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Report

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Molten Salt
Safety Study

MARTIN MARIETTA

Badger

MCR-80-1305
Contract 83-3638

Final Report   January 1980

**MOLTEN SALT
SAFETY STUDY**

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FOREWORD

This report was performed by Martin Marietta Aerospace under Contract 83-3638, Internally Insulated Thermal Storage System Development Program, from Sandia Livermore. Badger Energy Inc (subcontractor) was involved in this study.

CONTENTS

The considerations concerning safety in using molten salt (40% potassium nitrate, 60% sodium nitrate) in a solar central receiver plant are addressed in this report. The considerations are of a general nature and do not cover any details of equipment or plant operation. The study includes salt chemical reaction, experiments with molten salt, dry storage and handling constraints, and includes data from the National Fire Protection Association. The contents of this report were evaluated by two utility companies and they concluded that no major safety problems exist in using a molten salt solar system.

A proposed central receiver solar power plant is shown in Figures 1 and 2. The plant generates 300-MW electric power and is described in the Advanced Central Receiver Power System, Phase 1 Final Report (EG-77-C-03-1724d). The plant consists of nine collector fields, each with 7711 heliostats (mirrors) surrounding a central receiver (essentially a heat exchanger atop a 155-m (510-ft) concrete tower), a thermal storage area, and a conventional steam turbine/generator subsystem. Molten salt at 561 K (550°F) is pumped up to the receivers where it is heated to 839 K (1050°F) by the solar energy reflected from the heliostats. The molten salt is then pumped into salt/steam heat exchangers or storage tanks or both, as required. Steam leaving the heat exchangers enters a reheat turbine at 783 K (950°F) and 16.5 kPa (2400 psi) and produces a 300-MWe net output. The salt leaves the heat exchangers at 561 K (550°F) and is either returned to the receivers or sent to storage. The storage salt is used to keep the plant operating at night and during cloud interruptions.
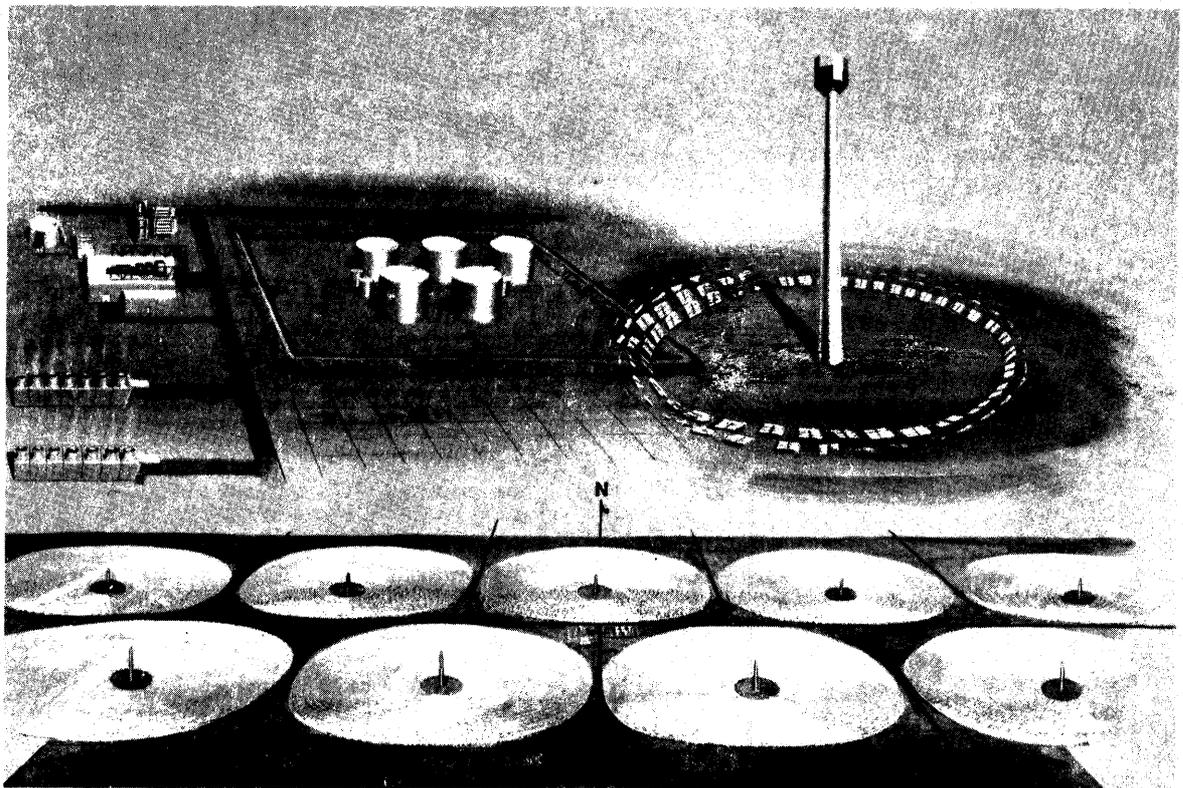

