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Testing Thermocline Filler Materials and Molten-Salt Heat Transfer Fluids for Thermal Energy Storage Systems Used in Parabolic Trough Solar Power Plants

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Abstract

Parabolic trough power systems that utilize concentrated solar energy to generate electricity are a proven technology. Industry and laboratory research efforts are now focusing on integration of thermal energy storage as a viable means to enhance dispatchability of concentrated solar energy. One option to significantly reduce costs is to use thermocline storage systems, low-cost filler materials as the primary thermal storage medium, and molten nitrate salts as the direct heat transfer fluid. Prior thermocline evaluations and thermal cycling tests at the Sandia National Laboratories' National Solar Thermal Test Facility identified quartzite rock and silica sand as potential filler materials. An expanded series of isothermal and thermal cycling experiments were planned and implemented to extend those studies in order to demonstrate the durability of these filler materials in molten nitrate salts over a range of operating temperatures for extended timeframes. Upon test completion, careful analyses of filler material samples, as well as the molten salt, were conducted to assess long-term durability and degradation mechanisms in these test conditions. Analysis results demonstrate that the quartzite rock and silica sand appear able to withstand the molten salt environment quite well. No significant deterioration that would impact the performance or operability of a thermocline thermal energy storage system was evident. Therefore, additional studies of the thermocline concept can continue armed with confidence that appropriate filler materials have been identified for the intended application.

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Acronyms/Abbreviations

API – American Petroleum Institute
BES – Back-Scattered Electron Spectroscopy
Ca – Calcium
$CaCO_3$ – Calcium Carbonate
CSP – Concentrating Solar Power

DI – Deionized Water
DOE – Department of Energy
EDS – Energy Dispersive X-ray Spectroscopy
HCE – Heat Collection Element

Hitec – Commercial inorganic salt formulation (sodium nitrate, potassium nitrate, sodium nitrite)
HitecXL – Alternative ternary formulation (calcium nitrate, sodium nitrate, potassium nitrate)
HTF – Heat Transfer Fluid

IC – Ion Chromatography
ICP/AES – Inductively Coupled Plasma/Atomic Emission Spectroscopy
ICP/MS – Inductively Coupled Plasma/Mass Spectroscopy

K – Potassium
Na – Sodium

NIST – National Institute of Standards and Technology
NREL – National Renewable Energy Laboratory (Golden, Colorado)
NSTTF – National Solar Thermal Test Facility (Albuquerque, New Mexico)
SEGS – Solar Electric Generating System (near Barstow, California)

SEM – Scanning Electron Microscopy
SNL – Sandia National Laboratories (Albuquerque, New Mexico)
TC – Thermocouple
TES – Thermal Energy Storage
VP-1 – Therminol HTF (used at SEGS plants)

EXECUTIVE SUMMARY

Parabolic trough solar thermal electric power systems will become an increasingly important and cost-competitive option for providing clean, renewable energy to the U.S. – and world – energy markets. The U.S. Department of Energy, in collaboration with its national laboratories, supports research and development of concentrating solar power using a systems-driven approach. This methodology helps define the markets, technology applications, systems and subsystems of those energy supply applications, and the most important and cost-effective use of R&D funding for materials, component-level, and system-level activities.

SunLab, a “virtual laboratory” comprising a partnership between Sandia National Laboratories in Albuquerque, New Mexico and the National Renewable Energy Laboratory in Golden, Colorado, has conducted trade studies to evaluate the viability and cost competitiveness of electric power production from parabolic trough solar electric generating systems. SunLab participants have recently focused research efforts on the integration of solar thermal energy storage (TES) as a viable means to enhance dispatchability and increase the value of concentrated solar energy.

There are a number of viable candidates for TES systems that might be developed and applied on a commercial scale for parabolic trough power plants. System studies conducted by SunLab have evaluated the more traditional two-tank energy storage systems and single-tank thermocline storage systems and have shown that “direct” thermocline-based energy configurations may offer the least-cost TES option. The single thermocline tank would use molten nitrate salts as the direct heat transfer fluid, storing energy gathered in the parabolic solar field, and transferring that energy when needed to the same power block heat exchangers that are served directly from the solar field. With the hot and cold fluid in a single tank, the thermocline storage system relies on thermal buoyancy to maintain thermal stratification and discrete “hot” and “cold” thermal regions of the TES system. A low-cost filler material used to pack the single storage tank acts as the primary thermal storage medium and reduces the overall required quantities of the relatively higher cost molten salt heat transfer fluid. Due to the potential size of TES systems and tanks for large power plants, properly specifying and qualifying the filler material as a significant component of this system is a major element for both first-cost and long-term maintenance costs associated with TES systems.

Ideal filler materials for thermocline storage tanks would need to be inexpensive and widely available, have a high heat capacity, a low “void fraction” (to reduce the amount of molten salt required), be compatible with nitrate salts, and be non-hazardous. Most of these parameters are fairly easy to characterize and quantify; however the compatibility of filler materials in hot, cyclic molten salt environments was unknown. Thus, a test program was developed to identify candidate filler materials, screen and test those materials in molten salt environments, down-select to the most viable candidate filler materials, and then perform rigorous testing to fully assess the potential of filler materials to withstand the demanding molten salt operating conditions.

Filler material screening studies and experiments conducted at Sandia identified a number of potential materials for further study, including limestone, marble, taconite, quartzite rock, and silica sand (used as an additional filler material in order to reduce void fraction). Initial thermal cycling of these materials identified quartzite rock in combination with silica sand as the best candidate for further studies. Sandia then designed, tested and evaluated a 2.3 MWh(t) pilot-scale thermocline storage system loop to model and consider the feasibility of the thermocline concept as well as test the candidate filler materials in hot molten salt environments typical of power plant conditions. Overall, the pilot-scale thermocline test was successful, demonstrating that a molten salt thermocline storage system is a feasible alternative for thermal storage in a parabolic trough power plant, and that the quartzite rock and silica sand work well as filler materials and should be further assessed for durability in molten salt. As such, a test plan was developed to extend the screening and feasibility studies to demonstrate conclusively the durability of these filler materials in molten nitrate salts over a range of operating temperatures for extended periods.

An isothermal test apparatus was developed to test rock and sand filler materials immersed in molten salt for a one-year test duration, at both 450ºC and 500ºC. Control salt pots containing only molten salt were included for comparison. Since a commercial storage system could go through 10,000 or more startup and shutdown cycles in a 30-year project life, a thermal cycling test was also conceived and developed to run for 10,000 thermal cycles in the 285ºC to 450ºC temperature range to simulate that typical 30-year plant life. The temperature range was chosen consistent with industry trade studies that evaluated the feasibility and design tradeoffs of pushing parabolic trough power plants to these higher temperatures using molten salt as the primary heat transfer fluid in the solar field and thermal energy storage system.

An extended period of pre-test evaluation of candidate molten salt formulations led to the use of a mixture quite similar to a commercial ternary molten nitrate salt product called HitecXL. The final mixture chosen for testing consisted of 44 weight percent calcium nitrate tetrahydrate, 12 weight percent sodium nitrate, and 44 weight percent potassium nitrate. Because the tetrahydrate form of calcium nitrate contains about 30 percent water, a process was developed to safely mix the salts, load the test apparatus, and then melt the salt mixture and boil the water off. With proper preparations and prudent precautions, this process worked well for these laboratory-scale experiments.

The startup and operation of the isothermal and thermal cycling tests of quartzite rock and silica sand filler materials were quite successful, with only minor operational issues. Of significance, gate valves of a simple stainless steel design installed for periodic isolation and shutdown mechanically froze in the open condition early in the thermal cycling test. Though these failures prevented periodic shutdown for qualitative observations of filler material condition, the limited benefits of these shutdowns did not justify the time, cost and risk of potential show-stopping failure of the test in order to replace the valves. Since a thermocline tank in a large power plant may be required to operate (economically) for the full 10,000-cycle life without rock/sand refurbishment or observation, the continuation of the thermal cycling test with no periodic shutdowns was thought more representative of the actual plant conditions.

Also noted during isothermal testing was significant deterioration of stainless steel sample baskets immersed in the molten salt that occurred during the 1-year test period. The baskets in the 500ºC test pot required repair and reinforcement in less than 6 months, and basically disintegrated on removal after one year. On the other hand, the sample baskets at 450ºC held up quite well for the entire test duration with no significant deterioration. A simple sample basket installed in the test chamber of the thermal cycling apparatus exposed to 10,000 cycles in the range of 285ºC to 450ºC also held up well.

Another condition noted during testing was significant calcium carbonate ($CaCO_3$) crust formation on the surface of the molten salt in one of the isothermal control pots at 500ºC. This crust also formed to a significant degree in the "cold" tank of the thermal cycling apparatus, which was open to atmosphere and maintained at approximately 280ºC to 285ºC for the 14-month duration of the thermal cycling test. This observation in testing raised concerns regarding the treatment and control of this scaling in large, commercial-scale power plants, particularly in the piping and solar field heat collection element absorbers.

Apart from these observations, the filler material testing was very successful. The quartzite rock and silica sand gained weight overall when exposed to both isothermal and thermal cycling conditions. The materials were removed at the end of testing and surface and subsurface examinations were conducted and the materials were evaluated by Sandia experts. The final sample net weight gain was an off-setting combination of early erosion and minor surface degradation coupled with minor nitrate salt intrusion/deposition and $CaCO_3$ crust formation, an "armor" that seemed to retard further growth or degradation. The deterioration of the quartzite rock and silica sand filler materials in both the isothermal and thermal cycling tests was considered minimal. Sandia recommends moving forward with additional studies of the thermocline concept armed with confidence that appropriate filler materials have been identified for the intended application.

INTRODUCTION

As people of the United States, and all nations of the world, contribute to and witness the dramatic growth of population, national economies, and complex infrastructures of the 21st century, the need for and supply of energy will become an increasingly critical issue. This report will not repetitively document what has already been said in thousands of articles and studies regarding these demanding technical, social, political, and economic issues. Rather, this paper focuses on material studies that support further development of energy supply systems based on capture of solar energy as a viable energy supply option.

The energy supply mix of the 21st century will be based on a strategic mix of existing supply sources and technologies as well as new and innovative supply technologies currently under development. Examples of those "new" alternative and renewable energy supplies include wind (both small and utility-scale), geothermal, biomass conversion, hydrogen-based approaches, photovoltaics (solar electric), and solar thermal technologies. In addition to the smaller-scale solar thermal energy technologies for applications such as residential and commercial space heating, water heating, and swimming pool heating, industrial and utility-scale solar electric generation can be supplied by what has been termed concentrating solar power, or CSP, technologies. Examples of those technologies include electricity generated by dish/Stirling engine systems, large power tower utility-scale systems, and industrial and utility-scale systems based on parabolic trough power generating plants. CSP technologies have the potential to provide the world with clean, renewable, cost-competitive power on a large scale.

Parabolic trough electric power generating plants have already been developed at the utility-scale, particularly in the United States. The Solar Electric Generating Systems (SEGS) near Barstow, California (Fig. 1) have accumulated over 145 years of operational experience generating electricity from concentrated solar thermal energy utilizing large fields of parabolic trough concentrators. A number of these SEGS plants, with total generation capacity of about 354 MWe, were built over a period of time in the 1980's and continue to operate successfully and economically. The operation of the SEGS plants has demonstrated the ability of this technology to compete in the commercial power supply market of southern California. As such, SEGS plants based on current and improved parabolic trough systems and components will constitute one of the highest priority technologies for consideration in national and international strategies for meeting the growing power demands of nations.

DOE, SunLab, and CSP

The U.S. Department of Energy (DOE) administers its CSP Program through two of its national laboratories – Sandia National Laboratories (SNL) in Albuquerque, New Mexico, and the National Renewable Energy Laboratory (NREL) in Golden, Colorado. These entities operate as a virtual laboratory known as SunLab created through cooperation, communication, and teamwork. SunLab has supported research and development in a systems-driven approach leading to field deployment of both experimental and commercial-scale CSP technologies. In addition to R&D activities in support of a large range of renewable and solar technologies, SunLab collaborates in the further development of the materials, components, subsystems and systems, potential applications, and markets for the CSP technologies. The focus of this report is on parabolic trough electric energy supply technologies.

Trough and Thermal Energy Storage Studies

SunLab participants have conducted trade studies [1,2] to evaluate the viability and cost competitiveness of electrical power production from parabolic trough solar electric generating systems. Studies and research efforts coordinated among SunLab participants [3,4] are now focusing on the integration of solar thermal energy storage (TES) as a viable means to enhance dispatchability and increase the value of concentrated solar energy. Fields of parabolic troughs alone are only able to economically generate power when the fuel resource – sunlight – is available during the day and when cloud cover and atmospheric haze cover are minimal. At other times, the plant must be placed in a standby or shutdown condition, decreasing capacity factor and reducing overall energy output relative to other power supply technologies (based on coal or natural gas for instance) which are not so constrained. Depending on solar field and storage system sizing and optimization, thermal energy storage can potentially remove most or all of this constraint, expanding the time frames when power can be supplied (on cloudy days and evenings and nights).

Figure 1 - Solar Electric Generating System - Barstow, CA

TES Design Approaches

Research and engineered applications have identified a number of potential viable approaches for TES systems for solar power plants. All of the various approaches have technology, performance, and cost tradeoffs that must be addressed in system design studies and optimization efforts. Figure 2 depicts a schematic diagram of an indirect, two-tank thermal energy storage system. When classified indirect, the system requires two heat transfer fluids (HTF), one that captures energy from sunlight in the solar field, and a second fluid that transfers the captured and stored energy to the traditional steam generation heat exchangers at the power block. Another heat exchanger or set of heat exchangers are required to transfer energy from the solar field HTF to the power block and TES HTF. These additional heat exchangers increase cost and reduce the overall efficiency of the plant but, at the same time, are relatively easy to control. This near-term thermal storage option for parabolic trough technology would circulate hot oil HTF, such as Therminol VP-1, in the solar field and pass the collected heat via the heat exchangers to another HTF (such as molten salt) used in the 2-tank thermal storage system. The “cold” tank stores and buffers lower temperature fluid after the power block and feeds the supply side of the solar field. After solar energy is captured, it is either fed directly to the power block heat exchangers and/or stored (via the interim oil-to-salt heat exchanger) in the "hot" tank for later use when it is required. This type of indirect, two-tank system was used at the Solar Two solar power plant built and operated in the mid-1990's. [5]

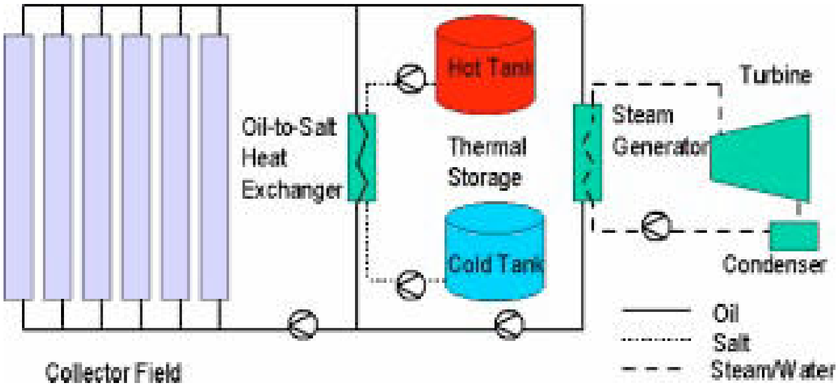


Figure 2 - Indirect, Two-Tank Thermal Energy Storage Schematic

The current baseline design of SEGS plants uses Therminol VP-1 heat transfer fluid in the collector field. Therminol VP-1 has a low freezing point (12°C) and is stable up to approximately 400°C, allowing these plants to use higher pressure, higher temperature and more efficient Rankine turbines. However, it is difficult to use this heat transfer fluid as a thermal storage media because its vapor pressure is too high to practically store it in any significant quantity at higher temperatures. Therminol VP-1 is relatively expensive, and is an environmental concern when leaks occur.

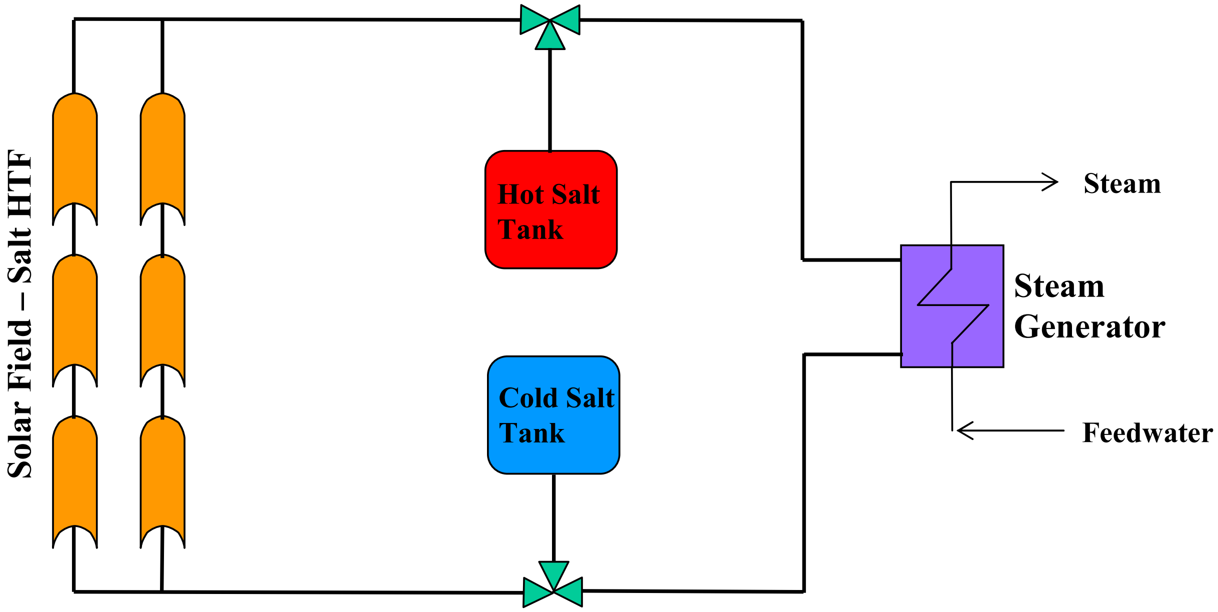


Figure 3 - Direct, Two-Tank TES Schematic

Rather than using an indirect TES system configuration, another option is designing a "direct" two-tank TES system (Fig 3). This allows the same fluid to be used in both the solar field and the thermal storage system, eliminating the need for the expensive heat exchangers. As part of the USA Trough Initiative, an industry/lab team led by Kearney and Associates [6,7] evaluated the option of using inorganic molten salts as both the solar field HTF and TES media in a trough solar power plant. This approach eliminates the expensive oil-to-salt heat exchangers. In addition, the solar field can be operated to higher outlet temperatures (450ºC to 500ºC) than currently possible with Therminol VP-1, increasing the power cycle efficiency and further reducing the cost of thermal storage. The primary disadvantage of most molten salt formulations is relatively high freeze points. Because of this, considerable care must be taken to make sure that the salt HTF does not freeze in the solar field. The higher outlet temperature also has some negative impacts as well, including higher heat losses from the solar field, concerns about the durability of the selective coating on the trough receivers, and the need for more expensive piping and materials to withstand the increased operating temperatures. Overall, initial findings for this direct molten salt HTF and thermal storage concept look encouraging, with the main issue being the relatively high freeze point of molten salts.

Another option to potentially reduce thermal energy costs significantly is to use direct, single-tank thermocline storage systems with molten nitrate salts as the direct heat transfer fluid (Fig 4). The thermocline storage system uses a single tank that is only marginally larger than one of the tanks in a two-tank thermal storage system (such as that used at Solar Two [5]). With the hot and cold fluid in a single tank, the thermocline storage system relies on thermal buoyancy to maintain thermal stratification. A low-cost filler material, which is used to pack the single storage tank, acts as the primary thermal storage medium. The filler displaces the majority of the molten salt that might be used in a comparable two-tank system. System studies [2,6,7] have evaluated the more traditional two-tank energy storage systems and single tank thermocline storage systems and have shown that thermocline-based energy storage configurations may offer the least-cost energy storage option. They offer potentially reduced capital costs for tank construction (and related pump, valve and piping costs). The use of lower cost filler media reduces the overall required quantities of the relatively higher cost molten salt heat transfer fluid. As such, in cost comparisons the thermocline system was found to be about 35 percent cheaper than the two-tank storage system.

