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WORKER HEALTH AND SAFETY IN SOLAR THERMAL POWER SYSTEMS

III. Thermal Energy Storage Subsystems

By
Alan Z. Ullman
Bart B. Sokolow
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October 1979

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University of California
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Solar Energy

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ABSTRACT

The effects of the use of thermal energy storage (TES) subsystems in solar thermal power systems (STPS) on operating failures and on worker health and safety are examined. Relevant near- and medium-term designs for TES subsystems are reviewed. Generic failure events are considered by an event tree methodology. Three generic categories of initiating events are identified which can lead to release of storage fluids and other hazards. Three TES subsystem designs are selected for, and subjected to, analysis. A fluid release event tree for a sensible heat TES subsystem using mixed media organic oil/crushed rock and sand, designed for the Barstow, CA, 10 MWe pilot plant, is developed. Toxicology and flammability hazards are considered. The effect of component failures, including ullage and fluid maintenance units, on subsystem safety is considered. A latent heat subsystem using $NaNO_3/NaOH$ as the working medium is studied, and relevant failure events delineated. Mechanical equipment failures including the scraped wall heat exchangers, are examined. Lastly, a thermochemical TES subsystem using SO_2/SO_3 interconversion is considered. Principle hazards identified include mechanical failures and storage fluid release. The integrity of the system is found to depend on catalyst and heat exchanger reliability. Dynamic response to off-normal system events is considered.

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1. Introduction

The use of solar thermal power systems (STPS) for the generation of electricity may develop within the next decade into a practical and economic energy source. In general, no technology can be presumed to be free of potential hazards, and this must be assumed to apply to the STPS, which is dependent on some significant extensions of current power generation technology. The potential hazards may include environmental effects in the most general sense, subsuming both ecology and impact on affected populations, including workers. This report is one of a series prepared to consider the problems of worker health and safety in an STPS.

The economic benefit of an STPS depends not only on the quantity of electric energy produced, but also on the time-dependent pattern in which power is generated. An STPS which produces power only a few hours a day, and is subject to interruption due to cloudcover, may not displace the need for additional generating capacity from other energy sources. It may prove desirable to decouple the power generation cycle from the solar power supply cycle even if some cost is entailed in doing so, since in general this shifting of patterns will involve an increase in capacity credit along with a decrease in peak plant output.

One STPS option for altering the power generation pattern incorporates an auxillary boiler or heater using fossil fuels in the plant. The boiler or heater works in parallel to a solar receiver. This hybrid plant has merit for some applications, in particular, the repowering of existing oil or coal power plants. This option can provide an expeditious application of solar energy, and will serve as a method by which production and operations experience may be gathered. A hybrid design would generally have a solar availability of only about 0.4, that is only 40 percent of its energy output would be of solar origin if used as a base load plant.

The second option is the provision for a solar energy-derived back-up system for times without sufficient solar input. In addition to the prompt conversion of solar energy to electricity and its delivery to the electric utility grid, several means of delayed conversion or storage can be incorporated into a generating plant. The solar energy can be promptly convected to electricity, and in turn this electric energy can be stored in the form of potential (e.g., pumped hydroelectric power), kinetic (e.g., fly-wheels), chemical (e.g., batteries), electromagnetic (e.g., superconducting storage rings), or other forms of energy. Reconversion and delivery to the grid can then be made at times when direct solar energy is unavailable, thereby increasing the capacity credit of the plant. The necessary scale for application tends to argue against this route. For example, a lead-acid battery system that would be needed to store 5 hours output of a 100 MWe STPS (i.e., 500 MWe-hrs) would require a battery with 2000 tons of lead transferred per charge/discharge cycle.

It may be more efficient to store energy in thermal form in an STPS, that is, prior to its conversion to electricity. Such a thermal energy storage (TES) system might be scaled such as to serve as a thermal storage buffer of several minutes between the solar receiver and the conversion subsystem. This is useful in the event of rapid transients, such as cloud cover. If provided with more capacity, these systems could produce power for hours or days. Several hours' peak capacity would be desirable to allow nighttime plant operation, while several days or more might be required for operation during extended periods of cloudiness. The 10 MWe pilot plant at

Barstow, California, Solar 1, will have a TES system which can store about four hours' thermal input. The storage will be based on the heating of an organic oil, such as Caloria 43®, in a mixed media bed with crushed rock and silica sand. This system will be described in more detail in Section 4.

The use of thermal energy storage is not limited to an STPS, but it does appear to have a substantial application in this area. The TES system may thus be considered to be a unique worker health and safety hazard associated with the STPS. To address the nature and level of this hazard, this report presents the technical basis of TES subsystem design, a delineation of generic system hazards and a detailed hazard analysis for several specific designs. The designs which have been selected for analysis are viewed as suitable for near- or medium-term application. Lastly, a review of system designs is developed to generate subclasses of TES systems for hazards identification.

2. Designs and Technical Basis of Thermal Energy Storage (TES) Subsystems

There are three principle types of TES subsystems: 1) sensible heat systems, in which energy is stored by raising the temperature of the storage medium; 2) latent heat storage , in which energy is stored as the heat of a phase transition (usually fusion) of the storage medium; and 3) thermochemical systems, where heat is stored through the use of reversible chemical reactions. In reading the forthcoming review of extant designs, one should bear in mind that the potential hazard to worker health and safety from TES subsystem will depend principly on the materials and the operating and maintenance procedures used in the plant. Of particular concern are potential release of fluids, since many proposed working fluids are hazardous or flammable. The hazard depends on the quantity of fluid released, the state of the fluid (e.g., temperature, pressure, phase), and the amount and type of worker exposure. There are a number of TES subsystems currently proposed for use in STPS plants, using a broad range of fluid storage media. These proposed systems have not been proven on the scale envisioned and in many cases are only conceptual in design. It is the purpose of this section to delineate some of the subsystems proposed, and to indicate the types of fluids and other hazards that may be encountered. The subsystems are partitioned in accordance with the tripartite classification given above.

2.1 Sensible Heat TES Subsystems

Sensible heat energy storage occurs when the temperature of the storage medium is raised. On discharge, the storage medium cools, and the energy is transferred to the working fluid used in electricity generation. The storage medium may be formed from either a solid or a liquid, or from a combination of these two. Working temperatures for a particular medium are limited by phase transitions, excessive vapor pressures, corrosion reactions, and material instabilities. Storage and conversion efficiencies and transfer fluid properties will also affect the choice of the working temperature range. Equilibrium and rate phenomena can have an important effect on the operation of a storage system and must be considered in the design. The TES storage medium may be heated either directly or indirectly by the solar receiver. In the latter case, heat transfer equipment must be provided between receiver and TES fluid loops.

Sensible heat storage is generally considered to be the simplest of the TES options. While sensible thermal energy storage places the fewest restrictions on storage medium, advantageous materials properties can be identified. It is desirable that the material have a high specific heat capacity, a high temperature capability, a high density, and a low cost. In addition, a low vapor pressure at elevated temperature can result in lower containment costs. Availability at an acceptable cost, biological and environmental hazards, and the existence of technology for the medium's use must be considered in the selection of a fluid for TES use. Finally, it is important that the material be stable in the cyclic high temperature enviornment in which it will operate.

Sensible heat storage TES subsystems are relatively simple, consisting of conventional components: one or more containers for the maintenance of the storage medium, heat exchangers for thermal interchange with the working fluids used in the solar receiver and/or the electric conversion cycle, and fluid transport pipes. Where the storage medium will thermally decompose over time, provision for reprocessing or replacing the storage medium, and for the repair or replacement of parts damaged by decomposition, must be made.

The thermal storage of an isobaric sensible heat storage material is its enthalpy change over the operating temperature range. This is given by

$$\Delta H = \rho \int_{T_L}^{T_u} C_p \, dT \qquad (1)$$

where:

ΔH = enthalpy change [=] J/m^3)

ρ = density of the storage medium ([=] kg/m^3)

C_p = heat capacity ([=] J/kg K)

T = temperature ([=] K)

and the subscripts L and U refer to the lower and upper temperature limits of operation. Depending on the design, some fraction of this storage may be unavailable due to thermal stratification, losses, or other non-idealities.

Table 1 contains a list of representative storage media appropriate for a sensible heat TES subsystem integrated into an STPS plant. The advantages and disadvantages associated with these media are considered below. Particular reference will be made to features affecting worker health and safety.

2.1.1 Water

A potentially advantageous media for a TES subsystem is water. Water is inexpensive, abundant, environmentally neutral, has a large specific heat (1), and has good heat transfer properties (3). Since the volumetric heat capacity of liquid water, ρC_p, is substantially greater than that for steam, pressurization at high temperatures (e.g., 3.4 MPa [33 atm] at 240°C) (1) is required. The fabrication of sufficiently large pressure vessels appears to be prohibitively expensive, potentially ruling out water as a sensible heat storage media in most STPS designs except solar ponds.

2.1.2 Heat Transfer Oils

Organic and inorganic heat transfer oils have been considered extensively for thermal energy storage. The use of organic heat transfer oils is common in the chemical industry for process heating and cooling, so a technology for their use is available. Their properties make them well suited for use in sensible heat storage process (1,3), include low vapor pressures at high operating temperatures, wide operating temperature limits, and, depending on the specific choice of fluid and temperature, acceptable chemical stability. Heat transfer oils proposed include the Therminol® oils by Monsanto and Caloria-HT43® manufactured by Exxon.

Table 1

Sensible Heat Storage

Storage Media	T_U (°C)	$T_U - T_L$ (°C)	Cost ($/KWe-hr)	Development Status	References
Water	210-300	87	8.0 - 22.0	Engineering Design	4
Petroleum Based High Organic Heat Transfer Oils					
Therminol 55 (Monsanto)	315	55	62	Engineering Design	5
Therminol 66 (Monsanto)	315	55	27	Engineering Design	6
Caloria-HT43 (Exxon)	302	83	11	Engineering Design	7
Packed Bed - Mixed Media					
Granite + Caloria-HT43	302	84	5.13	Preliminary Design	6
Molten Salts					
HITEC (Dupont) [$NaNO_2$, $NaNO_3$, KNO_3]	350	300	4	Engineering Design	5 6 7
Liquid Metal					
Na	800?	?	?	Conceptual Design	8

Organic heat transfer oils are petroleum-derived materials. The heat capacities and other thermal properties dependent on the length of the paraffin chains constituting the oil. Studies of Caloria-HT43 (9), and Therminol (3) have shown decomposition from thermal cracking of the oil during normal operation. This degradation produces volatile species (e.g., methane, ethane) (10-12) and decomposition products which collect on pipe surfaces, reducing the effective thermal conductivity; the specific heat of the oil is reduced due to product formation. Additionally the gases produced from degradation can produce a significant pressurization in the container. Water leaking into the TES container can result in the sudden generation and expansion of steam, and a rapid pressure rises in the heat exchangers (3). Hot TES fluid may then be splashed out of its vessel by this process. There is also a corresponding flammability problem since operating temperatures exceed the oils' flash point.

These characteristics of synthetic oils lead to additional complexities for their use as TES mediums. Continuous oil reprocessing or replacement may be necessary to limit oil degradation, and scrapers or other mechanical devices might be needed to remove the deposits from internal heat transfer surfaces. If charging of the TES system is accomplished by using superheated steam from the receiver, as at Solar 1, a steam desuperheater will be required to prevent excessively high temperatures and rapid degradation of the oil, significantly reducing the thermodynamic cycle efficiency. Furthermore, ullage units must be provided to control the inert nitrogen atmosphere and to purge the volatile degradation products from the container.

Like most thermal storage systems, heat must be provided at a higher temperature than that at which it is withdrawn. This tends to reduce the thermodynamic efficiency of electrical generation during the discharge cycle. If a steam Rankine cycle is used, the use of a multiport steam turbine may be required to handle the variable steam conditions. Operating procedures for sensible heat TES subsystems must account for the variability of storage steam conditions during the discharging cycle. For example, storage tanks can be operated with a moving thermal boundary between hot and cold fluids, stabilized by fluid density variations, or by providing multiple hot and cold fluid tanks. Either of these operational modes increases capital costs or decreases thermal efficiency.

Inorganic heat transfer oils,principly silicone or organic-silicone polymers, are readily available. There oils generally have greater chemical stability at high temperatures, and are proposed for use as heat transfer materials in STPS receiver subsystems. Their high costs may prevent their significant application in TES subsystems unless integrated directly with the receiver subsystem.

The environmental hazards associated with oil release involve skin and eye irritation, burns, inhalation of toxic vapors, fires, and physical damage caused by the spreading of a large quantity of oil over a large unprotected area.

2.1.3 Mixed Media - Organic Oils

The mixed media TES subsystem is a variant on the organic oil design described above. Such a system uses a solid packed bed with oil filling only the void volume. Packed bed systems need less oil, and thus reduce system costs. One such system combines Caloria-HT43® with crushed granite rock. The system proposed for the STPS pilot plant at Barstow would use 4,500 tons of crushed rock and course silica sand, and 530 m^3 of Caloria-HT43 to produce 7 MWe for a maximum of 5 hours (12). The potential hazards described for the organic oils will be common to the hazards from this mixed media system. Some problems may be amplified, such as decomposition of the oil due to interactions with the rock.

Should mechanical devices fail or other problems develop inside the TES storage container, the use of crushed rock may exacerbate the difficult task of repair. Designs such as the Barstow 10 MWe pilot plant have not specified the means of access into the storage tank or the procedure for cooling and draining the container. Such access will lead to the venting of the container, increased fire hazards, and the possible emission of toxic vapors from the container. In the absence of detailed designs and procedures, no quantitative estimate of hazards are attempted, but the potential hazard and the need for greater system definition in this area should be noted.

2.1.4 Molten Salts

Molten mixtures of inorganic salts, such as HITEC® (consisting of 40% wt. $NaNO_2$, 7% wt. $NaNO_3$, and 53% wt. KNO_2), produced by DuPont, have been suggested (1) for sensible heat storage at temperatures above the practical limits of the organic heat transfer oils. These molten mixtures can provide more favorable behavior due to their thermal properties, temperature range,and stability. Unfavorable factors include the system costs and handling problems of these potentially reactive or corrosive materials. While HITEC has a low melting point and a relatively high upper temperature limit, it can decompose at high operating temperatures releasing NO, NO_2, and other oxides. Costs of these systems are currently projected to be high (2). Due to their thermal properties, this cost may be acceptable for systems in which these fluids can be used in both the storage and receiver subsystems. Such dual use will allow the electric generation subsystem to operate at the same capacity independent of whether the energy comes from storage or from the solar receiver directly.

2.1.5 Liquid Metals

The use of liquid metals, particularly sodium, will exhibit characteristics and areas of applicability similar to those of molten salt systems. Although temperatures may be somewhat higher, the problems of chemical reactivity are generally more severe.

2.2 Latent Heat Storage

Latent heat storage methods can be more economical than sensible systems, because their storage volume and material requirements are smaller and energy storage densities are greater (3). Latent heat systems may be operated as hybrid sensible/latent heat systems by heating the molten salt substantially beyond its melting point during the thermal charging process.

Although experience with latent heat materials for thermal storage is limited, the research in molten salt chemistry, various high temperature battery programs, and the molten salt reactor experiment has provided results which are relevant.

Many materials can be considered for application in latent heat TES systems. Over a thousand inorganic compounds have been compiled which could, in principle, be considered for thermal storage. Additionally, combinations of these compounds to form binary and ternary eutectics greatly expand the candidate compounds.

There are basically three characteristics to be considered for an ideal latent storage material - a material's: (1) heat of fusion, (2) heat capacity, and (3) thermal conductivity. While it would be desirable to optimize these characteristics on both a weight and volume basis, special system requirements may dictate the relative importance of one over the other. For example, the heat capacity is important only insofar as a hybrid sensible/latent heat storage operation is desired. Additional attributes of a good storage system include a low vapor presssure at elevated temperatures, a low thermal decomposition rate, and low toxicity of the storage medium. It is desirable, too, that contamination of the storage system not result in a hazardous situation, and that any contamination be easily and economically reversed. Another consideration is that there should be a minimum of physical and chemical interaction between the storage media and the containment system, with the containment system materials choices constrained by the usual economic considerations.

The economic availability of the salt material is the final major requirement to be met. Bulk quantity prices vary dramatically for the various inorganic salts. A major concern in the pricing of inorganic salts is the acceptable impurity level for each system. Impurities affect not only the cost of the materials, but also the thermophysical properties, the kinetics of phase transformations and side reactions, and the chemical interactions of the molten material with the containment system.

The processes which affect the availability of stored thermal energy include the transfer of heat between receivers, storage, and working media, and the losses of energy from the system. In situations where the storage medium is also one or both of the heat transfer fluids, the transfer processes are not needed. The transport of heat will always result in a reduction in work availability due to thermodynamic irreversibility. The impact of a loss of energy from a storage system depends upon the type of system under consideration,in particular the number of full-power hours of heat to be stored. In a sensible heat system, energy losses will always result in a drop in storage temperature and consequently, a loss in total availability. On the other hand, the loss of energy from a pure latent heat storage system does not affect the phase change temperature and thus the specific availability is unaffected. However, in both systems the total availability must necessarily decrease since the total amount of heat is reduced due to energy loss.

A latent heat storage system utilizes the properties of an isothermal, or nearly so, phase transformation system. Most commonly a phase change from solid to liquid (fusion) is used. When the system's storage medium's temperature is increased to the melting point, a change of phase occurs, absorbing the latent heat of fusion of the material. The latent heat is then released when thermal energy is extracted from the storage medium, reversing the phase change.

Latent heat thermal energy storage systems can withdraw heat at a nearly constant temperature without design complexities such as stratified beds or multiple tanks.

Several latent heat TES systems are currently in the preliminary design stage focusing on the identification of appropriate materials. Questions to be resolved includes the effect on efficiency of non-equilibrium processes such as superheating and subcooling of the medium. Material decomposition due to thermal cycling, and long-term stability (1,3), must be examined under realistic experimental conditions. Due to basic similarities, only a generic discussion of system design will be given here.

Table 2 contains five representative media which are in various stages of development for potential use in a TES subsystem in an STPS plant. A principle problem associated with most solid-liquid phase transformation systems is the low effective thermal conductivity of the crystallizing solid material, requiring expensive heat exchanger designs (3). The adherence of solids to the heat transfer surfaces exacerbates this problem.

The first system listed in Table 2 employs the NaF/NaF_2 eutectic. Due to its high operating temperature 680°C (1256°F), small scale tests have used mercury as the heat transfer fluid (1). The environmental hazards, technical difficulties, and costs related to mercury will likely preclude its use in the receiver. Most receiver subsystems other than gas-cooled designs cannot achieve the more than 720°C (1328°F) temperature needed to use this eutectic, and the thermal coupling of a gaseous heat transfer medium may present several technical problems.

LiH has exhibited good performance characteristics, but only in small scale tests. Its applicability for STPS is yet to be demonstrated. It will be expensive system to employ on the scale needed for STPS applications.

$KNO_2/NaNO_2$ has serious difficulties with containment and corrosion prevention (1,13). In addition, a mechanically complex heat exchanger system must be used to gain full efficiency from this system.

Another proposed system is a germanium sulfide compound, $Ge_{0.4}S_{0.6}$. If used, the properties of the material prevent it from sticking to heat exchanger surfaces because the solid is less dense than the liquid. The properties of germanium sulfide are still under investigation, and the cost of germanium remains prohibitively high (1, p. 43).

Table 2

Latent Heat Storage Media

Storage Media	T (°C)	Cost ($/KW(e)-hr)	Development Status	References
NaF/NaF (Eutectic)	680	21	Conceptual Design	14
KNO_2-$NaNO_2$	254	17	Preliminary Design	15
$Ge_{0.4}S_{0.6}$	590	--	Conceptual Design	16
LiH	680	--	Orbital Solar Energy Experiments	17
$NaNO_3$-NaOH	475	--	Experimental Designs	1

(Adpated from Reference 1)

The final system listed in Table 2 is a 99% $NaNO_3$/1% NaOH mixture. Although NaOH is corrosive in the presence of water, the amount of NaOH used is small, and may not present significant problems (18).

In addition to the above, a technical assessment of other candidate latent heat storage materials was performed by researchers at Sandia Laboratories (1). Their analyses revealed that numerous fused salt systems are available for use in TES subsystems. Many of them possess certain economic and technological problems which must be evaluated before testing. For example, a fluoride salt system appears to have a substantial cost disadvantage if LiF is used, and a toxicity problem is BeF_2 is used. Other problem areas identified among commonly considered choices for the TES medium include corrosion in chloride systems due to the presence of very small amounts of water and oxygen in the melt, exothermic chemical reactions with water or steam in alkali metal hydroxide systems, and excessive decomposition, corrosion, and vapor pressures in carbonate ternary eutectic mixtures.

2.3 Thermochemical Energy Storage

The third approach to thermal energy storage is through the use of reversible chemical reactions. The storage of thermal energy using reversible chemical reactions is a relatively new idea which has several advantages as a storage mechanism when compared with sensible and latent heat storage. Thermochemical energy storage systems employ an endothermic reaction for energy storage (charging) and the reverse exothermic reaction for energy release (discharging). The energy stored per unit mass and volume is about a factor of ten greater than in latent heat systems. Further, energy may be delivered and recovered at a constant temperature, while long term storage at ambient temperature is possible. However, thermochemical technologies are the least developed of the thermal energy storage systems, and considerable time, money and effort will be required to develop the commercial potential of thermochemical energy storage systems.