Figure 1 Artist's Concept of Solar Central Receiver Plant

7018.0
(23025'-0")

MODULE #5

℄ TOWER

POINT "A"

SEE ENLARGED PLAN

152.4
(500')

MODULE #4

MODULE #6

262 ROAD
(25')

697.99
(2290'-0")

697.99
(2290'-0")

1403.6
(4605'-0")

PLAN
NO SCALE

N

WATER TREATMENT AREA
30.4 m 30.4 m
(100' 100')

EXCHANGER AREA

SLEEPERWAY

ROADWAY

POINT "A"

45.720
(150'-0")

POWER PLANT
68 m × 58 m
(224' × 190')

POINT "B"

ROADWAY

SLEEPERWAY

DD-101C
DD-101
DD-101A

SALT STORAGE TANK (TYP)

DRAIN TANK

HOT SALT SUMP (TYP)

SLEEPERWAY

DIKE

22.860
(75'-0")

65.532
(215'-0")

36.576
(120'-0")

36.576
(120'-0")

28.956
(95'-0")

ENLARGED PLAN
SCALE IN METERS

POINT "A"

68.27
(224')

60%
(200')

POINT "B"

9.9
(32.5')

70.14
(230')

97.54
(320')

97.54
(320')

COOLING TOWER PLANE
SCALE IN METERS

NOTES:
1. DIMENSIONS ARE GIVEN IN THE FOLLOWING MANNER UNLESS OTHERWISE NOTED:
   METERS ON TOP,
   FEET/ INCHES BELOW.

Figure 2 Alternative Central Receiver Plot Plan

Molten salt is pumped between the receivers and the turbine/storage areas in large stainless steel pipes. A 300-MWe plant like the one described previously may have from 70 to 105 million kg (150 to 230 million lb) of salt. The storage area is diked to contain the salt in the event of a major leak.

The selected salt is a mixture of 60% sodium nitrate and 40% potassium nitrate and has a melting point of 494 K (430°F). Both nitrates have been used in their solid states as fertilizers since the 19th century and are neither explosive nor flammable. The National Fire Protection Association Association classifies both sodium nitrate and potassium nitrate as "Class I oxidizers," the least hazardous of the four classes. This is defined as "an oxidizing material whose primary hazard is that it may increase the burning rate of combustible materials."

Molten salts have been used in industry in open baths for heat-treatment of metals since the turn of the century and are also commonly used as heat transfer media in the petroleum and chemical industries. Currently about 45 million kg (100 million lb) of molten heat transfer salt are in use worldwide. Safety procedures for handling both dry and molten salts are well established and have contributed to accident-free plant operations for up to 60 years. Potential hazards can be avoided by recognizing the salt as an oxidizing agent and by treating the molten salt like any hot liquid. The use of molten salt in a solar thermal power plant represents nothing new in this respect except for the quantity of salt involved.

Experiments have shown that organic liquids and vapors introduced into molten salt do not react with the salt but burn at the salt surface when they gain access to oxygen in the air. Chemical reaction with the salt can occur with finely divided particles of organic materials and some metals.

II. PUBLIC UTILITY COMPANIES EVALUATION

The two public utility companies that evaluated the contents of this report were Arizona Public Service (APS) Company and Public Service Company (PSC) of Colorado. APS has been actively involved in studies of molter salt solar central receiver systems. PSC has had no involvement with molten salt systems.

Both utility companies concluded that using molten salt in a solar central receiver power plant is acceptable, that no major problems exist, that this report gives adequate safety definition, and that the report forms the basis for preparing operating procedures.

The definition of hardware operation and requirements will have to be addressed but this subject is out of the scope of this report.

The use of molten salt with a fossil fuel plant was questioned by PSC. The stored fuel should be separated from any possible salt leaks. Since coal plants result in coal dust permeating the site, a possible salt spill could contact powdered coal. It would be advantageous to test the possible reaction of molten salt with coal dust under plant conditions.

III. SAFETY INVESTIGATION

Molten salts are commonly used as heat transport media in metallurgical heat treatment and in the chemical process and petroleum industries. These are usually nitrate, nitrite, chloride, fluoride or carbonate compounds of the alkali or alkaline earth metals. These compounds may be mixed in varying combinations and proportions to match the properties of the salt to the application.


A. TYPES OF NITRATE-NITRITE SALT MIXTURES

The most widely used heat transfer salt (HTS) is a eutectic mixture of 40 weight percent sodium nitrite ($NaNO_2$), 7 weight percent sodium nitrate ($NaNO_3$), and 53 weight percent potassium nitrate (KNO_3). This salt is marketed under the trade name HITEC by Coastal Chemical Company and as PARTHERM 290 by Park Chemical Company. Draw salt, a common metal-treating salt, is a eutectic mixture of 54 weight percent potassium nitrate (KNO_3) and 46 weight percent sodium nitrate ($NaNO_3$). It is marketed by Park Chemical as AL-2.

