THERMOCLINE THERMAL STORAGE TEST FOR LARGE-SCALE SOLAR THERMAL POWER PLANTS

Abstract

Solar thermal-to-electric power plants have been tested and investigated at Sandia National Laboratories (SNL) since the late 1970s, and thermal storage has always been an area of key study because it affords an economical method of delivering solar-electricity during non-daylight hours. This paper describes the design considerations of a new, single-tank, thermal storage system and details the benefits of employing this technology in large-scale ($10MW_e$ to $100MW_e$) solar thermal power plants. Since December 1999, solar engineers at Sandia National Laboratories' National Solar Thermal Test Facility (NSTTF) have designed and are constructing a thermal storage test called the thermocline system. This technology, which employs a single thermocline tank, has the potential to replace the traditional and more expensive two-tank storage systems. The thermocline tank approach uses a mixture of silica sand and quartzite rock to displace a significant portion of the volume in the tank. Then it is filled with the heat transfer fluid, a molten nitrate salt. A thermal gradient separates the hot and cold salt. Loading the tank with the combination of sand, rock, and molten salt instead of just molten salt dramatically reduces the system cost. The typical cost of the molten nitrate salt is $800 per ton versus the cost of the sand and rock portion at $70 per ton. Construction of the thermocline system will be completed in August 2000, and testing will run for two to three months. The testing results will be used to determine the economic viability of the single-tank (thermocline) storage technology for large-scale solar thermal power plants. Also discussed in this paper are the safety issues involving molten nitrate salts and other heat transfer fluids, such as synthetic heat transfer oils, and the impact of these issues on the system design.

Introduction

Solar thermal-to-electric power plants have been studied extensively since 1979 when Sandia National Laboratories finished construction of the National Solar Thermal Test Facility (NSTTF) located in Albuquerque, New Mexico. Engineers at SNL helped develop and test two types of solar power plant technologies, central receiver and parabolic troughs. Both types of power plants use conventional power blocks, meaning they use conventional steam-turbine generators to produce electricity. The difference between fossil fuel power plants, such as coal, and solar power plants is the means of generating heat. In a coal power plant, the fossil fuel is burned until the temperature required to operate the steam turbines is reached. In a solar power plant, mirrors reflect sunlight and concentrate it onto a receiver. A heat transfer fluid passes through this receiver and is heated up to the temperature required to operate the steam turbines. Thus, the sun provides the fuel in a solar power plant. It is renewable and will last as long as the life of the power plant. Below are examples of the two types of solar power plants.

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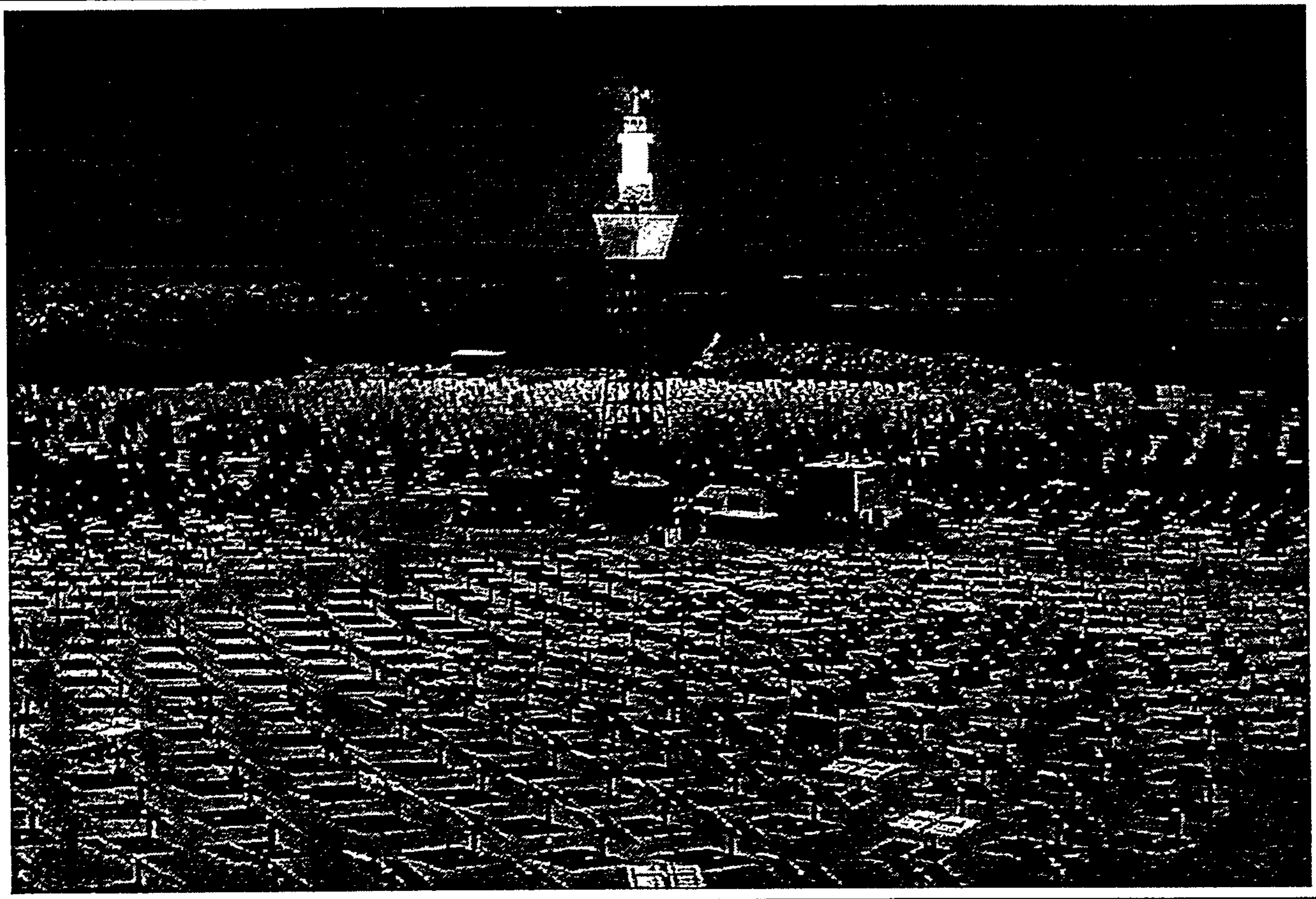


Figure 1: Solar Two, an example of a Central Receiver Solar Power Plant.

Central receiver power plants, often referred to as power towers, use molten nitrate salts as their heat transfer fluid. Surrounding the tower are thousands of slightly-concave sun-tracking mirrors called heliostats. The receiver is located at the top of the tower. All the heliostats reflect and concentrate the sunlight onto the receiver. At Solar Two the molten salt experienced temperatures between 290°C and 560°C. Solar Two was a $10MW_e$ test solar power plant that was connected to the power grid in Southern California. Southern California Edison (SCE) was the head of a consortium of utilities that demonstrated Solar Two with SNL and the DOE. Solar One was the first large-scale central receiver power plant to be constructed and tested. It was located at the same site as Solar Two. The difference was Solar One used a water-steam receiver and an oil-rock thermocline storage system. Solar Two substituted molten salt as the heat transfer fluid instead of water and also molten salt as the storage medium instead of the oil.