Even in mature form, thermochemical systems will probably be more complex than sensible and latent heat systems, incorporating as they must aspects both of a thermal storage device and a chemical processing plant. For example, gaseous products of a reaction must be separated and stored until the reverse reaction is needed, thus necessitating fractionating columns and additional pumps and tanks. Not only will individual components be complex, but integration of various components will be needed to achieve acceptable overall system efficiencies. Any sensible or latent heat of the reaction products which is lost during the storage time will have to be supplied for the reaction reversal, which results in an energy loss from storage which must be accounted for. Some storage schemes involving chemical reactions require a substantial input of energy to cause the reaction reversal which liberates the stored energy.

Various reactions have been proposed as the basis of thermochemical storage, and some small lab scale experiments have been conducted. Criteria for selection include:

- suitable operating temperatures and enthalpy change in reaction
- reversibility with no significant side reactions
- reaction rates rapid enough to satisfy energy input and output requirements
- easily controllable endothermic and exothermic reactions

- reactants and products easily and inexpensively stored
- materials exhibit acceptable safety, corrosion, and toxicity characteristics
- comparable costs and availability of materials.

Detailed lists of possible reactions for TES systems have been compiled (19,20,21). Table 3 list some characteristic thermochemical storage systems which are under investigation, with pertinent references. Most of the systems are only in the conceptual stage of development and detailed analyses are not yet available. Table 4 presents a description of the chemicals proposed for the thermochemical systems. Many additional systems which have been proposed are excluded from these lists due to temperature requirements beyond the range of current STPS designs. The hazards noted in this table are preliminary assessment of intrinsic hazards. The general categories are described below.

2.3.1 Inorganic Hydroxide Chemical TES Subsystems

The first type of system listed in Table 3 is based on inorganic hydroxides and oxide reactions. Alkali and alkaline earth element hydroxides, on the addition of heat energy, dehydrate to form their oxides and water vapor. Separation of oxide and water provides for long-term chemical energy storage. This stored energy can be released with the addition of superheated steam. The $Ca(OH)_2/CaO$ system has the advantage of having the lowest material cost of any system described in Table 3. $Ca(OH)_2$ can cause alkali burns (see Table 4) while $Mg(OH)_2$ appears to be of a minimal environmental and safety hazard. The use of superheated steam is common in power production systems and should not pose new hazards. The temperature range specified can be varied modestly as the steam pressure is varied, but will

Table 3

Proposed Thermochemical Storage Systems

Proposed System Reactions	Heat of Reaction, Q		Operation Temperature (C°)	Material Cost ($/kWt-hr)	Development Status	References
	(kWt-hr/kg)	(cal/g)				
Type I: Inorganic Hydroxides						22-25
$Mg(OH)_2(s) + Q = MgO(s) + H_2O(g)$	0.288	166	375-350	0.62	Lab Scale	
$Ca(OH)_2(s) + Q = CaO(s) + H_2O(g)$	0.366	240	520-490	0.07	Experimental	
Type II: Methane-based Rxns(gas)						26,27
$CH_4 + H_2O + Q = CO + 3H_2$	1.8	1451	1100-800		Conceptual	
$CH_4 + CO_2 + Q = 2CO + 2H_2$		980	676-538		Conceptual	
Type III: Metal Hydrides						28
$FeTiH(s) + Q = FeTi(s) + 1/2H_2(g)$	0.078		100	28	Conceptual	29
$VH_2(s) + Q = VH(s) + 1/2\ H_2(s)$	0.105		100	105	Conceptual	
$LaNi_5H_5 + Q = LaNi(s) + 5/2H_2(g)$	0.48		100	1060	Conceptual	30
Type IV: Heats of Dilution						
H_2SO_4(dilute + Q = $H_2O(g)$ + H_2SO_4 (conc.)	0.107		238	0.45	Lab Scale	31,32
Type V: SO_3 Decomposition						
$SO_3(g) + Q = SO_2(g) + 1/2O_2(g)$	0.343	360	722	.16,16.4*	Conceptual	20,33-35

* Includes storage system costs

Source: Based on Reference 1, pp. 45, 85 and 87

Table 4

Description of Some Chemicals Proposed for Thermochemical Storage Systems

Chemical	Characteristics/Description/Uses
$Mg(OH)_2$	Magnesium hydroxide - classified as a nonsystemic antacid, main component of "Milk of Magnesia" (7.0 - 8.5% suspension, low solubility
MgO	Magnesium oxide - hydrates readily to magnesium hydroxide and has similar uses, O.E* fumes is 15,000 μg/m^3
CaO	Calcium oxide - hydrates readily to calcium hydroxide - component of cement and wall plasters, may cause alkali burns to eyes
$Ca(OH)_2$	Calcium hydroxide - sparingly soluble (saturated solution, 0.15%, pH = 12.4), cause severe lime or alkali burns in the eyes, very difficult to remove once in the eyes
CH_4	Methane - combustible, physiologically inert, simple asphyxiant (prevent body tissues from receiving adequate oxygen when inhaled at 20 - 30% by volume)
CO	Carbon Monoxide - Chemical asphyxiant (prevents the body from utilizing an adequate oxygen supply), mechanism - has a 200 times greater affinity for hemoglobin, the bloods oxygen carrier, 0.1%, 1-hour exposure dangerous to life, 0.35% exposure fatal in less than one hour
CO_2	Carbon Dioxide - minor atmospheric component (300 ppm), respiratory gas, simple asphyxiant (see methane)

* O.E. is Occupational Exposure limits for 8-hour exposure.

Table 4, (Continued)

Chemical	Characteristics/Description/Uses
H_2SO_4	Sulfuric Acid - severe eye damage at pH greater than one, chronic and acute effects on pulmonary function for sulfur particulates, conc. H_2SO_4 is a strong acid (typically 36 N solution) and destroys tissue on contact
SO_3	Sulfur Trioxide - reacts rapidly with moisture to form sulfuric acid
SO_2	Sulfur dioxide - causes eye irritation (10 ppm), lung irritation and severe coughing (20 ppm), affects pulmonary function

(Source: Reference 13, 36)

generally remain below the 535 to 565°C (1000 to 1050°F) temperature range for steam generation in a modern steam Rankine cycle plant. Materials separations are relatively simple for this system, since the products are heterogeneous in phase under the reaction conditions.

2.3.2 Methane Reactions for Chemical TES Subsystem

The second group of reactions listed in Table 3 are the methane-based reactions. These closed-looped chemical systems utilize a temperature of 1100°C (2010°F) in the forward direction for the water-gas reaction, and catalytic methanation of CO in the reverse direction at a temperature of 800°C (1470°F). Obtaining the high temperatures needed will be a significant problem in STPS plants (1). Further, the storage requirements for containment of gaseous reactants and products is expensive. Methane and carbon dioxide are simply asphyxiants, and prolonged worker exposure to large concentrations (20-30% by volume) is hazardous. Carbon monoxide as a chemical asphyxiant, can reduce blood oxygen concentration by displacing xoygen molecules on hemoglobin molecules, and is hazardous at a concentration of 0.1% in air.

Corresponding reactions between CO_2 and CO alone are also possible, but achieving the temperature and pressure ranges at which these become possible requires extremely exotic technology.

2.3.3 Metal Hydride Chemical TES Subsystems

Several metal hydrides have been proposed for solar thermal energy storage. In the energy storage phase, the metal hydride is decomposed and the hydrogen gas is generated and stored. Energy is released through a rehydriding process. Since metal hydrides can be created in a number of chemical combinations, many desired pressure - temperature relationships are possible by varying the alloy composition. Hydride reactions have been applied in other areas such as vehicle propulsion (37), and off-peak energy storage for hydrogen-oxygen fuel cell power generation (38,39). While hydride systems appear to be technically feasible, they suffer from high costs associated with chemicals, heat exchangers/reactor components, and hydrogen containment.

2.3.4 Heat of Dilution Chemical TES Subsystems

The fourth type of system described in Table 3 is based on the heat of dilution of concentrated acid solutions. Utilization of this method of energy storage is a rather old idea (31) that has gained recent attention (32). While aqueous systems have a limited operating temperature range, temperature boosting is possible and material costs are low. Operational temperatures, however, will probably have to be kept down to protect materials from corrosion at elevated temperatures. In the proposed system, sulfuric acid is used. Since sulfuric acid manufacturers have experience in handling large amounts of the acid, safety aspects of this system may be well understood. Sulfuric acid presents a fluid hazard since it is an extremely damaging respiratory irritant.

2.3.5 Sulfate Reaction Chemical TES Subsystems

The last type of thermochemical storage system list in Table 3 is based on sulfur trioxide (SO_3) decomposition. This system utilizes catalytic decomposition of SO_3, at a temperature of about 722°C for heat intake. The product species are separated and stored for energy storage. The reaction is reversed in a catalytic reformer at a reduced temperature in the discharge cycle. Preliminary system costs are encouraging, in part due to the utilization of some proven technology associated with sulfuric acid manufacturing. There is some concern that the capital costs of an SO_3/SO_2 energy storage system may be higher than anticipated. Detailed designs have been proposed for a thermochemical TES system using SO_3 gas dissociation (34). A recent review (40) suggests that substantive development problems associated with the SO_3 system include an effective catalyst for the high temperature endothermic reaction. Construction with materials that can withstand the corrosive environment may be technologically or economically unfeasible.

2.3.6 Other Thermochemical TES Subsystems

Many types of thermochemical energy storage systems have been proposed for use in solar thermal power plants. In addition to the systems discussed above, proposals include: coupled reactions, in which two chemical reactions are coupled via a common product/reactant species (41,42), hexamine reactions (43); hydrated (44), ammoniated (45), and methanolated salts (46); and alkali metal and alkaline earth carbonates (47,48).

2.4 Design Summary

Direct storage of high temperature thermal energy is technically feasible in the near term with sensible heat TES technology. Latent heat systems have the potential to be more cost effective, and thermochemical systems may be more flexible. Latent heat and thermochemical technologies are at an early stage of development, requiring additional research before the potential of these systems can be realized. The environmental, health and safety hazards associated with the release of many of these fluids require further analysis.

3. Hazard Identification in Thermal Energy Storage (TES) Systems

3.1 Hazard Categories

The source of worker injuries in hypothetical energy technologies has been examined in a separate report (49). In accordance with the procedures established by the California Department of Industrial Relations, Division of Labor Statistics and Research, the sources of accidents can be partitioned into ten categories, listed in Table 5. Also listed in that Table are the ten categories of injury types. To both lists must be added a general category for miscellaneous sources or types. Many of these categories are related to the environment in which the worker must function. For example, pairs of accidents sources such as hand tools and machines, or injury types such as falls from elevation and falls on the same level, may reflect comparable accidents in somewhat modified settings. The modifications reflect the functions and needs of the industrial operation performed, and the procedures workers will follow.

It would be constructive to compare the accident categories in Table 5 with the operation of a TES subsystem to ascertain the nature of injuries to workers. We would contend that many aspects of the design and operation of a TES subsystem are insufficiently well defined to allow a complete comparative analysis. At a preliminary stage of technology development, many of the design aspects which will have a profound effect on the nature and rate of injury to workers are, in essence, only petty details in terms of the design as a whole. For example, one would not care to spend too much time examining aspects of working surfaces at such an early stage in technology development.

Certain aspects of the design are clearly not in this "petty details" category and, equally clearly, can profoundly affect workers health and safety. Principle among these will be the hazards falling into the source category of chemicals, with the presumptive injury types of bodily reaction

Table 5

Categories of Accident Sources and Injury Type (from Reference 50)

Accident Sources

- Containers
- Chemicals
- Furniture and fixtures
- Hand tools
- Hoisting apparatus and conveyors
- Machines
- Metal items
- Vehicles
- Wood items
- Working surfaces

Injury Types

- Struck by or against
- Fall from elevation
- Fall on smae level
- Caught in or between
- Rubbed or abraded
- Bodily reaction
- Overexertion
- Contact with electric current
- Inhalation and absorption
- Motor vehicles accidents

or inhalation and absorption. As will be demonstrated in the subsequent sections of this report, the hazardous chemicals are very much an integral part of the TES subsystem, and the hazard of these chemicals will differ in nature and magnitude between the designs considered. The potential for, and events leading to, the release of fluids will therefore be considered in detail. Concommitant events, such as missile generation, will be considered as they relate to fluid releases.

Restricting the consideration of worker hazards to this narrow subclassification is not intended to imply that these hazards are the most serious in the system, or that the hazards are in any absolute sense of large magnitude. As we have reasoned elsewhere (49), injury rates from chemical exposure are expected to be quite small except in a most singular industry. We see no reason to believe that the STPS is likely to present a particularly great hazard with respect to chemical use. In contrast to chemicals hazards, however, many of the routine hazards in the TES subsystem are amenable to "add-on" safety at a later stage in development, largely by the specification of operating procedures. The consideration of fluid and chemicals release hazards, by contrast, presents an intrinsic hazard of a particular design. This hazard may be increased or decreased by careful design, but it will nonetheless be an integral part of a particular system concept. This type of hazard, we believe, should be considered at an early stage, and in the context of the choice between alternatives.

3.2 Description of Generic TES Fluid Release Analysis

The external release of TES working fluids may lead to several consequences of general environmental concern. These consequences include health effects resulting from worker exposure to TES fluid, ecological damage caused by TES fluid effects on biota, and secondary release of additional TES or other fluids, or damage to other subsystems, as a result of physical damage caused by TES fluid release. To mitigate against these consequences, the causes of off-normal release of TES fluid into the environment have been examined.

A generic description of TES fluid release modalities can identify and elucidate the overall hazards associated with the TES subsystems. In these analyses it is possible to assess adverse effects of interactions between the TES subsystems and other subsystems. It is also possible to develop categories of initating evenst useful in specific subsystem analysis. However, the specific design and operating characteristics of sensible, latent, and thermochemical TES subsystems do differ considerably. For this reason, specific sensible, latent, and thermochemical TES techniques were evaluated, based on available designs and data. The particular examples of a sensible, latent, or thermochemical TES subsystems selected have been developed through the phase of engineering design and operation description, and have near- or medium-term prospects for STPS application. This two-phase analysis is intended to point out both the generic and specific considerations which deserve attention prior to the implementation of a particular TES subsystem in an STPS.

3.3 Event Tree Delineation of Generic TES subsystem Fluid Release

The construction of appropriate event trees is among the most powerful tools for the delineation of the various causative events which leads to a particular undesired consequence. Figure 1 is such an event tree for various phenomena leading to normal fluid release from a TES subsystems. Events in this diagram are considered in a wholly generic way. Central to the event tree are the interactions which can occur between the TES subsystem and other subsystems, including the receiver and power generation subsystems

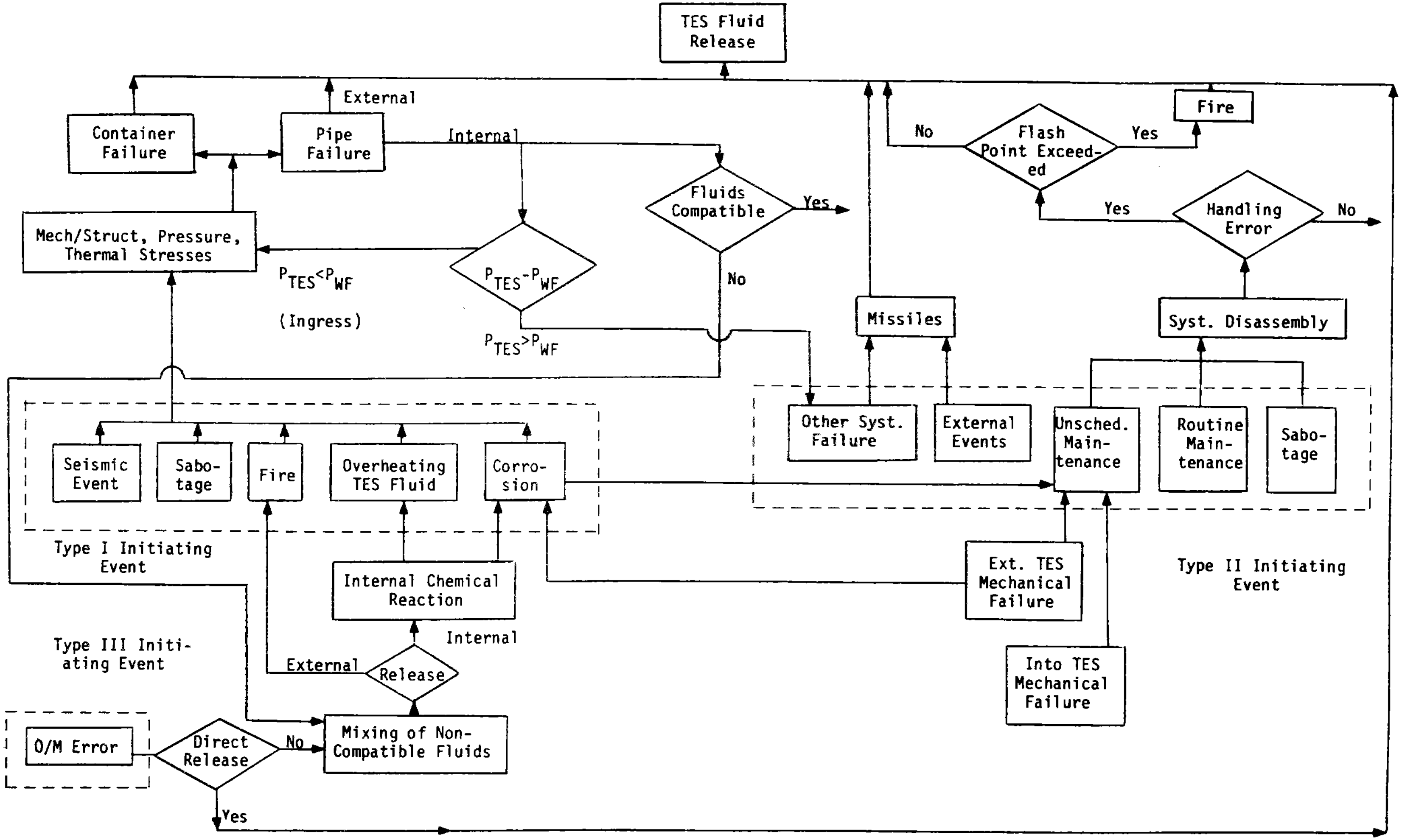


Figure 1. Event Tree for TES Fluid Release

with which it interchanges heat. Consideration is also given to self-generated events in the TES subsystem. The diagram contains the pathways leading from a variety of initiating events to the external release of TES fluid. In this section the relationships between the events and the pathways in Figure 1 are developed.

The external release of TES fluid can occur as either the direct or indirect result of some set of circumstances. Events which lead directly to the release of TES fluid, or which start a sequence of events which lead to the external release of TES fluid, are defined as initiating events. These initiating events may be partitioned into several classes. The first class of initiating events are those in which a material design limit of some subsystem component is exceeded. These are denoted in Figure 1 as Type I initiating events. For example, the temperature or pressure rating of a vessel might be exceeded, leading to vessel failure and fluid release. A second class of initiating events consists of off-normal events generally outside the scope of specific design requirements of TES construction methods or materials. These are denoted in Figure as Type II initiating events. This type of initiating event occurs with uncertain frequency and may be large and disruptive in magnitude. These events include normal and off-normal maintenance, and events initiated by other STPS subsystems. The last class of initiating events are those which result from use of substandard materials, failure to maintain operation standards in TES subsystem construction, or from other inappropriate actions taken in normal or off-normal TES operation and maintenance. These are denoted in Figure 1 as Type III initiating events. In Type III events, design requirements have been determined but not implemented.

Initiating events which can cause particular design capability to be exceeded include:

- seismic events - where ground acceleration is greater than maximum design strength
- sabotage - due to deliberate tampering with valves, controls, or other equipment
- fire - temperature stress resulting from combustion of reactants external to TES fluid containers
- TES fluid overheating - due to fires or internal chemical reactions from mixing of non-compatible fluids
- Corrosion - due to external TES mechanism: failure, overheating, or internal chemical reactions

These Type I initiating events, shown in Figure 1, lead directly to an activating mechanism, such as those created by stresses which exceed the mechanical/ structural, pressure, or temperature limitations of a construction material. Surpassing these limitations may lead to direct or indirect fluid release. The delineation of these Type I initiating events tacitly assumes that it is uneconomic, infeasible, or unwarranted to design the system to withstand these initiating events. For example, some level of seismic stress will be within the design limits of the plant. It is likely that this design level can be exceeded no matter how high it is set, leading to a Type I initiating event. (Of course, the probability of exceeding the design limit is reduced as the limit is increased, but it is not the purpose to quantify these effects at this time.)

The Type II initiating event will include:

- other STPS subsystem failures - (e.g. turbine, boiler, or collector failure
- Off-normal events external to the TES system - (e.g. aircraft accident)
- external or internal TES mechanism failure - leading to failure may be direct or indirect communication with the thermal energy storage media (e.g. scrapers, reprocessors, catalysts)

The distinction between Types I and II initiating events stems from the existence of specific design standards relevant to Type I events. Thus, Type I events have probabilities of occurance directly subject to TES subsystem design standards. These second types of initiating events, with the exception of sabotage, lead directly to other activating mechanisms. Other STPS component failures and external events can lead to the creation of missiles, which can penetrate the structural vessels and pipes containing TES fluid. In addition, TES mechanism failures and routine operating and maintenance procedures may lead to system disassembly, which in turn may permit fluid to be released.