Potassium nitrate (KNO_3) is slightly more expensive than sodium nitrate ($NaNO_3$). Where small quantities of salt are to be used, the cost differential is unimportant. For thermal storage in commercial—scale power plants, however, enormous amounts of salt are required and the cost differential becomes significant. For this application the of a mixture of 60 weight percent $NaNO_3$ and 40 weight percent KNO_3 is proposed. This is marketed as PARTHERM 430 by Park Chemical. It is not a eutectic mixture; the freezing point (the tem- peratures at which the first solids appear on cooling) is 494 K (430°F). The chemical properties are approximately the same as those of draw salt.

B. CHEMISTRY

Both HITEC and draw salt belong to a general system of mixtures of two salt pairs: $KNO_3/NaNO_3$ – $NaNO_2/KNO_2$. A freezing point diagram is presented in Figure 3. This system is more closely interrelated than most other similar ones in that the nitrate and nitrite ions are related through a simple oxidation-reduction reaction

$$2NO_3^- \rightleftharpoons 2NO_2^- + O_2.$$
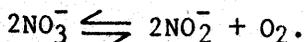
Thus, one may start with a particular mixture of the salts and, given the proper conditions and enough time, find that the composition and properties of the mixture have changed considerably.
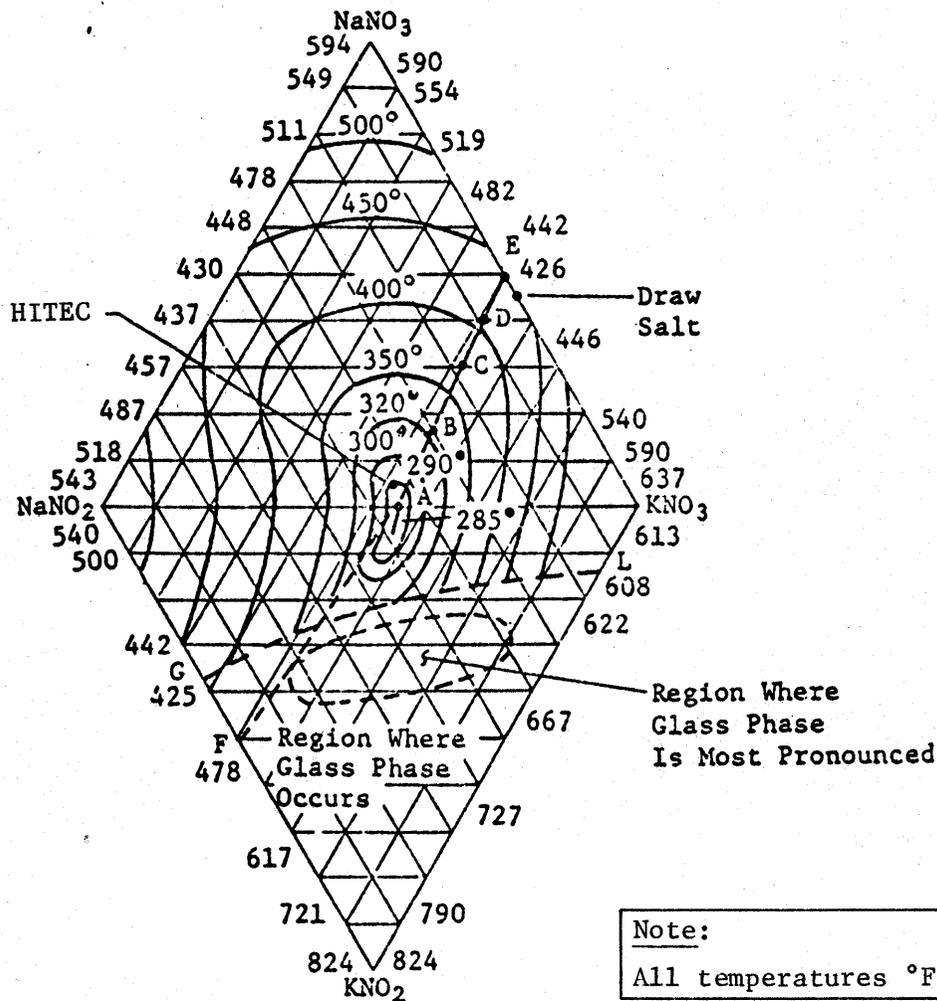
(From A. Alexander, Jr. and S. G. Hindin, "Phase Relations in Heat Transfer Salt Systems," I & EC XXXIX, 1 (1947), 1044.

Figure 3
Freezing Points of Alkali Nitrate-Nitrite Mixtures
with Compositions Given in Weight Percent

HITEC is blended to give all the good qualities of a heat transfer salt (high heat transfer coefficient, high heat capacity) while maintaining a low melting point [415 K (288°F)] and a relatively low cost (less than $0.30 per pound). Forty percent of the mixture is sodium nitrite, which is significantly more expensive than the nitrate components but is the nitrite salt that produces the low melting point. If HITEC is allowed to remain in contact with air in the molten state at elevated temperatures, the nitrate salt in the mixture will gradually be oxidized to nitrate and the melting point will rise to something in excess of 477 K (400°F). If one intends to use 150-psig steam to melt the salt, [saturation temperature 459 K (366°F)], this "degradation" of HITEC is of great importance. The final composition of the salt in equilibrium with air is close to that of draw salt. HITEC is generally used in a temperature range between 422 K (300°F) and 672 K (750°F) and in an inert gas atmosphere.