A thermocline is defined as a stratification in a fluid according to its temperature. So a thermocline tank houses a fluid that maintains a temperature gradient (layers at different temperatures) from top to bottom.

The other type of solar power plant is the parabolic trough plant. See photo below.

Figure 2: Solar Energy Generating System (SEGS) four through seven, an example of Parabolic Trough Solar Power Plants.

These plants are more commercial than central receiver power plants. In the mid-1980s SCE signed a thirty-year contract to buy electricity from nine SEGS plants that would be constructed. An Israeli company called Luz developed the majority of the technology for these parabolic trough power plants. SNL did some supportive testing. Today these plants are connected to the utility power grid and serve tens of thousands of homes and businesses in Southern California. Construction of the SEGS power plants began in the mid-1980s and finished in the early 1990s.

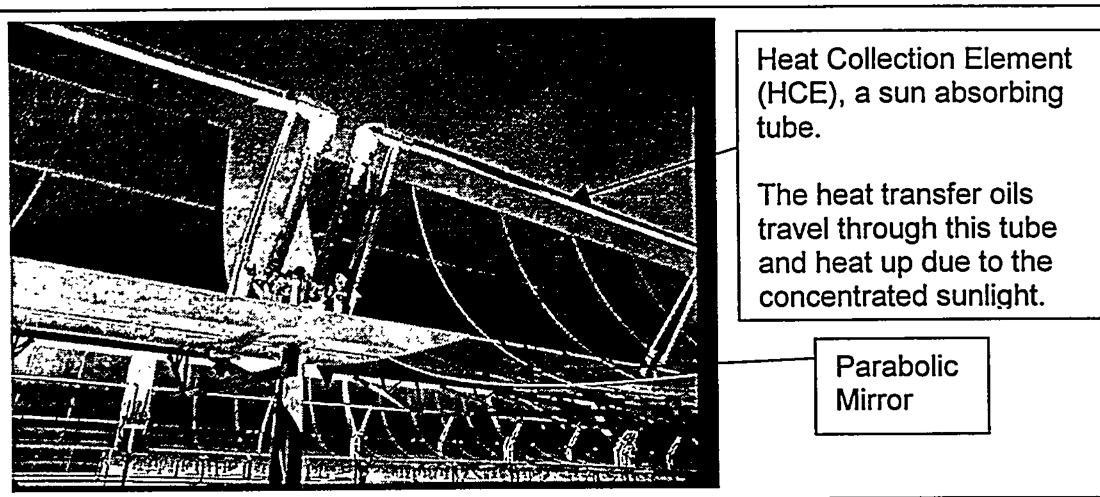


Figure 3: Close up of a section of a parabolic trough concentrator.

These plants consist of many rows of parabolic-shaped mirrors to concentrate sunlight onto a tube that runs along the focal point of the mirrors. Temperatures in SEGS Two – Nine reach 390°C, and the heat transfer fluid is a synthetic oil called Therminol. In SEGS One a mineral oil called Caloria is used as the heat transfer fluid. The SEGS One plant runs its power cycle at temperatures of 220°C and 310°C. In SEGS One there are two tanks that provide some storage for the power plant. These two tanks house the heat transfer fluid, Caloria. In SEGS Two – Nine there is no storage because Therminol can reach higher temperatures than its Caloria counterpart at SEGS One. The power cycle temperatures at SEGS Two – Nine are 290°C and 390°C. The higher temperatures yield a higher efficiency in the steam turbine. Additionally the Therminol boils at 260°C and atmospheric pressure. Thus, it must be pressurized. The cost of a pressurized storage tank is not practical in the SEGS Two – Nine plants.

Thermal Storage in Solar Power Plants

Since the fuel source cannot be accessed on a 24-hour basis, thermal storage is a key element in the design of solar power plants. In designing a solar power plant, one can size the mirror field to meet or exceed the energy requirement of the steam-turbine generators. This is known as the solar multiple, the ratio of the thermal capacity of the mirror field to the thermal requirement of the steam generator.

Engineers designed Solar Two's solar multiple at 1.2. This means that if all the heliostats were in operation, then the thermal capacity of the heliostats would exceed what the steam generators demanded. Thus, Solar Two's thermal storage was sufficient to produce electricity after sundown or during periods of long cloud cover. Incidentally, the solar multiple of 1.2 was not always achieved because some days the heliostats would malfunction.

Solar One had a single thermocline tank. The tank contained a mixture of rock, sand and a mineral oil (as the heat transfer fluid). They filled that tank with rocks and sand to displace as much volume as possible before adding the oil. This reduced the price of the plant, as the oil is more expensive than the rocks. Caloria costs $530/ton versus the rocks, which cost $70/ton.[2]

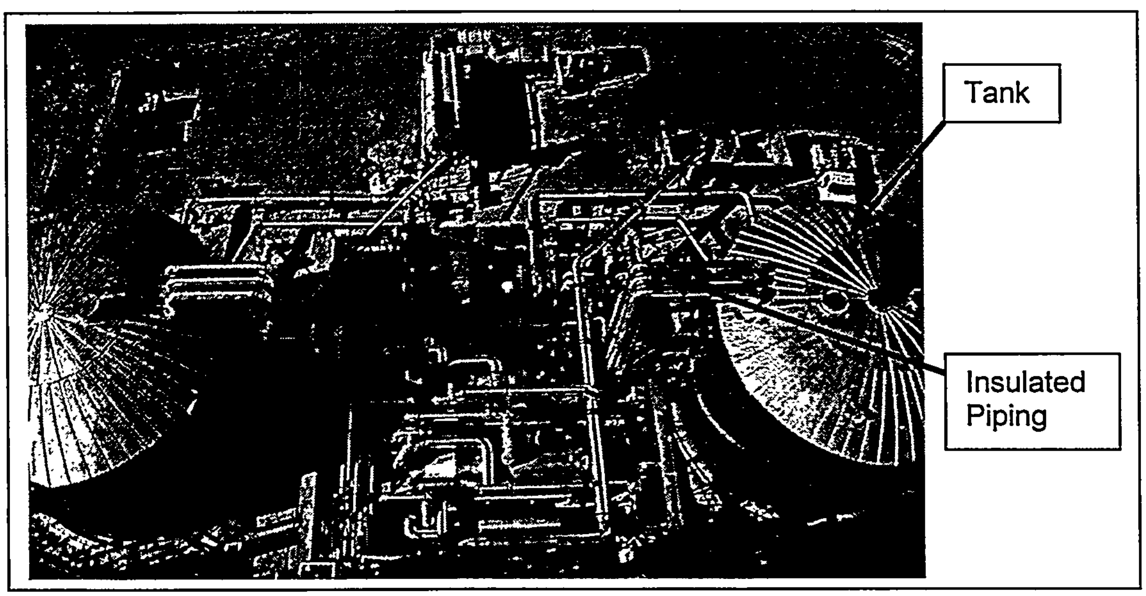


Figure 4: Cold and hot tanks at Solar Two.