The last Type of initiating events are those which result from incorrect or negligent actions taken during normal or off-normal TES subsystem operations. These events may include operation and maintenance errors and inproper system operation.

Several scenarios may be useful to illustrate the relationships between the events and the pathways proposed. A Type III, operation/maintenance error may result in direct release of TES fluid, producing an immediate hazard to workers. An indirect (internal) release may lead to mixing of noncompatible fluids (e.g. heated oil and air, concentrated acids and water), which creates an internal chemical reaction. This internal release may lead to a Type I initiating event such as a fire. In turn a container or pipe may be stressed beyond its thermal design limits, producing an external release. Likewise, fire may cause overheating of TES fluids (thermal stress) which may produce corrosion (material stress) and both events can lead to external or internal fluid releases. Internal fluid release may lead to additional events; if the pressure of the TES fluid is less than that of other fluids (i.e. the electric generator working fluid, WF), then further pressure stress may occur, causing the container and pipes to fail. If the pressure for the TES fluid is greater, it may escape and create other system failures (a Type II initiating event). For example, if a dense TES fluid were to egress into the turbine working fluid and reach the turbine blades, the turbine could fail, possibly generating missles. In turn, this could lead to additional fluid release. Other systems failures may also be responsible for these type of initiating events. In either case, internal fluid release may lead to mixing of non-compatible fluids which could initiate other undesired events.

In another example, an external fluid reprocessing unit is necessary if high-temperature organic oils or a thermochemical storage fluid that has side reactions were used as the TES fluid. Alternatively, internal contrivances such as heat exchanger scrapers or catalysts may be required. Failure of these components may lead to unscheduled maintenance, a Type II initiating event. In this situation, handling could initiate a direct release. If the fluids reach the autoignition or flashpoint, a fire could occur, leading to off-normal fluid release. This fire may be a Type I initiating event, leading to other possible hazards.

Figure 1 presents pathways and events which cause the release of fluids. It is recognized that other events and pathways may exist, but at this time whether such pathways are generic to TES subsystems cannot be ascertained. The nature and probability of occurrence of these pathways should be determined in future studies. To ascertain some of these pathways, three specific systems have been selected for further study. These are: (1) an organic oil-mixed media sensible heat TES subsystem; (2) a two component nitrate/hydroxide molten salt latent heat TES subsystem; and (3) a sulfate thermochemical energy TES subsystem. Each is well documented and, within its category, a relatively near-term option.

4. Safety Considerations of an Oil/Rock Mixed Media Sensible Heat TES System

4.1 Design Description

A sensible heat thermal energy storage (TES) system for use in a solar thermal electric power plant has been proposed by the McDonnell Douglas Corporation (51). The availability of documentation on the McDonnell Douglas sensible heat TES design and its near-term application to solar thermal power systems suggest its suitabiltiy as a candidate for a thorough safety analysis.

Figure 2 is a schematic of the 10 MWe Pilot Plant TES subsystem proposed by McDonnell Douglas. The design and performance characteristics of the 10 MWe TES is briefly summarized below (51).

The 10 MWe Pilot Plant TES system employs sensible heat storage using dual liquid and solid media for the heat storage in a single tank, as shown in Figure 3. The thermocline principle is applied to provide high-temperature extractable energy at a rate and temperature largely independent of the total energy stored. Caloria HT43®, manufactured by Exxon, is the selected oil based on volumetric storage, stability, and cost considerations. A commercial granite crushed rock and a course silica sand were chosen as the most applicable and cost effective particulate solid medium.

The TES subsystem as designed has an extractable storage capacity of 103.8 MWt-hr, which provides 7.5 MWt-hr for a turbine hot start and

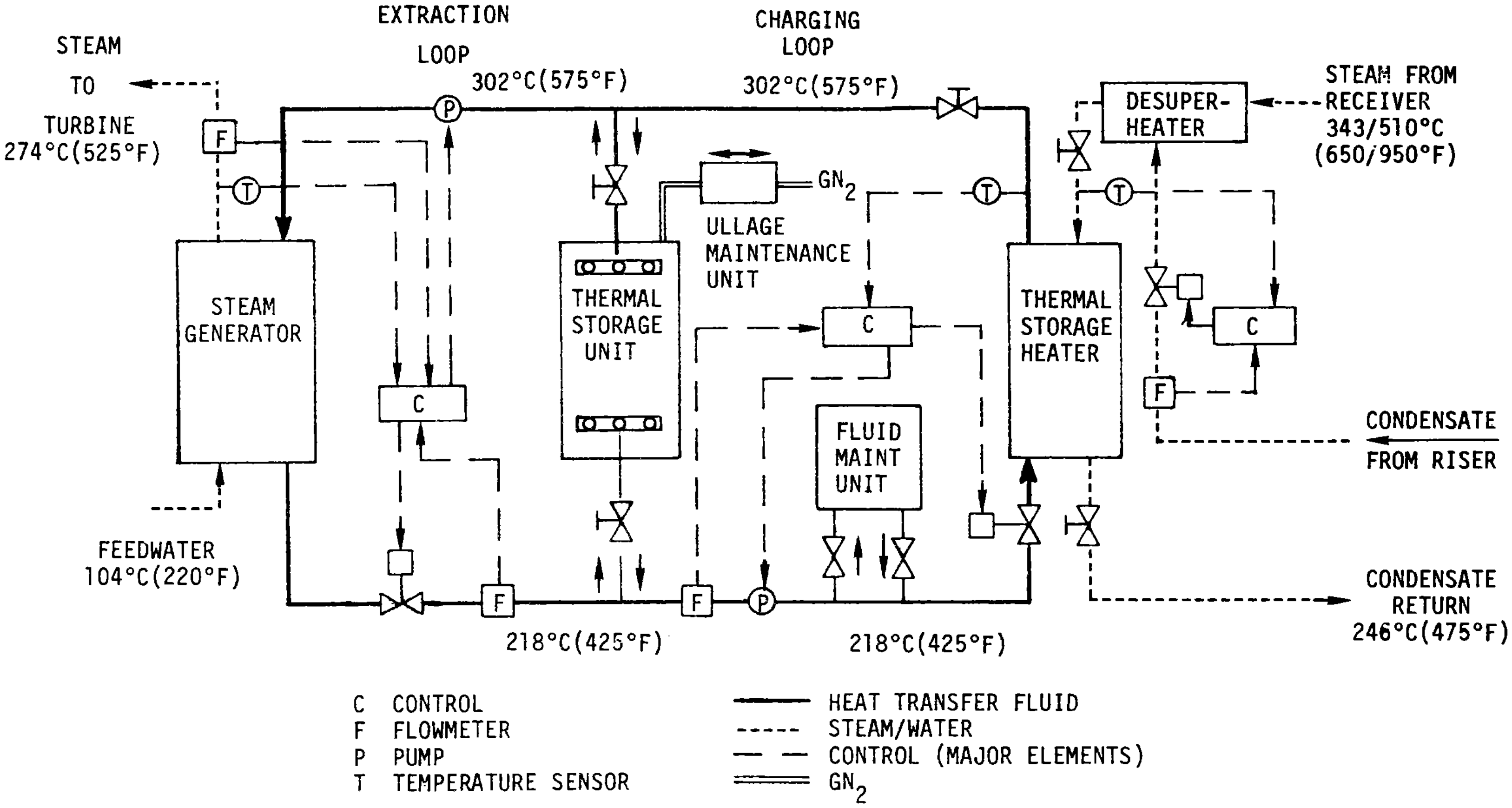


Figure 2. Schematic of 10 MW e Pilot Plant Thermal Storage System
Source: Reference 11

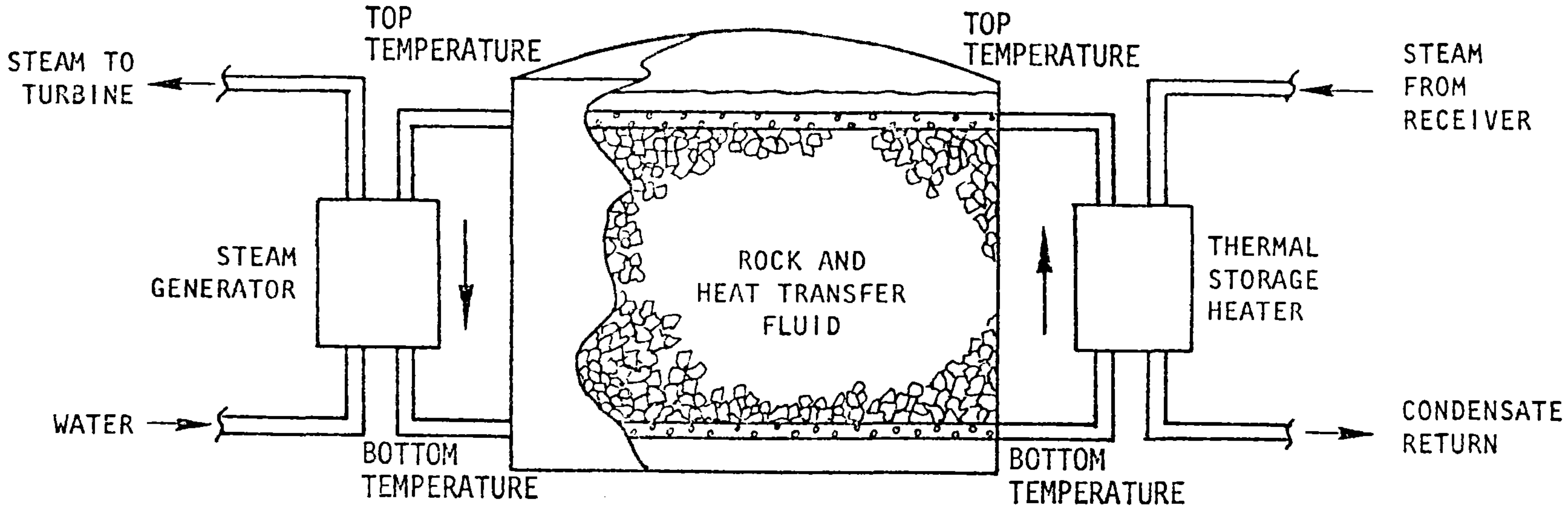


Figure 3. Dual-Medium Thermal Storage Concept

96.3 MWt-hr for the generation of 7 MWe net (7.8 MWe gross) for 3 hours following turbine startup. The charging rate range is 1.5 to 30 MWt, and the maximum allowable heat loss starting in a fully charged condition is 3% of extractable capacity in 24 hours. The subsystem is required to provide nighttime seal steam at a temperature of at least 135°C (275°F), at a rate of 0.33 MWt for approximately 16 hours. The design storage temperatures are 302°C (575°F) maximum and 219°C (425°F) minimum, with allowable degradation of TES fluid temperature of 8.3°C (15°F) during extraction (51).

There are five fluid streams crossing the boundaries of the TES system, all water or steam flows. The subsystem is designed to accept steam from the receiver at 10.1 MPa (1465 psia) and 343°/510°C (650°/960°F); the two temperatures correspond to derated and rated steam operation, respectively. The supply steam from the TES steam generator is at 2.76 MPA (400 psia) and 277°C (530°F).

The TES subsystem is divided into nine components:

1) thermal storage unit (TSU): a tank which stores and dispenses thermal energy via the Caloria HT43 heat-transfer fluid
2) ullage maintenance unit (UMU): provides an inert nitrogen gas cover over the fluid surface in the tank
3) fluid maintenance unit (FMU): removes suspended and dissolved impurities from the fluid
4) desuperheater (DSH): limits incoming steam temperature
5) thermal storage heater: served to transfer heat from the condensing steam to the fluid
6) thermal charging loop: comprises the charging fluid pump and associated equipment
7) steam generator: transfers heat from the fluid to generate steam for the power plant
8) extraction loop: comprises the extraction fluid pump and associated equipment
9) controls and instrumentation: provides operational control for the subsystem

Figure 4 and 5 are schematic illustrations of the fluid and ullage maintenance components integral to the selected sensible heat oil storage system. These components are required for the maintenance of on-specification conditions for the TES storage medium.

4.2 Identification of Fluid Release Modes

Examination of the sensible heat TES subsystem described above reveals that failure of any one of several units can lead directly to fluid release. The thermal storage, heat exchanger, fluid maintenance, ullage maintenance, and desuperheater units have direct pathways to fluid release via one or more component failure mechanisms. Personnel can also become exposed to TES fluids or cause fluid release during the maintenance operations recommended by McDonnell-Douglas on TSU, FMU, and UMU. There will, therefore, be a routine exposure hazard if maintenance is attempted particularly while the subsystem is hot. The fact that ignition temperatures are exceeded during normal operation indicates that fire can occur, potentially initiating further fluid release.

Several pathways of fluid release are shown in Figure 6. A desuperheater failure or a fluid maintenance unit failure could give rise to an increase in oil temperature. The oil could exceed the auto-ignition temperature, causing an explosion or fire if sufficient oxygen were present. The increase in oil temperature would also cause an increase in thermal cracking rate, with safe venting of the gas produced. A similar situation can occur during the charging cycle if the ullage maintenance unit fails. During charging, the gas displaced by the expanding oil must be vented. On subsequent discharge of the TSU, the oil volume will decrease and a UMU failure might allow air into the ullage space. Thereafter a fire hazard could exist, since the oil which is above the flash point during normal operation is exposed to air. The hazard of fluid release can occur wherever and whenever oxygen and hot oil come in contact.

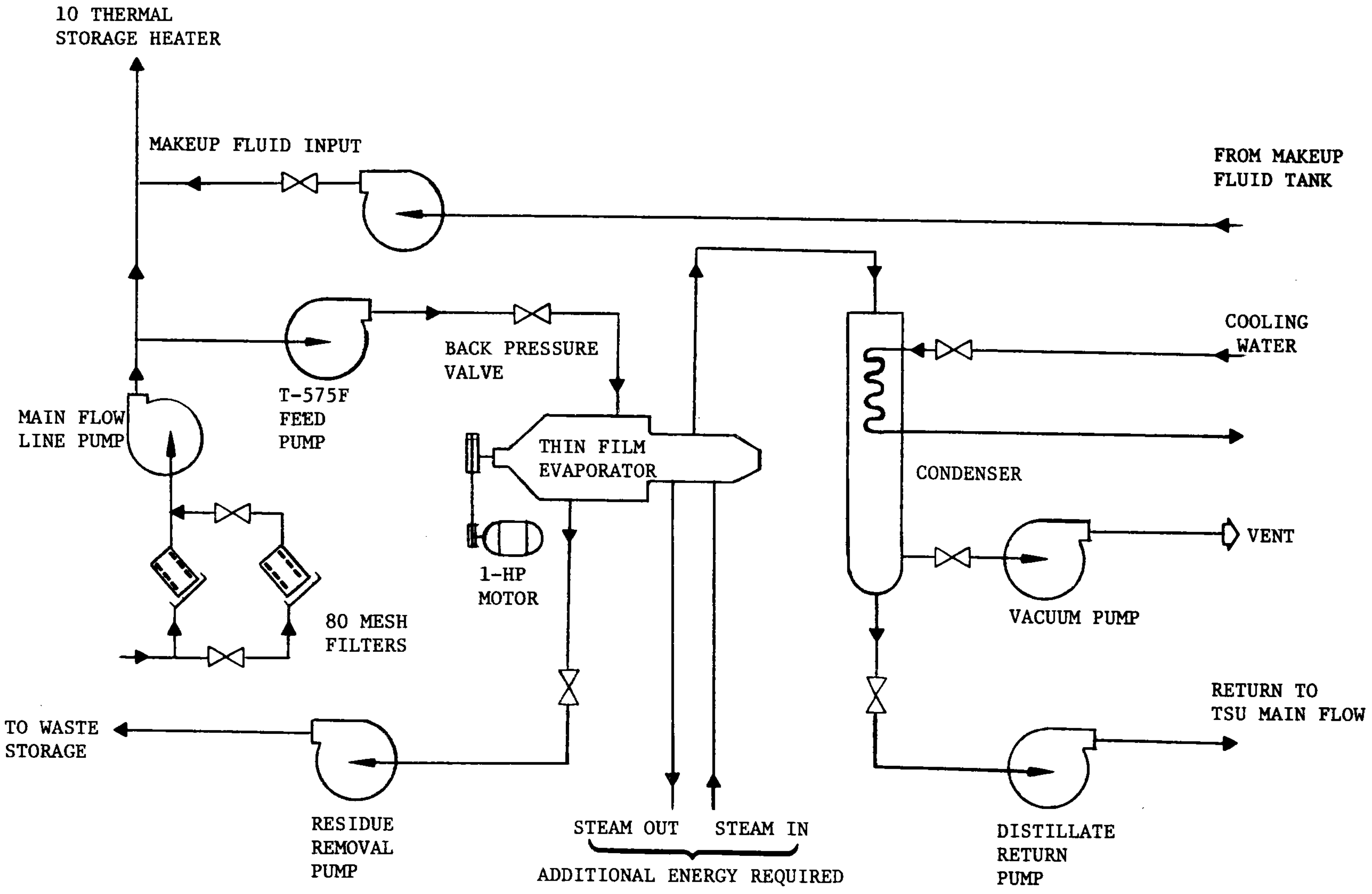


Figure 4. Fluid Maintenance Unit Design for 10-MWe Pilot Plant

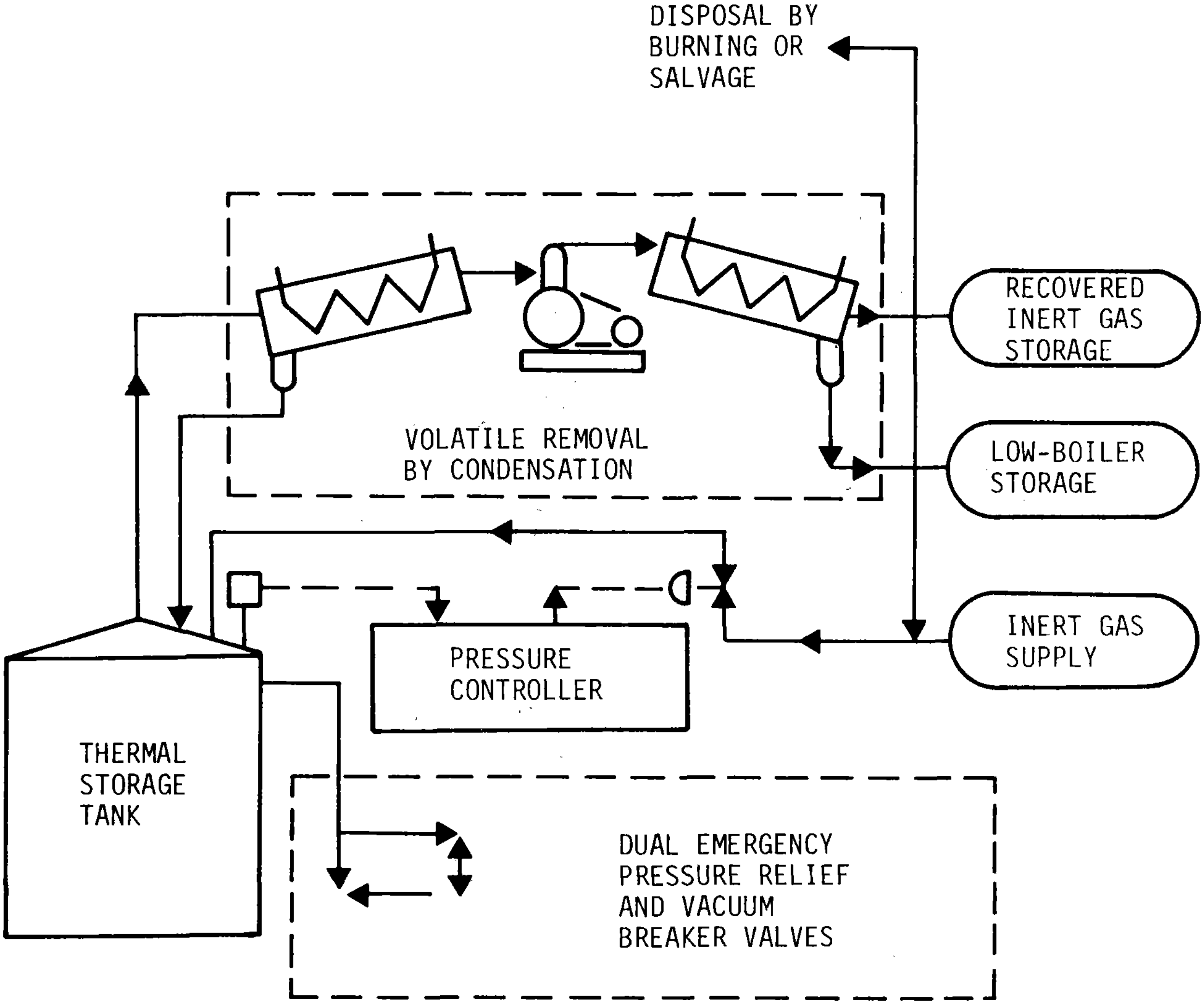


Figure 5. Conceptual Design of Ullage Maintenance Unit for 10 MWe Pilot Plant
SOURCE: Reference 11, pp. 4-74.