The nitrite salts are susceptible to degradation by a different sort of reaction

$$2NaNO_2 \rightleftharpoons Na_2O + N_2O + O_2.$$

The gaseous products can include any or all of the oxides of nitrogen and nitrogen and oxygen depending on the conditions. Sodium monoxide is not normally stable and will react with any available carbon dioxide or water to form sodium carbonate or sodium hydroxide. The equilibrium of this reaction and the conditions necessary for it to go forward are not well understood. It is known that the reaction is slow at temperatures at least as high as 922 K (1200°F) and that, although nitrate salts react similarly, they are more stable than the nitrites.

In metallurgical heat-treatment applications, low melting point is not an important consideration. Salt baths are kept hot by electric resistance heating or direct firing of tank walls. The baths are open to the air and chemical stability is important. For these applications, draw salt is frequently used. it is less expensive and chemically more stable than HITEC because it is not made with nitrite salts.

Draw salt or indeed any mixture of sodium nitrate and potassium nitrate is neither explosive nor flammable. It has been shown to be stable at temperatures in excess of 922 K (1200°F). Any potential fire hazard due to the salt is caused by its high temperature and/or its oxidizing properties.

C.   DRY STORAGE AND HANDLING

The National Fire Protection Association classifies both sodium nitrate and potassium nitrate as "Class I oxidizers." This is the least hazardous of four classes, and is defined as "an oxidizing material whose primary hazard is that it may increase the burning rate of combustible materials." Standard storage and handling procedures are adequate for handling these dry, solid salts. They should be stored dry and segregated from organic and combustible materials including wooden floors. Spills should be swept up and disposed of immediately. This is more a precautionary measure than a stringent requirement. If spills were allowed to permeate a wooden floor over a long period of time, the salt would increase any fire hazard. Nitrate salts are commonly shipped, however, in paper bags and on wooden pallets.

Olin Chemicals, the major producer of sodium nitrate, and Park Chemical, a major producer of draw salt and other nitrate salt mixtures, both ship their products in paper bags. The bulk handling of these materials presents no special problems. Both the Olin and Park installations were visited by a Badger engineer who verified their salt-handling practices.

Olin Chemical's sodium nitrate plant at Lake Charles, LA was built in 1949 and currently has an annual production capacity of over 90,900 kg (200,000 lb). Sodium nitrate ($NaNO_3$) is made from the acid

neutralization of nitric acid (HNO3) with sodium hydroxide (NaOH) or sodium carbonate (Na2CO3). Temperatures over 589 K (600°F) are used in parts of the process. Olin has had 30 years of accident-free operation.

Park Chemical blends, packages, and distributes nitrates and other salts to be used in molten salt baths. They have been handling, packaging and shipping dry powdered nitrates for over 60 years without an explosion or fire.

Both potassium nitrate and sodium nitrate in their solid state are used in fertilizers. The use of sodium nitrate fertilizer dates back to the 19th century. Most of the natural sodium nitrate is mined and refined in Chile. The solid product consists of pellets ranging from about 8 to 29 mesh and has a purity of greater than 98%. It is stored in large silos and transported in ships having a 10 x 10 kg bulk capacity. There is no history of explosions or serious fires occurring during the dry bulk shipment of these salts.

Nitrate salt explosions such as the infamous Texas City disaster [also Brest, France (1947) and Red Sea (1952)] have nothing to do with either sodium nitrate or potassium nitrate. The explosive agent in these cases was ammonium nitrate that was coated with an organic material. Needless to say, ammonium nitrate is no longer produced in this way.

Amonium nitrate (NH4NO3) is a strong oxidizing agent. When mixed with combustible materials, it is used as an explosive. These explosive mixtures are known as blasting agents or nitro-carbo-nitrates. One example is that of 95% ammonium nitrate and 5% fuel oil. This mixture has an energy equivalent of 890 cal/gm compared to that of TNT, which is 820 cal/gm. Since ammonium nitrate is not shock-sensitive because of its slow rate of energy release, these explosions must be initiated by dynamite.

Theoretically a similar explosive mixture could be produced using either potassium nitrate or sodium nitrate. In fact, black powder, a Class B low explosive, contains sodium nitrate. However, several points must be made in this regard:

1) The exothermic yield (energy release) is only about 56% of the corresponding ammonium nitrate mixture;

2) The theory for thermal initiation of an explosion assumes a first--order reaction and an optimum fuel-salt mixture. These are worst--case assumptions. There is no evidence that such a reaction is in fact first-order;

3) Initiation of a detonation by shock is most unlikely to occur, even granting the supposed optimum mix;

4) The "supposed optimum mix" is most unlikely to occur since neither sodium nitrate nor potassium nitrate are coated or mixed with organic substances in shipping, handling and storage;

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5) Countless tons of sodium nitrate and potassium nitrate have been shipped and stored in bulk for almost 100 years without an explosion occurring.