Solar Two used a two-tank system. There was a hot tank 560°C filled with just molten salt, and a cold tank containing molten salt at 290°C. The molten salt was used in Solar Two because it can reach higher temperatures than the mineral oil, Caloria, used in Solar One. The molten salt can reach 560°C whereas Caloria's peak temperature is 310°C. A higher temperature yields a more efficient cycle, thus the substitution of molten salt for mineral oil made sense.

One of the largest challenges for large-scale solar thermal power plants taking off commercially is their large cost compared to the cost of conventional power plants such as coal. Currently, the average coal power plant produces electricity for a cost of $0.02 - $0.04 per kWh.(3) Solar power plants produce electricity for a cost of $0.12 per kWh.(3) If solar power plants were to take off and an industry created for the production of all the component, then the cost of solar-thermal electricity would go down. There are projections that put the cost of solar-thermal electricity at $0.08 per kWh should the industry take off.(3) However, the current situation is $0.12 per kWh, and as a result the motivation behind the thermocline test is reducing cost.

The thermocline thermal storage test is set to be tested here at the Sandia National Laboratories' NSTTF at the beginning of September. The primary goal of this test is to reduce costs by testing a single thermocline tank that is lower cost than a two-tank molten salt storage system. The thermocline thermal storage could be employed in both central receiver and parabolic trough type power plants.

To sum up, the thermocline test investigates the following new concepts:

- A single thermocline tank for storage instead of two separate tanks.
- Mixing rocks together with the salt in the tank. (Decreases cost by reducing the amount of salt needed.)
- Introducing Calcium Nitrate ($CaNO_3$) into the nitrate salt formula. (Lowers melting point of nitrate salt mixture.)

Note: It is true that the thermocline tank could be used with central receiver solar power plants; however, the current test will run its cycle with temperatures of 290°C and 390°C. Central receiver solar power plants run their cycle at higher temperatures 290°C to 560°C. Thus, the materials selected would have to be proven at a test stage with the appropriate temperature range before implementation at a central receiver power plant. The focus of the thermocline test is for the parabolic trough solar power plants.

Details of the Single Thermocline Tank

Engineers conceived the design for the thermocline test in December 1999. Ordering valves, piping, pumps, heat trace, thermocline tank, and performing the construction all began in February 2000. Many components were reincarnated parts from older experiments. We brought in a pump from Solar Two, reused many valves and flow meters from old experiments, resurrected a propane heater from the original power tower experiments conducted back in the early 1980s, and we reused a cooler from a previous experiment. With all this provisions, the cost of materials for this project only reached around $200,000.

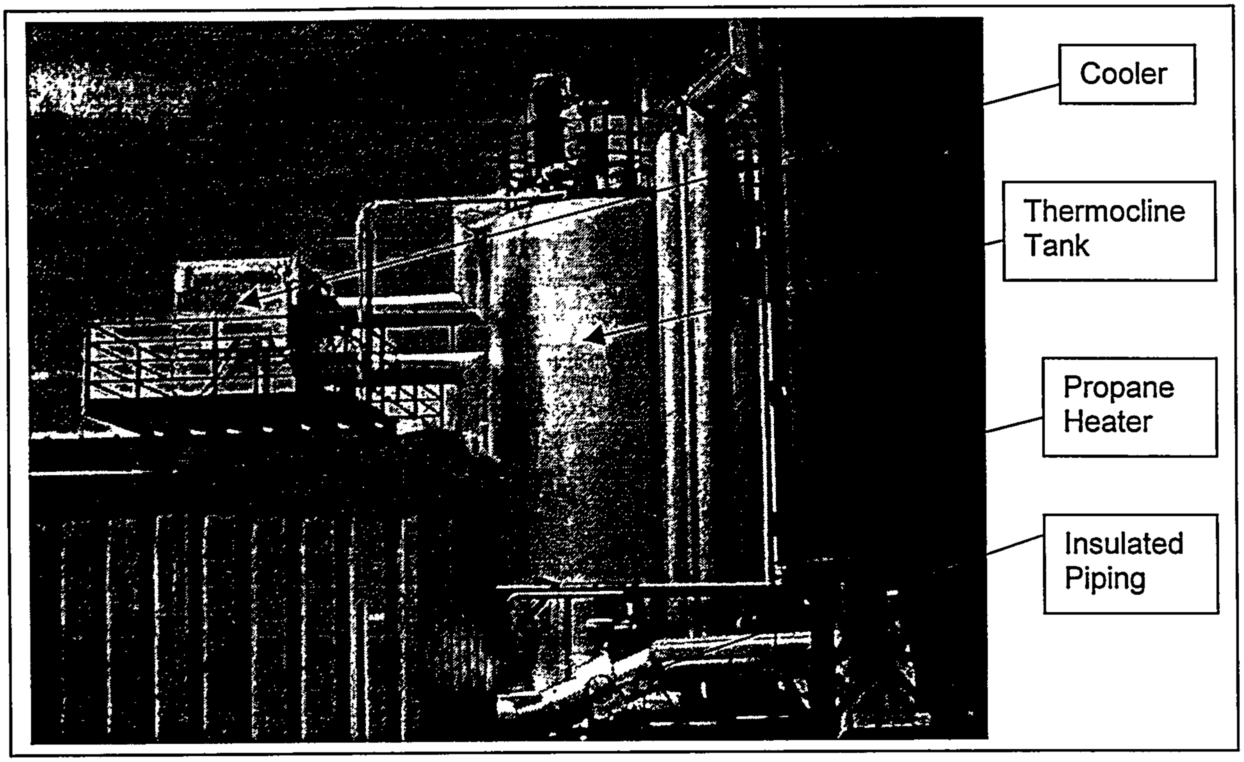


Figure 5: Side view of entire thermocline system.

The thermocline tank is 20' in height and 10' in diameter. It has a thermal capacity of 1.5 MWh.