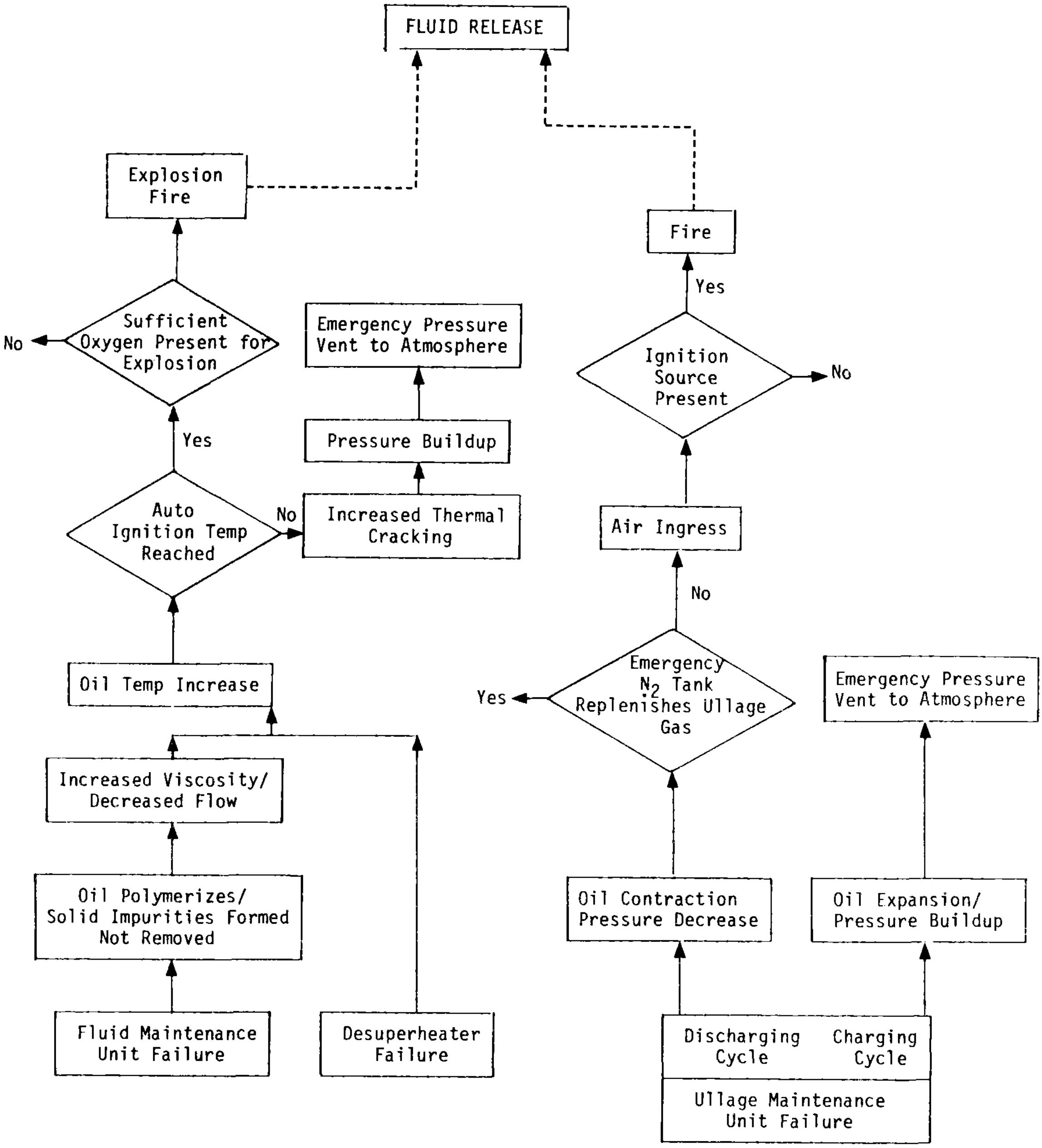


Figure 6. Fluid Release for Sensible Heat TES System

Failure to observe appropriate care in the choice of the oil and rock combination or long term changes in mechanical properties may initiate various failure modes. With the expected settling of the rock in the tank, differential expansion and contraction of the rock and the wall of the container may produce large cyclic stresses on the tank walls during heating and cooling cycles. It is also conceivable that mineral contaminates on the rocks or as a constituent of the rock may chemically react or promote decomposition.

The major pathways of fluid release which can occur during the operation of the McDonnell-Douglas TES subsystem have been described. Precautions intended to prevent worker exposure and TES fluid release are presented in the subsections which follow.

4.2.1 Thermal Storage Unit (TSU)

The TSU contains the TES fluid and solid particulate material necesesary for storage of thermal energy. Although expected to require no maintenance, the TSU has two potential problems associated with its operation. Thermal ratcheting (51, pp.4-50) can result from differential thermal expansion/contraction of a more elastic tank wall surrounding a less elastic solid particulate material; and 2) decomposition of TES fluid may be accelerated by cracking of TES fluid on the solid particulate material. An example of this phenomena would be a component of rock acting to catalyze the cracking of Caloria HT43 when high temperatures are reached.

The McDonnell-Douglas design calculations for container stress from thermal ratcheting use conservative stress values (11). Insofar as it is possible to predict the behavior of mixed solid media over the thirty year life of the plant, it should be possible to maintain such stresses within a satisfactory margin of safety for the tank structure. It is not clear that this phenomenon is well understood. Should an unforeseen circumstance cause these predicted design values to be exceeded, fluid release could occur due to wall stresses, and a potentially serious safety hazard would result.

4.2.2 Ullage Maintenance Unit (UMU)

The Ullage Maintenance Unit (UMU) is shown in Figure 4. Failure of the ullage maintenance unit could cause a condition within the TSU in which pressure is no longer controlled and an oxygen-free environment can no longer be assured. The failure of the UMU might lead to the release of TES fluid, in particular, if plant operation were permitted following a failure of the UMU. A rough estimate of the ullage space above the oil during heating and cooling can be made using dimensions estimated from Figure 3. The ullage space consists of a conical roof of average height ∿0.5 m. The ullage space includes ∿0.9 m of tank height when thermal energy is completely extracted (when the fluid is at the minimum temperature , 219°C), or 0.3 m when completely charged (when the fluid is at the maximum temperature, 302°C). The hot and cold effective ullage space heights are then the sums, ∿0.8 and ∿1.4 m, respectively. The ratio of pressures should the UMU fail is given by the ideal gas law as:

$$\frac{P_{hot}}{P_{cold}} = \frac{V_{cold}}{V_{hot}} \frac{T_{hot}}{T_{cold}} = \frac{(1.4m)(302 + 273)\ K}{(0.8m)(219 + 273)\ K} \cong 2 \qquad (2)$$

This ullage space pressure ratio of ∿2 should present little intrinsic concern. As a precaution, manual venting of gases from the TSU during heating can be performed using the vents designed into the TSU. This would prevent development of signfiicant overpressurization. Failure to close the vents during discharge would lead to TES fluid at temperatures of 219° to 302°C (above the flash point of 204°C) in the presence of oxygen. Oxygen monitoring of the ullage gas and TES fluid should be performed continuously. Should the UMU fail and auxiliary nitrogen gas fail to compensate for underpressurization of the system during extraction of thermal energy, it is possible that the air vents may be manually opened.

To reduce the chance of malfunction of the UMU, it is suggested (51) that daily inspections and required maintenance of the UMU and its auxiliary equipment be performed. It is also recommended that operational personnel take weekly samples of the organic fluids passing through the unit during operation. Annual maintenance requires temporary disassembly to inspect the UMU to be sure the mechanism is clean and functions properly.

4.2.3 Fluid Maintenance Unit (FMU)

The Fluid Maintenance Unit (FMU), which is shown in Figure 5, functions to remove components of very low volatility, principly polymerized material formed over long periods of time via pyrolysis, and solid residues from the heat transfer fluid. The FMU also maintains a constant fluid inventory. The FMU contains devices such as filters, pumps, a condensor, and a thin film evaporator.

McDonnell-Douglas estimates that the bulk fluid can function properly with a concentration of 10% polymerized matter. The FMU will be designed to maintain that 10% level by reprocessing 60 1/day of the approximately 600,000 1 inventory of fluid in the Pilot Plant (11, pp. 4-89).

However, we note that the polymer production rate estimates by McDonnell-Douglas is only 6 1/day. This suggests that employing an FMU may not be necessary. The 10% maximum concentration of polymers would not be reached for approximately

$$600{,}000 \ \ell \text{ oil} \times \frac{0.1 \ \ell \text{ polymer}}{\ell \text{ oil}} \times \frac{1 \text{ day}}{6 \ \ell \text{ polymer}} \times \frac{1 \text{ year}}{365 \text{ days}} \approx 30 \text{ years}$$

This is approximately equal to the plant lifetime. Therefore, it may be unnecessary to install a unit that will not be needed for 30 years, and more economical routes (e.g. partial replacement of oil) may exist. For example, the replacement of 60 ℓ/day of oil would suffice to stabilize the 10% polymer concentration without on-stream reprocessing. It is recognized that oil will degrade, and at a rate that could be substantially greater than that predicted. If this were the case, then the use of the FMU would be necessary for proper function of the system.

The FMU and UMU are ancillary devices in the TES subysstem. Off-normal operation of the FMU (e.g. clogging of filters) can be handled by the manual diversion of the circulating TES fluid from the FMU. Any other failure or leak in the FMU can be handled similarly until it is effectively repaired. Presumably, the repair could be accomplished within a time to prevent degradation products from accumulating in the TES fluid, reducing TES performance.

4.2.4 Desuperheater

A desuperheater is employed to lower the steam temperature during the TES changing cycle. The desuperheater reduces the peak temperature of the receiver steam from 510°C to about 343°C by injecting water into the superheated steam. As a result, the thermal degradation of the TES fluid due to contact with hot metal parts is reduced. Should the desuperheater fail, not only will the oil undergo significant cracking but it may also achieve its autoignition temperature of 404°C. A failure of the desuperheater will raise the peak temperature of the steam in the heat exchanger. However, the temperature at which the steam will condense will not change, since that is fixed by the steam pressure. For the heat exchanger to reach temperatures above normal therefore requires not only that the desuperheater fail, but also that all or part of the heat exchanger tubing be dry and exposed to dry (unsaturated) steam. Depending on the design, desuperheater failure is most likely to lead to above normal rates of degradation of oil due to excessive wall temperatures only when the TSU is fully charged or nearly so. The degradation may occur at other times if the heat exchanger is designed in a way which leads to poor steam circulation and local hot-spots. In either case, however, the maximum rate of heat input to the TSU is unchanged unless the normal practice is to use subcooled rather than saturated liquid for the desuperheater. That possibility will depend on how the TES and steam generation equipment are integrated. Even if such were the normal practice, the rate of heat input would increase only modestly. Consequently no dynamic analysis has been performed. Consideration should be given to the use of a thermal sensor at the steam exit of the desuperheater and to the provision of manual valving able to divert the steam from the TSU. Since the maintenance schedule of the desuperheater is not specified, failure may result from an accumulation of chemical deposits or particles in the water spray nozzles.

4.2.5 Heat Exchangers

Conventional shell and tube heat exchangers are used to transfer heat from the incoming steam to the TES fluid, and to extract heat from the TES fluid to generate steam for the turbine. The mixing of water and oil, leading to rapid water vapor generation and damage to the heat exchanger, is a potential source of worker hazard. Another potential hazard arises from tube conversion on the water side. Although relatively large amounts of water will overload the UMU, water is not considered detrimental to fluid life (1). To prevent these problems, McDonnell-Douglas recommends daily walk around inspections of these heat exchanger assemblies and monitoring for water in the vented gases in the UMU for detection of small leaks.

Other failures might include oil flow failures during the discharge cycle, permitting liquid water to reach the steam turbines. Consideration should be given to use of a dropout drum to prevent fluid reaching the turbine blades, subsequently causing their erosion and possible release as missiles.

As was suggested in the previous sections, a continuous inspection process is suggested to reduce the probability of serious problems from developing. Routine operating precautions are appropriate for this unit. Since maintenance and operational personnel will be in the TES operating area continusouly, protective garments and eye cover should be mandatory. Exclusion zones should be properly labeled, and maintenance should be performed only in those areas which have cooled down well below possible burn hazard limits. The McDonnell-Douglas document includes these recommendations and suggests that containment aresa and barriers be constructed to restrict to a minimum the area of exposure during a major fluid release. In addition, fire extinguishing equipment should be readily available due to the potential flammability of the TES fluid.

5. Safety Considerations of a Sodium Nitrate/Sodium Hydroxide Latent Heat TES System

5.1 Technical Basis

Thermal Energy Storage in an STPS can be accomplished using a medium which undergoes a nearly isothermal phase transformation. Modest storage volumes, low operating vapor pressures, and thermal energy extraction at a nearly constant temperature are among the characteristics which may make latent heat thermal energy storage attractive when compared to other alternative thermal energy storage schemes.

A number of attributes considered important in selection of a latent energy storage system have been suggested by a recent Sandia Laboratory review (1), including

- a high heat of fusion, heat capacity and thermal conductivity
- low material vapor pressure at elevated temperature
- minimum decomposition over the system lifetime
- the inadvertant contamination of the storage system will not result in a hazardous situation and can be easily and economically reversed
- components are not toxic during any phase of operation
- minimum of physical and chemical interaction between the storage medium and the containment system

and

- a storage medium which is relatively inexpensive

At the present time, a TES system utilizing 99 wt% $NaNO_3$ and 1 wt% NaOH developed by Honeywell (18) appears to be among the most favored, based on these considerations for near-or medium-term application. Since its documentation is relatively complete, the Honeywell design was selected for this safety evaluation.

5.2 Design Description

As developed by Honeywell, the basic features of the TES subsystem for a 10 MWe STPS pilot plant include the following design capabilities

- 345 MWt-hr storage capacity
- Salt phase change materials $NaNO_3$ - NaOH
- Array of 5 insulated cylindrical tanks
- Ground level storage

- Modular heat exchangers
- Self-regulating control system
- 40 year storage life
- One hold up storage tank

The performance of the subsystem is specified as

- Deliver 7 MWe net for 6 hours
- 6.5 MPa/307°C discharge cycle (28°C supheat)
- 12.0 MPa/510°C charge cycle
- Heat losses less than 0.35% per hour when fully charged

In the storage concept proposed as the baseline design, the mixture 99 wt% $NaNO_3$ and 1 wt% NaOH undergoes a solid/liquid phase change as the thermal energy storage material. The medium may also be heated above the homogeneous melt temperature, thus performing as a hybrid sensible/latent heat system. For the thermal storage (charging) cycle, the latent heat of condensing steam inside a bundle of tubes is transferred to the salt outside the tubes as the salt's latent heat of fusion. Bulk heat transfer occurs by convection and thermosyphon effects. Discharging heat is transferred from the freezing salts surrounding circular tubes to water circulated through these tubes. The water generates steam vapor and is supplied to a steam drum separator where saturated steam is withdrawn. The crystallized salt is removed from the outside of the tubes by mechanical scrapers. The configuration of the pilot plant design is given in Figure 7. The systems can be partitioned into these areas as follows:

1. Thermal Storage Unit (TSU): an insulated rectangular tank containing the salt material. The tank supports the vaporizer and condenser modules, as well as the vaporizer scraper mechanisms and instrumentation.

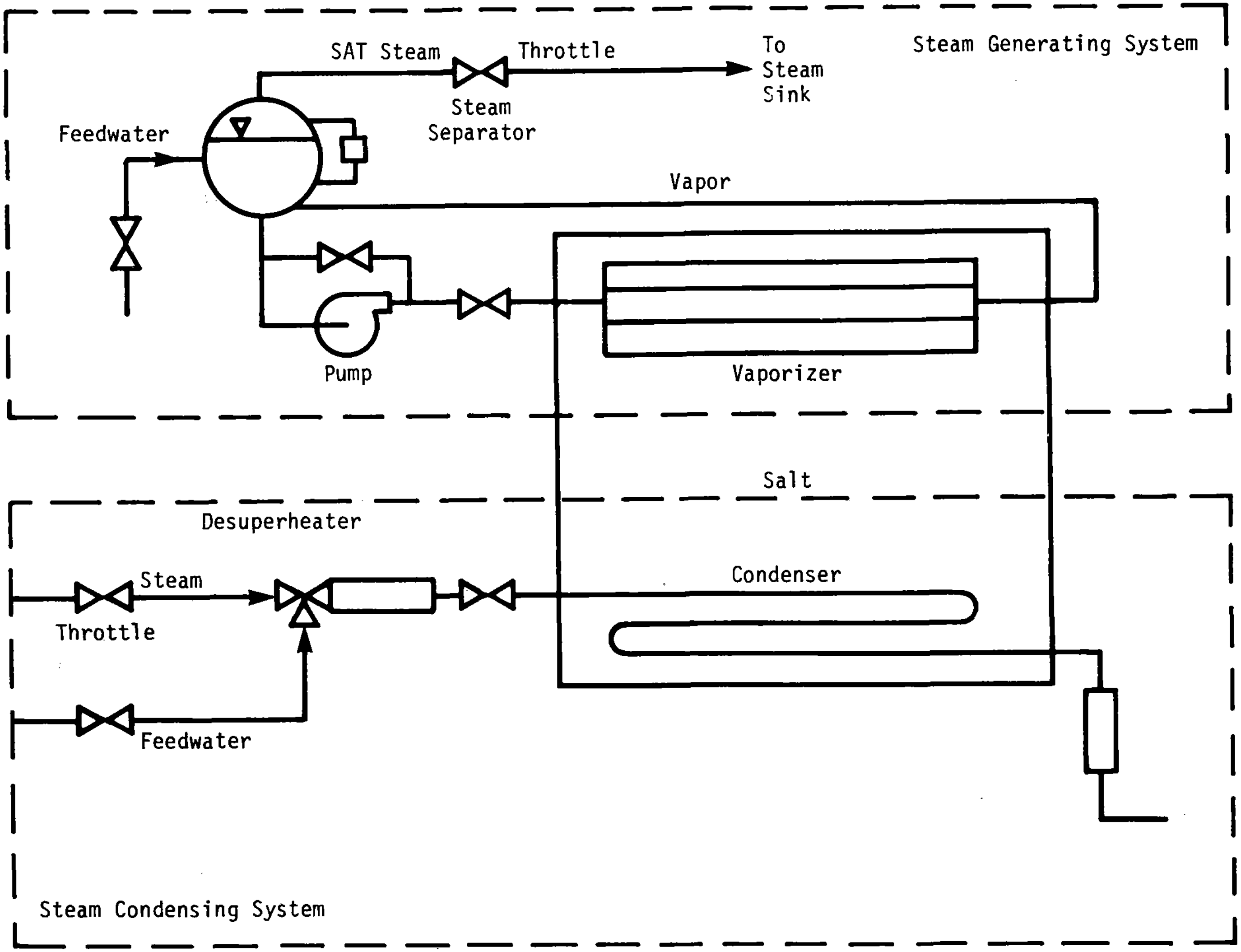


Figure 7

Latent Heat TES System Pilot Plant Design

2. Steam Generating System: consists of the vaporizer, steam drum separator, pump, controls, valves and piping. Feedwater is pumped through the vaporizer and saturated steam is withdrawn from the steam drum. The steam throttle valve places the same type of demand on the system as the turbine throttle valve.

3. Steam Condensing System: consists of a condenser module, desuperheater, and steam trap, with control valves and piping. The desuperheater provides saturated steam to the condenser module and the condensed steam is discharged from the condensate receiver. The steam throttle valve loads the system in the same manner as the Receiver Steam Generator supply valve.