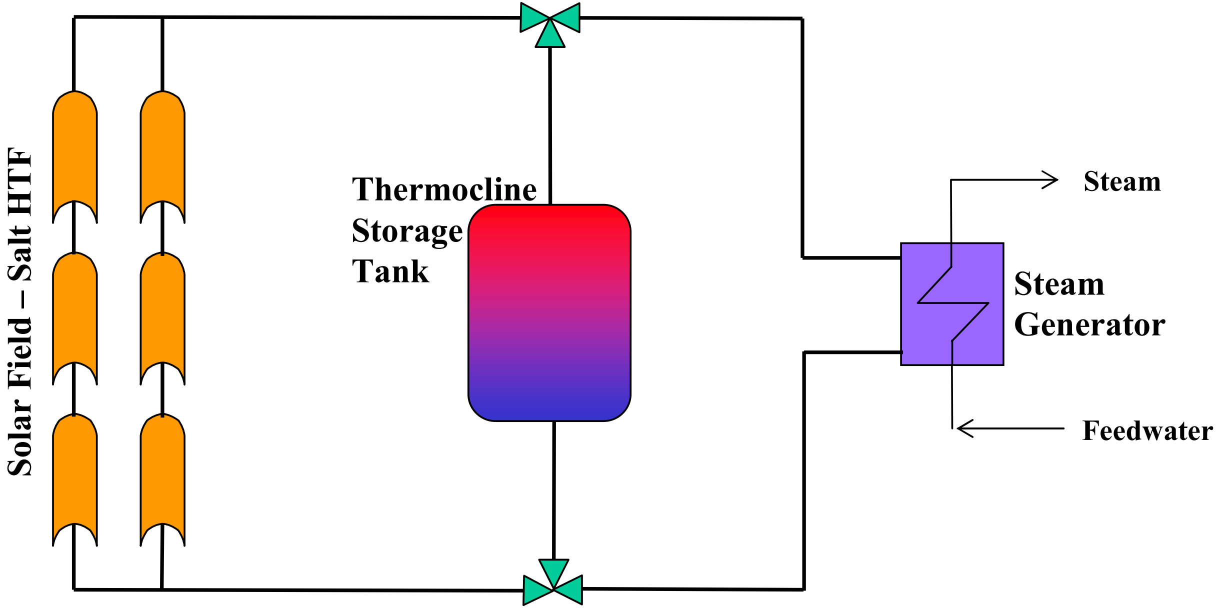


Figure 4 - Direct Thermocline TES Schematic

Important Parameters of Successful Filler Materials

Ideal filler materials for thermocline storage tanks would need to be inexpensive and widely available, have a high heat capacity, a low void fraction (0.25 or less to reduce the amount of liquid required), be compatible with nitrate salts, and be non-hazardous. Most of these parameters are fairly easy to characterize. However, the compatibility in hot, cyclic molten salt environments was unknown. So, it was deemed important to develop a test program to identify candidate filler materials, screen and test those materials in molten salt environments that would be typical of the systems and design conditions specified in the industry trade studies, down-select to the most viable candidate filler materials, and perform additional rigorous testing to fully assess the potential of filler materials to withstand the demanding molten salt operating conditions.

Summary of This Report

This report summarizes the SunLab-sponsored thermocline filler material testing program conducted at the Sandia National Laboratory National Solar Thermal Test Facility (NSTTF) in Albuquerque, New Mexico. The initial filler material screening tests began during the 2000 and 2001 time frame, and more comprehensive molten salt, isothermal, and thermal cycling tests of filler materials occurred during 2002 and 2003.

The section on Background Tests and Evaluations summarizes the earlier series of thermocline and filler material screening tests conducted at Sandia, including molten salt assessment conducted during a much earlier period. That background discussion is followed by a summary of the Test Objectives for the later follow-on comprehensive tests of filler materials and molten salts, including a detailed discussion of the test apparatus used for isothermal and thermal cycling tests at the NSTTF. A summary of the post-test analysis plan is also included.

The Operations and Test Experience section summarizes the pre-test, operations, shutdown, and post-test activities associated with the isothermal and thermal cycling tests that were conducted. Detailed summaries, procedures, schedules and checklists are provided in Appendices.

The section on Analytical Trends and Results provides a comprehensive summary of the findings of this test program, again with the details relegated to Appendices. Observations, trends, plots and interpretations are provided – for both isothermal and thermal cycling conditions – to document changes in molten salt chemistry, filler material condition and degradation, and interactions with and impacts on the sample basket materials and test apparatus.

Conclusions and recommendations are provided, including commercial operational considerations that will require investigation in the next phases of TES design and assessment for parabolic trough plants.

BACKGROUND TESTS AND EVALUATIONS

This section summarizes a series of studies and experiments that were conducted by Sandia researchers, primarily at the NSTTF. First, a series of screening assessments were conducted to identify potential thermocline filler materials, to identify and perform initial assessments of possible molten salt mixtures and safety issues (when used with Therminol VP-1), and to perform initial thermal cycling tests of the best candidate filler materials in the selected molten salt. Second, a pilot-scale thermocline demonstration test was conceived and conducted. Models were developed to predict and characterize the thermal behavior of thermocline thermal energy storage tanks. Finally, additional molten salt experiments were conducted to gain more experience with various mixtures and to document initial characterization of molten salt freeze/thaw behavior and handling issues.

Filler Material Screening

A number of candidate filler materials, from a list of commonly mined minerals and crushed rock, were identified in consultation with a geologist and nitrate salt expert. The initial list included seventeen minerals: anhydrite, barite, bauxite, carborundum, cassiterite, corundum, fluorapatite, hydroxyapatite, illmenite, limestone (from Kansas – KS), limestone (from New Mexico – NM), magnasite, marble, quartzite, scheelite, taconite, and witherite. These were all considered relatively pure materials that could be easily found and delivered at a low cost.

To evaluate the seventeen candidate materials, a test plan was developed for a series of isothermal tests to immerse the materials in two commercially available nitrate salt mixtures. All of the materials were weighed, photographed, and immersed in HitecXL nitrate salt – a mixture containing calcium nitrate, sodium nitrate, and potassium nitrate salts. The materials were removed at specified intervals (after 10, 100, and 1000 hours of exposure) and washed, weighed, and photographed again following removal. Four of the materials (limestone, marble, quartzite, and taconite) were also tested in "solar salt" (a mixture of 60 weight percent sodium nitrate and 40 weight percent potassium nitrate) and removed after 400 hours. Samples of the salts were taken for analysis of contaminants.

The screening process based on isothermal testing was straightforward (see Appendix A for details). The witherite and barite samples reacted with the calcium nitrate during their initial 10-hour exposure to HitecXL. Bauxite, illmenite, and KS limestone samples crumbled after exposure to the nitrate salts. Anhydrite experienced significant weight loss. Carborundum and taconite gained weight, most likely due to their porous structure and the difficulty of removing trace amounts of salts after exposure. The most successful candidate filler materials included quartzite, taconite, marble, NM limestone, apatite, corrundum, scheelite, and cassiterite. Because taconite, marble, NM limestone, and quartzite are readily available in bulk quantities for reasonable prices, attention was focused on these materials to conduct the next phase of screening using thermal cycling tests.

The purpose of the thermal cycling tests was to evaluate how well the materials selected in the isothermal tests would hold up in thermal cycling conditions typical of a thermocline system based on molten salt HTF. During the design and development of the thermal cycling apparatus and test plan, filter sand was added to the test matrix because this material is similar to quartzite and drastically reduces the void fraction in a thermocline tank (see Appendix A for discussion of void fraction determination).

The initial thermal cycling test apparatus was similar in concept but significantly different from that documented later in this report; the details will not be repeated here (see Pacheco [8] and Appendix A). Two vessels – a hot tank containing molten salt at 400ºC and a cold tank at 290ºC – were alternately pressurized and vented, forcing first hot, then cold, molten salt through a test chamber that contained the filler materials being tested (Fig. 5). Hitec XL salt was used for the thermal cycling tests. Hot and cold soak times were nominally about one-half hour each, and typically 15 to 19 cycles were completed each day. After the specified number of cycles (generally 350 for each test), the experiment was stopped and the samples were inspected.

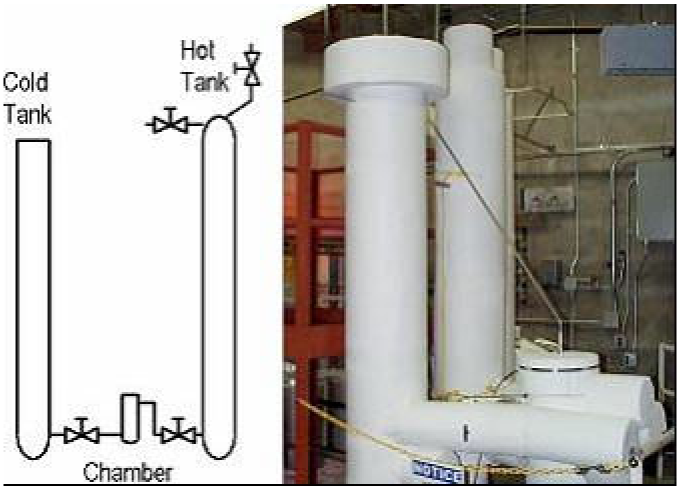


Figure 5 - First Thermal Cycle Test Apparatus

The NM limestone, a sedimentary rock consisting of hydrated calcium carbonate, should be insoluble to nitrate salts. It fell apart after 365 cycles, softening to the consistency of mud (Appendix A). This material fared the worst and was deemed unacceptable as a filler material. Marble is a metamorphic rock, which is calcium carbonate that has been exposed to extreme temperatures and pressures. The marble held together after cycling, but softened. The individual grains in the samples appeared to grow in size and prominence during the test. At these temperatures, it is possible that the grains were re-crystallizing into larger crystals. Another explanation is that the surface was being preferentially eroded by an unknown process during the test, making the surface features higher in contrast. The marble also became discolored, most likely due to oxidation of entrapped iron. This material fared poorly and was considered unacceptable as a filler material.

The taconite pellets held together fairly well (see Appendix A). Because the pellets were porous, salt wicked into the pellet pores, but this did not seem to affect them. There were some fines produced, but not so much that system clogging would be a concern. Some of the fine material may have been present in the initial material.

The quartzite rock held up to thermal cycling remarkably well, showing no significant decomposition of the material after 553 thermal cycles (Appendix A). The edges of individual rocks appeared sharp and unaffected. Some pieces of quartzite changed from a bluish to slightly reddish color. The change of color was likely due to oxidation of iron that is present in the quartzite. White pieces of quartzite did not change color or appear affected at all. The silica sand behaved similarly to the quartzite. Some grains appeared slightly reddish in color after exposure, but held up well overall. Thus, based on the initial screening studies on candidate filler materials, quartzite rock in combination with silica sand (thus reducing void fraction significantly) appeared compatible with nitrate salts and are widely available and low in cost. These materials were chosen for use in a pilot-scale thermocline storage system test, reported next.

Thermocline Studies

During FY00 - 01 a test was conducted at the Sandia National Laboratories' NSTTF of a molten salt thermocline storage system [8]. This 2.3 MWh(t) pilot-scale test used quartzite rock and silica sand filler materials to displace a binary mixture of sodium nitrate and potassium nitrate salts ("solar salt" - 60 wt% $NaNO_3$ and 40 wt% KNO_3). The goal of this test was to verify the operation and performance of a molten salt thermocline system on a larger-than-laboratory scale. The main purposes of the test were to 1) verify the heat capacity of a thermocline system, 2) evaluate the size and shape of the thermocline, 3) evaluate the change in shape of the thermal gradient over time, and 4) evaluate the heat loss of the thermocline tank. A number of tests were planned to achieve those objectives: initial charging test, full discharge test, full charge test, partial charging test, partial discharging test, and a heat loss test.

A carbon steel tank, 6.1 m tall by 3.0 m diameter, was fabricated to meet American Petroleum Institute (API) Code 650 Appendix J. A thermocouple tree was placed in the middle of the tank with thermocouples every 15 cm, vertically. In addition, thermocouples were placed on three radial arms each at three discrete levels from the tank bottom. The tank had a radial flow distribution manifold at 10 cm from the bottom, which was connected to a standpipe, housing the cold pump. The hot pump was supported from below to pump salt from the top of the tank. A number of electric mineral-insulated heat-trace cables were wrapped on the exterior surface of the tank to provide heat input during the initial heating process and make up for heat loss. The tank was insulated with 23 cm of fiberglass insulation on the sides and with 20 cm of calcium silicate ridged block insulation on the top of the tank. Figure 6 provides an overall view of the actual system installation. See Appendix A for test apparatus fabrication details and illustrations of the installation process.

Figure 6 - Aerial View of Thermocline Test Apparatus

Based on the results of the isothermal and thermal cycling screening tests of filler materials, the tank was filled with a mixture of quartzite rock and silica sand. First, a 3-cm layer of sand was laid on the bottom of the tank, followed by a 20-cm layer of quartzite rock. A fine mesh stainless steel screen was laid down to prevent the sand from working down to the manifold. All manifolds within the tank had the stainless steel screen installed to prevent filler material from entering the piping system. Next, 5-cm layers of a 2:1 mixture of quartzite rock and sand were added and compacted in place until the fill level reached 5.2 meters. Prior to tank filling, tests were completed to determine the highest packing density of quartzite rock and silica sand. In half-drum quantities using the 2:1 ratio of rock to sand, void fractions of approximately 0.25 were achieved. The final void fraction measurement of the rock/sand mixture in the tank was 0.22 based on actual quantities of salt used. In total, 49.9 tonnes of rock and 21.9 tonnes of sand were loaded into the thermocline tank.

A schematic of the flow system is shown in Figure 7. The system incorporated a propane heater to simulate the heat input from an oil-to-salt heat exchanger that would be incorporated into the commercial TES loop. The salt-to-air cooler was included for heat rejection from the system (Fig 8). To charge the system, cold salt was drawn off the bottom of the tank through a manifold using a multistage turbine pump. The cold salt was heated with the propane heater and returned to the top of the tank. Both the flow rate of the salt and the heat input from the propane heater could be controlled. In general, the flow rate was fixed, then the propane flow valve was adjusted to achieve the desired salt outlet temperature. As the hot salt made its way through the rock and sand, it heated the filler materials and established a thermal gradient in the tank. To discharge the system, hot salt was drawn off the top of the tank through a manifold and pumped through the forced-air salt cooler to reject the heat from the salt. The cold salt exiting the cooler returned to the bottom of the tank. At the end of a given test, both the heater and cooler were drained into a sump, from which the sump salt inventory was then pumped back into the tank.

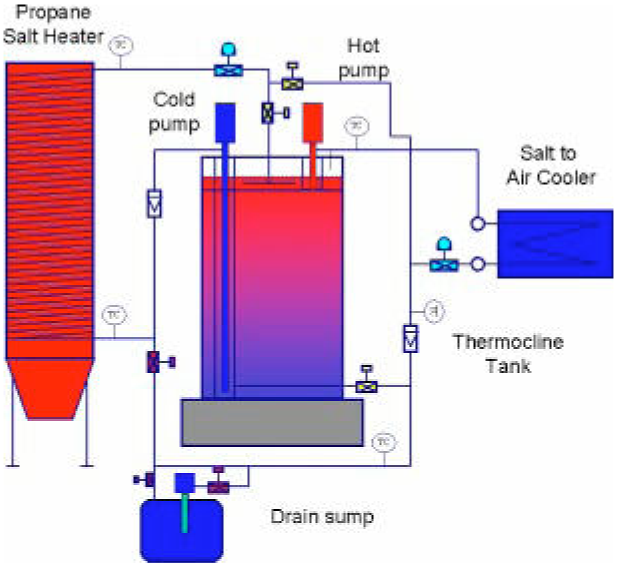


Figure 7 - Thermocline Flow System Schematic

As noted earlier in this section, HitecXL was used for the isothermal and initial thermal cycle screening tests of filler materials. However, because of time constraints related to receiving technical-grade calcium nitrate, a nearly eutectic mixture of sodium nitrate and potassium nitrate, without calcium nitrate, was used for the pilot-scale thermocline test apparatus charge. The thermocline tank and inventory of rock and sand filler material were initially heated by energizing the exterior heat trace and forcing hot air from a small propane heater using a venturi into the lower manifold at the bottom of the tank. Once the entire volume was above about 260ºC, the salt melting process began. Equal numbers of 23-kg bags of sodium nitrate and potassium nitrate were loaded into a propane-fired salt melter located on the top of the tank. The salt was melted and heated to about 290ºC, and then a valve was opened to dump the salt batch into the tank. Once enough salt was melted so the cold pump could be started, the propane heater was brought online and solid salt was added directly to the top of the tank to be melted by the hot salt returning from the heater.

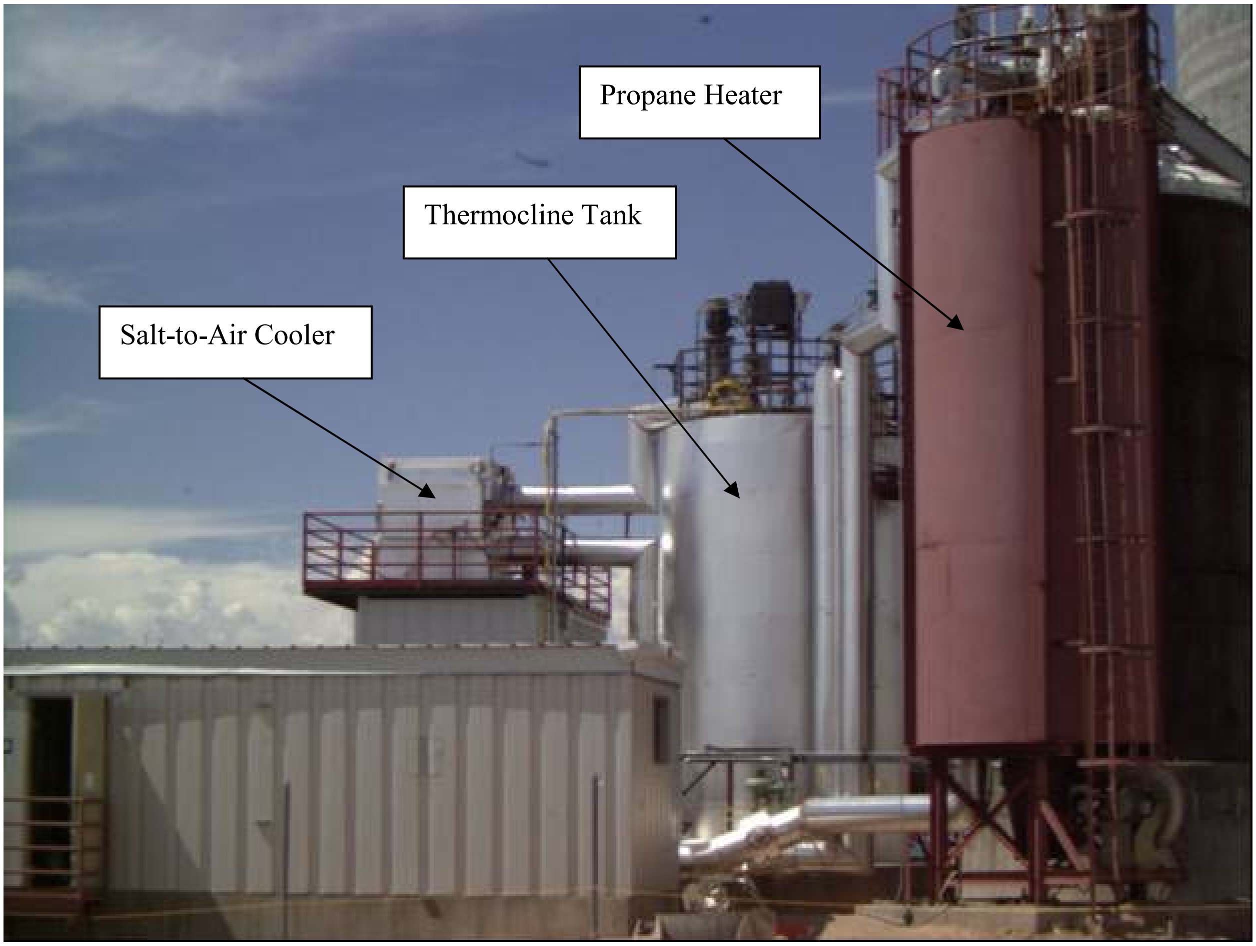


Figure 8 - Thermocline Test Equipment

In general, the charging and discharging tests went well and achieved thermal gradients and temperature profiles nearly as predicted by models that were developed and run prior to testing. The models suggested that, because of the height required for the gradient, taller tanks with smaller diameters would be preferred over shorter tanks with larger diameters. In general, during the charging cycle, the temperature of the cold salt entering the heat exchanger is constant until the gradient reaches the bottom of the tank. At that point the temperature of the salt coming out of the bottom of the tank starts to rise. Similarly during the discharge cycle, the hot salt coming off the top of the tank is nearly constant until the gradient rises to the upper portions of the tank. At that point, the hot salt temperature begins to decay.