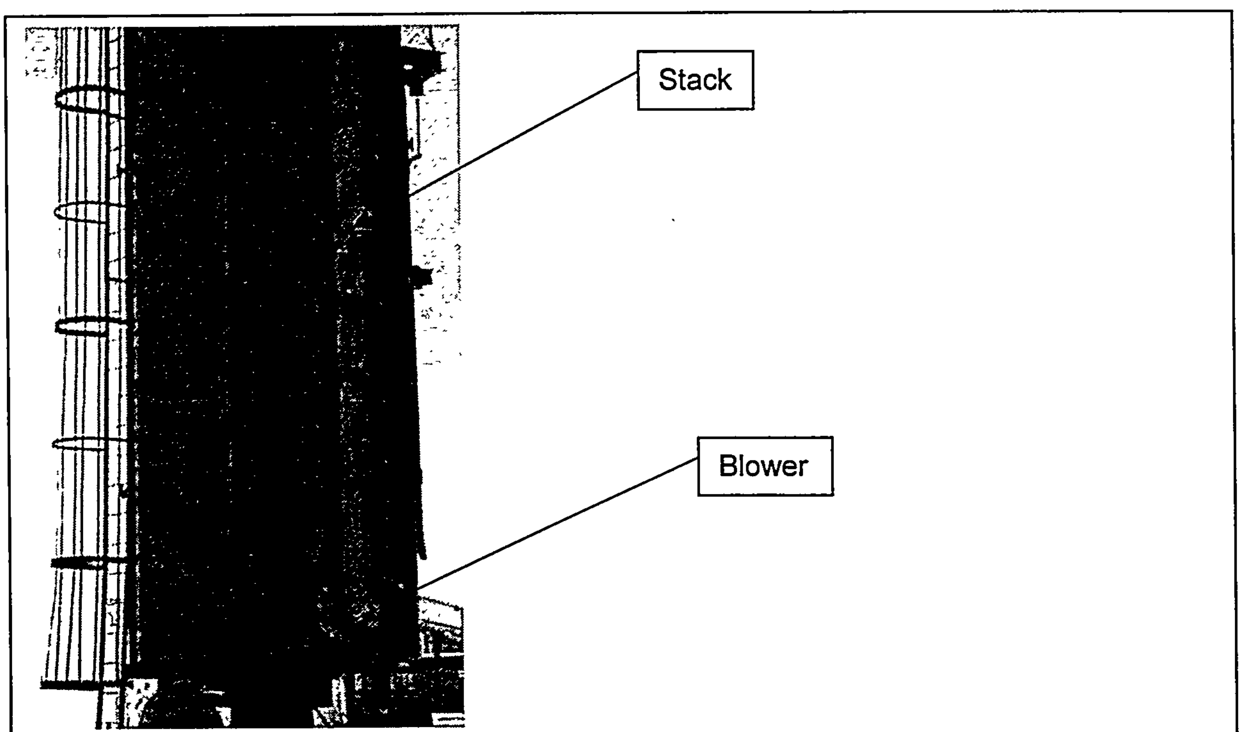


Figure 6: Propane heater

The propane heater was used in the original test back in the early 1980s. We made good use of this existing piece of equipment. The thermocline test will require about 1/6 to 1/3 of the heater's capacity for the thermocline test.

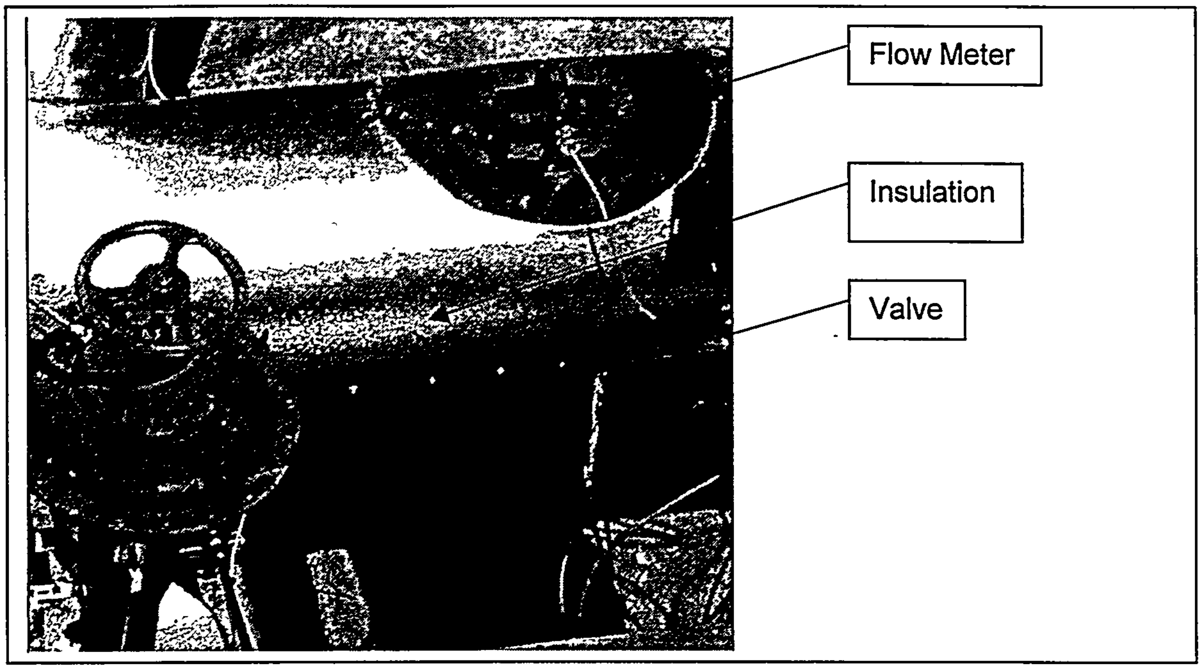


Figure 7: Valve and flow meter with insulation.

This close-up picture shows some of the equipment that we reused from previous experiments.

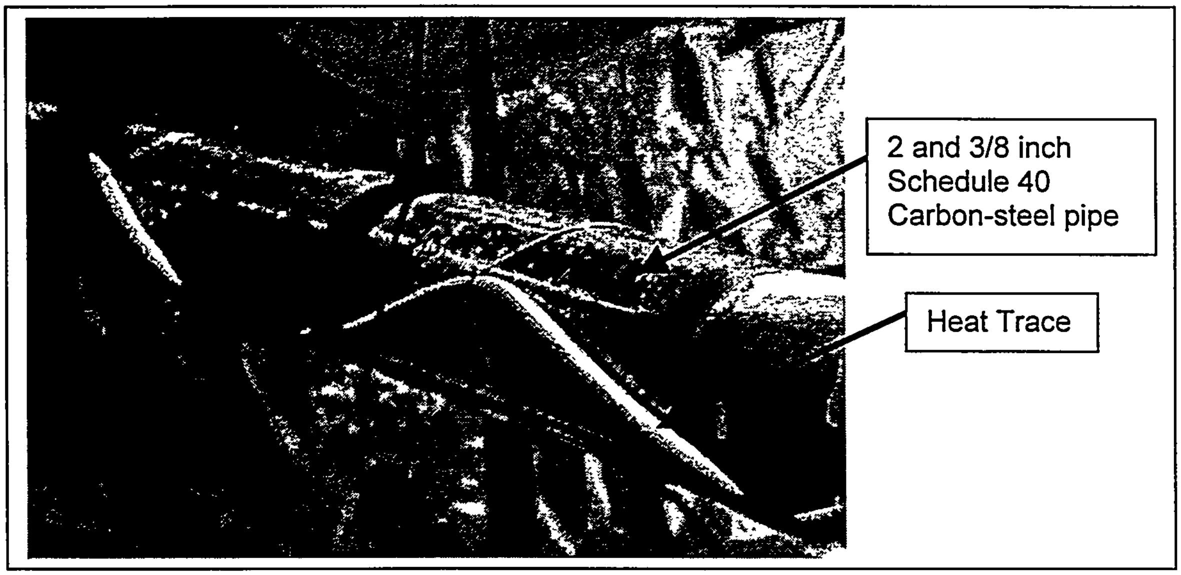


Figure 8: Heat trace on piping

The piping needs to be wrapped with heat trace, a resistance wire that will maintain heat on the pipes, to prevent freezing of the salt.