D. EXPERIMENTS WITH HITEC

Experiments have been conducted to determine the flammability of various organic materials in contact with molten HITEC (see 5., Bibliography). Combustible vapors generally reacted relatively slowly with HITEC and escaped before complete combustion occurred. Gasoline vapors, high in unsaturated compounds, were bubbled through molten HITEC for two hours at 866 K (1100°F). The results indicated that over 90% of the gasoline was recovered unchanged. The reaction between HITEC and ammonia was also studied under similar conditions. The results indicated that less than 50% of ammonia reacted with the HITEC. Changes in the salt composition were negligible in both experiments.

Flammable liquids vaporize rapidly in contact with molten HITEC and burn at the surface just as on any hot surface. Crude oil burned similarly on the surface of molten lead at the same temperature. Motor gasoline, cracked gasoline, gas oil, and crude oil were separately mixed with sulfur and released below the surface of an open container of HITEC at 866 K (1100°F). In each case, the hydrocarbons vaporized and burned. Considerable spattering of hot salt due to rapid, subsurface vaporization occurred with the crude oil and gasoline mixtures. There was little change in the salt composition, indicating that the principal reactions were between the vaporized hydrocarbons and the air above the salt bath and not with the salt itself.

Combustible solids such as wood, coke, paper, plastics, cyanides, chlorates, ammonium salts and active metals such as magnesium must not come in contact with molten HITEC. Heat-treatment of aluminum parts in molten HITEC is a common and safe practice when suitable precautions are taken.

Violent combustion resulted when ground petroleum coke was held beneath the surface of HITEC at 894 K (1150°F). Subsequent analysis revealed that the HITEC had taken part in the reaction. If HITEC is contacted with iron filings, a thermite-like reaction would occur. Similarly, mixtures of fine aluminum and iron filings reacted with HITEC at 811 K (1000°F), producing enough heat to burn through a nickel crucible.

Fine charcoal flared up and burned vigorously when placed on the surface of HITEC at 922 K (1200°F), but grease burned quietly under the same conditions. When an oxygen-balanced mixture of HITEC and paraffin was heated rapidly to 866 K (1100°F), the paraffin merely volatized and burned, leaving the salt practically unchanged. However, an 80% HITEC/20% nylon mixture burned vigorously at 672 K (750°F) with subsequent analysis indicating that the HITEC had taken part in the reaction.

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Experimental data indicate that HITEC is not explosive. HITEC, or mix-
tures of HITEC and paraffin, petroleum, nylon or topped Houdry conden-
sate, could not be detonated at 464 K (375°F) and 25 in. of mercury
using a No. 8 blasting cap or 0.23 kg (0.5 lb) of blasting gelatin.
HITEC was similarly insensitive to explosion at 866 K (1100°F).
Oxygen-balanced mixtures of HITEC and finely divided char- coal or
topped Houdry condensate could not be detonated by vigorous heating
under confinement. Pressures of 5.66×10^6 kPa (18,000 psi) were
attained during this experiment.

Draw salt or any other mixture of sodium nitrate and potassium nitrate
is expected to act similarly to HITEC. These mixtures, however, are
somewhat stronger oxidizing agents since they do not contain nitrite
salts. These experiments indicated that liquid and gaseous oxidizable
materials do not react or react only very slightly with these molten
salts. The only danger of serious explosion would involve salt react-
ing with finely divided solids.

E.   MOLTEN SALT BATHS

The industrial use of molten salt for the heat-treatment of metal orig-
inated in England at the turn of the century and quickly spread. It
became popular in the United States during World War II when it became
necessary to stress-relieve large structures such as airplane wing sec-
tions. Molten salts are chemically stable and form an inert heating
medium in which the metal work is immersed. The outstanding character-
istic of the molten salt bath is the uniform and rapid rate of heat
transfer from the molten salt bath to the metallic part. Draw salt, or
similar nitrate combinations, is extensively used in the annealing,
quenching, and tempering of metals. It is estimated that 3 to 5 mil-
lion kg (7 to 10 million lb) of this salt are currently being used for
this purpose in the United States. Metal-treatment is performed in
open baths at salt temperatures of 422 K (300°F) to 866 K
(1100°F). The pieces are hung on racks or conveyor belts and are
dipped into the open baths of hot molten draw salt. The baths are
melted and kept molten with either gas firing or electric resistance
immersion heating. No extraordinary safety precautions are required
and it is common for workers to go about their business in close prox-
imity to these open baths.

The chief hazards connected with nitrate molten salt baths are due to
their high temperature and their character as oxidizing agents. One
famous explosion occurred when a worker erroneously dumped a bag of cy-
anide salt into a molten draw salt bath. The combination of a finely
divided combustible and a hot oxidizing agent had the predictable re-
sults. This type of accident is virtually impossible in the type of
salt system proposed for energy storage and transport. The tanks will
be closed and inaccessible. In addition, no combustible solids will be
available for dumping into the tanks. The second explosive hazard
sometimes reported in the literature is the water explosion. This,
however, is due to the rapid vaporization of water and not to any chem-
ical reaction or combustion.