During a 41-hour period, the average heat loss was measured to be approximately 20 kW, and found to be much higher than the predicted value of 12 kW [8]. Due to changes in the internal energy of the tank, heat loss measurement uncertainty is high. Also, in this smaller tank, penetration heat sinks (for the pumps in particular) were not accounted for in the heat loss model. The penetrations in a larger commercial-scale system would have less affect on the overall system heat loss. During the 41-hour test when no heat was added, the initially flat thermocline profile became more tapered. Because the tank had a low volume-to-surface-area ratio, edge effects were more pronounced than would be the case in larger tanks.

In the Sandia test, with a 60°C temperature difference between the hot and cold fluids, the thermocline occupied between one and two meters of the tank height. As such, the thermocline system seems to be best suited for applications with a relatively small temperature difference between the hot and cold fluids. One way to quantify the practical storage capacity of a thermal storage system is to compare it to the amount of energy the storage media could hold if the entire inventory were at its upper temperature and discharged completely to its lower temperature. This is termed the *percent theoretical capacity*. In a two-tank molten-salt system, the percent theoretical capacity is typically about 85 percent because each tank has a heel of salt (about 1 m deep) which cannot be used for its storage capacity. In a thermocline storage system, the percent theoretical capacity is a function of the tank height and is typically about 69 percent because of the space required by the thermal gradient.

Overall, the pilot-scale thermocline test was successful. Relatively simple cost analyses were conducted to compare the costs of materials, molten salt, and filler materials for a larger commercial-scale thermocline TES system with a similar-sized two-tank TES system. According to the cost analysis from Pacheco [8], the thermocline system was about 66 percent of the cost of a two-tank molten salt system. This test demonstrated that a molten salt thermocline storage system is a feasible alternative for thermal storage in a parabolic trough plant.

Molten Salt Assessments

As already noted, earlier filler material and thermocline tests were conducted using both the binary "solar salt" and ternary mixture known as Hitec XL. In the Solar Two power tower project, solar salt was used because of its stability at temperatures up to 600ºC, its low cost, its compatibility with common piping and valve materials, and its favorable performance in many past tests conducted at the NSTTF. The biggest disadvantage with solar salt is its high freezing point of approximately 230ºC.

A good candidate alternative molten salt formulation also available at a reasonable cost is a commercial ternary molten salt mixture known as HitecXL. The commercial formulation is shipped premixed dissolved in water. To remove the water requires initial conditioning and heating to boil off the water. After the water is driven off, HitecXL has a reported (claimed) freezing point of about 120ºC and is claimed to be stable to temperatures around 500ºC. SunLab trade studies were based on an assumed upper solar field temperature of 500°C, but past studies at Sandia [9,10] indicated significant decomposition of similar ternary molten salt formulations near 460°C. Thus, characterization of freeze/thaw behavior, thermal stability and upper temperature limits of molten salt HTF formulations were a concern.

Appendix B summarizes some of the evaluations conducted for various molten salt formulations. Based on those preliminary results, the exact nitrate salt mixture selected for the follow on testing documented in the remainder of this report consisted of 44 weight percent $CaNO_3$, 12 weight percent $NaNO_3$, and 44 weight percent KNO_3. This mixture, in these studies, appeared to offer the lowest melting and freezing range (approximately 120°C to 133°C) for this ternary formulation. Sandia decided to procure the three "dry" constituent salts to work with (calcium nitrate is only available in tetrahydrate form, requiring some boil off). Only A.C.S. reagent-grade salts were procured for this series of tests due to concerns about unknown and inconsistent levels of impurities in lower (but more economical) grades. Funding and time did not allow an extensive investigation and characterization of the ternary salt formulation similar to HitecXL that was chosen for the test. The primary purpose of the isothermal and thermal cycling tests was to determine the durability of quartzite rock and silica sand in molten nitrate salt over long periods.

The results of evaluations of molten nitrate salts and relatively simple assessments of freeze/thaw behavior pointed to the need for further study and, eventually, engineered solutions for handling large quantities of these salts for initial plant startup and during daily load changes. Maintaining minimum system temperatures to avoid freezing and salt disassociation; measuring physical properties (density, viscosity, heat capacity, thermal conductivity); characterizing and understanding molten salt viscosity, pumpability, and pump costs; maintaining adequate or continuous field flow and mixing; and optimizing use of heat trace in critical areas (and the related parasitic costs) are all elements of an engineering analysis that should be undertaken. The engineering to address these issues was well beyond the scope of this testing effort.

TEST PLAN AND APPARATUS

During FY02, test personnel at the Sandia NSTTF began plans and preparations to enhance and extend earlier testing of thermocline filler materials in molten salt environments.

Test Objectives

Prior thermal cycling evaluations demonstrated the promise of quartzite rock and silica sand as potential filler materials in thermocline energy storage systems. This new series of experiments sought to extend those studies in order to demonstrate conclusively the durability of these filler materials in molten nitrate salts over a range of operating temperatures for extended timeframes. The primary objective of the isothermal and thermal cycling tests [11] was to determine if the selected filler materials could withstand thermal cycling and isothermal tests at elevated temperatures in molten salts without decomposition.

Isothermal tests were conducted at 450°C and 500°C for one-year total immersion of quartzite rock and silica sand filler materials in a ternary nitrate salt mixture (equivalent to HitecXL). Controlled melts of the ternary molten salt mixture at identical temperatures but without rock/sand samples were included. Since a commercial storage system could go through 10,000 or more cycles in a 30-year project life, the thermal cycling test was designed to run for 10,000 cycles in the 285°C to 450°C temperature range to simulate a 30-year plant life. The temperature range was raised consistent with industry trade studies and past studies regarding the chemical stability of HitecXL and similar ternary molten nitrate salt formulations [9,10].

Isothermal Test Apparatus

Isothermal tests were set up to evaluate the long-term durability of quartzite rock and silica sand statically immersed in ternary molten salt at both 450°C and 500°C. Four melting pots were included – two at the test temperatures with samples, and two control pots at test temperatures without samples (Fig. 9). Three 316 stainless steel sample baskets were made up for each of two salt pots, consisting of a 2:1 mixture (by weight) of quartzite rock and silica sand, quartzite rock alone, and silica sand alone, respectively.

Zones 1 and 2 contained the rock and sand samples in molten salt at 450°C and 500°C, respectively. Rock and sand samples were carefully washed, dried, weighed, and photographed prior to insertion in the melting pots. The "control" pots without samples – Zones 4 and 5 – were established at the same temperatures. Because of supply limitations, less than one-third the quantity of salt was melted in the control pots. This resulted in an identical molten mixture, but more than tripling the effective surface-volume ratio in these pots as compared to the Zones 1 and 2 pots containing the samples. See Table 1 for a summary of these isothermal zones. On a monthly basis for the one-year duration, the rock and sand samples were removed, washed and dried, observed and weighed, and salt samples were taken for chemical analysis. Upon test completion, careful analyses of rock/sand samples, as well as the molten salt, were conducted to assess long-term durability in these test conditions.

Table 1 - Explanation and Summary of Isothermal Zones

Zone	Salt Quantity	Samples	Test Temperature
1	20 kg	Rock/Sand	450ºC
2	20 kg	Rock/Sand	500ºC
4	6 kg	Control	450ºC
5	6 kg	Control	500ºC

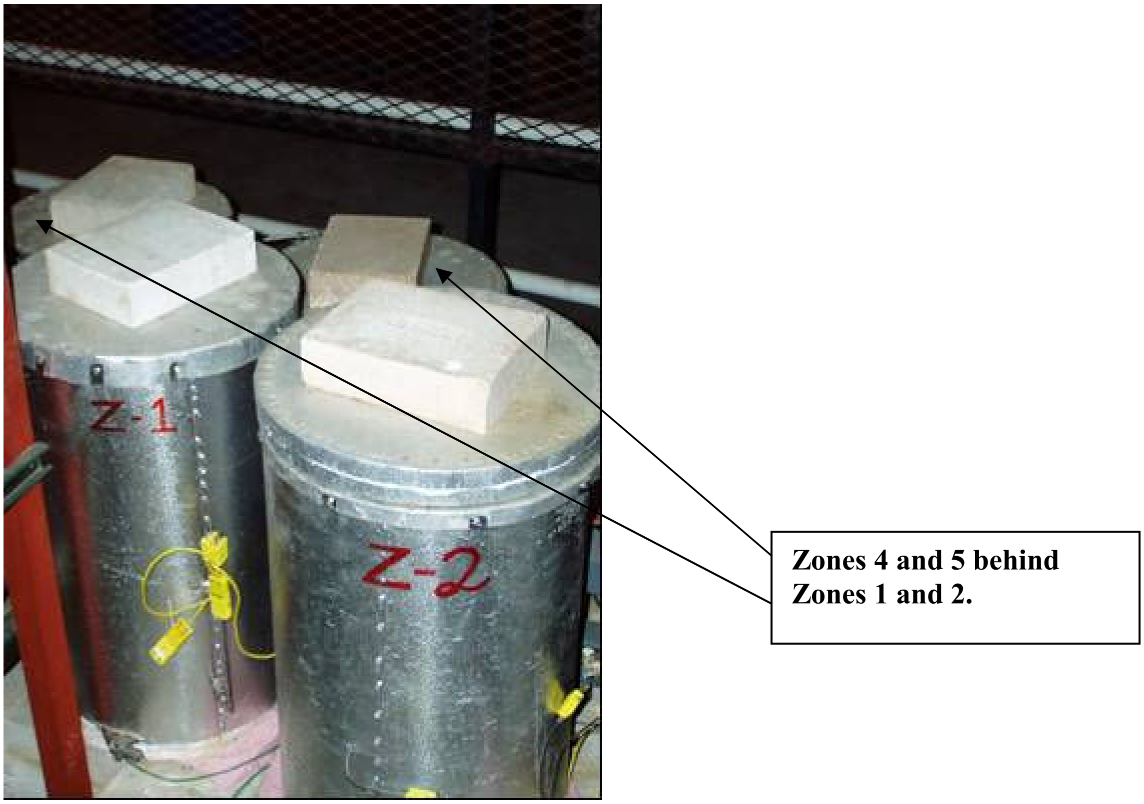


Figure 9 - Isothermal Test Pots

An important condition to note: other than convective currents in the pots, none of the pots were mechanically stirred or plumbed for flow conditions for the duration of testing, so these were truly static tests. Though not strictly representative of expected conditions in an operational solar power plant, these tests did provide valuable information regarding the ability of the rock and sand samples to withstand test conditions in molten salt, and they also provided direct observations of changes in molten salt in the early (first-year) stage of such exposure.

Thermal Cycling Test Apparatus and Controls

Figure 10 depicts the basic schematic arrangement for the thermal cycling apparatus. The entire system was constructed using welded 316 stainless steel piping and components. A small 10.2 cm (4 in.) diameter test chamber 35.56 cm (14 in.) tall containing filler material was placed between two vessels – the hot and cold tanks – each 25.4 cm (10 in.) in diameter by about 152 cm (5 ft.) tall. The hot tank was designed to contain molten salt at 450°C and the cold tank at about 285°C (the target temperature range consistent with industry trade studies [1,3,4,6,7]). Figure 11 shows the final thermal cycle test apparatus after insulation. The test chamber arrangement (prior to insulation) is shown in Figure 12. Two gate valves and a drain valve were installed for periodic isolation and draining for sample observations.

After mechanical fabrication, the entire system was carefully heat traced, thermocouples were installed, and the system was insulated to minimize heat loss yet allow thermal cycling to occur. The rock/sand test chamber and components were carefully fabricated to ensure containment of the rock/sand samples and yet allow molten salt flow in either direction during cycling operation. The net forces on the filler material at the bottom of a 12-m (40-ft) commercial thermal storage tank were calculated to be approximately 0.55 bar (8 psi). To simulate this, a weight of approximately 45 kg (100 lbs) was installed on a tall rod above the test chamber and transmitted to a porous plate on top of the filler material surface. A hydraulic piston/pulley/displacer setup was fabricated to cycle the molten salt through the filler material. Note that the system was not pressurized and was open to atmospheric conditions.

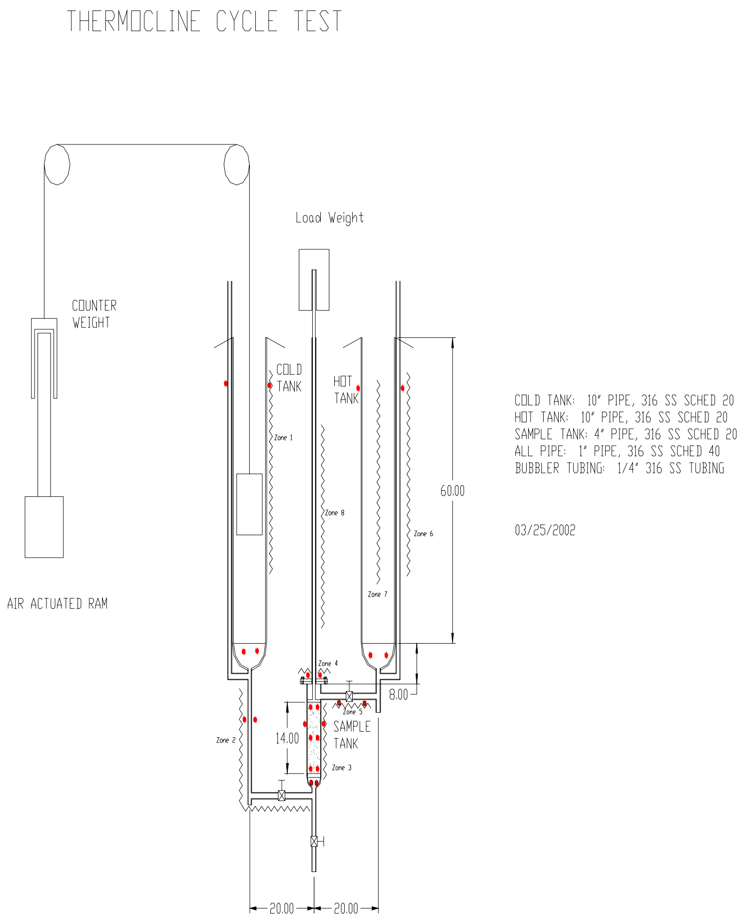


Figure 10 - Thermal Cycle System Schematic Drawing

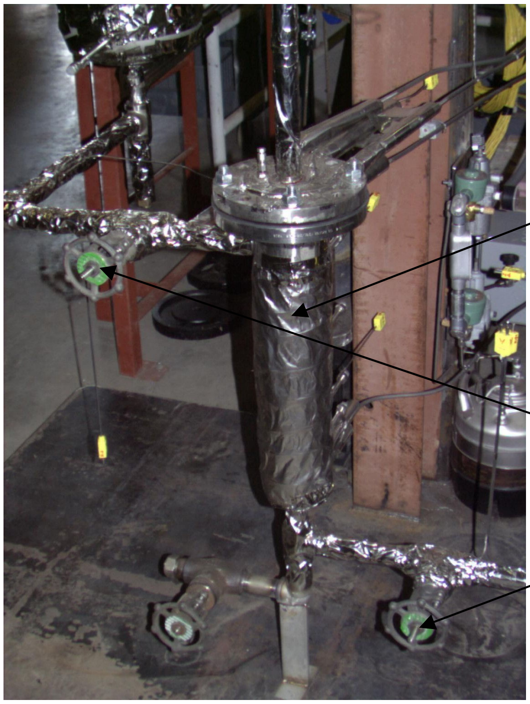
To cycle salt at both hot and cold test temperatures through the filler material in the test chamber, the displacer in the cold tank was first lowered into the salt, slowly forcing the cold salt through the system and filler material and consequently displacing the level of the salt equally (with some level variation due to density differences) in the hot and cold tanks. This cold fill process introduced some relatively cold salt into the hot tank (temperatures were maintained through selective timing of heat trace and bubblers). After a 15-minute cold soak, the displacer weight was slowly retracted back to its initial position, allowing the hot salt to flow through the filler material, and to an extent into the cold tank. This hot fill step was followed by a 15-minute hot soak, completing one full cycle. With approximately 15 minutes for each cold and hot fill, the cycling process continued 24 hours a day, averaging approximately 23-24 cycles per day. Displacement volume was calculated to ensure salt flow approximately six times the test chamber volume on each stroke to obtain the required heat transfer between the salt and filler material.

Hot Tank

Cold Tank

Test Chamber

Figure 11 - Thermal Cycle Apparatus Insulated



All 316 Stainless Steel
Test Chamber
4” dia. By 14” high

316 Stainless Steel
Isolation Gate Valves

Figure 12 - Test Chamber, Isolation and Drain Valves

Before startup, rock and sand samples were weighed and photographed prior to installation in the test chamber, and initial salt samples were taken. According to the original test plan, after 1000, 2500, 5000, and 7500 cycles, the system was to be temporarily shut down and isolated, the test chamber drained and opened, salt samples taken, and rock and sand samples observed and inspected for breakdown and signs of rock/sand contamination in the salt. Upon completion of 10,000 cycles, final salt samples were to be taken for chemical analysis and comparison with initial salt samples, and the rock and sand would be washed, dried, and weighed. Qualified personnel would carefully analyze the surface and internal composition of the aged quartzite rock and silica sand against control materials to assess degradation mechanisms in long-term molten salt thermal cycling conditions.

Thermal Cycle Control System

The control program for the thermal cycle test was written in National Instruments LabVIEW with the Datalogging and Supervisory Control add-on module. The Data Logging and Supervisory Control module allows the use of tags for input/output and memory, automatic data logging, and real time and historical data trending.

The program was written to be easy to use for someone not totally familiar with all aspects of the test. The main display panel, or Pipe Panel, for the program was designed so that the experimenter could tell at a glance where the system was in the test. The other panels provided additional functionality such as setting set points, heat trace control, test control, temperature plots, and watchdog timer control.

The program started up from a simple panel with buttons to “press” to bring up additional panels to control the test or view temperature trends. The start up panel is shown in Figure 13.