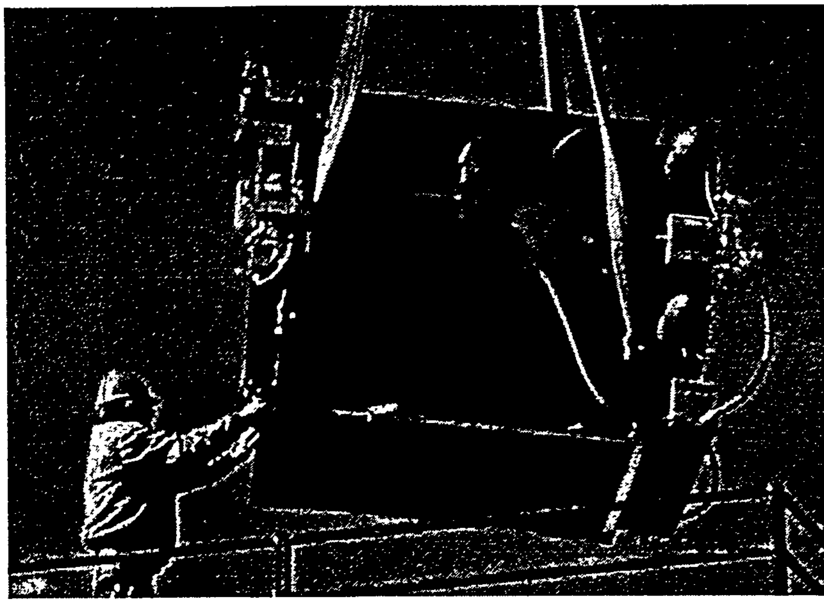


Figure 9: Cooler

Details on the Rock Selection and Packing

A first major step was choosing the appropriate rock that would not corrode or deteriorate due to its submersion in the molten salt. To determine what rock would endure this environment the best, a small-scale test called Hot Rocks test began in March 2000.

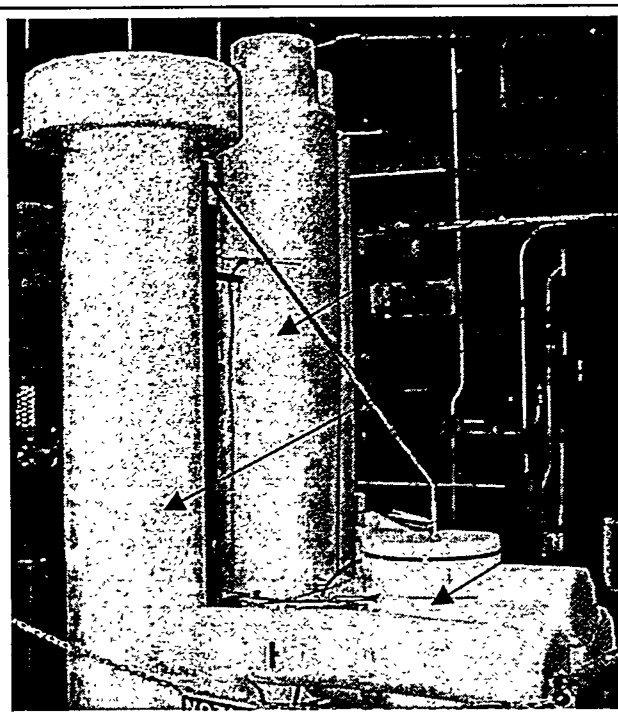


Figure 10: Hot rocks test. (Shows original insulation of tanks and piping.)

The hot rocks test explored the durability of each rock sample by cycling hot salt (400°C) and cold salt (290°C) through a basin of the given rock sample. These are the temperatures at which the thermocline test will operate. A total of 17 different rocks were selected as possible candidates for use in the thermocline tank. Five were tested in the hot rocks experiment. The other 12 were eliminated based on their cost, availability, and instability when immersed in the molten salt (tested in the laboratory on a small scale). As seen in Figure 10, two tanks were located on both sides of a small chamber. One tank held salt at 400°C and the other tank held salt at 290°C. The rocks would soak in the 400°C salt for 20 minutes, then the 290°C salt was cycled through and the rocks would bathe in that salt for twenty minutes. We cycled the molten salt through the rock candidates at least 360 times. Since the thermocline tank is designed to cycle every 2 – 4 hours and the thermocline test needs operators to run, we calculated that 360 cycles was equivalent to a year of actual testing.

(4 hours hot soak) + (4 hours cold soak) = 1 cycle = 1 workday (Eq. 1)

One sensitive issue is the freezing point of the salt. We encountered many problems with the salt freezing in the pipes at the start of the hot rocks test. Depending on the composition of the salt it can freeze between 120°C and 230°C. The original insulation job was not sufficient to prevent freezing near the valves. See Figure 10.