The vaporization of water at atmospheric pressure is accompanied by a 1600-fold volumetric increase. Water added to a hot molten salt bath would boil instantaneously. This would have an effect similar to dropping water into a frying pan of hot bacon grease. Gradual and carefully controlled additions of water cause no difficulties. In fact, some metal treaters slowly inject water into draw salt baths to enhance their heat transfer properties. A heat exchanger leak in the proposed system would not cause an explosion. Either the leak would already be steam or the water would flash through the crack. The first probable indication of such a leak would be a steam plume appearing at the cold-salt storage vent.

Some dangers from fumes in salt bath installations have also been reported. The fumes are not due to the salt as such. They arise from the following application. Plastic or rubber-coated metal objects are immersed in the salt bath to burn off the coating and salvage the metal. The fumes are the partially oxidized remnants of the organic coating. This hazard also does not apply to an energy storage installation for obvious reasons.

Several explosions have been reported over the years in metal-treating plants. One factor is comon to nearly all of these incidents: the salt bath was allowed to overheat due to poor temperature control. In some instances, temperatures over 977 K (1300°F) were reported before the accident. At that point, the salt probably reacted violently either with the sludge that collects at the bottom of poorly maintained metal-treating baths or with the mild-steel bath containers. These accidents are a matter of carelessness, poor operating techniques or bad housekeeping. Companies that are careful about the control and condition of their baths have had many years of explosionand fire-free operation. Some examples of companies contacted by phone or in person are listed in Table 1. In all cases, their operations have been free from serious accidents throughout their operating history.

Table 1   Some Nitrate Salt Bath Installations

| Company | Salt | Bath Temperature | | Quantity, | Years |
		°K	°F	kg	
Hoover Steel Treating	AL-2 PARTHERM 375	811 477	1000 400	2,100 115	20-25 20-25
CAPCO, Inc. Automotive Parts - Heat-Treating	PARTHERM 375	589-644	600-700	330,000	15
Voltek Corporation - Polyethylene Treating	PARTHERM 290	422	300	82,000	9-10
Sun Steel Treating	AL-2	533-922	500-1200	22,000	15
Teledyne-Howell-Penncraft	AL-2	533-822	500-1020	2,000	35

Despite the fact that accidents have occurred in metal-treating applications of the nitrate salts, the conditions that caused the accidents are entirely preventable. Moreover, none of the causes of these accidents--the possibility of overheating, metal-treating sludge, and carbon steel in salt service over 900°F--will be present in an energy storage system.

F.   CHEMICAL PROCESS INDUSTRY

The petroleum industry was the first to begin using molten salt as a heat transfer media in the mid-1920s. By 1939, heat transfer salt was being used by Socony-Vacuum Oil Company and Sun Oil Company in their Houdry catalytic cracking units. These units used approximately 0.5 million kg (1 million lb) of the molten salt per unit for removal of the heat of combustion from spent catalyst at 900°F. By 1947, at which time the use of this process was at its peak, about 13.6 million kg (30 million lb) of heat transfer salt was being used in these plants. Socony-Vacuum Oil Company later used heat transfer salts in their Thermofor kilns for the regeneration of lube-oil decolorizing clays.

More recently the chemical industry has adopted heat transfer salts to provide heating and cooling for high-temperature reactions. The widest use has been in phthalic and maleic anhydride catalytic converters where naphthalene or benzene are oxidized by air at temperatures of 616 K (650°F) to 727 K (850°F). Another similar application is in alkylamine converters that operate at 621 K (659°F) to 755 K (900°F). Both operations involve cooling of the reactor bed with salt and generation of steam from the waste heat in the salt. Heat transfer salts are now being used for sulfur distillation at temperatures as high as 805 K (990°F) and for concentration of sodium and potassium hydroxides. They are also used for cleaning plastic and rubber-molding equipment. Coastal Chemical Company, the distributor of HITEC, estimates the current worldwide usage at approximately 45 million kg (100 million lb).

Major users of HITEC for heat transfer in chemical processes include Diamond Shamrock, Koppers, BASF Wyandote, Celanese, Rohm and Haas, Exxon, DuPont, American Cyanamid and Monsanto. These installations have about a 15-million-lb salt inventory. The salt is used as a coolant for phthalic anhydride and acrylic acid reactors and as a heating medium for drying caustic soda.

Two additional users of molten nitrate salts for heat transfer were contacted by phone and in person. Neither company would allow its name to be mentioned in a public report. They also required assurances that details of their operations that included proprietary information would not be divulged.