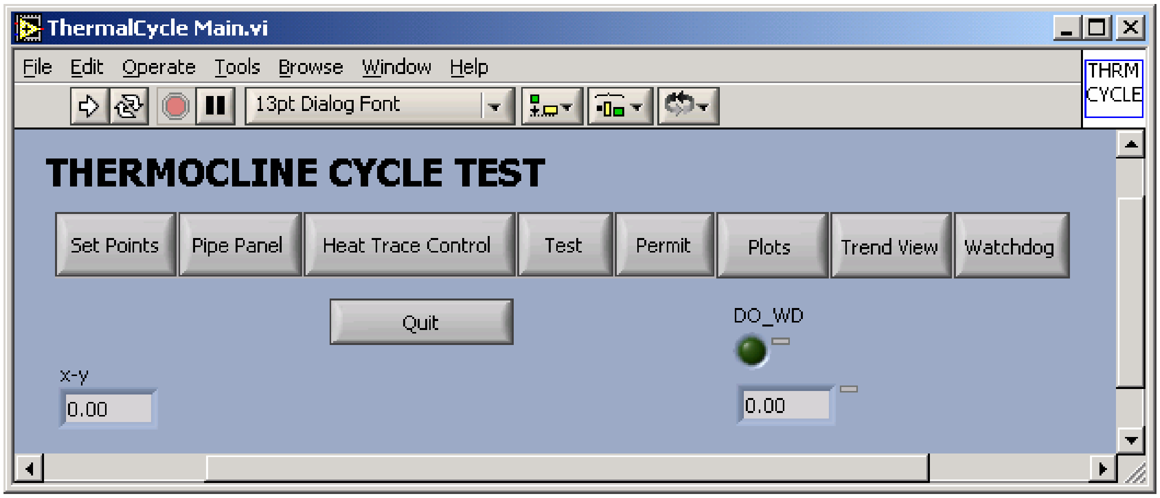


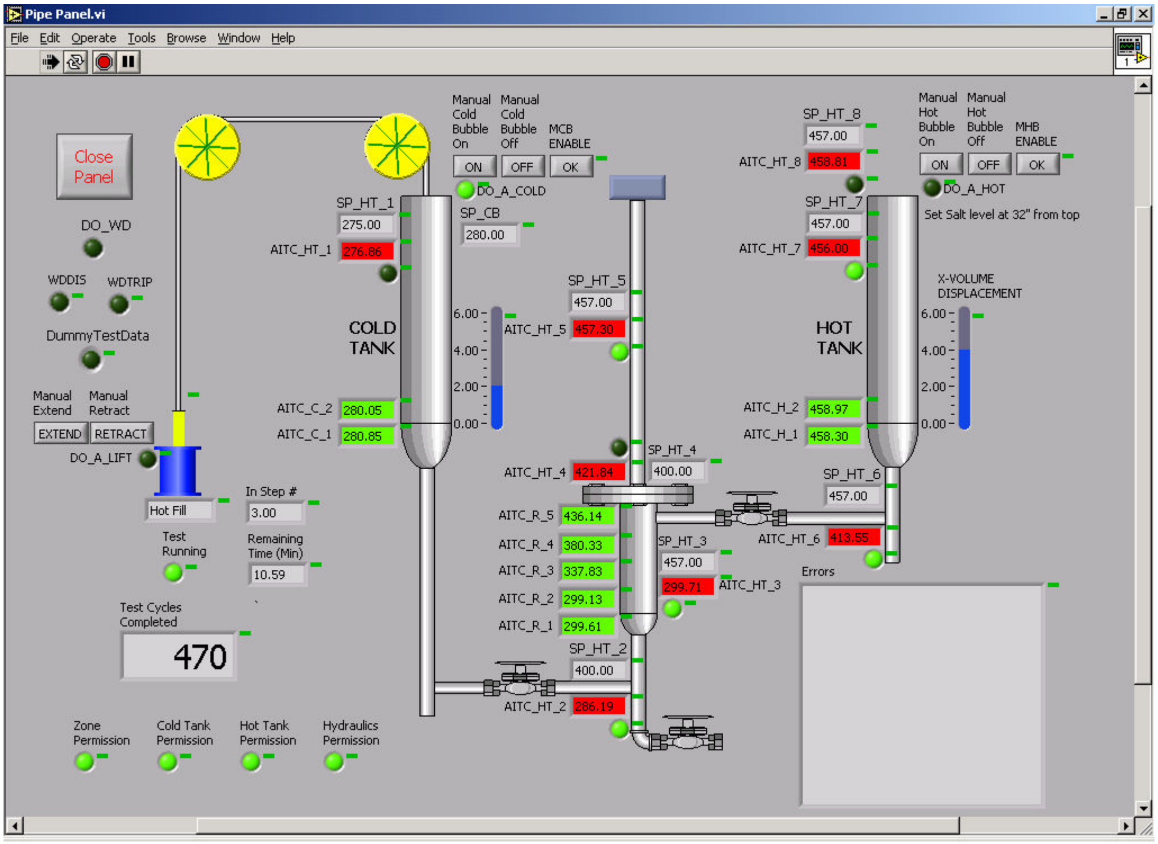
Figure 13 – LabVIEW Main Panel

The panels available in the start up program are:

Set Points
Pipe Panel
Heat Trace Control
Test
Permit
Plots
Trend View
Watchdog.

The Set Points module allowed establishing the hot and cold set points and dead bands for each temperature zone along with timing functions and counters. The data for this panel are stored in data files which can be recalled as necessary.

The Pipe Panel was the main panel for the test. It graphically displayed the salt levels in the tanks, the hydraulic ram position, the bubbler status, and all heat trace zone settings and thermocouple readings as well as the status of the heat trace control relays. A view of the Pipe Panel is shown in Figure 14.



SP_HT_1 275.00
AITC_HT_1 276.86
SP_CB 280.00
SP_HT_8 457.00
AITC_HT_8 458.81
SP_HT_7 457.00
AITC_HT_7 456.00
SP_HT_5 457.00
AITC_HT_5 457.30
AITC_C_2 280.05
AITC_C_1 280.85
AITC_H_2 458.97
AITC_H_1 458.30
SP_HT_4 400.00
AITC_HT_4 421.84
SP_HT_6 457.00
AITC_HT_6 413.55
In Step # 3.00
Remaining Time (Min) 10.59
AITC_R_5 436.14
AITC_R_4 380.33
AITC_R_3 337.83
AITC_R_2 299.13
AITC_R_1 299.61
SP_HT_3 457.00
AITC_HT_3 299.71
SP_HT_2 400.00
AITC_HT_2 286.19
Test Cycles Completed 470

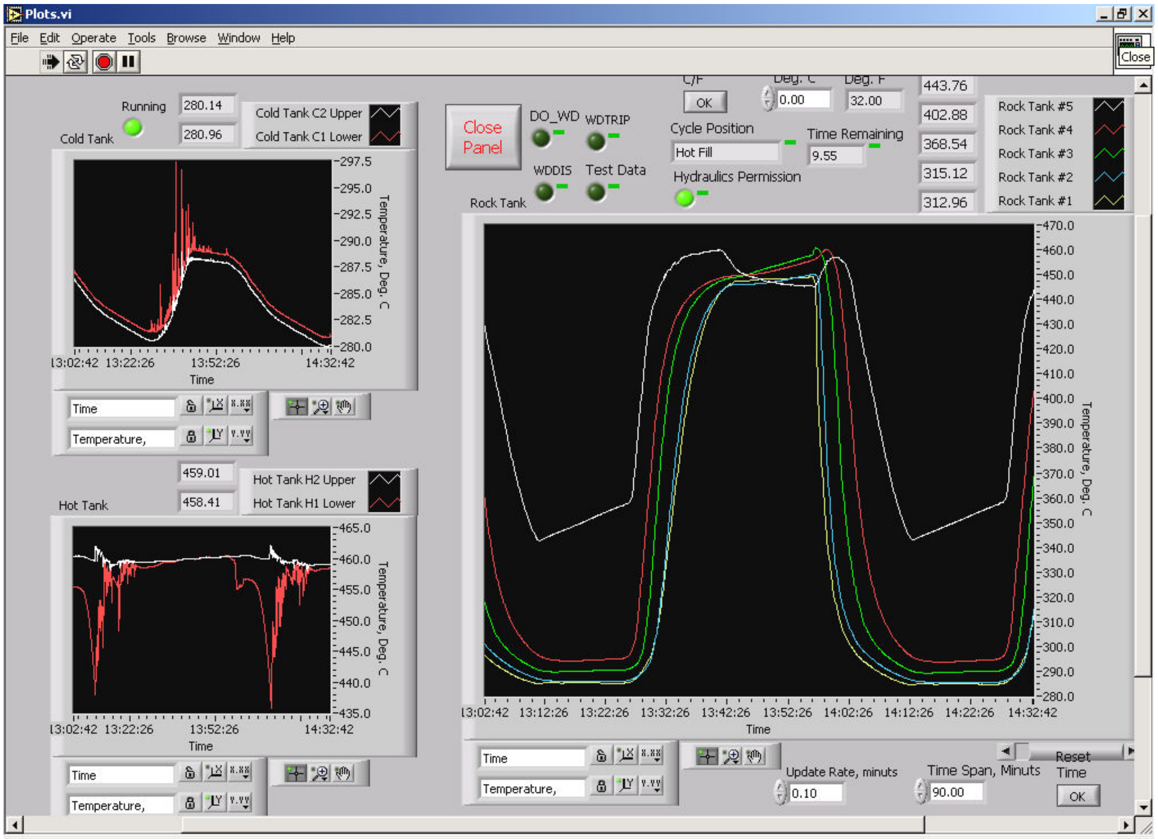
Figure 14 – LabVIEW Pipe Panel

The Heat Trace Control panel displayed all the necessary data and status of the heat trace zones such as set points, dead bands, high and low temperature limits, and heat trace relay status all on one panel so the operator could clearly see the status of the heat trace.

The Test panel was used to start and stop the test and reset the Test Cycles counter if necessary. All of the test parameters were shown on this panel.

The Permit panel displayed the status of the program permissions. This program monitored thermocouple zones and tripped the watchdog timer if any temperatures were out of limits. If flow temperature limits for the cold tank or hot tank temperatures went out of limit, the beginning of the test cycle was suspended, and then continued when the temperatures were restored to within the proper range for that cycle.

The Plots panel displayed real time plots of the cold tank thermocouples, the hot tank thermocouples, and the rock tank thermocouples. A sample Plots panel is shown in Figure 15.



Running: 280.14, 280.96

Hot Tank: 459.01, 458.41

Deg. C: 0.00

Deg. F: 32.00

Cycle Position: Hot Fill

Time Remaining: 9.55

Rock Tank: 443.76, 402.88, 368.54, 315.12, 312.96

Update Rate, minuts: 0.10

Time Span, Minuts: 90.00

Figure 15 – LabVIEW Plots Panel

The Trend View panel allowed the operator to view plots of any tag or multiple tags in the system.

The Watchdog panel controlled the watchdog timer. If the program hung up or key temperatures went out of range, the watchdog timer would trip, turn off all heat trace relays, and page up to four telephone numbers to notify test personnel that the test had a problem. The watchdog timer had to be reset manually.

Analysis Plan

Molten salt

A chemical analysis plan was developed for initial and periodic sampling and analysis of salt, rock, and sand samples. Primary objectives included analysis of changes in the salt given variables such as time, temperature, thermal stability, and potential impurities introduced as (and if) the rock and sand samples degraded over time.

One parameter of concern was the ratio of Ca:Na:K initially and over time. The objective was to identify potential decreases in the calcium concentration with salt decomposition and precipitation of calcium as carbonates and oxides form. Inductively coupled plasma/mass spectroscopy (ICP/MS) and ICP atomic emission spectroscopy (AES) methods were used in that determination. The Sandia team was also concerned with changes in nitrite levels and used ion chromatography (IC) assay methods to monitor nitrite over time. ICP/MS techniques were used to look for metallic constituents and silica that might be present if the rock and sand began to degrade as well as other metals or impurities due to potential reactions with the test apparatus. The following provides a detailed description of those analytical techniques, tools, apparatus and procedures.

Inductively Coupled Plasma-Atomic Emission Spectroscopy

The samples were quantitatively analyzed for sodium (Na), potassium (K), and calcium (Ca) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Each sample was prepared in triplicate as follows. Approximately 0.1 gram of sample was weighed to the nearest 0.1 mg into a clean plastic beaker. Next, 5 mL of a 3% solution of nitric acid (prepared from Fisher Scientific Optima™ grade concentrated nitric acid and deionized (DI) water, resistivity ≥ 18 MΩ-cm) was added. 10 mL of a 1000 µg/g rhenium (Re) standard (National Institute of Standards and Technology (NIST)-traceable) was added and the solution was then diluted to 100 mL with DI water. 5 mL of this solution was accurately transferred to a clean plastic container and 5 mL of concentrated nitric acid (Optima™) was added. Finally, this solution was diluted to 100 mL with deionized water. The resultant solution can be described as containing 0.1 gram of the sample, diluted to 2000 mL in an aqueous 5 wt.% nitric acid matrix, and containing a ~ 5 µg/g rhenium internal standard.

A Perkin Elmer Optima 3000 ICP-AES spectrometer system was used to analyze the solutions. The spectrometer has a reciprocal linear dispersion less than 1 nm/mm (1st order), an acid resistant sample introduction system, and is also capable of: (1) generating and storing working calibration curves based on atomic emission intensities, (2) measuring the emission signal from an internal standard element (e.g., Re) and correcting analyte emission intensities for fluctuations due to minor changes in the operating environment, (3) conducting wavelength scans of spectral regions within 1 nm of the emission line of interest in selectable increments, and (4) measuring off-line background intensities and correcting line emission intensities for background fluctuations. Analyte concentrations were measured at the following wavelengths: Na – 589.592 nm, K – 766.490 nm, and Ca – 317.933 nm. The Re internal standard was measured at a wavelength of 197.240 nm. Quantitative analysis was performed with calibration curves generated using aqueous standards prepared from NIST-traceable Na, K, and Ca standard solutions. Each solution was analyzed in triplicate on the ICP-AES instrument. The result for each sample was reported as the average of the 9 measured values (triplicate ICP-AES measurements on triplicate sample preparations). Estimated uncertainties were reported as 95% confidence limits, which represent fit of standard calibration curves, instrument precision, and triplicate sample preparation.

Inductively Coupled Plasma-Mass Spectroscopy

The samples were analyzed for trace levels of ~ 60 additional elements (besides Na, K, and Ca) by inductively coupled plasma-mass spectroscopy (ICP-MS). The solutions prepared for ICP-AES analysis (see above) were used for this analysis, which was performed using a Perkin Elmer 6100 DRC ICP-MS instrument. Samples were first analyzed using the Total Quant analytical program to detect the presence of trace elements with concentrations greater than 0.5 ppm in the original sample. The samples were then quantitatively analyzed for these elements using calibration curves generated from NIST-traceable standards.

Ion Chromatography

The samples were quantitatively analyzed for anionic species (nitrate, nitrite, *etc.*) by ion chromatography (IC). The samples were dissolved in DI water (resistivity ≥ 18 MΩ-cm) and analyzed using a Dionex DX-500 ion chromatograph equipped with a 25 µL sample loop and Dionex AS15 and AG15 columns (4 mm diameter). The eluent was 48 mM KOH flowing at 1.6 mL/min. Autosuppressed conductivity detection at 30 °C (external water mode) was used to detect and quantitate the eluted anionic species.

Filler materials

Analysis of the thermocline filler materials involved the following suite of samples:

- Quartzite rock control (no salt exposure)
- Silica sand control (no salt exposure)
- Zone 1 (450°C) rock – 1 year exposure
- Zone 1 (450°C) sand – 1 year exposure
- Zone 2 (500°C) rock – 1 year exposure
- Zone 2 (500°C) sand – 1 year exposure
- Rock – 10,000 thermal cycles
- Sand – 10,000 thermal cycles
- Collected fines and other degradation products

Scanning Electron Microscopy (SEM) and Back-Scattered Electron (BES) microphotographs of samples from all of the experiments at various magnifications (100x, 1000x, 10,000x) were planned to document any differences in the morphology of the surfaces compared to the control samples. Analyses by Energy Dispersive X-ray Spectroscopy (EDS) while in the Scanning Electron Microscope determine if any chemical changes/additions have occurred and guide the determination of the need for more detailed chemical analyses with the Electron Microprobe X-ray Analyzer. Particle size and porosity of the control samples were measured and evaluated with respect to the exposed samples and their weight gain. If reactions took place and new phases formed and/or significant degradation of the sample surfaces was noted, then a few samples were cross-sectioned by metallography personnel and sent to the Electron Microprobe X-ray Analyzer laboratory for more detailed elemental work.

The analysis plan included evaluating sample porosity, soaking selected samples in deionized water for an extended period to attempt to remove embedded salt, and analyzing the leachate. Also, “fines” collected from the test apparatus were analyzed for material properties and origin, and to assess the degradation of solid samples and/or precipitation of dissolved solids. Finally, samples of crust layers on the 500°C sample pots and thermal cycling test cold tank (discussed below) were analyzed to ascertain material properties.

OPERATIONS AND TEST EXPERIENCE

This section provides summaries of the test experience during pre-test activities, startup, normal operations, and shutdown. See Appendix E for more details of observations and notes taken during the operational phase of the test program.

Summary of Pre-Test Activities

Isothermal Test Preparations

Once the trial mixing and melting of the three dry nitrate salts were completed (see Background Tests and Evaluations, and Appendix B), setting up for the long-term isothermal testing was simple and straightforward. Due to the need to allow full immersion of the three sample baskets, and to allow for monthly salt samples for one full year, it was desirable to fill the test pots completely. This required mixing, melting, initial boil off, and serial additions of new dry salt (and boil off) a number of times in order to accommodate slump and volume reduction as pot charging progressed. Each of four pots were filled with the 44:12:44 (Ca:Na:K) mixture and stabilized at the test temperatures (two at 450°C, two at 500°C).

During the filling process on one of the pots, the team experienced a rather surprising and sobering event that demonstrated the need for caution when working with molten salts. While adding dry salt to one of the pots that already contained a significant quantity of hot, molten, partially dehydrated salt, the new salt "bridged" and formed a "snowball" that persisted on the surface of the melt. Test personnel had had significant experience with manually mixing the partially molten salt during the trial melts, so this situation was familiar to deal with. The ball of salt was pushed down in the melt with a handheld thermocouple to encourage its breakup and solution in the melt. This time, however, the entrained water (and air) reached the right temperature and had no place to go but up and out. A portion of the dry and molten salt vigorously boiled and bubbled out of the pot for a few seconds duration, making a mess, but posing no direct threat to personnel (who were clothed and prepared to work under these conditions). This event pointed to the need for patience and provided a valuable lesson-learned in preparation for charging the thermal cycling tanks.

A detailed but simple process was developed and followed to wash rock and sand samples, dry, weigh, photograph, then insert in the sample baskets. The baskets were then carefully inserted in each pot; on August 1, 2002 for the 450°C pot and August 2, 2002 for the 500°C pot. Salt samples were taken just prior to sample insertion. Appendix C provides a copy of the monthly schedule, procedure and checklist that was followed to periodically sample and document observations of the condition and weight of the rock and sand samples as the test progressed. These pictures show initial rock and sand samples.

Thermal Cycling Preparations

There were many details involved in setting up for thermal cycling once the basic apparatus was designed, fabricated, instrumented, insulated, and the control system designed and implemented. The system was filled with water and flushed and drained a number of times. This allowed a check on calculated salt volumes, and also provided an opportunity to begin exercising the system in limited fashion with hot water. Note that special chemical flush agents were not used, so the system may have retained some small amount of residual contamination from the original piping and/or fabrication/welding process. Final checks of heat trace and thermocouple circuits and data acquisition channels were performed. A salt mixing plan and spreadsheet were developed to automate the calculations needed during batch mixing and salt loading. A simple procedure supplemental to the test plan was developed (based on isothermal and trial melt experience) to guide the team through salt weighing, mixing, charging, melting, boil off, and system heat up, plus final valve-in. The rock and sand samples were carefully washed, dried, weighed, and prepared for insertion in the test chamber. The test chamber was prepared, internal components fabricated and installed, and readied for loading.

On August 20, 2002, the test chamber was carefully loaded with a 2:1 by weight mix of rock and sand, with all additions carefully weighed and documented. A controlled sample of rock and sand was enclosed in a wire mesh basket (similar to that used for the isothermal test baskets) and inserted mid-height in the test chamber, with the goal of providing a carefully controlled sample for analysis at the end of testing.