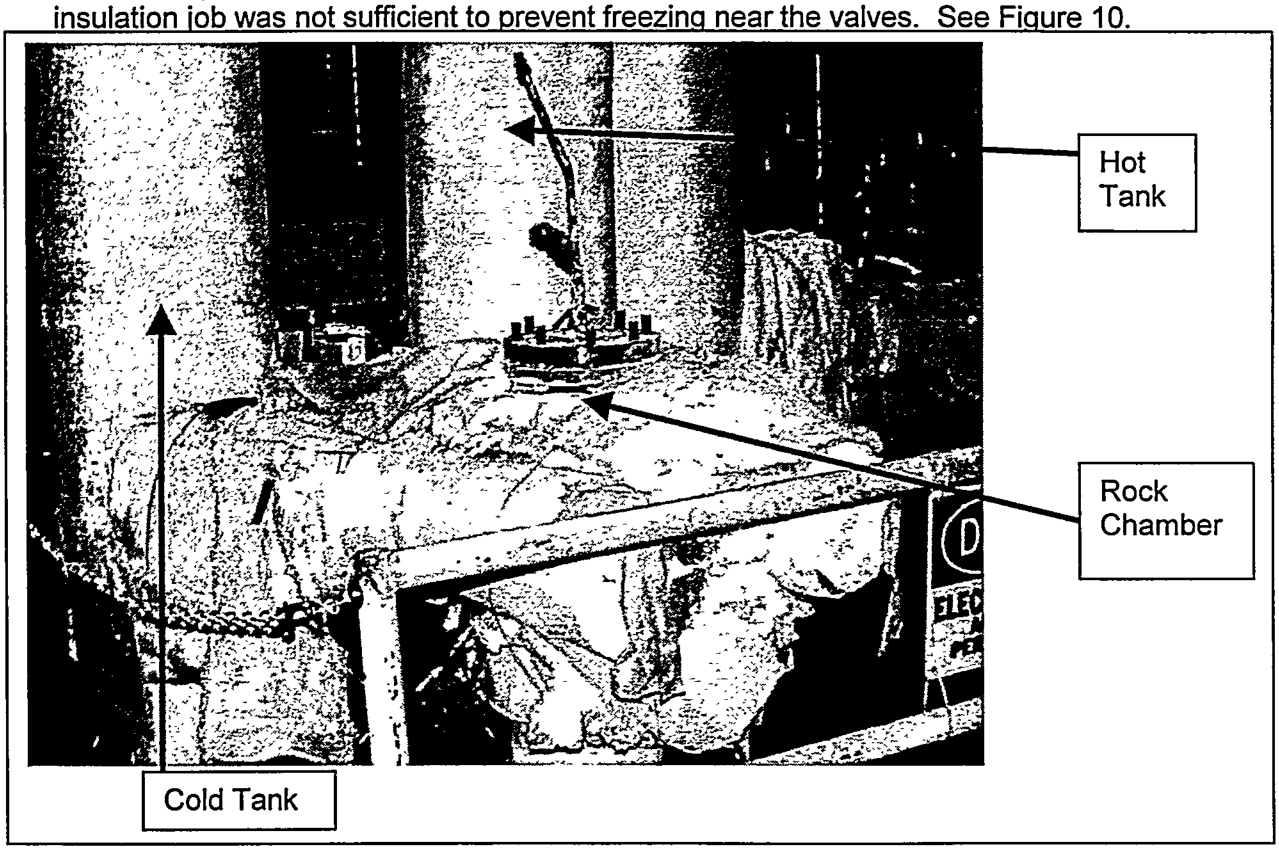


Figure 11: Hot rocks test running smoothly in late March after much patchwork on the insulation.

Note the difference between Figures 10 and Figure 11. It took a lot of additional insulation to ensure that the salt did not freeze in the pipes.

Below are some examples of rock candidates that did not endure the molten salt environment.

Figure 12: Limestone before (left) and after (right) experiencing 360 cycles of molten salt.

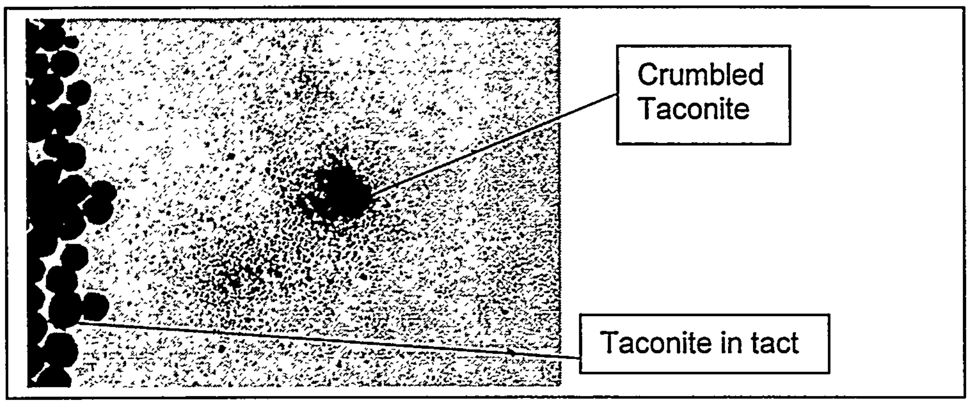


Figure 13: Taconite after exposure to molten salt for 360 cycles.

Some pieces were easily crushed between two fingers. We believe it was due to the molten salt exposure, even though the taconite seemed to hold up well overall.

According to the data from the hot rocks experiment, quartzite rock was chosen as the filler material in the thermocline tank. Along with quartzite rock, we selected silica sand to mix with it.

Figure 14: Quartzite Rock before (left) and after (right) experiencing 533 cycles of molten salt.

Note: The rocks on the right are mixed with water. We were cleaning the tank to prepare for another test.

Figure 15: Silica Sand before (left) and after (right) experiencing 360 cycles of molten salt.

Silica sand has the same chemical composition as the quartzite rock, and it performed well in the hot rocks test. From Solar One's thermocline storage tank data, we know we could obtain the best void fraction by mixing sand with rock.[2] This is true because given a certain void space between the quartzite rock, that void space will decrease if sand is added and that sand then occupies that void space. The combined void space of the sand and rock together should theoretically be:

$$\left(Void_{quartzite}\right)\cdot\left(Void_{sand}\right) = Void_{combined} \quad \text{(Eq. 2)}$$

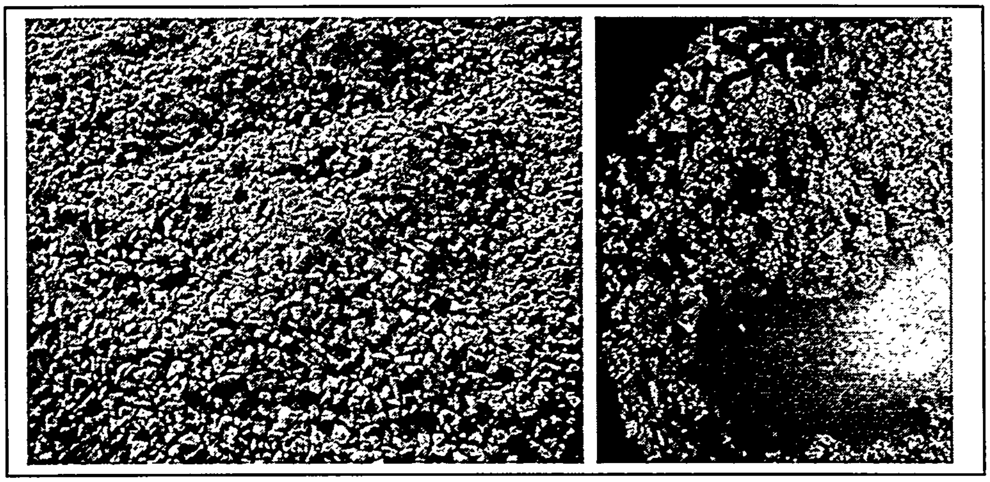
The numbers from Solar One were 40% void for the rock alone and 40% void for the sand alone. Using Eq. 2, the combined theoretical void was 16%. In practice they attained a void space of 22%.[2] For the thermocline test, we predicted the combined void space by using 55-gallon drums. See Figure 16 below. We discovered from the literature that to obtain a reliable value for void fraction, the diameter of your tank must be 50 times the diameter of the largest rock.[1] Originally we had done experiments in a bucket with a 1-foot diameter. Since the quartzite rock averages ¾" in diameter, the buckets gave us erroneous values for the combined void fraction. We measured about 37% for the combined void fraction using the 1-foot buckets. Therefore we could not confide in the values obtained using the 1-foot buckets. Nor could we calculate the void fraction using Eq. 2. Thus we performed two experiments using the 55-gallon drums from which we concluded the following:

Table 1: Void Fraction Results.