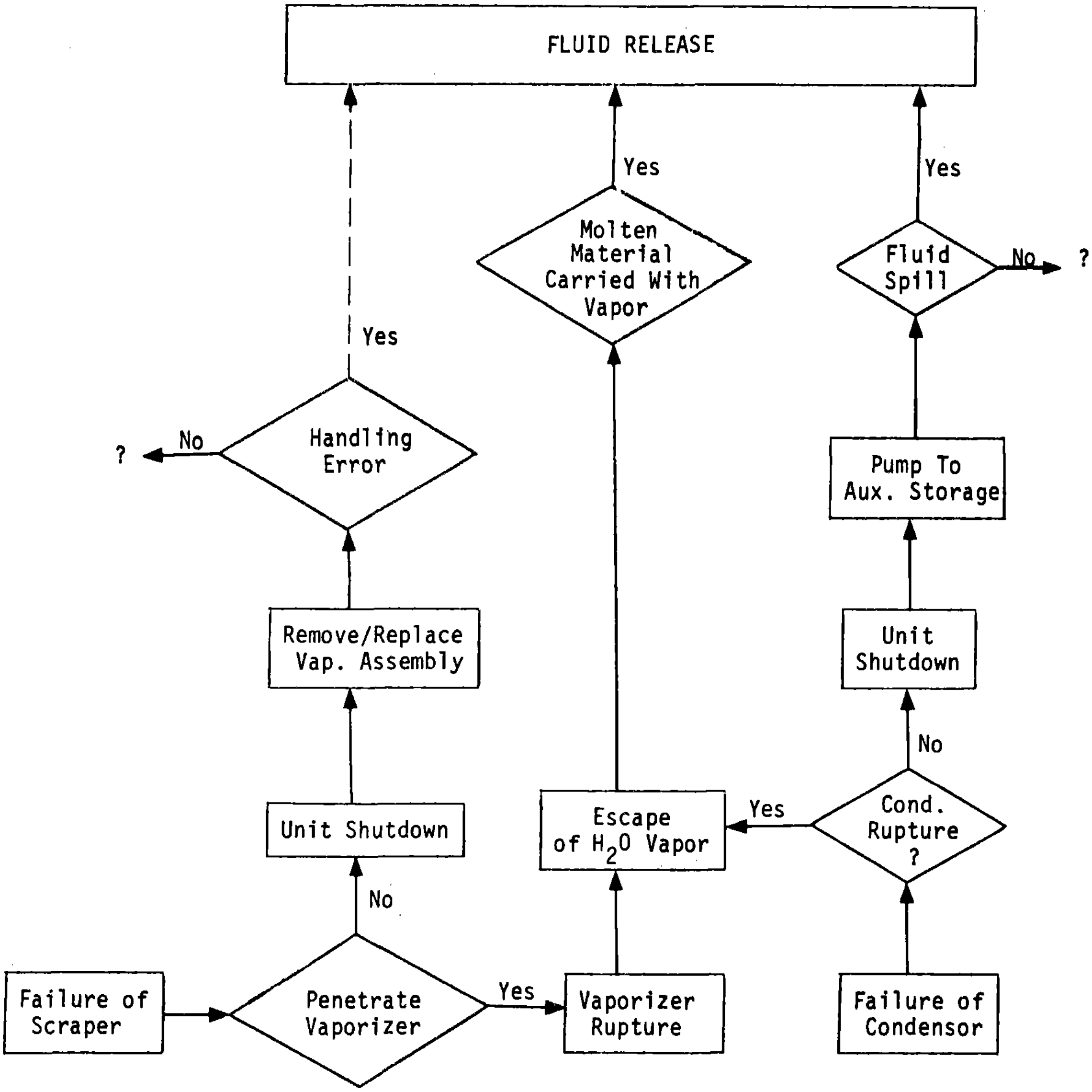
5.3 Identification of Fluid Release Modes

Figure 8 presents the fluid release pathways identified for this latent heat subsystem. Principle initiating events include scraper and condenser failures. As shown in this Figure, there are three major pathways leading to fluid release.

The first two event sequences proposed may be initiated by a failure in the scraper system. The scraper system is the least technically developed component of the storage system. If the scraper failure does not rupture the vaporizer apparatus, the storage unit can be shut down and the entire scraper/vaporizer system may be removed and repaired or replaced. A nominal amount of fluid may be released due to normal or off-normal handling of the subassembly. If the scraper penetrates the vaporizer, however, ingress of water or steam into the salt mixture can occur.

Figure 8.

Latent Heat Storage Fluid Release Event Tree



Escape of water or steam into the salt mixture may also be possible if rupture of the condenser, initiated by a unit failure (e.g. pipe corrosion, pipe fatigue), occurs. Any water ingressing into the salt mixture will rapidly flash to steam due to the decrease in the pressure of the water/steam stream and high temperature of the molten salt. Salt material may be entrained with escaping gas, giving rise to a fluid release. To control possible discharges, Honeywell proposes to restrain the moveable main cover vents by hooks, chains, or hinges on one side. A personnel and equipment exclusion zone would be required to minimize the potential hazard during venting. As specified in the preliminary design, it appears that water or steam ingress into the salt is not explosive, and poses minimal worker hazard other than from contact with hot fluid. The salt apparently will not react with the water vapor, and should readily return to its anhydrous state. However, the water vapor needs to be properly vented to avoid a severe pressure increase from occurring.

The third event sequence occurs when the condenser fails. Since the condenser is at the bottom of the tank, the salt may have to be removed to another tank if damage occurs to the condenser guide structure. Potential release hazards may be caused by transfer of the hot salt as well as contact hazard with fluids at or above 300°C. It should be possible to effect such a transfer with acceptable safety hazard to personnel, assuming that appropriate precautions are observed. Potential problems of freezing and plugging may lead to additional worker hazards.

The mitigating measures suggested by Honeywell may be adequate for preventing serious damage or injury (8, pp. 2-44). It is suggested that proper orientation be made of rotating shafts, scraper drives and other devices to avoid spraying molten salt from the tank. Workers should be required to wear protective clothing and full length face shields when performing tasks near the molten salt storage medium. Since the salt is highly oxidizing causing rapid burning of exposed combustible materials, equipment which can come into direct contact with the molten salt must be nonflammable. Another consideration is that condenser leakage can cause the rapid movement of bubbles to the tank surface, releasing water vapor. This discharge of steam not only increases the pressure above the liquid in the tank but can also disperse salt around the tank. Therefore, an exclusion area for equipment and personnel is recommended. Vaporizer/scraper assemblies are manufactured and installed for easy detachment and replacement. Finally, the system design does not require gas blanketing or ullage space, which may reduce both cost and safety hazards.

It appears that for any liquid-solid latent heat system, a workable and reliable scraper system must be demonstrated for near-term applicaton.

6. Safety Considerations of an SO_2/SO_3 Thermochemical TES System

6.1 Technical Basis

Thermochemical energy storage is being examined as another means by which heat energy from a high temperature STPS may be stored. The thermochemical storage technique, although in a conceptual state, presents several advantages over other types of TES subsystems. These advantages include greater energy storage densities, increased fluid transportability, capability to store reactants and product for long periods at near ambient temperatures, and lower raw material costs.

Several investigations (52-54) of energy storage using an SO_3/SO_2 gas dissociation reaction have been made. A summary of the major technical issues and conceptual design results was published by EPRI (33).

The SO_2/SO_3 thermochemical storage concept involves the storage of thermal energy as the chemical heat of reaction of sulfur dioxide. In the heat generation mode, sulfur dioxide and oxygen combine to form sulfur trioxide.

$$SO_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow SO_3\ (g) \qquad (3)$$

This reaction is exothermic, releasing 1.2 MJ/kg reagent. In the heat consumption mode, SO_3 is decomposed to SO_2 and $\tfrac{1}{2}\ O_2$ within the solar receiver, via the reaction.

$$SO_3\ (g) \rightarrow SO_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \qquad (4)$$

Both the forward and reverse reactions in this system require a catalyst to achieve useful reaction rates.

6.2 Design Description

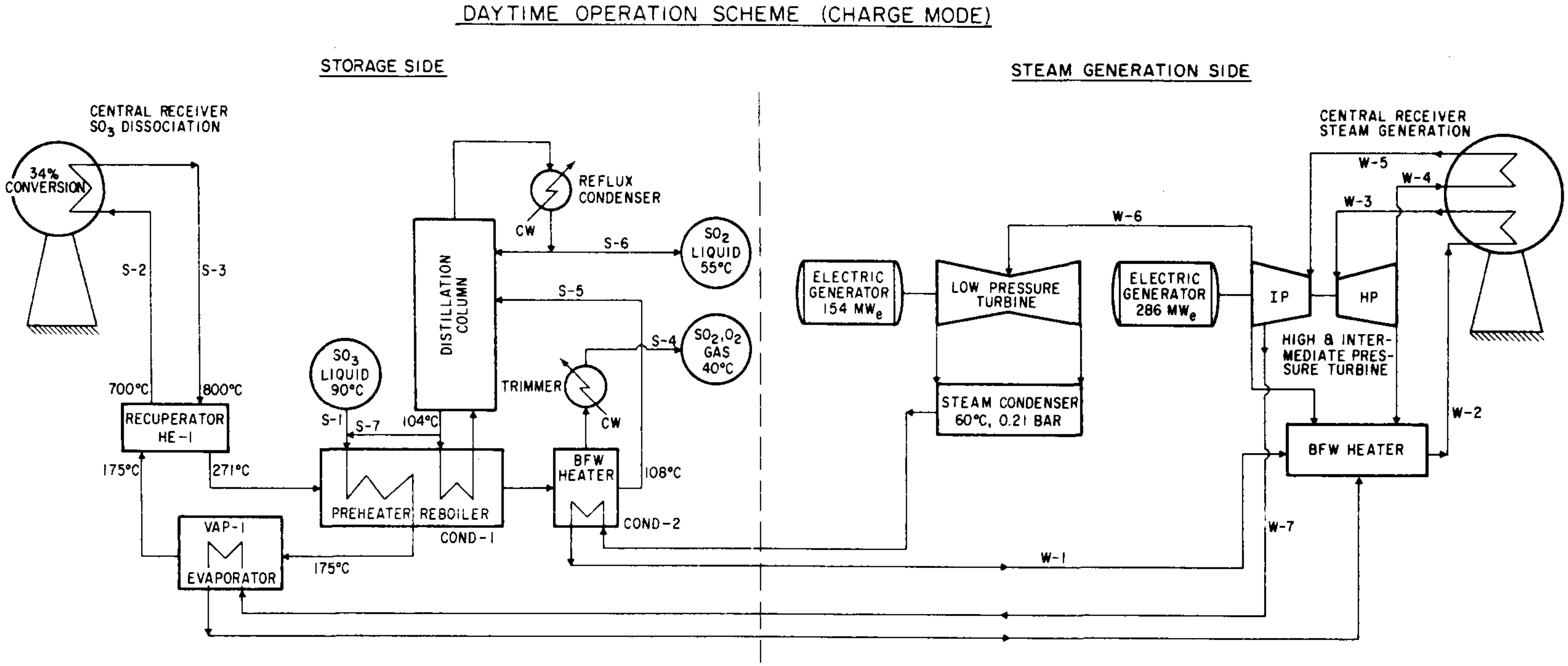
A design concept for an SO_3/SO_2 thermochemical energy storage system has been developed based on the Boeing gas-cooled receiver design (55). This design integrates energy storage with power generation. During the day-time cycle, steam is generated in a central receiver solar power plant (56). In addition, in a separate tower SO_3 is cracked partially to SO_2 and $\tfrac{1}{2}\ O_2$ within receiver tubes contaning a catalyst. At night, steam for electric power generation is produced from heat generated by a catalytic oxidation of SO_2 similar to the process used for commercial sulfuric acid production. This system has a well documented design and appears easily incorporated into an STPS. Therefore, it was chosen for this safety assessment. An explanation of the operation of this design follows.

6.2.1 Daytime Cycle

The operation of the daytime cycle is depicted in Figure 9. The SO_3-rich liquid from the product separator at 104°C is combined with the liquid SO_3 stored at 10 bar and 90°C. This combined fluid stream, at a temperature of 100°C, is pressurized to 40 bar and sent through a preheater condenser (Cond-1). Here it is heated by the exit gas stream from the recuperator (HE-1) to 175°C. This stream then enters the evaporator (VAP-1) where it is vaporized by steam from the intermediate pressure turbine. SO_3 vapor flows from the evaporator through a recuperator (HE-1) where it passes counter current to hot gases leaving the receiver. The heat exchanged in the recuperator raises the stream temperature to 700°C. This superheated SO_3 vapor then flows into the central receiver. The SO_3 vapor is heated to a temperature greater than 800°C in central receiver tubes containing a catalyst for the dissociation reaction. The preliminary calculations (34) assume that by using the central receiver as a high temperature reactor approximately 34 percent of SO_3 is converted to SO_2 and $\frac{1}{2}$ O_2.

After exiting the central receiver the effluent stream which consists of 57% SO_3 plus the products SO_2 and O_2, passes back through the series of heat exchangers described above. The stream passes in turn through the recuperator (HE-1) and the condenser (Cond-1). In this latter unit SO_3 is heated as a liquid from 110°C to 175°C, and the distillation column reboiler is supplied with the heat needed for operation. The cracked stream is then sent to condensor-2, where boiler feedwater (BFW) is preheated.

Approximately 85% of the effluent stream from the receiver is condensed to a liquid (SO_3 + SO_2) during this heat recovery process. The liquid is depressurized and fed to the distillation column operating at 10 bar, while the



MAIN STREAM DATA - SULFUR (S) SYSTEM

Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7
Flow (kmole/sec)	1.94	5.76	6.72	1.06	5.66	1.84	3.82
Composition* (mole%)							
SO_2	1.0	1.0	28.7	8.2	32.1	99.0	1.0
SO_3	99.0	99.0	56.8	1.2	67.9	1.0	99.0
Temperature (°C)	90	700	800	40	108	55	104
Pressure (bar)	10	40	40	40	40	10	10
State (L-liquid; G-gas)	L	G	G	G	L	L	L

MAIN STREAM DATA - WATER (W) SYSTEM

Stream	W-1	W-2	W-3	W-4	W-5	W-6	W-7
Flow (kg/sec)	287	426	426	374	374	287	66
Temperature (°C)	140	243	538	316	538	349	427
Pressure (bar)	4	208	167	37	33	8	15
State (W-water; S-steam)	W	W	S	S	S	S	S

*Oxygen content makes the balance.

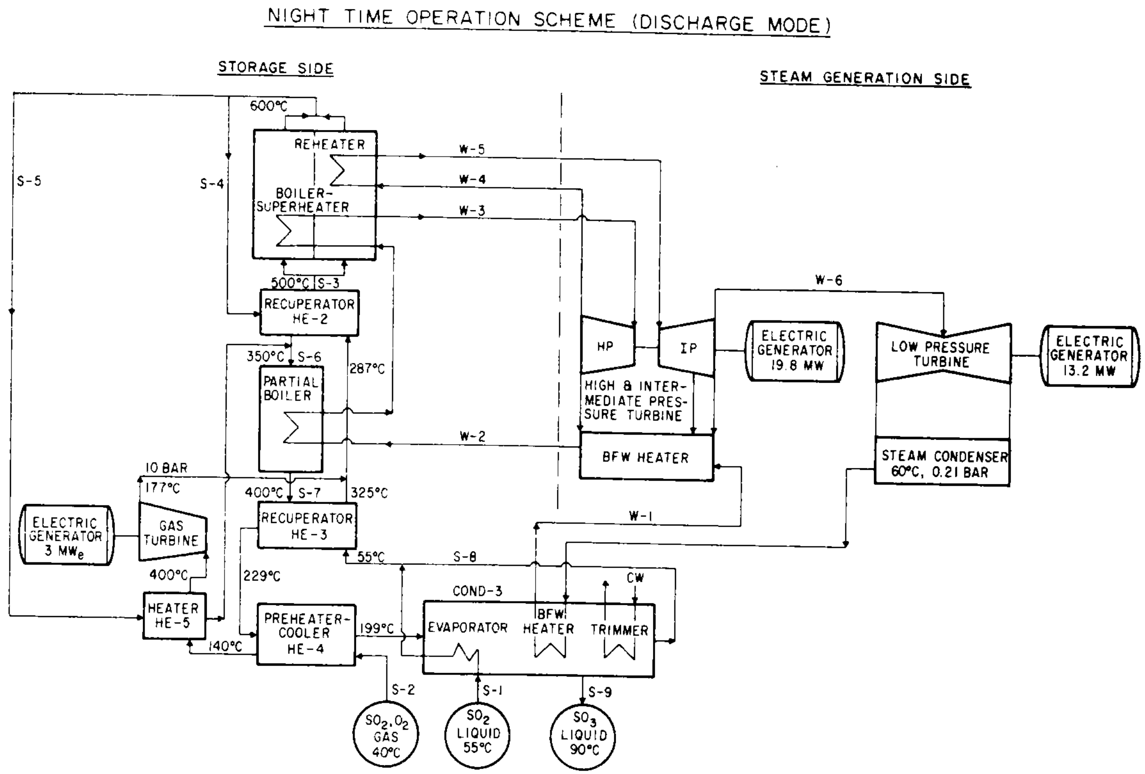
FIGURE 9. DAYTIME OPERATION SCHEME OF THE SO_2/SO_3 THERMOCHEMICAL TES SUBSYSTEM (FROM REF. 34)

uncondensed gas, mainly O_2, is stored at 40 bar and 40°C. The distillation column separates the SO_2 from unconverted SO_3. The liquid SO_3 can then be recycled back to the solar reactor, while the liquid SO_2 is removed from the top of the distillation column and stored at 10 bar and 55°C.

6.2.2 Nighttime Cycle

The operation of the nighttime cycle is depicted in Figure 10. The chemical heat generating process used to produce steam in the absence of solar insolation is accomplished in the following manner. Liquid SO_2 at 10 bar and 55°C and gaseous O_2 and SO_2 at 40 bar and 40°C are withdrawn from their respective storage containers. Liquid SO_2 is sent to the evaporator (Cond-3), and then mixed with a recycled stream of O_2, SO_3, and SO_2. (This latter stream is the vapor from the partial condensor in which SO_3 is removed as liquid.) This mixture is heated in a recuperator (HE-1) to 325°C. In parallel, the O_2-SO_2 gas stream at 40 bar passes through heat exchangers (HE-4 and HE-5), raising its temperature to 400°C, and through a gas turbine for power generation. The temperature and pressure of the gas at the turbine outlet is 177°C and 10 bar. These two streams are then mixed, and have a temperature of 307°C. The combined stream flows through a recuperator (HE-2) where the temperature is elevated to 500°C.

The gas mixture then enters two parallel V_2O_5 catalytic reactors operating at temperatures in the range used in commercial sulfuric acid catalytic oxidation reactors, 500-600°C. The heat produced by the exothermic reaction to form SO_3 removed by steam flowing through tubes in the fixed-bed catalytic reactors. One of the reactors functions as a boiler and superheater for the stream flowing from the partial boiler, while the other reactor is used as a reheater. The superheater/boiler raises the steam temperature to 538°C (1000°F), and reheater takes 37 bar (530 psi) steam from 316°C (600°F) back to 538°C (1000°F). 85% conversion of SO_2 to SO_3 is specified, and the



MAIN STREAM DATA - SULFUR (S) SYSTEM									
Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Flow (kmole/sec)	0.96	0.53	1.50	0.80	0.26	1.06	1.00	0.007	0.993
Composition* (mole%)									
SO_2	99	8.2	66	11	11	11	1.3	1	1.4
SO_3	1	1.2	1	83	83	83	98	9	98.6
Temperature (°C)	55	40	500	600	600	350	400	40	90
Pressure (bar)	10	40	10	10	10	10	10	10	10
State (L-liquid; G-gas)	L	G	G	G	G	G	G	G	L

*Oxygen content makes the balance.

MAIN STREAM DATA - WATER (W) SYSTEM						
Stream	W-1	W-2	W-3	W-4	W-5	W-6
Flow (kg/sec)	24	29	29	26	26	24
Temperature (°C)	140	243	538	316	538	349
Pressure (bar)	4	208	167	37	33	8
State (W-water; S-steam	W	W	S	S	S	S

FIGURE 10. NIGHTTIME OPERATION SCHEME OF THE SO_2/SO_3 THERMOCHEMICAL TES SUBSYSTEM (FORM REF. 34)

effluent stream is at 600°C. The reported temperature limit for the V_2O_5 catalyst is about 625°C.

Recovery of the sensible heat of the products leaving the reheater takes place in the recuperator (HE-2). There the hot products pass countercurrent to the reactants, and are cooled to 350°C. The cooled products then enter a partial boiler which is cooled by water from the BFW heaters. In the partial boiler most of the remaining SO_2 is converted to SO_3 in a catalytic bed operating at 400°C. The product gas is then cooled using a series of heat exchangers (HE-3 and HE-4) and the stack of condensers (Cond-3). Most of the SO_3 will be condensed (Cond-3) for storage as liquid at 10 bar and 90°C. The uncondensed gas, containing mostly O_2 and unreacted SO_2 will be recycled back to the reactant feed stream.

6.2.3 Steam Generation

The steam generation process is separated into two modes, a daytime mode, in which steam is generated directly in a central receiver, and a nighttime mode, in which steam generation is achieved by using the SO_3/SO_2 storage system. During daytime operations, steam production drives a high pressure steam turbine of the type used in conventional fossil fuel power plants. At night the storage system provides steam which drives the same high pressure steam turbine at 8 to 20 percent of the day time power.

6.3 Hazards Assessment

As a precursor to the identification of hazards, the distinctive features of this SO_3/SO_2 TES subsystem should be noted. These include:

- A catalytic process is proposed for the exothermic reactions similar to the one used for industrial sulfuric acid production. Once developed, the catalyst for the thermochemical storage reaction will be placed in tubes in the receiver.
- The entire system is pressurized (from 10 to 40 bars).
- Liquid and gaseous storage is required.
- Heliostats focus solar radiation on a Boeing design cavity receiver which directs the radiation onto heat exchanger tubes containing either energy generating fluid or storage fluid.
- A high pressure steam turbine of the type used in fossil fuel power plants is employed for the water/steam cycle. In addition, a gas turbine is used to lower the pressure of the SO_2-O_2 gas stream during storage discharged, and in the process provide a generating capacity of 3 MWe.