Salt loading began the afternoon of August 20 and progressed rapidly. Due to the size of the hot and cold tanks, the team was able to add over 360 pounds of salt, one bucket at a time, to the system that day and begin the melting and boiling process. The total approximate mass of salt required to fill the system was calculated (and verified with water). Allowing for rock and sand in the test chamber, the addition of about 422 pounds dry salt (after water boil off) was anticipated. To account for measurement uncertainty, a total of almost 444 pounds of salt was added as boiling progressed. It was deemed easier to remove excess than add dry salt to molten salt at test temperatures.

Boiling started in the range of 130°C to 135°C and progressed smoothly. Some control system problems were experienced early in the salt loading phase that extended the time required to boil off water. Once the control system database problems were resolved, boil off ramp up to test temperatures occurred the rest of that week and through the weekend of August 24-25. At that point, all heat trace zones were set to allow for startup. The test chamber flange was insulated and a few other minor adjustments and component fixes were completed.

Initial salt samples were taken from each of the hot and cold tanks. Appendix D provides a copy of the schedule, procedure and checklist that was followed to periodically sample and document observations of the condition and weight of the rock and sand samples, and salt, as the thermal cycling test progressed. Due to slight variations in hot and cold fill times (because of hydraulic system sensitivity to ambient conditions – see below), and uncertainty regarding the length of time required to shutdown and restart at the sampling times, the dates in the schedule were approximate.

Summary of Startup Activities

Isothermal Test

Isothermal test startup requirements and activities were minimal. The first monthly samples were taken on September 3, 2002. There were no operational problems with any of the isothermal pots during the first month of testing. The samples all looked quite normal after removal, washing, and drying. No obvious crumbling or other deterioration was noted as the samples were photographed and weighed. There was a whitish color to the samples after washing that was either due to salt deposition or slight scaling from the washing process (tap water was used for the initial rinse and deionized water for final washing). As such, the samples weighed in just slightly higher (rock up 0.5 percent, sand up about 2.5 percent) than the original weights after the first month of testing.

Thermal Cycling Test

Thermal cycling test startup began the week of August 26 following last minute adjustments and repairs as noted above. The system was valved in with no difficulties, though the isolation gate valve seats were "stuck" somewhat because they were closed when cold. The process of installing the displacer, checking levels, and dipping excess salt was a bit tedious due to the difficulty of determining levels internal to the tanks. A net amount of 23 pounds of salt was removed, leaving approximately 421 pounds in the system, nearly identical to the calculated amount.

Thermal cycling was initiated early afternoon August 27. On startup, the thermal response and stratification in the test chamber that would occur throughout the thermal cycle test was immediately observed. Because of the almost immediate and excellent response of the system (due in no small part to the design, preparations, and pre-start exercises and experience with the LabVIEW control system), the Sandia team was able to declare startup from the initial cycle. From the beginning, very near the hot and cold salt temperatures desired in the rock/sand test chamber were achieved. Initially, the hot side was a bit low and the cold side a bit high, but not enough to negate or not "count" those thermal cycles in the actual test sequence. By adjusting the hot and cold tank temperatures slightly and making very slight changes in heat trace, the temperature range was broadened to achieve the test chamber targets of 285°C and 450°C (within the limits of the system thermal response and natural stratification that occurred in the chamber). In order to approach and reach the desired hot soak temperature required setting the hot tank heat trace control at 460°C, with salt temperatures slightly in excess of that (461°C-462°C). Due to documented thermal stability limits of the ternary nitrate salt mix at those temperatures, the team was unwilling to go any higher. See Appendix E for more details.

In summary, the startup process went exceptionally well. The most tedious part of startup was initial timing and adjustment of displacement times (with the hydraulic system) and synchronizing those times with the LabVIEW system. As it turned out, the hydraulic system was sensitive to ambient changes at the test location, so the facility room temperature was closely monitored and controlled for the 14-month duration of the test.

Operational Experience and Observations

Isothermal Test

Given the relatively simple test apparatus and setup, the operational experience with the isothermal tests was routine and almost without incident for the 12-month test duration. The melting pot Chromalox controllers were visually monitored on a daily basis to ensure setpoint temperatures were maintained. Each month, a portion of a day was devoted to temporarily removing, washing, drying, weighing, and photographing – and then reinserting – the rock and sand samples, and taking salt samples from both sample and control pots for both test temperatures. Observations and sample weights were recorded in a test logbook. Salt samples were analyzed off-site at another Sandia facility, and the results were recorded and plotted in an Excel spreadsheet. See Appendix E for more operational details.

There were three significant observations made during testing; details of these trends will be discussed at length later in this report. First, the rock and sand samples gradually increased in weight, most likely due to intrusion of molten salt and other chemical constituents in the small pores and cracks on the surfaces of the rock and sand materials. Second, the samples baskets in the Zone 2 test pot at 500ºC significantly degraded over time, with very little comparative degradation in the Zone 1 test pot at 450ºC. Third, a very significant crust formed on the surface of the salt in the Zone 5 control pot at 500ºC, with very little similar formation in the Zone 2 pot (with samples) at the same 500ºC temperature.

Thermal Cycling Test

Testing began August 27, 2002, and 10,000 cycles were achieved at approximately 2:00 am, October 29, 2003. Other than the few operational notes documented in logbook entries during testing (see Appendix E for operational details), the test was very successful and operated with no significant concerns during the 14-month test duration.

There were three significant operational notes of interest during the thermal cycling test. First (as already noted), due to system thermal response it was necessary to increase the bulk temperature in the hot tank to approximately 460°C in order to achieve the desired profile in the test chamber. Based on studies by Bradshaw [9,10] on the thermal and chemical stability of these salts, this was the highest temperature deemed appropriate. Over time, the team had to almost eliminate activation of cold tank heat trace, and increase bubbling times, in order to achieve the low-end temperatures desired in the test chamber temperature profile. This operational constraint may have contributed to conditions noted during testing: notably, intermittent operation of the cold tank bubbler line, and what was assumed to be minor quantities of frozen salt buildup on the displacer and top interior portions of the cold tank.

Second, the Sandia team installed a “caged” controlled sample of rock and sand midway in the test chamber, with the hoped-for objective of periodically removing, observing, and weighing that well-defined mass of rock and sand. It was postulated that the screen mesh used to hold the sample might provide a collection point for corrosion products and provide a means to “filter” and retain fines from rock/sand degradation. Though any captured material might “backflush” during the alternate fill period, this condition was a concern. However, throughout testing, no significant deterioration of the desired thermal response was noted.

Third, it became impractical to shut down the system at the planned periodic intervals to observe the rock and sand in the test chamber. In summary, the two isolation gate valves on the hot and cold tank legs were mechanically “frozen” open early in testing, preventing the isolation required to open the system. After debate with test personnel and interested industry partners, Sandia decided to resume testing through the entire 10,000-cycle duration without periodic observations. It was felt that the limited benefits of an extended shutdown to attempt correction of the problem could not justify the time, cost, and risk of potential show-stopping failure of the experimental apparatus. The original test plan called for periodic disruptions of the controlled volume of rock and sand filler materials in the test chamber, including return to ambient, washing, drying, and removal (with minimum disturbance) of the original rock/sand state in this simulated thermocline tank. In an operating plant, apart from major maintenance or replacement, a large thermocline tank may be required to operate for the full 10,000-cycle life without rock/sand refurbishment or conditioning. As such, the revision to the test plan necessitated by valve failure allowed the experiment to more closely simulate those conditions.

Shutdown Summary and Observations

Isothermal tests

Shutdown of the isothermal tests was quite simple. Final salt samples were taken, and the final process of extracting, rinsing, drying, weighing, and photographing rock and sand samples occurred. The rock/sand samples were then bagged and labeled for eventual detailed analysis by Sandia experts. Figure 16 depicts the condition of the Zone 2 samples baskets that had deteriorated during the test sequence. Note that the baskets in that test pot at 500ºC required repair during the course of testing, yet still continued to deteriorate. Figure 17 shows the typical nature of the crust that formed on the surface of the molten salt in the Zone 5 control pot at 500ºC. These observations will be discussed in more detail in the Analytical Trends and Results section of this report.

Figure 16 - Blackened Zone 2 Sample Baskets

Figure 17 - Zone 5 Typical Crust Formation

Testing Thermocline Filler Materials

Thermal Cycling Test

Preparations for the thermal cycle test shutdown process began during October 2003. A detailed procedure was developed outlining the steps required spanning almost a week of effort. Materials and tools needed to carefully shutdown and capture all relevant samples, observations, and other important information were arranged for.

There were a number of objectives to accomplish during the shutdown process:

- Safely shutdown the thermal cycling apparatus to a cold standby condition, ready for any potential follow-on testing.
- Fully drain, cooldown, and capture all molten salt, degradation products, salt samples, and filler materials from the test chamber.
- Document the final operational status of all components, including valves, bubblers, heat trace, thermocouples, hydraulic system, and the LabVIEW application and computer/DAQ hardware.
- Download, backup, and store all historical data for potential reduction and analysis.

Preliminary Activities

On October 29 and 30, historical data through the required test duration of 10,000 cycles were downloaded and copied to alternate locations for safekeeping and future access. The final molten salt samples were taken from both the hot and cold tanks. The system and test area were prepared for shutdown (Figure 18). However, due to other testing activities and the weekend approaching, thermal cycling continued through another weekend.

Figure 18 - Drain Pan for Thermal Cycle Shutdown

On Sunday, November 2, at the completion of cycle number 10,108, thermal cycling was discontinued and the control system was re-configured to support shutdown. All heat trace zone setpoints were adjusted to ensure stable molten salt temperatures adequate for the drain-down operation.

Summary of Shutdown Operations and General Observations

Shutdown operations began the morning of November 3, 2003. Initial efforts involved insulation removal and thawing out the drain valve and discharge piping (due to inadequate heat trace at that location of the apparatus). Once the drain valve was broken free, the team attempted to grab and screen the first samples of salt and any other products collected in the small "deadleg" near the drain valve. Unfortunately, the salt flow was too fast, and too hot to safely capture and filter any significant sample before onset of freezing. However, a small sample of the first discharge stream was obtained. Qualitatively, the team observed very little material (degradation products of rock/sand, or other un-dissolved solids) in the initial molten salt flow. Samples of material that collected in the small drain pipes below the hot and cold tanks were also obtained. The remainder of approximately 25 gallons of molten salt flowed into a large drain pan (Figure 19) and was allowed to freeze prior to disposal. All heat trace were set to control temperatures of approximately 85ºC to 90°C to ready the system for water flushing. Cooldown was very slow, taking overnight and into the next morning.

Figure 19 - Molten Salt Following System Draining

Early morning, November 4, 2003, portions of the insulation were removed and fans installed to accelerate cooldown. Late morning, water flushing both hot and cold tanks began. At that time, after removing the displacer from the cold tank, a significant crust buildup on the displacer and on the walls of the lower half of the cold tank was noted (Figure 20). It was first assumed the crust was due to salt separation, a non-repeatable phenomenon noted during earlier isothermal experiments that occurred after a number of freeze/thaw cycles. So, the team attempted to soak the material in hot water and flush the system a number of times. As the material broke away from the walls and collected in the bottom of the cold tank, drain flow was nearly stopped and the material did not readily dissolve and flush out of the system. Due to the heat and limited accessibility to the cold tank, it was difficult to accurately measure scale thickness. Small samples ranged from 1.5 to 3 mm (1/16- to 1/8- inch) thick, a significant buildup. Samples were taken and sent to a Sandia chemical lab for analysis. Later analysis, documented in the next section of this report, confirmed that the crust buildup was primarily composed of calcium carbonate ($CaCO_3$). A similar crust buildup in the Zone 5 isothermal pot, which was at 500°C (Fig 17) was also noted, but it was significant to see the extent of this buildup at 280°C to 285°C in the cold tank. There was also a very small (but not appreciable) amount of similar white crust in the hot tank.

Figure 20 - Calcium Carbonate Crust in Cold Tank After Breakup

On November 5, after repeated attempts to flush the system as well as the open test chamber, water flushing was suspended and heat trace was activated to dry the system out. (One note: throughout cooldown and shutdown, the isolation valves that “froze” open early in testing remained inoperable.) The test chamber top works was removed and extraction of rock and sand began (see observations next section). Removal of thermocouples was routine as rock and sand were removed, but the lower portion of the test chamber required additional drying overnight. The remainder of the rock and sand was removed the morning of November 6.

ANALYTICAL TRENDS AND RESULTS

Isothermal Test

Qualitative observations of the rock and sand samples and condition of the molten salt were recorded monthly in a test logbook. There were three primary areas of interest from these logbook observations: salt condition, rock/sand condition, and sample basket condition.

Molten Salt Chemistry

Qualitative observations of the molten salt varied significantly among the four isothermal test zones as testing progressed. Molten salt in all of the zones very early turned various shades of yellow, apparently due to chromium leaching from the melting pots, sample baskets, and/or chromium impurities in the original dry salt mixture. The Zone 2 salt (500°C with rock/sand samples) was a deeper shade of yellow; the other three zones quickly ramped up to and maintained a relatively consistent yellow tint. Figures 21 and 22 depict the upward trend of chromium levels in all four zones; notably, Zone 2 was about five times higher concentration than the corresponding Zone 5 pot at 500°C.

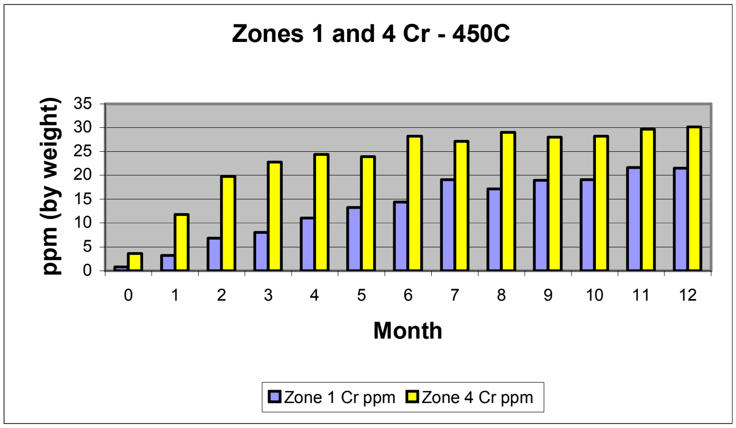


Figure 21 - Chromium Concentration at 450ºC

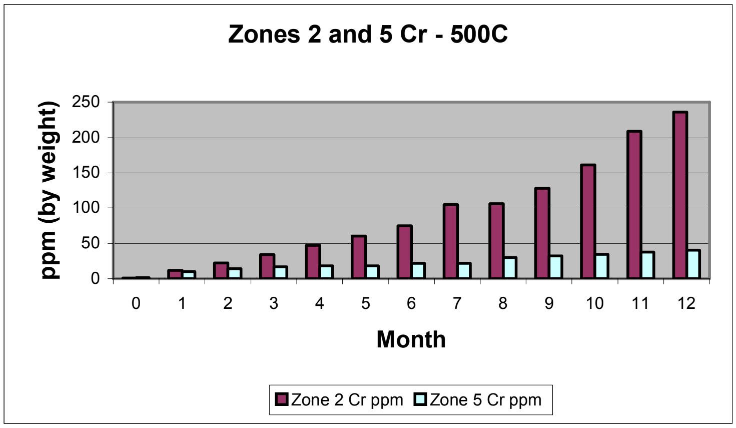


Figure 22 - Chromium Concentration at 500ºC

The ratio of Ca:Na:K in three of the four isothermal mixtures did not vary significantly over time. The calcium weight percent in Zone 5 dropped slightly over time (Fig. 23). Nitrite levels spiked to high levels early in testing, then attained a rough equilibrium with significant variation due in part to large measurement and analytical uncertainty.

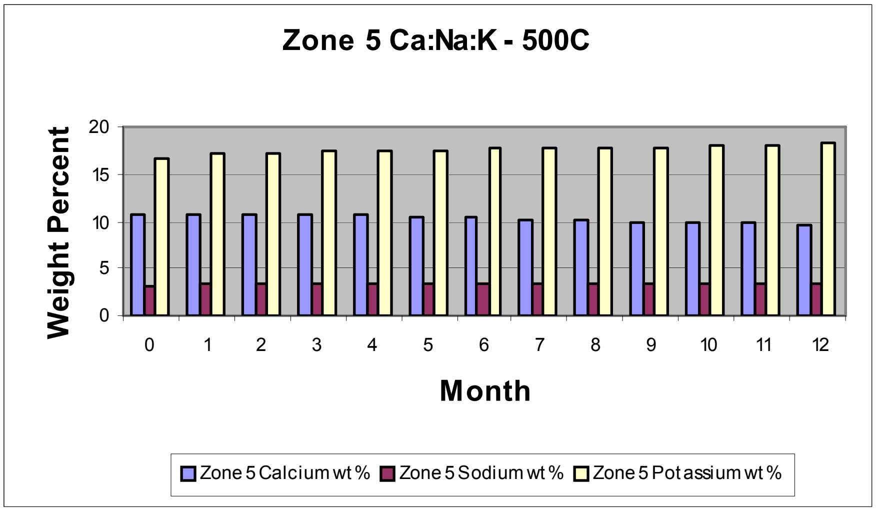


Figure 23 - Zone 5 Calcium Concentration Change

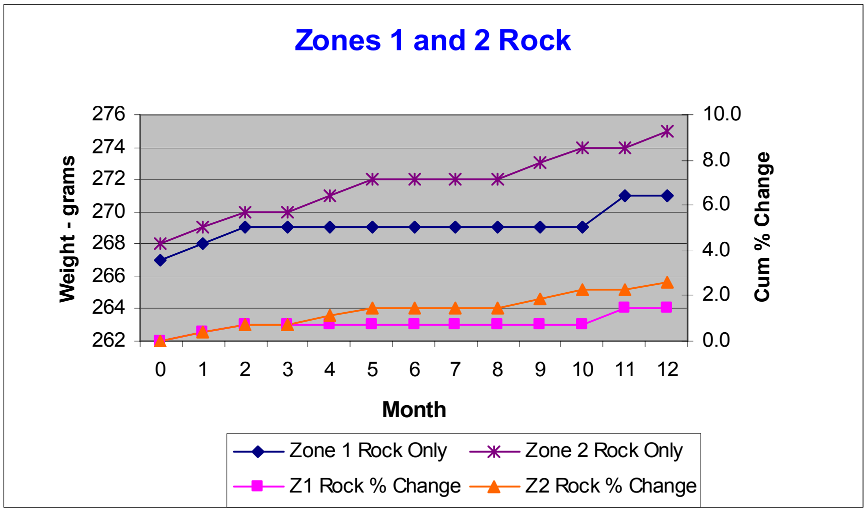
Over the 12 months of testing, very little visible change (other than color) occurred in the molten salt at 450°C, with or without rock/sand samples. However, significant changes occurred early in the Zone 5 control pot at 500°C. After the first month, a very thin layer of clear flocculant was observed on the surface of the Zone 5 pot. Based on Figure 23, the team suspected $CaCO_3$ precipitate (later verified as such via chemical analysis). This $CaCO_3$ crust layer thickened over the months (Fig. 17). Due to the difference in surface-volume ratio, but all other things apparently equal, the team anticipated seeing a similar buildup by about the third or fourth month in the 500°C Zone 2 pot containing rock/sand samples. However, that did not happen. It was not until June 2 (Month 10) that relatively minor yet evident $CaCO_3$ precipitate formed around the sample basket support wires in the 500°C Zone 2 pot. By the end of testing, there remained a small amount of crust formation in Zone 2, and even more crust in Zone 5. The Sandia team was unable to explain the different rates of $CaCO_3$ buildup between Zones 2 and 5. Appendix B contains a discussion of molten salt chemistry, $CaCO_3$ formation, and control approaches.

Filler Material Changes and Salt Interactions

Throughout the 12-month isothermal test, there were no visible signs of rock or sand crumbling or other signs of significant deterioration. Over the months, gradual changes in color and surface sheen occurred, more noticeable with the rock. It appeared that molten salt intruded into the fine surface irregularities and crevices of the rock samples. At the same time, the team also noted an early rampup in sample weights that, for a time, leveled off somewhat. Later in the test period, additional though less pronounced weight gain continued (Figs. 24 and 25). In aggregate, the rock gained 1.5 percent at 450°C, and about 2.6 percent at 500°C. The sand gained 3.6 percent at 450°C and about 6.5 percent at 500°C.