The total amount of molten salt installed in these two plants is about 0.7 million kg (1.5 million lb). One plant uses HITEC, the other a salt with a composition close to draw salt. They are typical of the users previously mentioned. Each of these plants has been operating for more than 10 years at salt temperatures between 644 K (700°F) and 755 K (900°F). Neither company has had any fires, explosions or serious accidents attributable to the use of heat transfer salt. Both have had experiences of molten salt leaking into the process side (including organics) of the equipment or steam leaking into the molten salt due to poor welds or corrosive boiler feed water. The leaks were not attributed to the salt; they had no effect other than causing some lost production due to downtime, and no serious damage occurred because of them. These operators are careful to clean up spills, provide safe drainage areas in case of major salt leaks, and keep the molten salt isolated from organic or other readily oxidizable materials.

The conclusions of this investigation are clear. Certain hazards are connected with the use of molten salt. The temperature and oxidizing nature of the material are the sources of these hazards. However, with proper care and ordinary safety precautions, one can expect an excellent safety record with a good deal of assurance. Moreover, the expertise for handling molten salt safety is in existence and many installations of all kinds have logged many years without any salt--related accidents. There is no reason to expect that solar and thermal storage applications should do any worse.

IV.   SAFETY PROCEDURES AND DESIGN PRACTICES

A.   DRY STORAGE

Sodium nitrate and potassium nitrate pose no special storage problems. Since they are oxidizing agents, they would aggravate a fire should one begin. Therefore, these salts should not be stored on wooden floors. Storage buildings should be constructed of fire-proof or fire-resistant materials.

Sodium nitrate and potassium nitrate are somewhat hygroscopic and tend to cake. They should therefore be stored in a dry place or in bags or drums.

These salts are neither poisonous nor particularly irritating. Nevertheless, good health and safety practices require that personnel be protected from ingesting or breathing the dust. Contact with the salts should be minimized by means of rubber or plastic-coated gloves and safety goggles. Operating personnel who work in the storage areas or who handle, package, load or unload these salts should wear clean uniforms daily. Cloth impregnated with draw salt has increased flammability and can also be irritating. Food should not be permitted in storage areas.

B.   MOLTEN STORAGE

Many of the safety precautions practiced in metal-treating plants would not be necessary in an energy storage system. There are no open baths in such a system and therefore the chance of the molten salt coming in contact with personnel or organic or combustible material is practically eliminated. If open draw salt baths can be operated safely for many years, there is every reason to believe that closed storage can be designed to be accident-free. Storage tanks should be diked individually so the dike will contain the entire tank inventory. This is to prevent hot salt caused by a possible tank rupture from attacking combustible material or damaging equipment. The diked areas should be kept free of combustible materials and large puddles of rain water.

The most likely sources of leaks in any plant are the pump seals. Pumps should therefore be checked every shift. Personnel should be protected from possible salt leaks by routing walkways away from potential leaks and shielding where necessary. Concrete drains should be provided to allow any salt leaks to flow away from the pumps, piping and equipment to a safe and isolated area. Molten salt should be allowed to solidify and cool before cleanup. The mass can then be chopped up and carted away by hand and the remainder flushed away with water.

Should the molten salt freeze in any tank or equipment, it should be melted from the free surface down. Salt trapped in a confined volume will expand on melting and possibly rupture the containment vessel or pipe line.

A small quantity of salt should be drained from the bottom of each storage tank periodically to prevent any sludge buildup. This will probably be done anyway to recondition the salt.

C.   HEAT TRANSPORT SYSTEMS

The main cause of serious accidents involving nitrate salts has been overheating of salt in contact with mild steel or some other readily oxidizable metal. Therefore all equipment should be designed so salt heated over 866 K (1100°F) does not contact mild steels. Incoloy 800, 347 SS or similar steels should be used for high-temperature service and in any places where hot spots or overheating can occur. This is necessary only in a solar receiver or fired heater. Salt cannot overheat in the heat exchange area since it is the heating medium.

Welded joints and expansion loops in draw salt service should be designed, installed and inspected with extra care for integrity. Draw salt is extremely penetrative when hot and can leak through a porous weld. All heat exchangers should be provided with liquid relief valves that are adequately heat-traced to ensure that the salt remains liquid in the valve and that the valve operates smoothly. These valves should discharge to safe locations away from equipment and personnel. All equipment should be designed and heat-traced to keep salt molten in critical places so valves and other safety devices will operate properly.

Thermocouple wells should be of a seamless construction and be thermally durable and corrosion-resistant. Thermocouples should be located to catch all possible hot spots of container walls, particularly in the case of fuel-fired furnaces. Solar receivers and salt heaters should be designed to allow the escape of steam discharged into the salt from a possible heat exchanger tube leak.

D.   FIREFIGHTING

Water from spray sprinklers or low-velocity fog nozzles is recommended for oil-fired salt heating units because the water will not sufficiently penetrate the surface of molten draw salt to cause dangerous spattering. Carbon dioxide and approved dry powder-type fire extinguishers can be used satisfactorily to extinguish fires in the vicinity of a salt unit. Vaporizing liquids (i.e. carbon

tetrachloride), foam, and aqueous types of fire extinguishers should not be used. In the case of a fire accompanied by a salt spill, self-contained breathing apparatus should be worn by firefighters. An adequate supply of clean, dry sand is recommended for slagging and diking to confine the spread of escaped molten salt.