Both SO_2 and SO_3 are hazardous chemicals due to their corrosive nature and potential for forming acid when combined with water. Other hazardous materials include the V_2O_5 catalyst, for which a threshold limit value (TLV) of 0.1 to 0.5 mg/m^3, depending on the condition of the V_2O_5, has been established. These chemicals, however, are handled routinely in the sulfuric acid industry. The scale of operation is somewhat larger than normal for sulfuric acid plants. The SO_3 night time formation rate (0.993 kmol/sec) corresponds to about 8500 tons/day of sulfuric acid, while sulfuric acid plants are generally in the 1000-1500 tons/day range. This difference in itself may not be that significant, and appropriate experience is likely to exist for properly handling the quantities needed for the TES process (21).

Since personnel can come into direct contact with the TES working fliuds during a fluid release accident, it is appropriate to discuss the potential hazards from a TES fluid release. After exposure to the environment, SO_2 can undergo the following reactions:

$$SO_2\ (g) + \tfrac{1}{2}\ O_2\ (air) \rightarrow SO_3 \qquad (5)$$

$$SO_3 + H_2O\ (air\ or\ rain) \rightarrow H_2SO_4 \qquad (6)$$

These reactions also occur during routine SO_2 release, such as in power plants, and result in acid rain formation. On release, both SO_2 and SO_3 can lead to personnel hazards through inhalation and direct skin or eye contact. Equipment damage by corrosion may occur, possibly initiating other hazards. The threshold limit values (TLV) are quite low, 13 mg/m^3 for SO_2 and 1mg/m^3 for H_2SO_4. Safety and treatment procedures therefore should be readily available throughout the plant.

6.3.1 Phenomenology of SO_2/SO_3 Release

The release of fluid from this (34) thermochemical TES subsystem constitutes serious environmental and worker health and safety problem. The phenomenology of external release of fluid(s) is therefore addressed. In considering the fluid release modes of the system, it is presumed that operation and maintenance standards adequate to assure acceptably low fluid release rates during normal TES operation are established. Thus it becomes necessary to determine the events leading to the off-normal operation of this system. In this way the potential pathways for fluid release which may not have been accommodated by the designers' standards can be distinguished, and the potential for mitigating measures evaluated. Figures 11 thorugh 13 are the event trees showing the primary events pathways resulting in fluid release from off-normal operation of the SO_2/SO_3 system. Principle initiating events include catalyst failures, mechnical equipment failures, and off-normal events in ancillary subsystems.

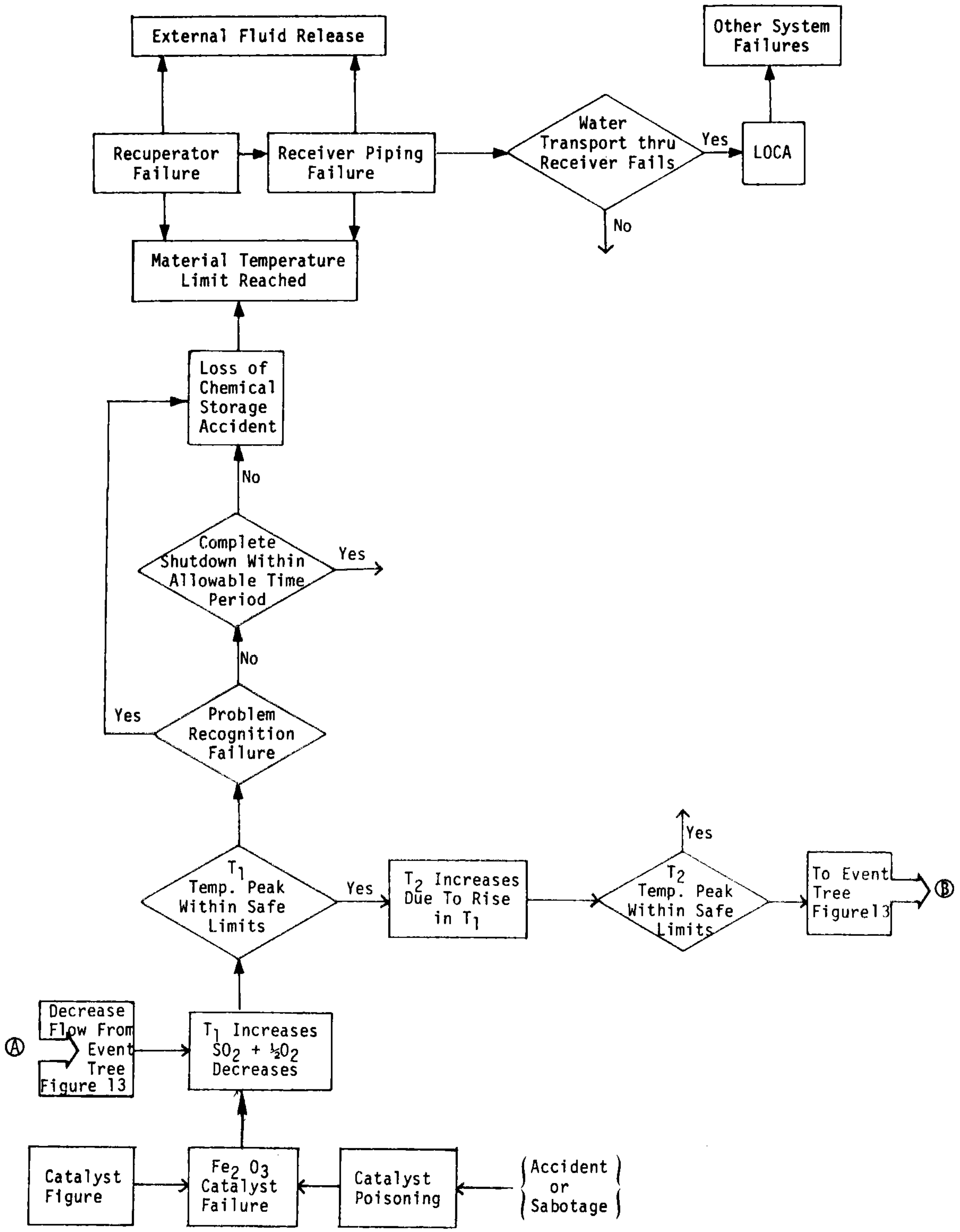


Figure 11. Fault Tree of Daytime Cycle Catalyst Failure

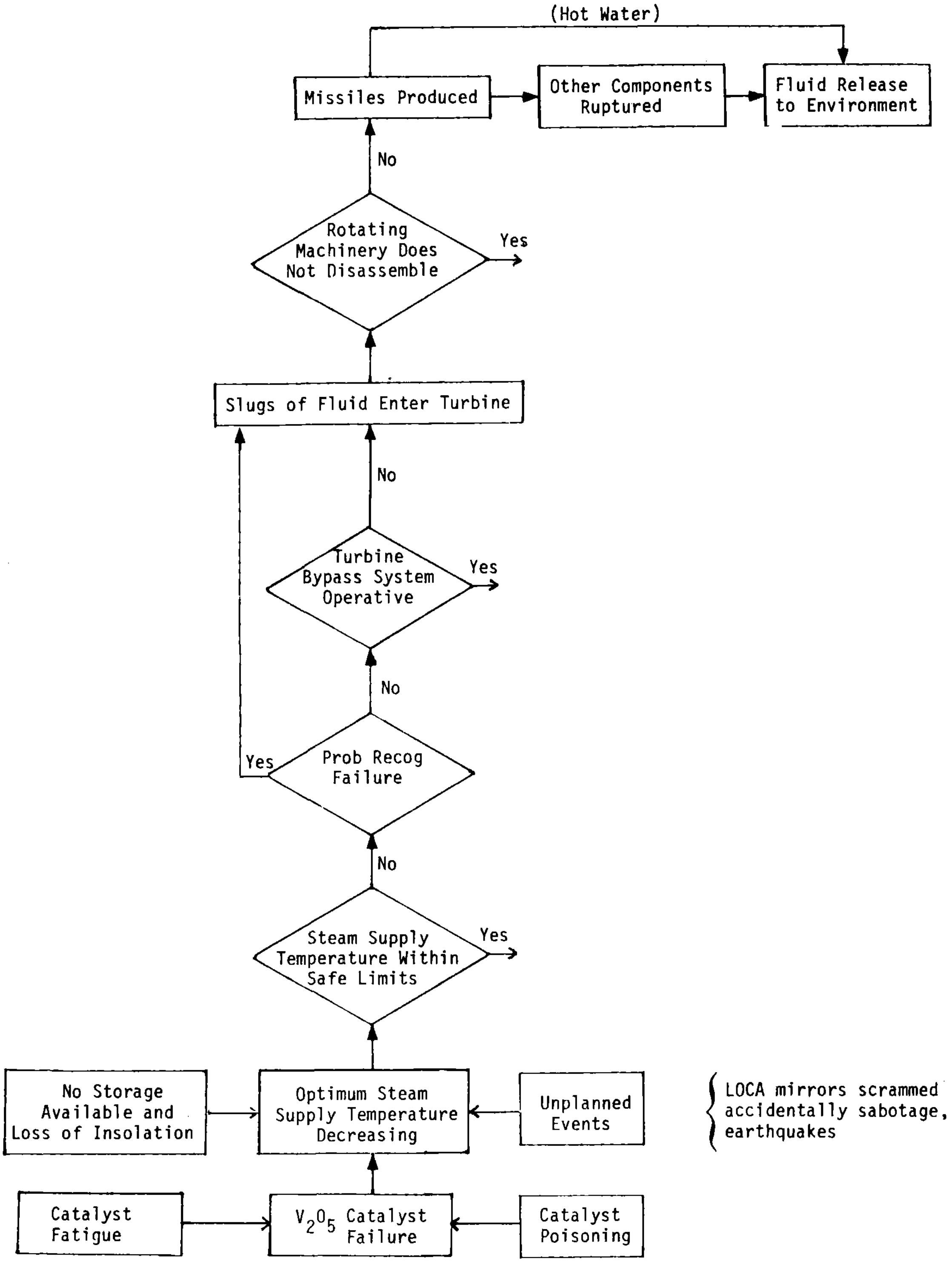


Figure 12. Fault Tree of Nighttime Cycle Catalysis Failure

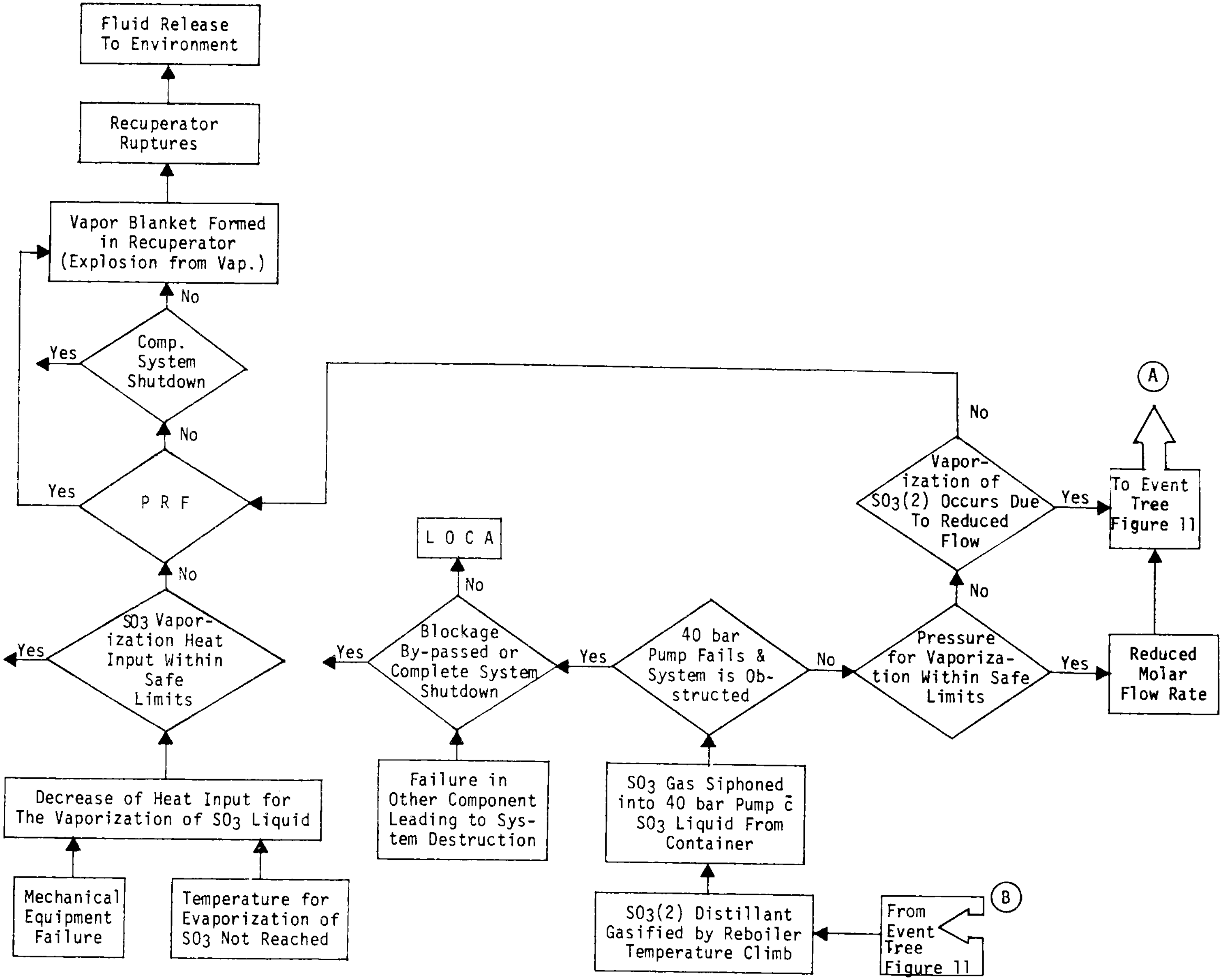


Figure 13. Fault Tree of Recuperator Failure

Figure 13 is the fault tree for a condition where the SO_3 decomposition catalyst fails to perform its function. This loss of activity of the catalyst can arise from any of several phenomena common to catalytic systems, including: loss of surface area by sintering, loss of active material by evaporation or other transport mechanisms (e.g., chemical reaction) and poisoning of active sites by contaminants (33). For the purpose of analysis, it is presumed that the catalyst fails unexpectedly, and this failure is undetected for some period of time. This situation might occur if a catalyst poison is accidentally or intentionally (e.g., by sabotage) introduced. It is presumed that either the failure of the catalyst is detected due to a lack of sensory monitors or poor sensor performance, or is detected, but an inappropriate or inadequate response is made.

6.3.2 Analysis of Receiver Behavior Due to a Catalyst Failure

In the absence of a catalyst, the chemical means of removing heat from the receiver ceases, and only a sensible heat mechanism remains. The significance of this may be found by comparing the thermal inputs to sensible and chemical heats under normal conditions as described in Figure 11. The sensible heat increases the temperature of the gas flowing at a rate, $\dot{n}$, of 5.72 k mol/sec from 700 to 800°C. The gas is taken as pure SO_3 with a heat capacity, C_p, of 76.0 J/molK at 1000K. The thermal input to sensible heat, Q_s, then is approximately

$$Q_s = \dot{n}\ Cp\ \Delta T \simeq 5.72\ \frac{\text{kmol}}{\text{sec}} \times 76.0\ \frac{\text{J}}{\text{moTK}} \times (800\text{-}700°\text{C}) = 43.5\ \text{MW} \qquad (7)$$

During passage through the receiver, 1.87 kmol/sec of SO_2 is formed, as calculated from the compositions and flow rates of the inlet and outlet streams. The heat of the reaction to form SO_2 from SO_3 is 97.6 kJ/mol at 1000K, hence the thermal input to chemical heat, Q_c is

$$Q_c = \dot{n}_{SO_2}\ \Delta H_f^\circ \doteq 1.87\ \frac{\text{kmol}}{\text{sec}} \times 97.6\ \frac{\text{kJ}}{\text{mol}} = 182.6\ \text{MW} \qquad (8)$$

In the absence of a catalyst, this latter heat must be shunted to sensible heat and to thermal losses from the receiver. For both reasons the gas temperature must rise. The increased temperature of the receiver output stream may overheat the heat exchanger (HE-1) and lead to its failure and to SO_3 release. The time required for this process is considered in Section 6.

The following calculations have been performed to describe quantitatively the above conditions. Figure 14 is used to obtain an approximate value of SO_3 stream temperatures exiting the receiver.

The recuperator and central receiver are shown in Figure 15. It is assumed to be a closed system with the exception of heat and mass inputs as indicated. In the recuperator, the net energy gained by the inlet stream equals that lost by the outlet stream. For a constant heat capacity:

$$\dot{n}\, C_p\, T_3 - \dot{n}\, C_p\, T_4 = \dot{n}\, C_p\, T_1 - \dot{n}\, C_p\, T_2 \qquad (9)$$

where $\dot{n}$ is the molar flow rate Thus:

$$T_3 - T_4 = T_1 - T_2 \qquad (10)$$

Note that during operation with a catalyst the composition and molar flow rate of inlet and outlet streams are quite different. However,

$$C_{p,\, SO_3} \simeq C_{p,\, SO_2} + \tfrac{1}{2}\, C_{p,\, O_2} \qquad (11)$$

hence the thermal mass is little affected by reaction. Q_{net}, the net solar heat input to the receiver, is a function of receiver outlet temperature, T_1, and is also the enthalpy gained by the stream as it proceeds through the receiver and recuperator system. The enthalpy

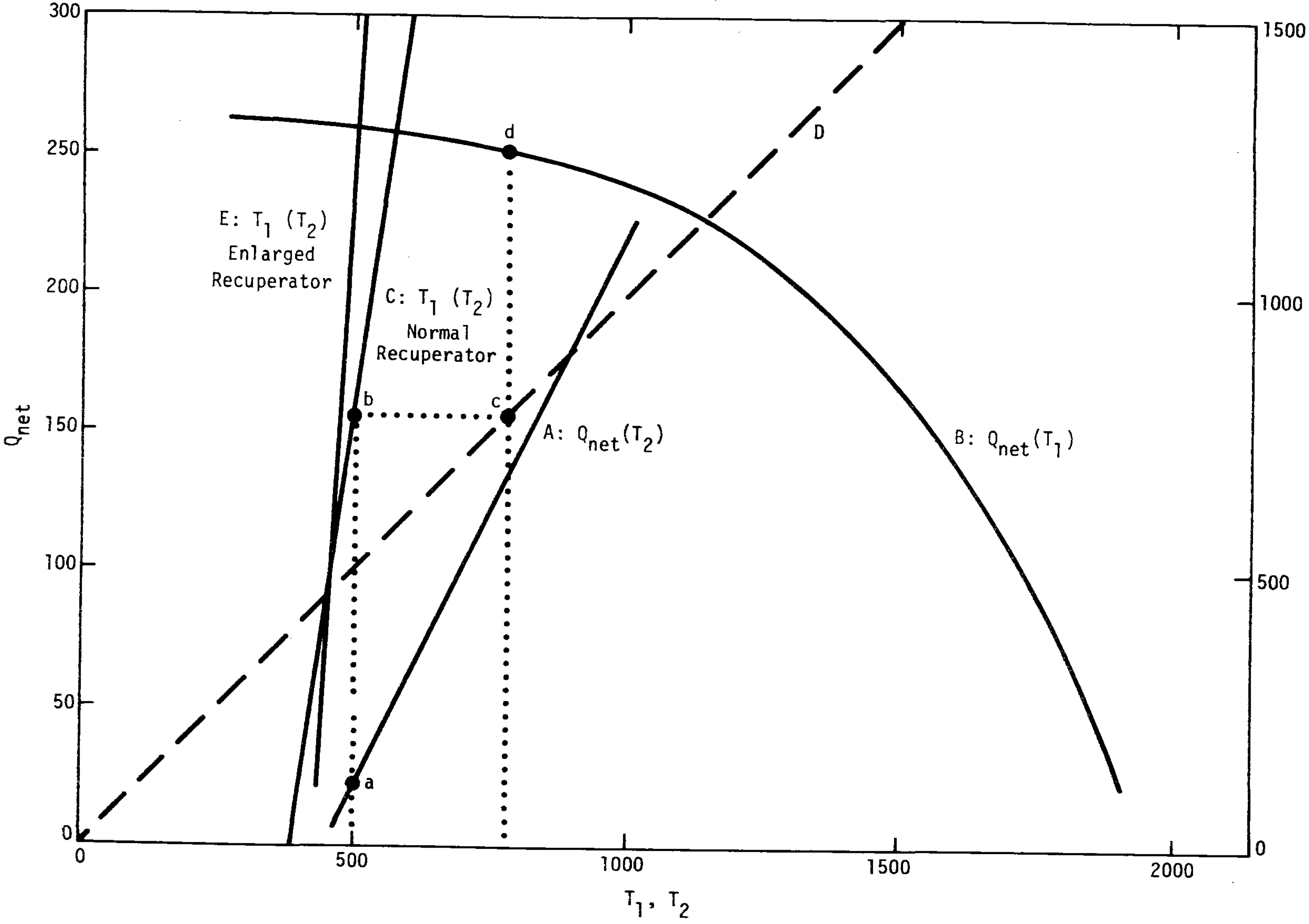
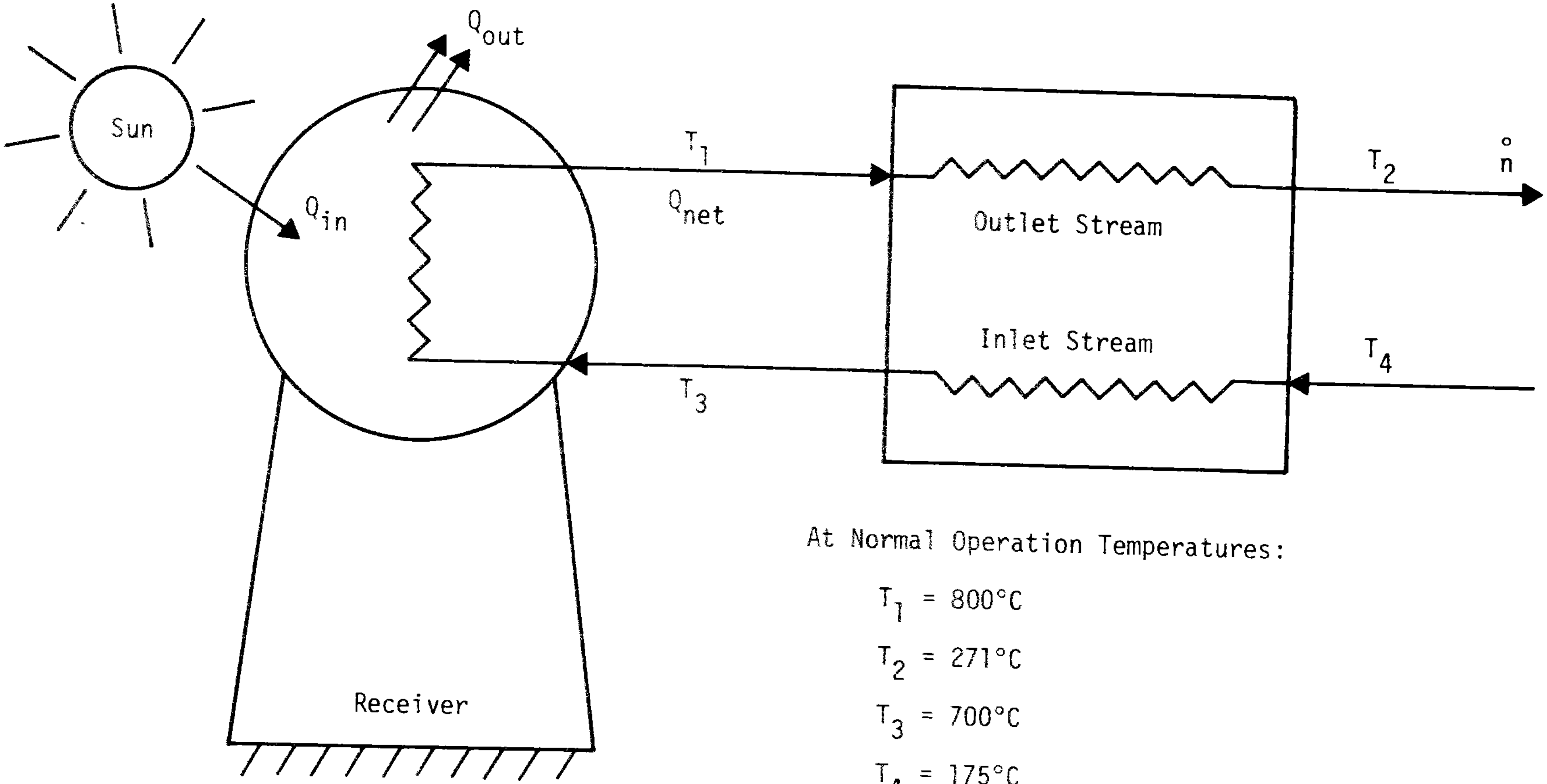