The team hypothesized that this weight gain was somewhat offset by surface deterioration of the samples. Images from scanning electron microscopy (see Appendix F) suggested a slow, relatively minor, early erosion process that may have involved removal of fine materials and impurities from the sample pores and very small surface irregularities. Those surface features were then refilled and smoothed by molten salt intrusion and calcite ($CaCO_3$) crust formation that were no longer removable during washing. See Figures 26 and 27. These off-setting conditions (e.g. surface erosion and molten salt intrusion plus calcite deposition) resulted in a net weight gain of the rock/sand samples.

Rock and sand coloration also changed over time (see pictures adjacent to Fig. 24 and 25). By May 1, 2003 (Month 9) a gradual increase in a greenish tint was observed, particularly on the sand in Zone 2 (500°C with samples). This seemed to coincide with accelerated deterioration of the sample baskets (summarized below). However, the Zone 2 (500°C) rock samples had a whiter appearance than the rocks in Zone 1 at 450°C. The end-of-test observations were similar, with an increasing greenish tint on the sand in Zone 2.



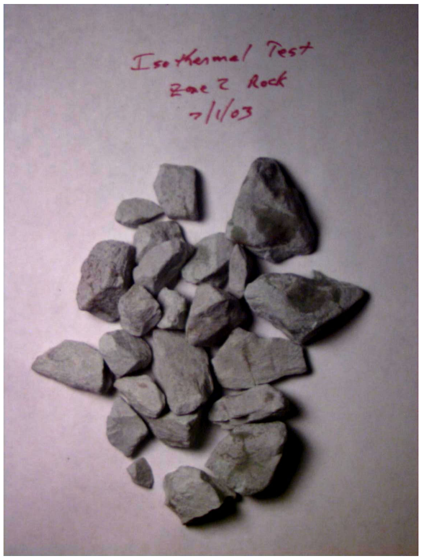
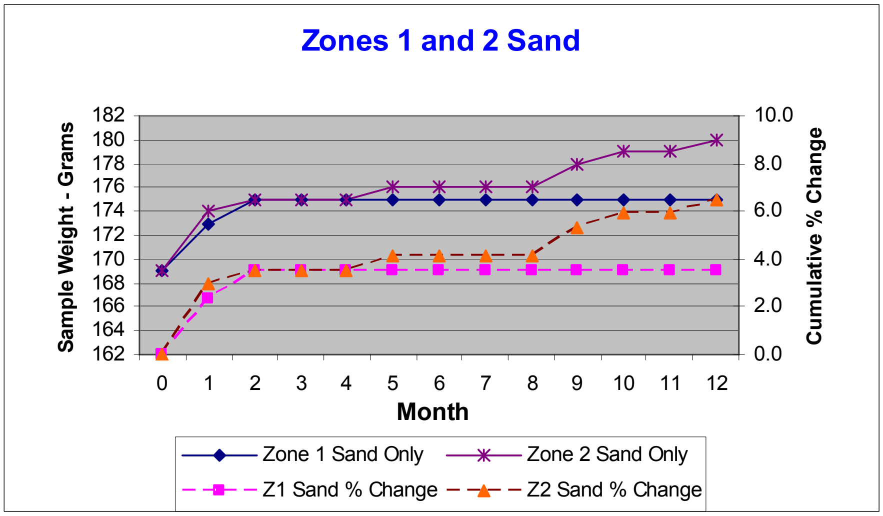


Figure 24 - Isothermal Rock Weight Change



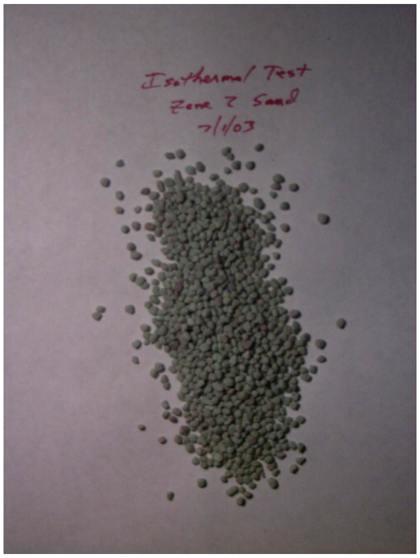
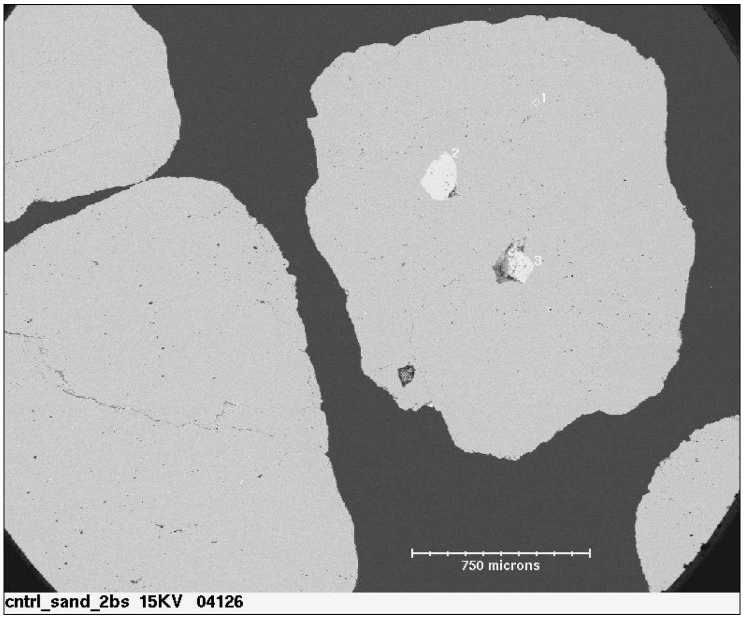


Figure 25 - Isothermal Sand Weight Change

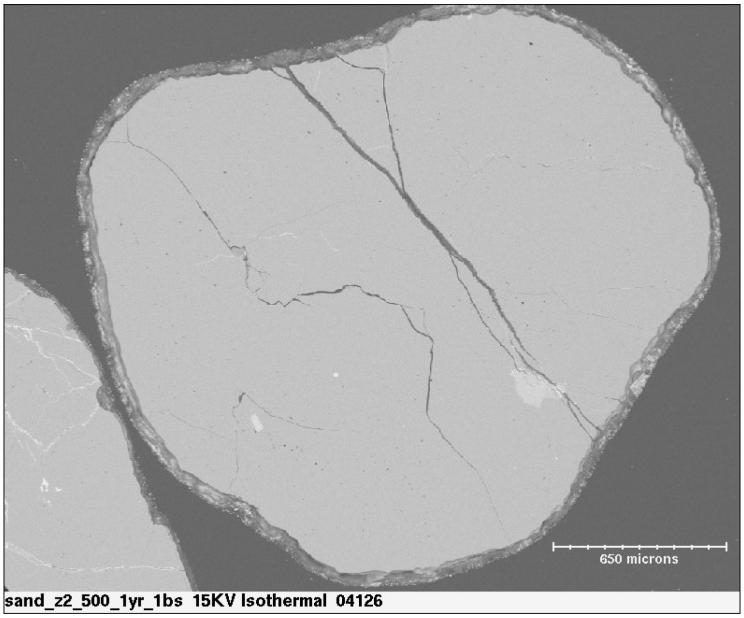
Sample Baskets

The condition of the 316SS sample baskets changed as testing progressed. By January (Month 5), deterioration (noticeable "blackening") of the sample baskets started in the Zone 2 pot at 500°C, along with surface deterioration of the covers and screen mesh (Fig. 16). At the same time, no notable deterioration occurred on the Zone 1 sample baskets exposed to 450°C salt. By February (Month 6), the Zone 2 sample basket containing sand required repair. External basket corrosion continued to worsen, and by Month 9 (May 1), was significantly advanced. Some additional basket reinforcement was added early June. By the end of isothermal testing (August 1, 2003), the Zone 2 sample basket was almost completely deteriorated and self-destructed upon removal for rock/sand assessment. By comparison, the Zone 1 (450°C) baskets were in very good condition.



This image shows some subsurface cracks, plus surface crumbling and slight deterioration that is natural, and typical, for this kind of silica sand. Funding limits did not allow quantification of the extent that aging led to more cracking.

Figure 26 - Back Scatter Picture of Control Sand (Typical)



Note the well-defined "crust" or "armor" that has developed around the periphery of the sand particle. This calcium carbonate layer explains to a large degree the typical weight gain of tested filler materials, both rock and sand.

Figure 27 - Back Scatter Picture of Zone 2 Sand

Thermal Cycle Test

Observations Prior to Shutdown

Observations for the thermal cycling test were more limited due to the operational inability to isolate and open the test chamber to remove the rock/sand samples. Throughout testing, there were no indirect observations based on system response that the rock or sand changed or deteriorated in a significant way. At the beginning of the test, the location of the weight rod above the rock/sand test chamber that provided a steady load on the filler materials was recorded. Apart from the initial thermal expansion on startup, that weight rod did not change position significantly. If rock or sand were degrading and the void fraction decreasing due to infilling and material slippage and compaction over time as the alternating salt flow occurred, a volume reduction and lowering of the rod could be expected. This did not happen.

Conversely, if the rock and sand were gaining mass due to molten salt intrusion similar to that seen in the isothermal tests, the control volume would expand and push the weight rod up; that also did not happen. These opposing effects may have happened to a minor extent, but the net volume change was negligible.

Molten Salt Chemistry

With respect to molten salt conditions, qualitatively, a notable observation was the clear color of salt samples from both the hot and cold tanks. There was almost none of the yellow coloration that was quite evident in the isothermal tests. A major difference in the tests was the constantly changing flow conditions of the thermal cycling test, conditions that led to significant mixing of salt between the tanks (air bubbler action enhanced this mixing on each cycle). Both sets of tests were at ambient pressure and only loosely covered with insulated covers, so there was no significant difference from that regard. Evidently, chromium leaching was much less pronounced under these test conditions.

Chemical analysis of molten salt samples showed insignificant changes in the Ca:Na:K ratio over time (Figs 28, 29), taking into consideration measurement and analytical uncertainty. Nitrite levels (Fig 30) significantly changed over time, ranging from 3000 to almost 5000 ug/ml, but from starting values of almost 2000 ug/ml. Iron content (Fig 31) also changed through a broad range, with high levels of measurement inaccuracy (not depicted on these plots). Chromium levels (Fig 32) were very consistent hot to cold and only slowly increased at low levels relative to levels noted in the isothermal tests. This explains in part the significant differences in salt color.

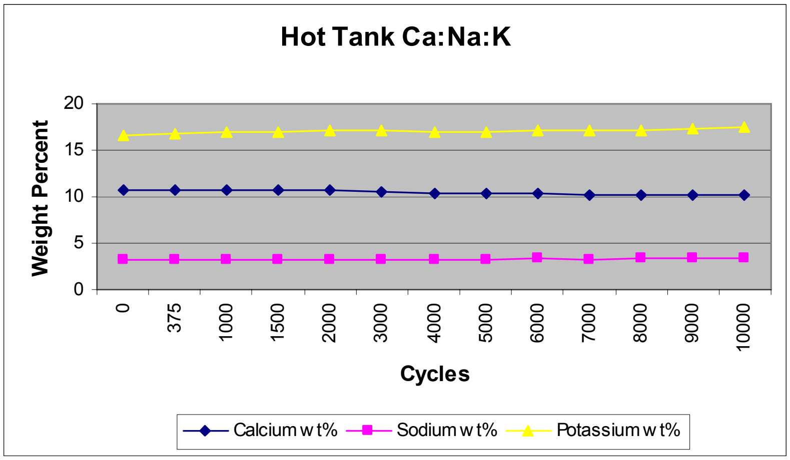


Figure 28 - Hot Tank Ca:Na:K Changes

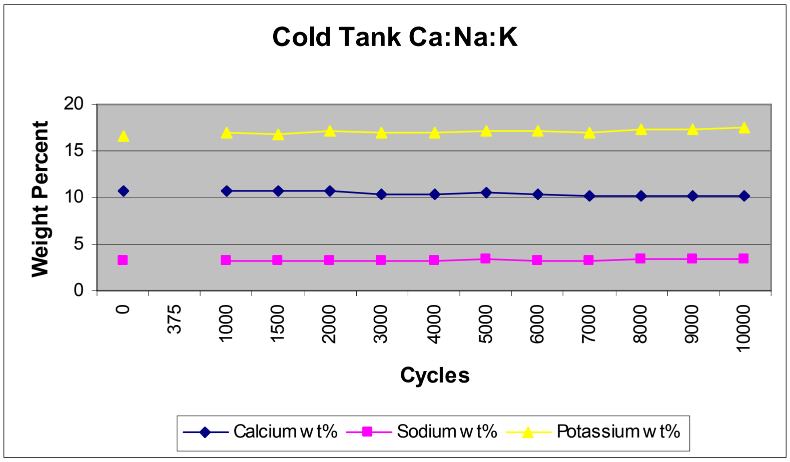


Figure 29 - Cold Tank Ca:Na:K Changes

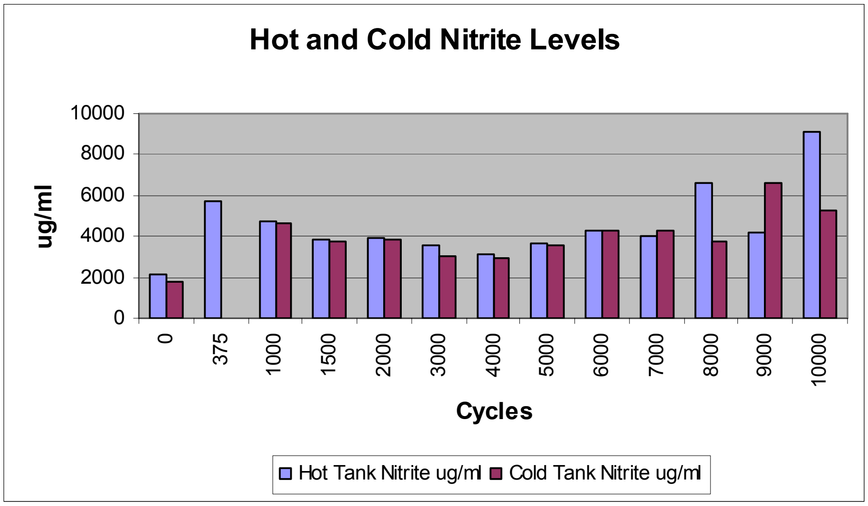


Figure 30 - Thermal Cycling Nitrite Changes

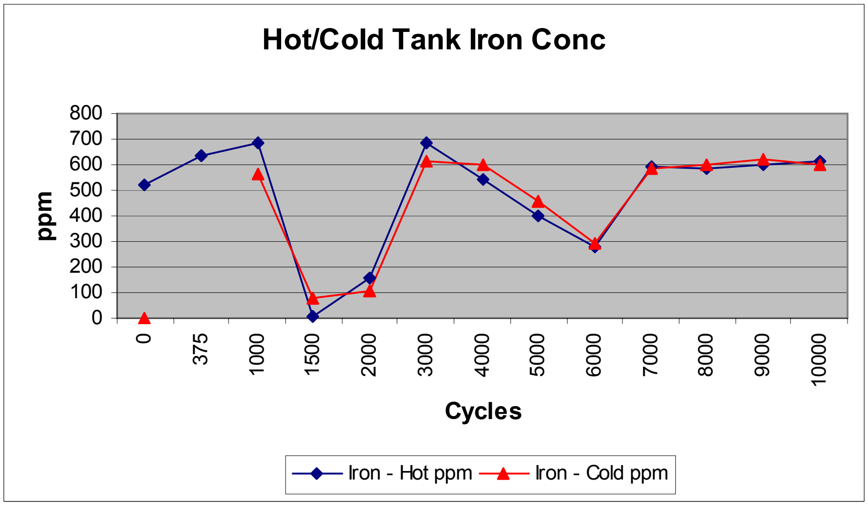


Figure 31 - Thermal Cycling Iron Concentrations

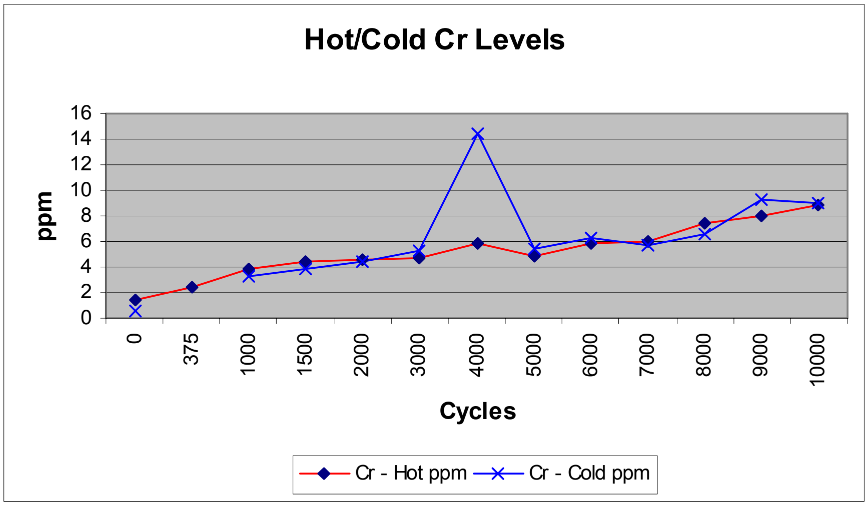


Figure 32 - Thermal Cycling Chromium Concentration

Filler Material Changes and Salt Interactions

General Observations at Shutdown

During extraction of rock and sand, a small amount of white powdery material was observed on the test chamber perforated top plate (Fig. 33). This was determined to be a very small fraction of salt and $CaCO_3$ crust flushed from the hot tank. The rock and sand were solidly packed into the test chamber but, as noted by the lack of weight rod displacement, had not changed in level or volume. Due to packing, fines, and small amounts of salt that very slightly "welded" the material, it was necessary to chip at the rock and sand with a screwdriver to break the material loose for removal. It is possible that this process led to some "pulverization" of the rock and sand. Though additional deterioration of the filler materials was likely very limited, it was also impossible to quantify.

Figure 33 - Open Test Chamber Showing Calcium Carbonate Crust

The initial layers of rock and sand removed contained a fine light brown powder (Fig. 34) that was eventually sieved and captured for analysis. The material was determined to be a mixture of rock/sand fines, very minor nitrate salt residue, the $CaCO_3$ crust, and very minor quantities of other degradation products. Notably, the sand did not turn a green tint as was evident during isothermal tests at 500°C. Succeeding layers were solidly compacted above the small, encaged sample that was installed approximately mid-height in the test chamber. Fines appeared to decrease as filler material removal progressed (Fig. 35).

Figure 34 - Initial Rock, Sand, Fines from Test Chamber

Figure 35 - Very Little Fines Above Caged Sample

The sample basket came out very easily and was in very good shape (Fig. 36). It looked much like the sample baskets removed each month from the Zone 1 isothermal pot at 450°C. There was no significant deterioration of the stainless steel basket material after 14 months of thermal cycling (in the range of 285°C to 450°C). As such, potential deleterious interactions of molten salt with the stainless steel materials used in this experimental apparatus were not a concern. There was also no indication that the sample basket acted as a filter or barrier to degradation or corrosion products.

Figure 36 - Caged Controlled Sample Basket Mid-Chamber

In the first layer of filler material below the sample basket (which fit tightly in the test chamber and likely did not move up or down as molten salt was cycled up or down), the rock and sand were not as tightly packed. After that, typical compaction continued to the bottom of the test chamber. There was not nearly the quantity of fines in the lower portion of the chamber as was found in the initial layers at the top. A thin layer of fine white powder was noted on the bottom perforated plate following removal of the bottom mesh. A sample was not obtained, assuming it was residue left from the cold tank $CaCO_3$ crust.