First Experiment	Second Experiment
30.7%	25.3%

In the first experiment, we attempted to pack the rock/sand down with a sledgehammer. This was not effective because the surface area of the sledgehammer hitting the rock/sand was too small with respect to the area of the rock/sand pieces. In the second experiment we used a 1-foot square piece of metal attached to a rod as our packer. Its packing area was much larger than the sledgehammer's area with respect to the rock/sand, and therefore we obtained a much better void fraction. The second experiment's results reflect what we expect in the thermocline tank. This is due to the fact that we will pack down the rock/sand with a packer in the thermocline tank.

By the two experiments performed, we discovered that critical factor for obtaining the optimal fraction is packing down the rock/sand very well.



<u>Figure 16</u>: Photo of a 2 to 1 mixing ratio of quartzite rock to silica sand respectively. Mixture spread out on the ground (left). Mixture filled with water contained in a 55-gallon drum (right).

In each experiment, we used a 2:1 ratio of quartzite rock to silica sand respectively. This should be used in the tank to obtain a void fraction near 25%. Also, it is practical because we can easily add 2 buckets of rock to 1 bucket of sand when we load the tank. At Solar One the mixing ratio was 7:4 (rock : sand). Regardless, we will stay with the 2:1 ratio, and we expect to obtain between 25% and 30% void space in the thermocline tank.

Salt/Oil Safety Test

This test explored the reactivity between Therminol and Caloria, and the molten nitrate salt. The molten salt used in this test was a commercially available mixture of 48% $CaNO_3$, 7% $NaNO_3$, and 45% KNO_3.[3] Its freezing point 87°C – 130°C.[3] This mixture is sold under the name Hi-TEC XL. The composition of these molten nitrate salts can be altered without much change on its material properties. For example, this Hi-TEC XL would behave very much the same in metal heat treating processes as would a mixture with different concentrations of $CaNO_3$, $NaNO_3$, and KNO_3. The factor that varies with changes in the concentration of the constituents is the melting/freezing temperature.

Therminol and Caloria are currently used as the heat transfer fluids in the SEGS solar trough power plants in southern California. Therminol is a synthetic oil; Caloria is a mineral oil. Since the intention of the thermocline is to provide thermal storage for the Solar Trough power plants, we needed to investigate the reactivity between the oils used in the SEGS plants and the molten salt. It is possible that the oils could come into contact with the molten salt at the operating temperature of 400°C due to a failure in the oil-to-salt heat exchanger. The subsequent reaction could cause a dangerous result such as a fire or explosion.

These tests involved introducing the oils underneath the surface of the molten salt at 400°C.

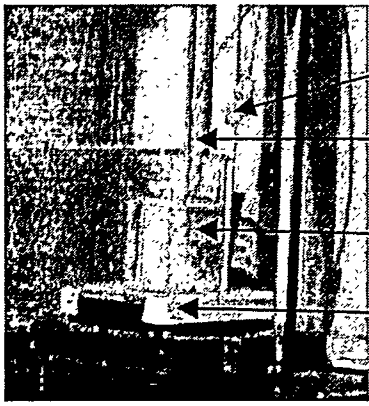


Figure 17: Set up of Salt/Oil Safety Test

The Therminol caused rapid bubbling and steaming when introduced into the salt. Bubbling continued for one minute and twenty seconds until the Therminol was completely boiled off. The bubbling is desirable because a failure in a Therminol-to-salt heat exchanger could be detected with a sensing mechanism that identifies a pressure rise. There were no flames.

The Caloria caused similar result as the Therminol. It bubbled and steamed for three minutes before all the Caloria was boiled off. Again this was satisfying because we witnessed no flames or explosion. After the Caloria boiled off we surrounded and covered the beaker with insulation in order to maintain the temperature of the salt at 400°C for the next experiment. Immediately upon covering the beaker we saw flames seeping through the gaps in the insulation. Right away we removed all the insulation from the beaker. The surface of the salt maintained the flame for just over two minutes.

The flames we saw in the Salt/Caloria safety test motivated us to repeat the salt/Therminol safety test, but this time implementing a spark plug in the headspace of the beaker. The Caloria vapors, mixed with oxygen from the air, caught fire when trapped by the insulation. Perhaps the Therminol would have reacted the same way had it been covered in its original test. The objective of this test was to determine if containing Therminol vapors and providing a spark would cause the vapors to ignite.

The Therminol vapors did ignite. Thus we deduced that if the temperature is above the boiling point of the oil (260°C for the Therminol and 320°C for the Caloria), then oil vapor will be present. If this vapor is contained and oxygen is available, then the oil vapors can ignite. If salt storage systems are to be incorporated into the Solar Trough power plants, care should be taken to monitor the oil-to-salt heat exchanger in case of a leak. A fire could result. One positive note was that both the Salt/Therminol and Salt/Caloria safety tests showed no signs that an explosion would occur. The flames in both tests ceased after a few minutes. The oil vapors just needed to burn off.

Larger safety factors could be incorporated into the design of the oil-to-salt heat exchangers to prevent the possibility of a leak. Also, pressure transducers could be used to monitor the pressure on each leg of the heat exchanger. Should there be change in pressure, valves could be shut off and the problem could be investigated. As long as no oxygen is present, there can be no flame. Thus, flooding the headspace in the salt tank with an inert gas would prevent ignition of the oil vapors. This technique could be employed to ensure no flame would ignite while investigating a suspected problem.

An important conclusion from these Salt/Oil safety tests is that monitoring the temperature of the salt would not reveal a leak in the oil-to-salt heat exchanger. The mixing of Therminol and Caloria with the salt did not cause a noticeable temperature alteration in the salt reservoir. The following graph shows the cooling curve for the salt when Therminol was introduced. The graph for when Caloria was introduced is equivalent. In both cases the temperature change upon introduction of the oil into the salt was negligible. See graph below.