Figure 14. Thermal Balances in the Receiver and Recuperator During Normal and Off-Normal Catalyst Operation



At Normal Operation Temperatures:

T_1 = 800°C
T_2 = 271°C
T_3 = 700°C
T_4 = 175°C
$\overset{\circ}{n}$ = molar flow rate

Figure 15. Schematic Representation of Receiver-Recuperator Thermal Operation

change for SO_3 from T_4 (450 K) may be found from the literature (57). We neglect the 1% SO_2, since it has a similar enthalpy increase. Thus:

$$Q_{net} \cong \dot{n}\,[(H^\circ - H^\circ{}_{298})_T - (H^\circ - H^\circ{}_{298})_{450}] \qquad (12)$$

where $(H^\circ - H^\circ{}_{298})_T$ is the SO_3 enthalpy change from 298 K to T. Q_{net} as a function T_2 is shown as line A in Figure 14. This value of Q_{net} includes only sensible, not chemical, heat input, and therefore applies only in the absence of reaction.

Next, we approximate the thermal losses from the receiver, Q_{out}, as a function of receiver output temperature. Various thermal losses are specified (55) at a normal operating temperature, T_o, of 1089 K. These are scaled as:

$$Q_{out}\ (\mathrm{MW})\ 10.3 + 23.4 \left(\frac{T_1}{T_o}\right)^4 + 6.3 \left(\frac{T_1 - T_a}{T_o - T_a}\right) + 2.1 \left(\frac{T_1}{T_o}\right) \qquad (13)$$

where T_a is the ambient temperature, ∿323 K, and the terms on the right hand side of equation (13) give thermal losses due to reflection, reradiation, convection, and conduction, respectively. The gross thermal input is 273 MW, hence:

$$Q_{net} = 273 - Q_{out}\ (T_1) \qquad (14)$$

Q_{net} is graphed as line B in Figure 14. At steady state Q_{net} as found from lines A and B should be equal when T_1 and T_2 are also steady state valves.

The link between T_1 and T_2 is found through the analysis of the recuperator. The thermal flow across the recuperator heat transfer surface is proportional to the mean temperature difference between the two fluids. We equate the enthalpy change of either stream to the heat flow between streams as:

$$\dot{n}\ C_p\ T_1 - n\ C_p\ T_2 = UA\ (T_2 - T_4) \qquad (15)$$

where

U = heat transfer coefficient across recuperator surface

A = area of recuperator heat transfer surface

Equations (9) and (10) have been used to eliminate T_3. Since $\frac{UA}{\dot{n}\ Cp}$ is essentially constant for a given system,

$$\frac{T_1 - T_2}{T_2 - T_4{}^\circ} = \frac{T_1{}^\circ - T_2{}^\circ}{T_2{}^\circ - T_4{}^\circ} \qquad (16)$$

where the superscript ° denotes normal (with reaction) operating conditions. It is presumed that the inlet temperature $T_4{}^\circ$ is constant and equal to 175°C (452 K) even without reaction, since the evaporator upstream controls this temperature. For the design considered (34),

$$\frac{T_1 - T_2}{T_2 - T_4{}^\circ} = \frac{T_1{}^\circ - T_2{}^\circ}{T_2{}^\circ - T_4{}^\circ} = \frac{1089-550}{550-452} = 5.68 \qquad (17)$$

or:

$$T_1 = 6.68\ T_2 - 2556 \qquad (18)$$

This is shown as line C in Figure 14. Equation (18) provides the needed link between T_1 and T_2. To facilitate graphical analysis, a reflection line D, is used along with line C to find allowed pairs of temperatures T_1 and T_2 on either axis of Figure 14. At one such pair, the two values of Q_{net} will be equal. A typical calculation is shown in Figure 14. A value of T_2 = 500 K is assumed, giving Q_{net} (T_2) (point a) and T_1 (T_2) (point b). T_1 is reflected on line D to give Q_{net} (T_1) (point d). The two values of Q_{net} are seen not to be equal. The solution is found iteratively as T_1 = 1789 K, T_2 = 650 K, and Q_{net} = 75 MW_t. This is shown as Case I in Table 6. The limiting temperature of 1789 K is above the design limits for conventional steels and inconels.

Table 6

Effects of Recuperator Size and Catalyst State on Daytime Operation of SO_2/SO_3 TES System

	Reaction	T_2-T_4	T_1	T_2	T_4	Q_{in}	Q_{out}	Q_{net}
CASE I	Yes	100 K	1118 K	550 K	450 K	$273MW_t$	$45MW_t$	$227MW_t$
	No	100 K	1790 K	650 K	450 K	$273MW_t$	$198MW_t$	$75MW_t$
CASE II	Yes	50 K	1275 K	500 K	450 K	$273MW_t$	$64MW_t$	$209MW_t$
	No	50 K	1895 K	537 K	450 K	$273MW_t$	$241MW_t$	$32MW_t$

CASE I is with the normal recuperator

CASE II is with the enlarged recuperator

6.3.3 Effect of Recuperator Efficiency

In the design considered, an SO_2/SO_3 mixture with a mole fraction ε of SO_2 is reacted. For 1 mole of $SO_2 + SO_3$ reacted, a product mixture is formed via the equation

$$\varepsilon\, SO_2 + (1-\varepsilon)\, SO_3 \rightarrow x\, SO_2 + y\, SO_3 + z\, O_2 \qquad (19)$$

where x,y, and z are the moles of SO_2, SO_3, and O_2 in the product mixture. Equilibrium will limit the amount of reaction, and is governed by the equilibrium constant

$$K = \frac{P_{SO_3}}{P_{SO_2}\, P_{O_2}^{\frac{1}{2}}} = \frac{y}{x} \left(\frac{x+y+z}{zP}\right)^{\frac{1}{2}} \qquad (20)$$

where P is the total pressure. Sulfur and oxygen conservation requires that

$$x + y = 1 \qquad (21a)$$

$$2x + 3y + 2z = 3-\varepsilon \qquad (21b)$$

From equations (20) and (21) the solutions are

$$y = 1 - x \qquad (22a)$$

$$z = \tfrac{1}{2}(x - \varepsilon) \qquad (22b)$$

$$\left(\frac{x}{1-x}\right)^2 (x - \varepsilon) = \frac{2}{PK^2}\left[1+\tfrac{1}{2}(x-\varepsilon)\right] \qquad (22c)$$

Standard tables are available (57) which give K as a function of temperature. From this data and equation (22) the equilibrium mole fraction of SO_2, $x/(x+y+z)$, may be found using the values (38) $\varepsilon = 0.01$ and $P = 40$ bar. This is shown in Figure 16 along with the operating point of the design under consideration.

Note that the design point assumes a particular degree of approach to equilibrium. Due to limitations on catalyst activity or size of catalyst receiver cavity, it may be necessary to operate farther from the

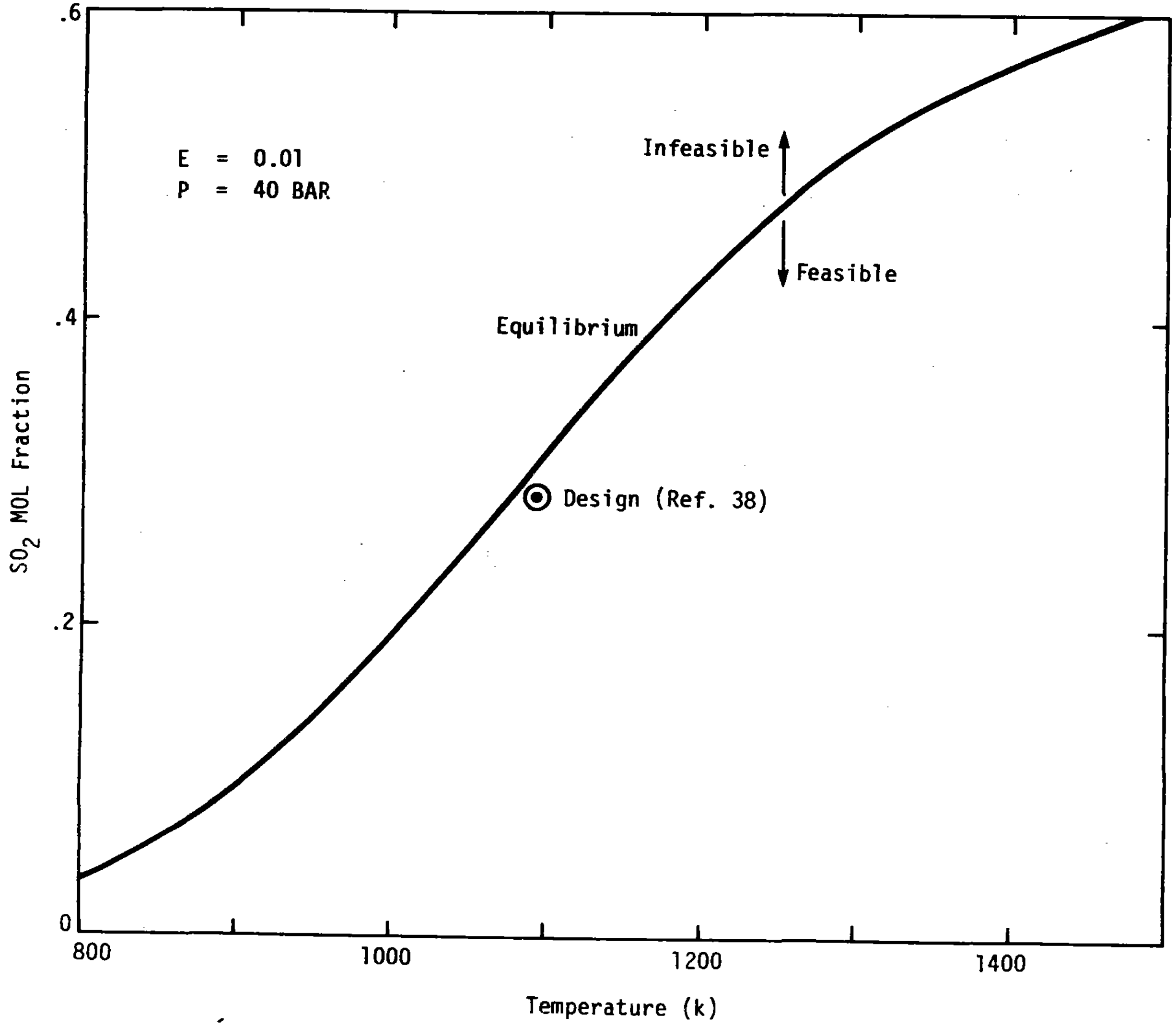


Figure 16. Equilibrium Constraint on Receiver Catalyst Operation

equilibrium line. This can be done by raising the temperature. To do this requires a larger recuperator. As an example, the same calculation done in section 6.3.2 can be repeated except that T_2 will be taken as 500 K. Thus, the temperature difference between streams, T_1-T_2, is 50 K, rather than 100 K in Case I. Assuming no change in composition, the thermal input is found from thermodynamic tables (51) to be 209 MW. From line A, Figure 14, this requires T_1 = 1275 K. For such a recuperator, equation (18) is replaced in accordance with equation (17) by

$$T_1 = 16.5\ T_2 - 6975 \tag{23}$$

This is shown as line E, in Figure 14. The solution is T_1 = 1895 K, T_2 = 537 K, and Q_{net} = 32 MW. This is listed as Case II in Table 6. Thus Q_{net} is further reduced and T_1 is a very high temperature.

6.3.4 Effect of Change in Flow Rate Through Recuperator

Flow from the reboiler will be approximately two-thirds of the total flow to the recuperator. Higher than normal values of T_2 may cause the reboiler to go dry and the feed pump to vapor-lock. If this liquid flow to the evaporator were to stop, the operating conditions in the receiver and recuperator would change. Using 1/3 $\dot{n}$ as the flow rate, the thermal balance on the recuperator becomes:

$$(T_1 - T_2) = \frac{UA}{1/3\ \dot{n}\ C_p}\ (T_2 - T_4°) \tag{24}$$

resulting in a new recuperator relation:

$$\frac{1}{3}\ \frac{T_1 - T_2}{T_2 - T_4°} = \frac{T_1° - T_2°}{T_2° - T_4°} \tag{25}$$

For $T_4°$ = 450 K and T_2 = 550 K, as in Case I, T_1 = 2250 K. Thus a large increase in the temperature through the receiver is expected to occur.

A conclusion from these calculations is that the same property which allows the recuperator to boost temperatures for enhanced kinetic rates may also make the entire system more vunerable should the catalyst fail.

6.3.5 Effect of Catalyst Activity on TES Subsystem Integrity

Other pathways for fluid release are related to catalyst failure and flow interruptions; these pathways are depicted in Figure 17. Either of these factors can, as shown in the previous section, lead to a reduced ability to transport heat away from the receiver tubes, eventually resulting in tube failure. There are various ways for SO_3 to come in contact with the water, including the melting of receiver tubes. In this event, both water and SO_3 are released in the receiver, with the expected formation of liquid H_2SO_4. This acid is extremely corrosive, and could lead to other material failures. System shutdown prior to recuperator failure would certainly reduce the potential consequences, but disassembly for repair could still be required. As we have indicated earlier in Figure 1, the act of repair itself can be a precursor to increased worker hazards. Finally, even if the temperature of SO_3 gas at the outlet of the receiver does not exceed design limits of the recuperator, gas at elevated temperatures leaving the recuperator may cause design temperatures to be exceeded in other components downstream, such as the boiler.

In summary, SO_3 decomposition catalyst failure represents an event which can cause the endothermic reaction to undergo thermal runaway. This situation then leads up a decision tree with further possibilities for influencing other system failures and the subsequent release of fluid.

6.3.6 Mechanical Failures in the TES Subsystem

Figure 13 details events leading to fluid release as a result of missiles penetrating containment materials. The missiles may be produced as a result of the disassembly of the rotating machinery of the high pressure steam turbine. The turbine failure can occur for several reasons, including excessive liquid in the fluid fed to or from the turbine. This event might occur if the catalyst from the night cycle, which liberates heat from SO_2 and oxygen, fails to perform adequately, and the failure is undetected, or is detected but the system is not protected. Catalyst failure can be imagined to occur for the same reasons mentioned in the discussion of SO_3 decomposition catalyst failure. The failure of the catalyst for this exothermic reaction is formally analogous to an endothermic reaction. The result is that the reaction is self-limiting, and temperatures needed to produce steam, estimated from information in Figure 11 to be 362 ± 10°C, are not obtained.

Another event pathway presented in Figure 12 leads to the inability to generate steam in the receiver subsystem due to a temporary loss of insolation during the day or the occurrence of events causing such a loss (e.g. seismic events, sabotage). The loss of steam generation may, for several reasons, coincide with either the failure to recognize the problem or a lack of capability to employ the TES or to protect the turbine from condensed fluid. Techniques exist for protection of the turbines under certain circumstances, but their use is not specified in the TES subsystem design.

Figure 13 assesses the problems which contribute to the loss of integrity of the recuperator (HE-1). One potential hazard is the generation of vapor blanketing if liquid is vaporized in the recuperator.

Depending on the recuperator design, the liquid might exert stresses on the recuperator as its unsteady boiling progresses. A developing vapor blanket might cause tube or weld failures to occur, leading to fluid release. Several events may initiate this condition. First, mechanical or equipment problems associated with pumps, evaporators, preheaters, or reboilers can cause the heat input for the vaporization of SO_3 to be insufficient. The heat input may also be reduced if the vaporization temperature is not reached at the evaporator due to a failure of the steam system. Possible operator actions during events leading to rupture of the recuperator may make it possible to ameliorate the more serious consequences. For example, if the system can be shut down within an allowable period of time, minimum damage can be expected and dealt with accordingly.

A vapor blanket in the recuperator (HE-1) might result from vaporization of SO_3 liquid distillant (Figure 11). This may occur if the dissociation catalyst were to partially deactivate. The recuperator would receive gas at higher than normal temperature from the receiver, and in turn, so would the reboiler. There the SO_3 distillant would be vaporized. Gas, instead of liquid, might return to the SO_3 supply line depending on the mechanical design. This gaseous SO_3 might then cause the 40 bar pump to vapor lock, either reducing or blocking further flow of fluid into the evaporator (VAP-1). If blockage were to occur and system shutdown not produced, the lack of coolant in the dissociation tubes of the receiver may result in tube failure, representing a situation previously discussed. On the other hand, if reduced molar flow rate was the result, then there is the possibility that pressure conditions of the fluid entering VAP-1 would not be proper for vaporization and a liquid would enter the recuperator

(HE-1). Another alternative might be that the reduced molar flow rate causes the temperature of the receiver exit stream to be increased, leading to a failure of the recuperator.

6.4 Dynamics of SO_2/SO_3 Recuperator and Receiver

The effect of a flow or reaction failure on the integrity of the SO_2/SO_3 recuperator and receiver will depend on the dynamics of the system. The equations for even the steady state behavior, equations (12), (13), (14), and (16), are non-linear, so the full solution of the dynamic response will be complicated. The following approximate analysis is used to establish a scaling of characteristic times.