Rock and Sand Weight – Summary and Compilation of Results

When the test chamber was first filled in August 2002, the rock and sand were carefully washed, dried, and weighed. A 2:1 weight ratio of rock to sand was used, consistent with earlier thermocline tests conducted at Sandia. Though the rock and sand were mixed and added in a number of relatively thin layers, it was impossible to remove and differentiate the original layers added to the test chamber. The test chamber volume was segmented into three discrete regions: top, middle sample, and bottom. Table 2 summarizes the results.

The original weight of the rock and sand installed in the test chamber is tabulated by section of the test chamber. After filler material removal, fines were first sieved out of the various portions of rock and sand. Upon analysis, it was found that about 75 percent of the fine material was $CaCO_3$, and the remainder included very small quantities of rock/sand degradation products and other sources (metal shavings or oxides). There was a relatively large quantity of fines in the top section, consistent with observations as the material was removed from the test chamber. Following fines removal, the rock and sand were thoroughly washed, dried, and re-weighed, yielding the final weight in Table 2. The difference in weight and percent change from the original installed rock and sand is noted. With fines removal and washing (a total of 27 grams of material were lost in the wash water), the final weight increased, with the exception of the top section sand. Overall, the difference from the original weight showed a positive weight gain throughout the test chamber. In aggregate, the rock gained about a quarter of one percent, the sand gained about 2.7 percent, and total filler weight increased just over one percent.

Table 2 - Thermal Cycle Filler Material Weight Changes

weights in grams	Original Weight	Final Weight	Weight Change	Percent Change
Top Rock	2520	2520	0	0
Top Sand	1260	1238	-22	-1.75
Middle Rock	244	247	+3	1.23
Middle Sand	122	126	+4	3.28
Bottom Rock	1502	1510	+8	0.53
Bottom Sand	751	826	+75	9.99
Total Rock	4266	4277	+11	0.26
Total Sand	2213	2190	+57	2.67
Total Filler	6399	6467	+68	1.06

The team expected, and confirmed in analyses, the existence of minor rock/sand degradation products, insignificant stainless steel component degradation materials, and the existence of $CaCO_3$ in the apparatus, notably in the cold tank. Though measurable, the deterioration of rock and sand filler materials in both the isothermal and thermal cycling tests was considered minimal. Also, as noted earlier, the lack of appreciable volume change of the filler material in the test chamber is a beneficial result from the standpoint of commercial thermocline tank operation.

As noted in the earlier discussion of the rock and sand analysis (page 32) and discussed in Appendix F, the exposed rock and sand filler materials exhibited evidence of early erosion of the surfaces, followed by nitrate salt intrusion into small surface pores and subsurface cracks, and formation of a calcite-based “armor” or scale/coating on the filler materials. These processes over time resulted in a net weight gain. It is notable from Figures 24 and 25, applicable to the isothermal tests, that an initial weight gain occurred, likely due to the early replacement of lost material by nitrate salt intrusion. That initial weight gain was followed by a period of relatively stable weight, and then a final period that showed a slow ramp up in weight, likely coincident with formation of calcite. Due to the inability to shutdown the thermal cycling apparatus and periodically monitor the filler material weight changes, similar information is not available. However, it is quite likely that, based on the changes noted in Appendix F, parallel weight change and surface/subsurface change processes occurred with these filler materials.

The very long-term impact of calcite formation on filler materials is unknown due to the time limitations of this test program. Assuming the thermal cycling test adequately simulated a 30-year plant life would suggest that no long-term ill effects would be expected. However, if time-related processes were not adequately captured during these tests, with the potential over longer periods for continued and worsening calcite formation, weight gain, or other undetected filler material degradation mechanisms, then additional assessments and/or lengthier tests would be warranted.

COMMERCIAL OPERATIONAL CONSIDERATIONS

The primary objective of this report was to document the results of thermocline filler material testing conducted at the Sandia NSTTF. That objective was met. However, enough was learned during this testing program that, in conjunction with lessons learned from past tests and evaluations of thermal storage systems, more discussion of the longer-term, larger-scale commercial applications seemed warranted. This section summarizes a number of key considerations regarding thermocline-based TES design, construction, startup, and operation. As this summary was largely outside the scope of this study, the discussion is neither comprehensive nor complete; additional studies are necessary.

Design Considerations

System optimization studies will be required in order to determine the best design approaches for direct thermocline-based TES systems. Factors include, but certainly are not limited to, power plant rated gross generation; solar field size and solar multiple; the solar resource at the plant site; ambient design conditions; the desired storage capacity (in hours or MWh ratings); the HTF used; power cycle design, temperature and pressure conditions, efficiency, and other performance parameters; the size and number of thermocline tanks; filler material selection; pump number, sizing, and configuration; piping and distribution piping internal to the tanks; and other important parameters. Design tradeoffs need to be identified, clearly understood, and evaluated with respect to installed cost, redundancy for operations and maintenance purposes, performance, and long-term operations & maintenance (O&M) cost.

Thermocline Tanks

The pilot-scale testing by Pacheco [8] identified a number of key issues relative to the thermocline tanks. The overall design and operability favored taller, smaller diameter tanks versus shorter, larger-diameter tanks. This larger height:diameter aspect ratio establishes key design constraints on the tanks. Designers will need to take into careful consideration design loadings from filler materials and molten salt and the required radial and circumferential hoop strength and wall reinforcement required, as well as foundation design and the design of the tank base. Material selection is important, given the preliminary findings in this report regarding molten salt interactions and impacts on stainless steels.

The number of tanks designed and installed for a given power plant application is a key parameter. There are practical limits on the design and field-installation (and operation and maintenance) of very large tanks, particularly thermocline tanks. Fewer tanks would mean fewer, but larger, pumps and less piping, fewer valves, fewer tank internals, and simplified controls relative to that required for many tanks. As noted in the Background Test discussion, the *percent theoretical capacity* of the TES system would need to be optimized, based on number and height of the tanks. The demands for establishing and maintaining the thermal gradient and the required height of the thermocline in the tank must be considered. A single large tank may have the lowest overall surface-to-volume ratio, minimizing the overall requirements for insulation, heat trace, associated controls, and thermal losses (thus, maximizing efficiency and plant performance). On the other hand, a single tank may be so large that construction, startup, operation, and maintenance may be very difficult to implement. See the following discussions for examples.

Tank Internals

Careful attention must be placed on the design of the internal manifolds and ring headers for the bottom cold suction and top hot suction pump headers. Placement of the headers (relative to the tank top and bottom, and the filler section) will partly determine the percent capacity of the system, but is also important with regard to installation and long-term access for maintenance. Selection of materials and screen protection to prevent filler material access to the headers, pumps, and piping are important design decisions. Considerations for pump installation and removal, standpipes, instrumentation (particularly thermocouples for thermocline performance monitoring), and freeze protection are all important.

Testing Thermocline Filler Materials

Filler Material Selection

This report provides an excellent basis for selecting quartzite rock and silica sand in combination as thermocline filler materials. However, many decisions must be made for large-scale applications. Supply sources at reasonable lowest cost must be identified and secured, with availability guaranteed for initial startup supply as well as long-term replacement requirements. The proper grade and quality of the rock and sand must be identified and specified and appropriate quality control requirements need to be established and implemented. Requiring screening, cleaning, and pre-treatment prior to shipment may minimize the field treatment of the huge quantities of filler material needed prior to installation. Proper packaging, shipment, and handling processes and procedures need to be established and implemented to ensure excellent filler material quality when it is ready for installation in thermocline tanks on site.

Pumps, Valves, and Piping

No attempt will be made here to discuss pump design requirements for thermocline TES applications. A number of Solar Two references [5,12,13] provide excellent discussions regarding experiences with pumps used in molten salt service. The development and evaluation of a long-shafted pump for high-temperature molten-salt applications at the Sandia NSTTF [14] showed that pumps for thermocline TES applications can be commercially and economically manufactured for mounting on the top of the molten-salt TES tanks. The long-shafted pump could be mounted directly above the salt storage tank, extending into the tank and drawing salt from the hot or cold regions of the tank (near the top, or from the bottom). Use of this pump configuration would eliminate the need for sump vessels, along with the associated isolation and control valves, piping, heat trace, and insulation. In addition, a number of failure modes could be eliminated, including sump overflow. Design of the system would need to consider pump sizing and redundancy, installation, operational requirements, access and provisions for removal and overhaul, and the interface with the tank internal manifolds and exterior piping and supports.

The Solar Two references also discussed valve issues identified during the test and evaluation and operational phases of the Solar Two Power Tower demonstration. Using binary “solar salt,” at higher temperatures than might be typical for parabolic trough molten-salt TES applications, gate, globe, some butterfly designs, and caged plug valves worked reasonably well. Ball valves did not perform well and were eliminated. All welded construction and welded installation were required. The simple gate valves in the thermal cycling test reported here failed open in moderate temperature service almost immediately when used in the ternary molten salt environment. A post-mortem was not performed, and it is possible these stainless steel valves were not appropriate for the application due to stem to bonnet clearances that were too small, resulting in stem galling and early seizure. Extended bonnet valves (as discussed by Kelly [5]) and bellows-type valves would probably perform well in high temperature molten salt applications, though care must be taken in the design and installation of the heat trace to prevent freezing in these valve types. Thermal cycling and operational cycling duty of the valves are factors that must be considered in valve design and specification. The design and programmed control of heat trace circuits for valves in hot service are important to the long-term successful operation of these valves.

Molten Salt

As discussed elsewhere in this report, the specification of the molten salt used in large-scale power plant applications will be important. A basic decision involves whether to procure an already-prepared commercial product such as HitecXL, or to procure the three constituent salts. Either decision then leads to further decisions regarding supplier and/or field pre-treatment of the molten salt prior to injection into the thermocline tank. Salt specifications need to be established with regard to grade, purity, availability, cost, and formulation. Assessments are required of the freeze/thaw behavior of the mixture and its thermal properties. As noted elsewhere, additional studies are required in order to establish the optimum mixture that provides the lowest freezing point, highest temperature rating without decomposition, and best thermal properties for the application, all at reasonable cost.

Construction and Installation

Some limited experience has been gained with the construction, installation, and characterization of thermocline-based TES systems. As noted by Pacheco [8], an early thermocline-based TES system was demonstrated at the Solar One power tower pilot plant [15] that used Caloria heat transfer fluid and rock and sand in a small thermocline TES system. Though the system was over-designed and not fully utilized during the operational phase of Solar One, the final evaluation report concluded that the system was a valuable source of design and operational experience. The thermocline concept worked well, with the ability to establish the thermal gradient and maintain the gradient until it was used. Heat loss from the tank walls was acceptable. Since the system operated for a limited period of time over 20 years ago, access to the experienced personnel from that era may not be easily achieved.

Field construction of large thermocline tanks, the materials used, shipping requirements and limitations, and the installation and fabrication methods chosen, while well beyond the scope of this report, are nevertheless very important practical considerations for a large commercial TES application. A single large tank, depending on the overall size of the plant, may not be practical. On the other hand, many small tanks would increase the complexity of the design, installation, and operational approach.

Filling the tanks with the rock and sand filler materials is another important consideration. The performance of a thermocline tank depends in part on how well the filler material is mixed and packed in the tank to minimize void space and settling over time. The experience at the Sandia NSTTF with the 2.3 MWh pilot-scale thermocline tank provided valuable lessons with regard to preparing the rock and sand, proper mixing in the 2:1 ratio and layered installation, and the need for packing as installation proceeds. Though a single large tank may be easier to access, full compaction when compared to smaller diameter tanks may be more difficult to achieve. Care must be taken in design and installation to provide adequate screening and separation of the rock and sand from the intake manifolds and ring headers in order to prevent entry of rock and sand fines into the piping system and pumps. The Solar One tank included a rock-only region around the manifolds to help achieve this. Sand was installed alone at the bottom below the cold manifold rock region. How the sand-only, rock-only, and mixed rock/sand regions were separated was not specified. Consideration should also be given in the design and installation for a means at the bottom of the tank to periodically collect and remove the very small fines that will develop over time (due in part to the inevitable fine material "contamination" during initial installation, and also longer-term degradation of the rock and sand due to the operational thermal environment).

Initial Preparations and Startup Considerations

There are a number of general considerations during startup that will need to be addressed, including tank and filler material heatup; conditioning, preparation, and initial molten salt charging; and design and operational provisions for freeze protection, initial circulation of the molten salt within the TES and throughout the solar field, and long-term maintenance of the thermocline charge and thermal gradient.

Tank and Filler Material Heatup

The experience at the Sandia NSTTF preparing the pilot-scale thermocline tank is valuable to draw upon. That system was small and the flow loop was limited to the propane heater and salt cooler. The system was initially heated with the tank heat trace, the propane heater, and the introduction of hot air through a venturi into the lower manifold at the bottom of the tank. This was a lengthy process, even for this relatively small tank. A single large commercial thermocline tank will require careful design of the methods and equipment needed to heat and maintain adequate temperatures in the tank and filler material prior to molten salt charging. Careful design of external heat trace and internal immersion heaters will be required. Otherwise, cold spots will quickly result in large areas of frozen salt that will be difficult to work with during the startup process. Given the contraction and expansion behavior of molten salt during freezing and thawing, any significant cold spots are to be avoided if at all possible.

Molten Salt Preparation

As noted earlier, the site preparation of the nitrate salts will depend upon the salt formulation purchased and the requirements placed on the supplier for factory preparation prior to shipment. Any commercial power plant in the sizes anticipated for parabolic troughs will require huge quantities of nitrate salts. Much thought must go into the safe and effective shipment, storage, and handling of these quantities. The commercial HitecXL formulation, while pre-mixed, would still require field treatment equipment (perhaps provided by the supplier) to pre-heat the mixture, flash off (and collect) the water, heat the salt to the fully molten state, and then introduce the molten salt into the thermocline tank. Filling the tank must include the critical phase of initial startup of the hot and cold pumps to circulate the molten salt in order to retain tank and filler material temperatures and to prevent salt freezing anywhere in the system.

An alternative to the “hydrotherm” liquid-phase molten salt preparation system just noted would be to procure the three individual “dry” salts. This system, while avoiding the bulk handling, storage, and boil off of massive quantities of water in the commercial HitecXL formulation, is not without its own set of issues and concerns. Supplier requirements will need to specify the size and quantity of shipping containers and provisions to protect the highly hygroscopic nitrate salts from exposure to moisture. Site storage will need to be arranged and storage time should be minimized by careful arrangements with the supplier. A well-designed plant material handling system would need to be provided, including provisions and equipment for unloading (truck or rail), storage, conveyance (mechanical, pneumatic), crushing, feed hoppers and conveyance for blending and mixing, melting (with some boil off of absorbed water and water from the tetrahydrate formulation of calcium nitrate), heating, and pumping into the tanks. The entire process requires careful attention to the accuracy of blending and mixing (to obtain the proper molten salt mixture with the desired lowest freeze point), the heating process and ramp rates (and the lengthy periods of time measured in weeks for these processes), monitoring tank temperatures and tank growth, maintaining salt flows and levels, and establishing soak times and thermal conditioning of the salt, and salt circulation. The experience at Solar Two with solar salt [13] included attention to magnesium nitrate impurities in the salt and the formation of gaseous nitrous oxide (reduced during thermal conditioning); tank venting and freeze prevention; recycling salt leakage back into the system; and restart after long outages. The observations will not be repeated here, but are valuable lessons learned for future plant startups.

Operations and Maintenance

Once successfully started, the routine operation and maintenance of the TES system, with molten salt and filler materials, should not pose insurmountable obstacles to success. The design should include provisions for periodic access to and inspections of the rock and sand filler materials, at least at the top surface in the tank. As noted earlier, routine removal of fines from the system should occur if design provisions allow it. Otherwise, though the fines could stabilize within the system, they are more likely to potentially build up, flow up and down through the filler matrix during charging and discharging cycles, and eventually collect at the bottom of the tank or on the screen surfaces around the manifolds. Internal stainless steel surfaces and upper manifold screen mesh (if it is made accessible in design) should be routinely inspected for evidence of corrosion or other degradation processes. Removal of the filler materials for tank refurbishment may not be possible without resorting to destructive measures that would require major operations to repair and refill the tank and put it back into service.

This report has documented a concern regarding formation of calcite (including calcium carbonate and dicalcium silicate) on the surfaces and intrusion of the nitrate salts into the pores and cracks of the filler materials, resulting in weight gain. The test duration was not adequate to assess the very long-term potential and risk for increased growth of the scaling deposits and net weight gain of the filler materials. As such, this condition is something that should be monitored throughout the life of the TES system thermocline tank and filler materials.

The report also suggested the potential for calcium carbonate formation and scaling in other portions of the system, including tank internals, piping, and within the solar field heat collection elements. If the latter scaling occurs, extremely negative impacts could occur with regard to solar field heat absorption, collector performance, and overall plant power cycle efficiency. Control and minimization of such formation are thus quite important from the standpoint of minimizing both operations and maintenance costs, as well as maximizing plant rated output.

It was well beyond the scope and timing of this project to evaluate the potential extent of occurrence of calcium carbonate scaling, or the best means to control or eliminate its formation. Elimination of carbon dioxide from the system through some system of ullage control is certainly one viable control method. See Appendix B for further discussion of molten salt chemistry, and potential methods for CO2 control that warrant additional study. This approach would involve design and operational tradeoffs with regard to cost, feasibility with a molten nitrate salt thermocline tank design, cost and control of the ullage system, venting of offgasses, freeze protection, and similar considerations. Other possibilities, perhaps implemented alone or in conjunction with the ullage system, are chemical acid treatment of the molten nitrate salt using a side-stream system (to add the appropriate chemicals and remove byproducts of the treatment process) or a carbonate removal system as briefly proposed and discussed in Appendix B. Once again, the specification and design of these types of treatment processes was well beyond the scope of this report.

CONCLUSIONS AND RECOMMENDATIONS

At the conclusion of the isothermal and thermal cycling experiments, the quartzite rock and silica sand that are being considered as thermocline tank filler materials appeared able to withstand the molten salt environment quite well. No significant deterioration that would impact the performance or operability of a thermocline thermal energy storage system was evident. Sandia would recommend moving forward with additional studies of the thermocline concept armed with confidence that appropriate filler materials have been identified for the intended application.

This experimental program raised concerns regarding characterization of HitecXL ternary nitrate salts in the large-scale power plant environment. In the long run, more comprehensive studies are required to better characterize, understand, and specify the ternary molten nitrate salt formulation recommended for commercial use. Additional studies are recommended to evaluate ternary molten salt freeze/thaw behavior and other engineering and thermal properties. Finally, engineering studies are needed for handling large quantities of these salts during initial plant startup and during daily load changes. These studies should address such factors as maintaining minimum system temperatures to avoid freezing and salt disassociation; characterizing and understanding molten salt viscosity, pumpability, and pump costs; maintaining adequate or continuous field flow and mixing; and optimizing use of heat trace.

Though the primary purpose of these experiments was assessment of thermocline filler materials, there were a number of other concerns and issues raised during the course of testing. Significant salt/metal interactions were evidenced by accelerated deterioration of stainless steel sample baskets in 500°C molten nitrate salt. It appears that these interactions may not be a significant concern as long as nitrate salt HTF is maintained at or below 450°C. However, the early inoperability of the thermal cycle apparatus isolation gate valves strongly suggested the need for additional evaluation of valve design, manufacture, and material selection that should be considered in long-term molten salt applications at temperatures similar to the experimental conditions. The significant level of $CaCO_3$ scale buildup in the cold tank suggested potential issues for the use of the ternary nitrate salt formulation in the industrial setting. Such scale buildup will present operational and maintenance challenges, particularly if present in the solar field heat collection elements. There are quite likely chemical treatment and/or other engineering solutions to this issue, but further targeted study is needed.

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APPENDICES

Appendix A - Details on Thermocline Testing Reported by Pacheco

Screening Thermocline Filler Materials

As noted in the body of the text, 17 candidate filler materials were tested in isothermal baths prior to the thermal cycling test. Of those, only four materials (taconite, marble, limestone, and quartzite rock and sand) were tested in the thermal cycling test.