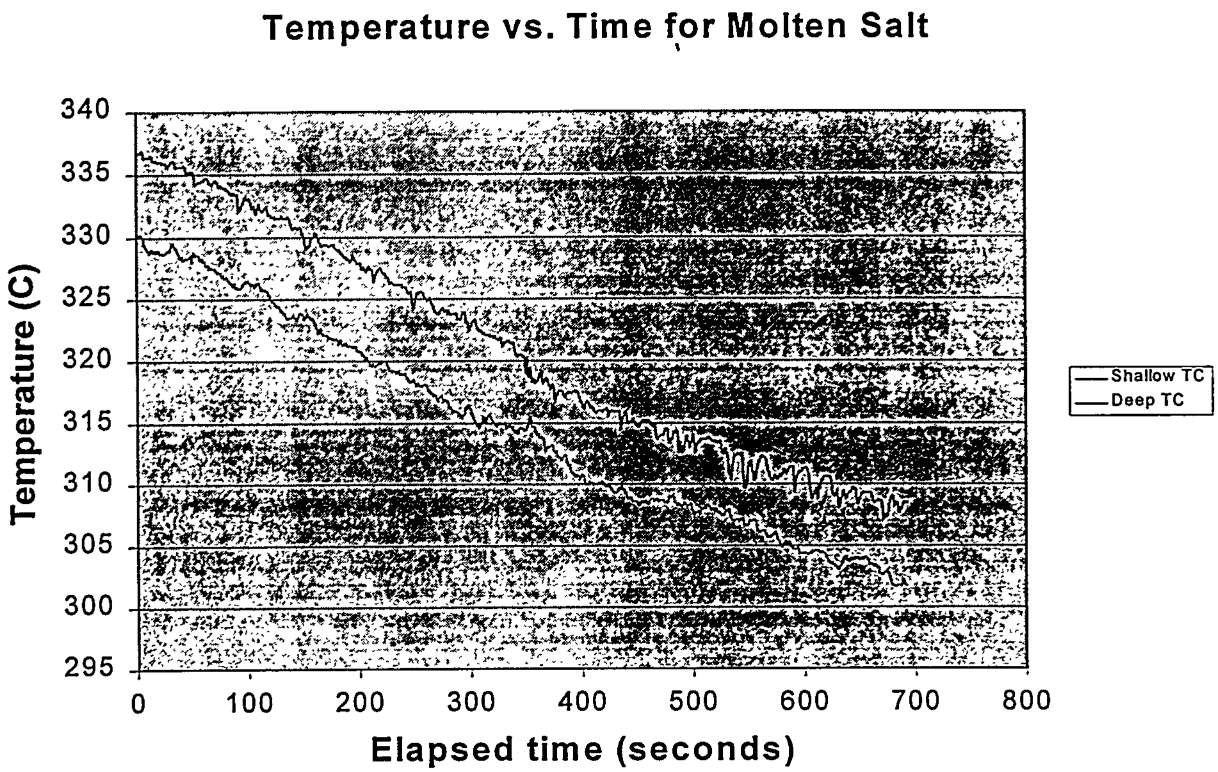


Figure 18: Graph of temperature vs. time for cooling of salt.

The salt was introduced 350 seconds. The temperature changes of the salt after the introduction of the Therminol varied by a few degrees Celsius at most. Thus, monitoring temperature would not be a good technique to detect a leak in the oil-to-salt heat exchanger.

Details on the $CaNO_3$ Element in the Nitrate Salt

As stated before the salt could cause a problem because it freezes between 120°C and 230°C depending on the composition. Therefore it is imperative to insulate and heat the piping. As seen in Figure 8, the piping needs to be wrapped with heat trace to prevent freezing of the salt. In Figure 7 the insulation can be seen. Molten salts have been used in metal industry for decades. Their ability to maintain very high temperatures (over 500°C) makes them good candidates for a heat transfer fluid in a power plant. That is why they have been employed in solar power plants.

A different component was added to the molten salt mixture for this experiment. It is Calcium Nitrate ($CaNO_3$). We wanted to mix our own salt for this test rather than use the commercially available Hi-TEC XL because it is much less expensive to buy our own salt and melt them together to get the composition we want. The cost of the Hi-TEC XL is $5,000/ton.[3] $CaNO_3$ lowers the melting point of the salt mixture. This is advantageous because it reduces the possibility of the salt freezing in the pipes. In Solar Two and in previous experiments dating back to the first days of solar power plant research the 1970s, primarily potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$) were used in the nitrate salt mixture. $CaNO_3$ was not as common as the other two nitrate salts. Also, $CaNO_3$ is more expensive than the other two constituents.

The following table displays the difference in price of the three nitrate salts.

Table 2: Prices of Nitrate Salts

$CaNO_3$	KNO_3	$NaNO_3$
$1300/ton	$560/ton	$360/ton

Even though the $CaNO_3$ is more expensive, we feel the trade off for a lower melting point will be more valuable. From pipe freezes experienced at Solar Two, we know the labor costs for thawing out the frozen salt in the pipes are troubles worth trying to eliminate. The thermocline testing will provide the comparison.

The combination (used in Solar Two) of 40% by weight KNO_3 and 60% by weight $NaNO_3$ melts at 230°C. For the thermocline test we investigated combining different percentages (by weight) of the $CaNO_3$ with the KNO_3 and $NaNO_3$. We varied the $CaNO_3$ concentration from 15% to 30%. After many laboratory experiments we decided to choose a mixture of 30% $CaNO_3$, 24% $NaNO_3$, and 46% KNO_3. We found in the laboratory that for the reagent grade (pure) salts, the given mixture melted between 140°C and 160°C). Yet we found with the technical grade salts (containing more impurities that reagent grade) that the given mixture melted between 120°C – 140°C. The mixture melted around 120°C. We expect between 120°C – 140°C as temperatures at which the 30% $CaNO_3$, 24% $NaNO_3$, and 46% KNO_3 salt mixture will melt and freeze. We will use this mixture in the thermocline tank. We expect these temperatures because we will use the technical grade salts in the thermocline system. This is fantastic because the pipes in the thermocline test are not as likely to freeze as the pipes at Solar Two, whose salt fusion temperature was 230°C.

Advantages of Thermocline Design

The primary advantage of this design is the cost reduction compared with a two tank-storage design. The thermocline design dramatically reduces the hardware needed. It eliminates piping, heat trace, insulation, foundation and the pumps associated with one of the tanks. Plus, it displaces over 70% of the volume inside the tank, thus eliminating 70% of the salt needed for the test. The 70% comes as a result of the 25% – 30% void fraction. All this translates to about a 1/3 cost reduction compared to a two-tank storage system.[3] The introduction of $CaNO_3$ into the salt mixture is advantageous because it reduces the risk of salt freezing in the pipes.

There is some thermal advantage to adding the rocks versus just having salt in the tank. On a volumetric basis, the specific heat of the rock is about five percent larger than the specific heat of the nitrate salt.[3] The rocks will hold the heat longer than the salt thus providing a thermal advantage over the salt. However the most important advantage of the rock/sand mixture eliminating the amount salt needed is the cost reduction associated with that. The cost difference is \$800/ton for the salt versus \$70/ton for the rocks and sand.

Finally, there are less thermal losses associated with a one-tank system than with a two-tank system. There is inherently more surface area with a two-tank system through which heat will be lost from the molten salt to the environment. A one-tank system reduces the amount of surface area exposed to the environment by eliminating a tank and the pipes associated with it.

Conclusions

The thermocline test will begin in September. The expected data will allow us to summarize the performance of the thermocline tank for storage and contrast it against the two-tank design. The performance of the Thermocline test will potentially confirm the following data.

- Mixing rocks together with the salt in the tank should yield the best advantage - reducing cost.
- A 1/3 cost reduction is expected from a one-tank thermocline thermal storage system compared to a two-tank system.[3]
- The cost of the nitrate salts is \$800/ton versus the rock/sand combination at \$70/ton.
- Quartzite rock and silica sand were chosen as the filler material in the tank. They performed the best in the hot rocks test.
- A 2:1 mixing ratio of quartzite rock to silica sand respectively will produce the lowest void fraction in the tank.
- That void fraction is expected to fall between 25% – 30%.
- Introducing $CaNO_3$ into the nitrate salt formula should help reduce the chance of the salt freezing.
- The melting/freezing range of the 30% $CaNO_3$, 24% $NaNO_3$, and 46% KNO_3 mixture falls between 120°C – 140°C.

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