Users of molten salt do not consider it to be dangerous. They do realize, however, that it must be treated with respect as is any high-temperature liquid. By following procedures such as those described, many operators have enjoyed long histories of accident-free use of molten nitrate salts.

Medium	Practical Temperature Range, °C	Cost, $/kg	Melting Point, °C	Heat Capacity, $J/kg^{-1}K^{-1}$	Film Coefficient,* h at 7.5 kW	Limitations
Dowtherm A[†]	180–370	0.22	13	2760	600	Leaks readily at seals and glands; poor rate of heat transfer; decomposition causes fouling.
HTS	205–540	0.44	142	1560	1400	Lines must be heated or steam-traced because of freezing point.
Draw Salt	260–550	0.25	220	§	1320	Lines must be heated or steam-traced because of freezing point.
Na	125–760	0.57	98	1300	4000	Requires sealed system; reacts violently with H_2O and other materials; needs special equipment.
NaK	40–760	3.50	18	1050	3000	Requires sealed system; reacts violently with H_2O and other materials; needs special equipment.
Lead	370–930	0.44	327	159	2080	Forms solid oxides that foul heat transfer surfaces and cause corrosion; needs high power; is toxic.
Mercury[†]	370–540	8.8	-39	138	1100	Very toxic; installation requires a high inventory cost.

*At 315°C and at a velocity to require the indicated power per 300 m of 7.6-cm pipe.

[†]All are used as liquid except Dowtherm A and mercury, with latent heats of evaporation at 1 atm of 3.25×10^5 and 2.92×10^5 J/kg, respectively.

§Value should be approximately that of HTS.

From M. D. Silverman & J. R. Engel: "Survey of Technology for Storage of Thermal Energy in Heat Transfer Salt," ORNL/TM-5682 (Oak Ridge National Laboratory, 1977).

APPENDIX A—COMPARISON OF HEAT TRANSFER MEDIA FOR USE AT HIGH TEMPERATURES

The National Fire Protection Association (NFPA) lists potassium nitrate and sodium nitrate in Hazardous Chemicals Data (NFPA No. 49). These data are given:

The NFPA Code for the Storage of Liquid and Solid Oxidizing Materials (NFPA 43A) classifies oxidizing materials as follows:

Class 1 Oxidizer

An oxidizing material whose primary hazard is that it may increase the burning rate of combustible materials.

Class 2 Oxidizer

An oxidizing material that can undergo vigorous self-sustained decomposition when catalyzed or exposed to heat.

Class 3 Oxidizer

An oxidizing material that can undergo vigorous self-sustained decomposition when catalyzed or exposed to heat.

Class 4 Oxidizer

An oxidizing material that can undergo an explosive reaction when catalyzed or exposed to heat, shock, or friction.

Both potassium nitrate and sodium nitrate are considered Class 1 oxidizers.

Potassium Nitrate KNO_3

Description:

White crystals or powder.

Fire and Explosion Hazards:

Oxidizing material. In contact with easily oxidizable substances it may react rapidly enough to cause ignition, violent combustion or explosion. Increases the flammability of any combustible substance.

Life Hazard:

Yields toxic gaseous oxides of nitrogen when involved in fire.

Personal Protection:

In fire conditions, wear self-contained breathing apparatus.

Firefighting Phases:

Use flooding amount of water in early stages of fire. When large quantities are involved in fire, nitrate may fuse or melt, in which condition application of water may result in extensive scattering of molten material.

Usual Shipping Containers:

Bottles, bags, boxes, cans, barrels, drums, bulk.

Storage:

Protect against physical damage. Store in cool, dry place. Separate from combustible, organic or other readily oxidizable materials. Avoid storage on wood floors. Immediately remove and dispose of any spilled nitrate.

Remarks:

See code for Storage of Liquid and Solid Oxidizing Materials (NFAP No. 43A).

Sodium Nitrate NaNO$_3$

Description:

Colorless, transparent or white crystals.

Fire and Explosion Hazards:

Oxidizing material. If sodium nitrate is in contact with easily oxidizable substances, violent combustion or explosion may result upon ignition from any source. Increases the flammability of any combustible substance.

Life Hazard:

Yields toxic gaseous oxides of nitrogen when involved in fire.

Personal Protection:

In fire conditions, wear self-contained breathing apparatus.

Firefighting Phases:

Use flooding amounts of water in early stages of fire. When large quantities are involved in fire, nitrate may fuse or melt, in which condition application of water may result in extensive scattering of molten material.

Usual Shipping Containers:

Multiwall paper bags, bottles, cans, metal or fiber drums.

Storage:

Protect against physical damage. Store in dry, cool place.
Separate from combustible, organic or other readily oxidizable
materials. Avoid storage on wood floors. Immediately remove
and dispose of any spilled nitrate.

Remarks:

See code for the Storage of Liquid and Solid Oxidizing Materials
(NFPA No. 43A).

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