6.4.1 Dynamic Model of the SO_2/SO_3 Recuperator

A schematic of the recuperator is shown in Figure 17. There are three layers, with the middle metal layer of thickness w and the two outer gas layers of thickness w_g. Assuming that thermal conduction is negligible in the direction parallel to flow, the thermal transport equations are:

$$\frac{\partial}{\partial t}(\rho(x)C_p w_g T)_{out} = -\frac{\dot{n}CpL}{A}\frac{\partial T_{out}}{\partial x} - 2U(T_{out} - T_w) \qquad (26)$$

$$\frac{\partial}{\partial t}(\rho(x)C_p w_g T)_{in} = \frac{\dot{n}CpL}{A}\frac{\partial T_{in}}{\partial x} - 2U(T_{in} - T_w) \qquad (27)$$

$$\frac{\partial}{\partial t}(\rho CwT)_w = 2U(T_{out} + T_{in} - 2T_w) \qquad (28)$$

where ρ is the density, C and C_p the wall and gas heat capacities, and the other variables are defined in Figure 17. Equation (26) balances the

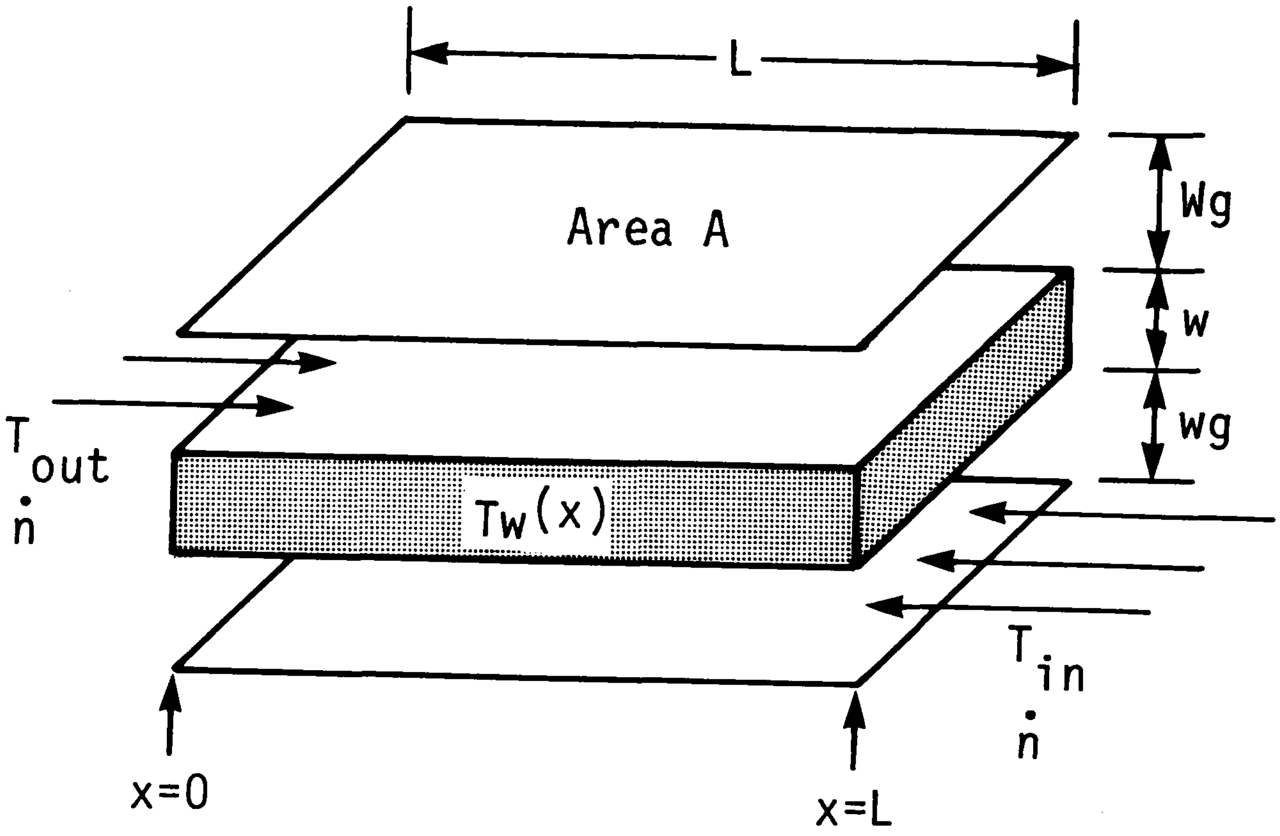


Figure 17

Recuperator Schematic

time variation of the thermal content of the outlet gas stream (left hand side) to the convective transport (right hand side, first term) and the conductive transport to the wall (right hand side, second term). (Note that the use of 2U as the gas-to-wall heat transfer coefficient in all of equations (26) - (28) will give an overall heat transfer coefficient U.) In equation (27), the time variation of thermal content is again equated to the convective and conductive transport terms. The differences in sign between equations (26) and (27) arise because the inlet (outlet) stream flows in the negative (positive) x direction. Equation (28) is a thermal balance on the wall, assumed to be isothermal perpendicular to the gas flow.

The gas is assumed to obey the ideal gas law, so the gas density ρ is given by P/RT. Then if the system is isobaric and of constant heat capacity the left hand sides of equations (26) and (27) are identically zero. The molar flow rate will be presumed to vary about some average value $\dot{n}^\circ$. Then dimensionless variables are introduced as:

$$\tau = tU/\rho wC \tag{29a}$$

$$\chi = xUA/\dot{n}^\circ \, L \, C_p \tag{29b}$$

Then equations (26) - (28) become:

$$0 = \frac{\dot{n}}{\dot{n}^\circ} \; \frac{\partial T_{out}}{\partial \chi} - 2(T_{out} - T_w) \tag{30}$$

$$0 = \frac{\dot{n}}{\dot{n}^\circ} \; \frac{\partial T_{in}}{\partial \chi} + 2(T_w - T_{in}) \tag{31}$$

$$\frac{\partial T_w}{\partial T} = 2(T_{in} + T_{out} - 2\,T_w) \tag{32}$$

In these equations a lumped model is used, in that the flow rate changes in the two gas streams are assumed to be synchronous.

Equations (30) and (31) are non-linear, and may be put into appropriate form for linearization by assuming that temperatures may be written as:

$$T_i\ (\chi,\tau) = \bar{T}_i(\chi) + \tilde{T}_i(\chi)\ g\ (\tau) \qquad\qquad i = \text{in,out,w}$$

and that the flow rate may be written as:

$$\dot{n}\ (\tau) = \dot{n}^\circ\ (1 + \nu\ g\ (\tau))$$

For Fourier analysis, we take $g\ (\tau) = \exp\ (j\ \omega\ \tau\ )$, where $j^2 = -1$. Then equations (30), (31), and (32) may be partitioned into six equations by collecting terms of like order in g and by dropping second and higher order terms. These are:

$$0 = -\frac{d\bar{T}_{out}}{d\chi} - 2(\bar{T}_{out} - \bar{T}_w) \tag{33}$$

$$0 = \frac{d\bar{T}_{in}}{d\chi} + 2\ (\bar{T}_w - \bar{T}_{in}) \tag{34}$$

$$0 = \bar{T}_{in} + \bar{T}_{out} - 2\ \bar{T}_w \tag{35}$$

$$0 = \frac{d\ \tilde{T}_{out}}{d\chi} - \nu\ \frac{d\ \bar{T}_{out}}{d\chi} - 2(\tilde{T}_{out} - \tilde{T}_w) \tag{36}$$

$$0 = -\frac{d\tilde{T}_{in}}{d\chi} + \nu\ \frac{d\ \bar{T}_{in}}{d\chi} + 2(\tilde{T}_w - \tilde{T}_{in}) \tag{37}$$

$$(4 + j\omega)\tilde{T}_w = 2(\tilde{T}_{in} + \tilde{T}_{out}) \tag{38}$$

In equation (38) use has been made of the equality

$$\frac{dg}{d\tau} = j\omega g$$

The first group of three equations may be solved by noting that, from equation (35),

$$\bar{T}_w = \tfrac{1}{2}\ (\bar{T}_{in} + \bar{T}_{out}) \tag{39}$$

This may be substituted in equations (33) and (34) to eliminate $\bar{T}_w$. Defining

$$f_{\pm} = \bar{T}_{out} \pm \bar{T}_{in} \tag{40}$$

the equations become

$$\frac{df_+}{d\chi} = 0 \tag{41}$$

$$\frac{df_-}{d\chi} + 2f_+ = 0 \tag{42}$$

The solutions are found readily on application of appropriate boundary conditions. These will be taken as a constant temperature of the inlet stream at its entrance, i.e.

$$\bar{T}_{in}(\Lambda) = T_{in}^{\Lambda}; \quad \tilde{T}_{in}(\Lambda) = 0 \tag{43}$$

where

$$\Lambda = \chi(x=L) = \frac{UA}{\dot{n}^{\circ}C_p} \tag{44}$$

and a variable temperature of the outlet stream at its entrance, i.e.

$$\bar{T}_{out}(0) = T_{out}^{o}; \quad \tilde{T}_{out}(0) = \tilde{T}_{out}^{o} \tag{45}$$

Than the solutions of equations (33) - (35) are

$$\bar{T}_{out} = T_{out}^{o} - \frac{T_{out}^{o} - T_{in}^{\Lambda}}{1 + \Lambda}\chi \tag{46}$$

$$\bar{T}_{in} = \frac{\Lambda T_{out}^{o} + T_{in}^{\Lambda}}{1 + \Lambda} - \frac{T_{out}^{o} - T_{in}^{\Lambda}}{1 + \Lambda}\chi \tag{47}$$

Equation (39) may be used to find $\bar{T}_w$. Then equations (36), (37), (38), (46), and (47) may be simplified as

$$\frac{d\,\tilde{T}_{out}}{d\chi} + \frac{4 + j2\omega}{4 + j\omega}\,\tilde{T}_{out} - \frac{4}{4+j\omega}\,\tilde{T}_{in} = 2N \qquad (48)$$

$$\frac{d\,\tilde{T}_{in}}{dx} + \frac{4}{4 + j\omega}\,\tilde{T}_{out} - \frac{4 + j2\omega}{4 + j\omega}\,\tilde{T}_{in} = 2N \qquad (49)$$

where

$$N = \frac{\nu(T_{out}^{\,o} - T_{in}^{\,\Lambda})}{2\,(1 + \Lambda)} \qquad (50)$$

In analogy to equation (40), we define

$$F_{\pm} = \tilde{T}_{out} \pm \tilde{T}_{in} \qquad (51)$$

Applying this to equations (48) and (49) gives

$$\frac{dF_+}{d\chi} + 2F_- = 4N \qquad (52)$$

$$\frac{dF_-}{d\chi} + \frac{j2\omega}{4+j\omega}\,F_+ = 0 \qquad (53)$$

Differentiating equation (52) and substituting into (53) gives

$$\frac{d^2F_+}{d\chi^2} - 4\,r^2\,F_+ = 0 \qquad (54)$$

$$r^2 = \frac{j\omega}{4+j\omega}$$

The solutions of equations (52) and (54) are then

$$F_+ = 2A\cosh 2r\chi + 2B\sinh 2r\chi \qquad (55)$$

$$F_- = 2N - 2\,rA\sinh 2r\chi - 2r\,B\cosh 2r\,\chi \qquad (56)$$

Then from equations (51), (55), and (56)

$$\tilde{T}_{out} = N + (A - rB)\cosh 2r\chi + (B - rA)\sinh 2r\chi \qquad (57)$$

$$\tilde{T}_{in} = -N + (A + rB)\cosh 2r\chi + (B + rA)\sinh 2r\chi \qquad (58)$$

From the boundary conditions, equations (43) and (45),

$$\tilde{T}_{out}^{\,o} - N = A - rB \qquad (59)$$

$$N = A\,(\cosh 2r\Lambda + r\sinh 2r\Lambda) + B\,(r\cosh 2r\Lambda + \sinh 2r\Lambda) \qquad (60)$$

Using the identities

$$\cosh x + a \sinh x = \sqrt{1-a^2} \cosh (x + \tanh^{-1} a) \tag{61}$$

$$a \cosh x + \sinh x = \sqrt{1-a^2} \sinh (x + \tanh^{-1} a) \tag{62}$$

the solutions for A and B can be found as

$$A = \frac{(\tilde{T}_{out}{}^{o} - N) \sinh (2r\Lambda + \tanh^{-1} r) + \frac{N\,r}{\sqrt{1-r^2}}}{\sqrt{1-r^2} \sinh (2r\Lambda + 2 \tanh^{-1} r)} \tag{63}$$

$$B = \frac{\frac{N}{\sqrt{1-r^2}} + (N-\tilde{T}_{out}{}^{o}) \cosh (2r\Lambda + \tanh^{-1} r)}{\sqrt{1-r^2} \sinh (2r\Lambda + 2 \tanh^{-1} r)} \tag{64}$$

Equations (57), (58), (63), and (64) provide explicit forms for the spacially-dependent temperatures. Of principle interest is the temperature at the entrance to the receiver, $\tilde{T}_{in}(0)$, which from equation (58) is $A + rB - N$. From equations (63) and (64), $\tilde{T}_{in}(0)$ can be computed, and will link three aspects of the dynamic response of the recuperator, $\tilde{T}_{in}(0)$, $\tilde{T}_{out}(0)$, and N. It is convenient to cast this equation in the form

$$\tilde{T}_{in}(0) = G_1 \tilde{T}_{out}(0) + G_2 N \tag{65}$$

where

$$G_1 = \frac{\sinh 2r\Lambda}{\sinh (2r\Lambda + \tanh^{-1} r)} \tag{66}$$

$$G_2 = \frac{2\left[r - \sqrt{1-r^2} \sinh (2r\Lambda + \tanh^{-1} r)\right]}{(1-r^2) \sinh (2r\Lambda + 2 \tanh^{-1} r)} \tag{67}$$

6.4.2 Dynamic Model of the SO_2/SO_3 Receiver

The receiver thermal balance may be approximated by the equation

$$m_t \frac{d \tilde{T}_{out}(0,t)}{dt} = Q_{net}(T_{out}) - \dot{n}\, C_p[(T_{out}(0) - T_{in}(0)] - \eta\, \dot{n}\, \Delta H_{RXN} \tag{68}$$

where m_t is the receiver thermal mass, η the fraction of SO_3 cracked ΔH_{rxn} the heat of reaction, and Q_{net} the net solar thermal input. It is assumed in this equation that a lumped parameter model for the receiver is adequate, such that only a single temperature is needed to describe the receiver state. The second and third terms on the right hand side are sensible and chemical heat terms for the reacting fluid, respectively. As with other variables, we write

$$Q^{=}_{net} = \overline{Q}^{=}_{net} - Q^{='}_{net} \tilde{T}_{out} (0) g \qquad (69)$$

$$\eta = \bar{\eta} + \tilde{\eta} g \qquad (70)$$

It is expected that $Q^{='}_{net}$ will be positive, since the net thermal input generally decreases with increasing temperature. The sensible heat term is found from equations (46), (47), and (65). Defining

$$R = \frac{m_t}{\rho w C A} \qquad (71)$$

$$J = \Delta H_{rxn}/C_p \qquad (72)$$

$$T_s = \frac{\overline{Q}^{=}_{net}}{\dot{n}^{\circ} C_p} \qquad (73)$$

$$G_3 = \frac{Q^{='}_{net}}{\dot{n}^{\circ} C_p} \qquad (74)$$

equation (68) may be linearized and separated into two equations of zeroeth and first order in g. These are

$$0 = T_s - \frac{T_{out}^{o} - T_{in}^{\Lambda}}{1 + \Lambda} - \bar{\eta} J \qquad (75)$$

$$(1 - G_1 + G_3 + j\omega R \Lambda) \tilde{T}_{out} (0) = G_2 N - T_s \nu - J \tilde{\eta} \qquad (76)$$

6.4.3 Joint Dynamic Model of the SO_2/SO_3 Recuperator and Receiver

Equations (65) and (76) may be combined to give the joint response equation

$$(1 + G_3 + j\omega R\Lambda)\ \tilde{T}_{out}\ (0) = \tilde{T}_{in}\ (0) - \tilde{T}_s \nu - J\tilde{\eta} \qquad (77)$$

Equation (77) links outlet temperature variations, $\tilde{T}_{out}$ (0), with those at the inlet, $\tilde{T}_{in}$ (0), with flow variations, ν, and with reactivity variations, $\tilde{\eta}$. All three variations determine $\tilde{T}_{out}$ (0) in the same way within a scalar constant, with the time response determined by the factor $1 + G_3 + j\omega R\Lambda$. The coupling between $\tilde{T}_{out}$ (0), $\tilde{T}_{in}$ (0), and ν is given in equation (65). There may be other couplings, particularly due to the effects of chemical kinetics or due to variations in temperatures and flow rates. The response of $\tilde{T}_{out}$ (0) is therefore determined by a simple first order demodulation factor

$$\frac{1}{1 + G_3} \quad \frac{1}{1 + j\,\dfrac{\omega R\Lambda}{1 + G_3}} \qquad (78)$$

The characteristics dimensionless response time therefore is

$$\tau_c = \frac{R\Lambda}{1 + G_3}$$

and the dimensional time is found from equation (29) as

$$t_c = \frac{m_t}{\dot{n}^\circ\ C_p\ (1 + G_3)} \qquad (79)$$

This equation may be written as

$$1/t_c = 1/t_s + 1/t_G \qquad (80)$$

where

$$t_s = \frac{m_t}{Q'_{net}} \qquad (81a)$$

$$t_G = \frac{m_t}{\dot{n}^\circ\ C_p} \qquad (81b)$$

The characteristic times t_s and t_G are for receiver temperature changes due to thermally-induced solar input variations and reactant gas variations. Thus, all of the perturbation considered, including temperature, flow, and reactivity, have the same characteristic response, which is the rate for the interruption of fluid flow (IFF) considered in a separate report. For futher application, a fuller analysis of couplings between the quantities in equations (65) and (77) will have to be developed, including kinetic effects, for quantitative predictions of the response.

6.5 Recommendations for the SO_2/SO_3 Thermochemical TES Subsystem

Although the SO_2/SO_3 TES system is only conceptual in design, there are several design requirements that can be identified from the foregoing hazard analysis. We presume that it will be of importance to monitor the state of the system components if one is to determine when and if system failures have occurred. Temperatures can be measured continuously throughout the plant, and if diagnosis of problems cannot be obtained readily through temperature monitoring alone, measures such as continuous gas stream composition monitoring may be necessary. In addition to recognition of these methods, shutdown procedures and bypass methods must be designed for all probable system failures.

Since any size leak can be potentially hazardous for human safety, proper precautions, such as carrying respirators and protective clothing when near SO_2/SO_3 piping, should be implemented.

Materials should be readily available which can quickly neutralize minor leaks if one is to mitigate damage from fluid releases. For example, SO_3 will "smoke" upon exposure to normal atmospheric moisture. This sulfuric acid mist can be hazardous, but the reaction can be reduced by covering the area with an inert fluorocarbon oil mixed with glass bubbles (37). This would allow location of the source rupture to be detected before a significant amount of material was released and the "smoking" obscured the leak. At this preliminary stage, it is unclear what additional diagnostic procedures are available or will be needed.

Our safety analysis was conducted on a thermochemical energy storage process which has technical attributes that make its near- to medium-term implementation feasible. The investigation revealed that attention should be focused on complications which can develop from events causing the failure of catalysts, and other equipment and process failures resulting from the off-normal operation of the process. These complications include system disassembly for unscheduled repairs, fluid release due to handling errors, deleterious health effects caused by release of the fluids, creation of acid, and the breakdown of equipment. Once these problems are elucidated and generalized to other TES systems, decisions can be made to implement the most appropriate way to prevent or mitigate the adverse effects. These mitigating measures might be comprised of the use of neutralizing compounds, the use of protective gear in close proximity to exposed feed throughs, pump shafts and valve stems, the inclusion of monitoring devices in system processes to evaluate operating conditions, and the use of turbine systems able to tolerate the off-normal conditions.

6.6 Discussion

To maintain normal operation of a TES system, TES fluids should not be permitted to communicate with other systems or the environment, since

TES fluids can be flammable, toxic, corrosive, and environmentally dangerous when released external to a TES system. Therefore, measures msut be used to limit TES fluid release and minimize the exposure of personnel during operation and maintenance.

Some of the more general measures for preventing adverse effects from TES fluid release include: 1) the construction of annuli to restrict fluid release to small areas, 2) fire prevention systems which are easily engaged, 3) protective garments and respirators worn by maintenance personnel coming into contact with TES fluid to reduce exposure, 4) placement of TES vessels as far away from other systems as is practical, 5) inclusion of pressure release mechanisms, fire insulation materials, and emergency spill tanks in TES construction design, and 6) use of turbines with mechanisms for preventing liquids from entering and eroding their blades.

At the present time, sensible heat systems appear to be the most technically and economically feasible systems for integration into STPS facilities. However, other energy storage technologies may present unique advantages which can lower costs and reduce the chances of personnel exposure to energy storage fluids at an STPS facility. For example, the Honeywell (20) latent heat storage system appears to require less maintenance than either the Dayan (38) SO_2/SO_3 system or the McDonnell Douglas sensible heat system (54). However, the Honeywell scraper mechanism appears to need further development before the system can be employed. Thermochemical energy storage appears to be the furthest from implementation since an effective, acceptable SO_3 dissociation catalyst has not been developed.

This study has not attempted to estimate the probability of the risks associated with TES systems of the types investigated. It is unclear that such estimates could be made at this time due to the lack of actual operating processes. Further investigation into this area will be needed so that the frequency of occurrence of particular events leading to fluid release or other hazards can be estimated.

Attempts should also be made to determine the mechanism of disposal of the TES fluids after expiration of their service life. Problems may exist for long-term storage in the finding of appropriate burial sites or appropriate chemical conversion mechanisms.

Finally, the advantages and hazards of not using a TES system should be addressed. Repowering may represent the best way to employ solar thermal electric power generation.

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