Void Fraction of Filler Materials

The void fraction of the filler materials was determined by simple tests using a uniform cylindrical bucket. Filler material was added to the bucket to a prescribed level and weighed, and then water was added to that level, and the contents weighed. The bucket was emptied, and then refilled to the same level with water alone. The ratio of the mass of water mixed with the filler to water alone determined the void fraction. However, this simple test was deemed and proven not to be representative of the final void fraction in a large commercial tank. The filler in a large tank will settle and be more compacted than in a small drum.

The void fractions for marble, NM limestone, and taconite were determined to be approximately 0.49, 0.42, and 0.52 respectively. These void fractions were higher than desired; test personnel determined that a void fraction of about 0.25 would be ideal. Additional tests were conducted with a 2:1 combination of quartzite rock mixed with silica sand. The void fraction, after packing, was about 0.25. Proper packing of the mixed filler material in the tank was determined to be a critical factor in achieving the lowest desired void fraction in the tank. The actual calculated and measured void fraction achieved in the pilot-scale thermocline tank based on actual quantities of salt used was 0.22.

Thermal Cycling Apparatus

This picture again depicts the finished and operational thermal cycling apparatus used for screening.

Testing Thermocline Filler Materials

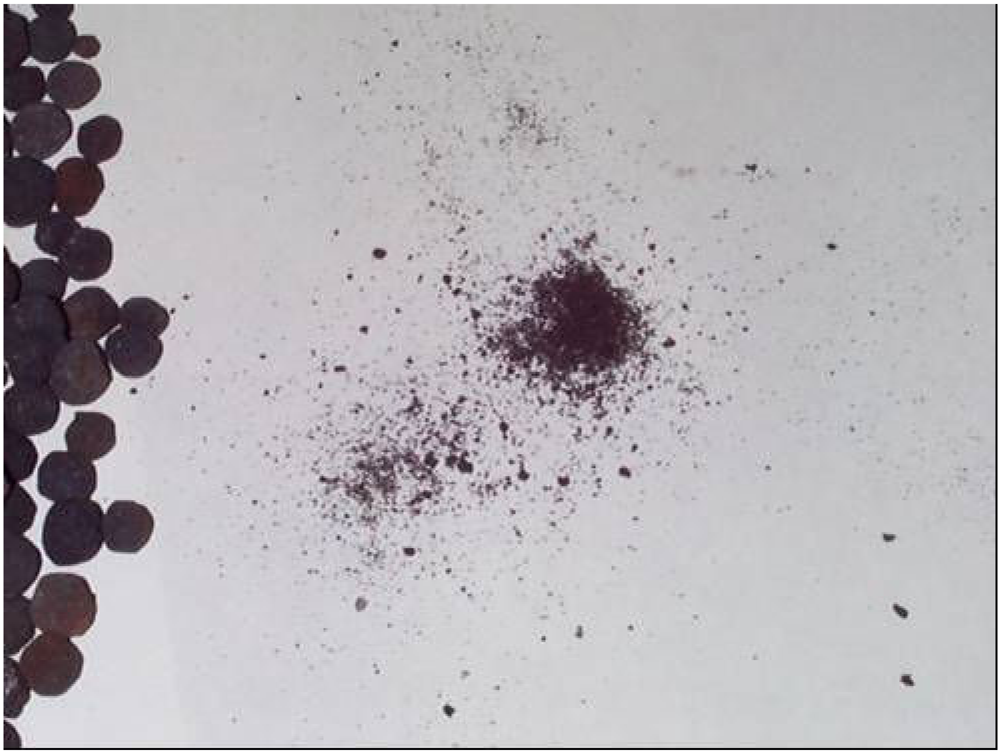
This “hot rocks” test explored the durability of each rock sample by cycling hot salt (400ºC) and cold salt (290ºC) through a basin or test chamber containing the sample. The test chamber was located between the hot and cold tanks. Using air pressurization, the salt was alternately cycled through the test chamber from either the hot or cold tank, with “soak” times that were typically on the order of 30 minutes. This apparatus, unlike that used for the later thermal cycling system for testing to 10,000 cycles, was pressurized with air. Thermal cycling control was reasonable, but difficulties were experienced which pointed to the desire for a new design for the longer-term test phase. Lessons were learned particularly with respect to heat trace and insulation requirements.

Results From Thermal Cycling Candidate Filler Materials

The following series of pictures shows the before and after condition of the samples tested. The limestone faired the worst in testing. This first picture is the initial condition of this material.

The following are two of the shots showing the condition of limestone after 365 cycles of testing.

There were no pictures available that depicted the condition of the marble filler material tested. The following pictures depict the taconite pellets and some of the fines that resulted from thermal cycling exposure conditions in molten salt. Some of the taconite pieces were easily crushable between two fingers, even though the taconite seemed to hold up well overall.



Testing Thermocline Filler Materials

The next set of picture depict the before and after condition of the quartzite rock which was tested for 553 cycles. Note that the picture taken after included water that was used to clean the tank in preparation for the next test. As noted in the main body of the report, this filler material did well in this screening test.

Finally, the silica sand that was chosen for use in combination with quartzite rock (in order to significantly reduce the void fraction) was also exposed to 360 thermal cycles. The before and after picture show remarkably little change in this material in these initial test conditions.

Selected Pictures of the Thermocline Installation Details

This first aerial photo shows the thermocline tank in the middle, the cooler on the right, and the propane heater on the left.

This image shows the insulated sump that collected molten salt from the heater and cooler at the end of a test. The inventory was then pumped back into the tank.

The above photo shows the thermocline tank fully heat traced, and the initial layers of insulation applied. The image below shows the completion of insulation, as well as the cooler on the right.

The photo above shows the thermocouple tree, the flow distribution manifold, and the hot and cold pump stand pipes, also noted in the picture below.

The finished product is noted on the following page.

Appendix B - Details on Molten Salt Studies and Issues

The primary purpose of isothermal and thermal cycling tests documented in this report was to determine the durability of quartzite rock and silica sand in molten nitrate salt over long periods. Funding and time did not allow an extensive investigation and characterization of the ternary salt formulation similar to HitecXL that was chosen for the test. However, a number of key issues and concerns with the nitrate salts focused the need for some investigations prior to testing.

Safety Issues Related to Salt-Oil Interactions

In parallel to screening tests conducted on thermocline filler materials, Sandia evaluated potential safety issues relative to possible heat exchanger interactions of oil HTF and molten salt used in thermal energy storage systems. In order to store energy for dispatch using an indirect TES system, heat from the oil HTF (for instance, Therminol VP-1) exiting the solar collector field would be transferred to the salt HTF through an oil-to-salt heat exchanger. Because the nitrate salt is classified as an oxidizer and the Therminol oil is a fuel, there was concern that having these two fluids in close proximity might pose an unacceptable hazard in the event of heat exchanger failures introducing oil into the salt or vica versa. Early studies were conducted with Hitec (a mixture of sodium nitrate, potassium nitrate, and sodium nitrite) and organic liquids. 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 593ºC. In each case, the hydrocarbon burned. The principal reactions were between the vaporized hydrocarbons and the air above the salt bath, and not with the salt itself. Experimental data indicate that Hitec is not explosive. Draw salt of any other mixtures of sodium nitrate and potassium nitrate were expected to act similarly to Hitec.

To verify that Hitec XL behaved similarly to Hitec, Therminol was introduced into a beaker of Hitec XL at approximately 400ºC three different ways: on the surface, below the surface, and trapped below the surface in a vial. In each case, the Therminol rapidly volatized when it came in contact with the hot nitrate salt. The oil did not burn under or on the surface of the salt. These tests were repeated with Caloria oil. The first two tests behaved similarly to the Therminol tests. However, in the third test after covering the beaker with insulation, trapped Caloria oil vapor caught fire and burned for approximately two minutes. The presence of a fuel, oxygen, and a heat source resulted in the small fire. The fire was not the result of a chemical reaction with the nitrate salts that were used. In fact, any heat source would have yielded the same result. As a follow up test, an ignition source was added to simulate an external source of ignition (such as a motor in a power plant) to verify a fire would occur under the right conditions. This ignition heat source did in fact ignite the Therminol vapors above the salt.

The safety concerns in power plants that use Therminol and nitrate salts in a heat exchanger are no more dangerous than using Therminol around other high-temperature heat sources. Accidentally mixing the two components should not create combustion, but combining hot Therminol vapors with oxygen from the air is dangerous. The design of the thermal energy storage system should address the unlikely event of having hot oil vapors released into the ullage space of a nitrate salt tank where oxygen could be present.

Handling and Processing Ternary Nitrate Salt Mixtures

The commercial aqueous formulation of HitecXL was procured and used in the early isothermal screening and initial thermal cycling tests conducted at Sandia. It was also intended for use in this current testing effort. However, in early phases of test setup, trial melts of the aqueous solution presented significant difficulties. Though possibly an artifact of the relatively loose temperature control on the melting pots, melting and boiling off the water from the HitecXL solution was very sensitive. Slight ramps in temperature at critical points caused uncontrolled and dangerous boiling and expulsion of hot salt solution from the melting pot. At higher temperatures, brown NOx emission was also a concern.

These experiences raised issues regarding the short-term ability to work with this molten nitrate salt formulation in the laboratory setting as well as longer-term issues handling and preparing huge quantities of aqueous ternary salt formulations in full-scale tests and operational plants. The engineering to address these issues was well beyond the scope of this testing effort. Future laboratory-scale experiments could be better controlled and dehydrated by bubbling air through the test apparatus. Air addition could nucleate boiling more uniformly, provide thermal uniformity and remove some of the moisture as it evolves. Removal of moisture would be limited by the air flow rate.

Nitrate Salt Formulations Evaluated for Thermal Cycle Testing

The Sandia team re-evaluated the original rationale for using the HitecXL formulation, its pedigree, availability, and (more recently) lack of supplier endorsement for this application. There were questions regarding past studies and inconsistency in documentation regarding the exact ternary mixture and formulation of HitecXL. Evaluations were conducted to better understand the best mixture of the three constituent salts to yield the lowest freeze point, and the supplier of HitecXL was consulted regarding the exact makeup of the product.

A number of different mixtures were studied, including melts to 450°C and 500°C. From supplier conversations and phase diagram analysis (shown below, [Ref. 16]), the optimum mixture appeared to be 45 wt% calcium nitrate, 11 wt% sodium nitrate, and 44 wt% potassium nitrate. The team also analyzed a 48:7:45 mixture and a 42:15:43 mixture (documented in prior Sandia studies), but the best results were obtained from the 45:11:44 mix. Sandia decided to procure the three "dry" constituent salts to work with (calcium nitrate is only available in tetrahydrate form, requiring some boil off). Only A.C.S. reagent-grade salts were procured for this series of tests due to concerns about unknown and inconsistent levels of impurities in lower (but more economical) grades. Future more detailed studies of nitrate salts that were beyond the scope of this task will need to address salt grades, costs, purity, availability, shipment quantities and packaging, etc..

KNO_3-$NaNO_3$-$Ca(NO_3)_2$

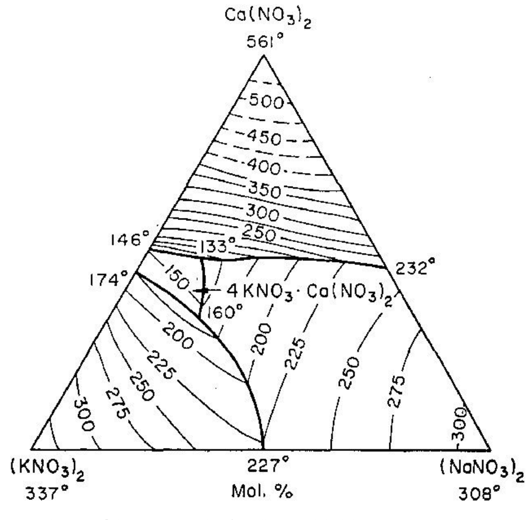


FIG. 1074.—System $(KNO_3)_2$-$(NaNO_3)_2$-$Ca(NO_3)_2$.

A. G. Bergman, I. S. Rassonskaya, and N. E. Shmidt, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei Neorg. Khim., Akad. Nauk S.S.S.R.*, **26**, 156 (1955).

Trial testing of the dry salts then occurred. The primary objectives of this trial phase were to gain experience with mixing, boiling off water, and melting the ternary molten salt mixtures, to better understand the freeze/thaw "behavior" of the molten mixture, and to refine the process needed to eventually charge the hot and cold thermal cycling tanks. With reasonable care, the process of boiling off the water (and quantifying the amount of water bound to the calcium nitrate) and melting the ternary mixture was straight-forward and repeatable. Boiling occurred around 125°C to 130°C and progressed vigorously but in controlled fashion as pot temperature was ramped up, until all water was gone (roughly in the range of 260°C - 290°C). There was no uncontrolled boiling, spitting, frothing, foaming, sludge, or NOx emissions, just water vapor. However, minor "brown cloud" emissions were detected going from 450°C to 500°C that varied with the ramp rate (though this was not quantified). It was fairly easy to safely add dry salt mixture to relatively cool molten salt during the boil off process. As-received salt samples and molten salt samples were chemically analyzed to understand the nature of impurities and how the molten salt changes at temperature (however, time and funding limits did not allow extensive chemical characterization).

Though the test mixture that seemed to yield best performance in these simple trials was 45:11:44 (Ca:Na:K) which was identical to the supplier-stated mixture for HitecXL, the mixture deemed most appropriate from the phase diagram was slightly different at 44:12:44. Due to concerns about limited supplies of calcium nitrate on-hand, Sandia decided to use the latter mix for the isothermal and thermal cycling tests. The team also had very good results with the 42:15:43 mix (with respect to low freezing points), suggesting the need and desire for more study of these ternary nitrate salt formulations. In the long run, further testing of various mixes in that limited region or trajectory of the phase diagram is recommended.

Thermal Stability and Limitations

The Sandia team was also concerned regarding thermal stability and the upper temperature limit of these nitrate salts. The SunLab trade studies were based on an assumed upper solar field temperature of 500°C, but past studies [9,10] indicated significant decomposition of similar ternary molten salt formulations near 460°C. There was an evident need to understand the chemistry: chemical decomposition processes, temperature limits, melting and freezing temperatures and behavior; as well as other engineering properties of the molten salt. Meetings were convened and many e-mail exchanges and teleconferences among the SunLab participants occurred to attempt to address the concerns and issues and arrive at a logical path forward. A preliminary conclusion was that, until further molten salt testing and characterization would be done, the current modeling assumptions and test conditions for inorganic salt HTF would need to fall at or below the 460ºC limit.

Freeze/Thaw Evaluations

Sandia conducted relatively simple and not-well-controlled (due to equipment limitations) assessments of freeze/thaw behavior of the various mixtures. The results were extremely interesting, but pointed strongly to the need for further study. Initial efforts to “freeze” the molten salt resulted in increasing viscosity that eventually led to a pot of clear, rubbery gel that became glass-like below about 110°C. Re-melting occurred over broad ranges with little repeatability, at times in the mid-120°C range, and other times from 130°C to 145°C. However, in follow-on freezing and melting cycles, the freeze/thaw behavior changed and appeared to track up in temperature. On freezing, crystals started forming around the edges of the pots and, in a few cases, sludge formed, and the freeze was very opaque. Re-melting required significantly higher temperatures, but stable melts were not an issue once achieved. The best guess was salt disassociation, leaving a binary melt with higher melting and freezing points; the ternary mixture behavior returned once the hot melt was well established. This experience pointed to the need for further study and, eventually, engineered solutions for handling large quantities of these salts for initial plant startup and during daily load changes.

The glassy freezing and melting behavior is a property of alkaline earth-alkali nitrate mixtures. Since high viscosity may be a problem in commercial operation, the best approach might be to simply avoid the glassy phase temperature region altogether as if it was a freezing point. This of course will impact minimum solar field temperatures, heat trace requirements, and the economics of plant parasitics. In addition, the molten salt mixture could be treated to create disorder or to breakup the glassy phase. Oxy-anions (such as nitrate, sulfate, carbonate) have strong physical forces that create relatively long-range order in liquid salts (the glassy phases). Adding other ion constituents that are not oxy-anions, such as NaCl (or other chlorides), may disrupt this order. Clearly, additional study on these approaches is warranted, including additional evaluations of materials interactions, both metals and filler materials.

Molten Salt Chemistry and Calcium Carbonate Issues

The formation of $CaCO_3$ (as documented earlier in this test report) is a consequence of CO_2 in ambient air that serves as the cover gas (in the experiments reported here) reacting with the molten salt. The primary reaction is probably between CO_2 and CaO, which forms as a minor decomposition product of the ternary molten salt mixture at the highest temperature of the system. Reaction of CO_2 with nitrate may also occur but likely to a lesser extent. The rate of calcite formation depends on temperature and access to CO_2, while the solubility of calcite depends mostly on temperature. At the same time, the rate and amount of CaO formation is very dependent on temperature, which affects both the rate of decomposition reactions and the degree to which they occur.

The solubility of ionic constituents other than nitrate in the molten salt mixture vary a great deal between the calcium-containing ternary salt and a calcium-free binary mixture (such as "solar salt"). The binary mixture can dissolve several weight percent of carbonate at temperatures near the freezing point. However, the solubility of $CaCO_3$ in the ternary molten salt is only a few tenths of a weight percent at nominally 450°C and much less at lower temperatures. Although dissolved carbonate accumulation can be removed by chemical treatment of the melt with nitric acid, such a procedure may not be a desirable way to operate.

The difference in the rates of calcite formation in the Zone 5 500°C isothermal pot (without samples), and the cold tank on the thermal cycling apparatus was unexplained. In the Zone 2 500°C pot (with samples), the CaO from decomposition reactions may preferentially react with the filler to form the coating seen on the filler materials. When no filler is present, CaO may then react with CO_2 to form the crust on the surface of the molten salt in the pot. This happens at 500°C because decomposition is most pronounced and the solubility limit of calcite is exceeded. In the cold tank (at 290°C), crust was found because the solubility is lowest at this minimum temperature, though the calcite formed mostly on the hot side. During cycling operation, dissolved calcite (in the hot tank) flowed with the salt to the cold side, where that solubility limit was exceeded and it deposited. The solubility of calcite at 290°C is the limiting factor.

Limiting access of CO_2 to the molten salt is the obvious means to prevent crust formation. However, air is the preferred cover gas because gaseous oxygen is necessary to chemically stabilize the molten salt at temperatures above nominally 450°C. Blanketing with nitrogen is not recommended because it will result in high concentrations of nitrite (NO_2^-). Nitrite forms due to the disassociation of nitrate according to a well-established thermodynamic equilibrium [9,10]. A nitrogen cover gas will also promote the formation of oxide species, which aggravate corrosion.

Limiting access to CO_2 could be accomplished even in a salt storage tank that is vented to the atmosphere. The design goal would be to minimize displacement of the molten salt surface during operation, thereby minimizing changes in the volume of the cover gas. Displacing the liquid surface acts similarly to a piston pump to bring fresh air, and thus CO_2, into the head space of the tank. Once gas exchange has been minimized by design and operating features, CO_2 can be effectively gettered at the vent openings with a variety of absorbents that are commercially available and are easily replaceable.

Much of the information above on molten salt chemistry, as well as the ideas presented next for carbonate removal, were contributed by Robert W. Bradshaw, Sandia National Laboratories, Livermore, California.

Carbonate Collector for Thermocline TES Tanks

Though not within the scope of this report, a potential approach for dissolved carbonate removal is suggested below and may warrant additional study, development, and testing. The purpose of this carbonate collector device is to remove dissolved carbonate from a nitrate-based molten salt before it can increase to a concentration that exceeds the saturation value at the lowest temperature in the salt circulation loop. This is accomplished by adding a small vessel on the cold salt return line to the thermocline tank that contains a removable metal surface (dip-leg) that is cooled slightly below the cold salt temperature. The carbonate crystallizes preferentially on the dip-leg rather than elsewhere in the fluid circuit. Figure 1 shows a simple schematic of the piping layout, which incorporates a bypass line to allow the collector to be removed from the vessel without shutting down the system. The solid deposit could be removed mechanically or dissolved with dilute acid.

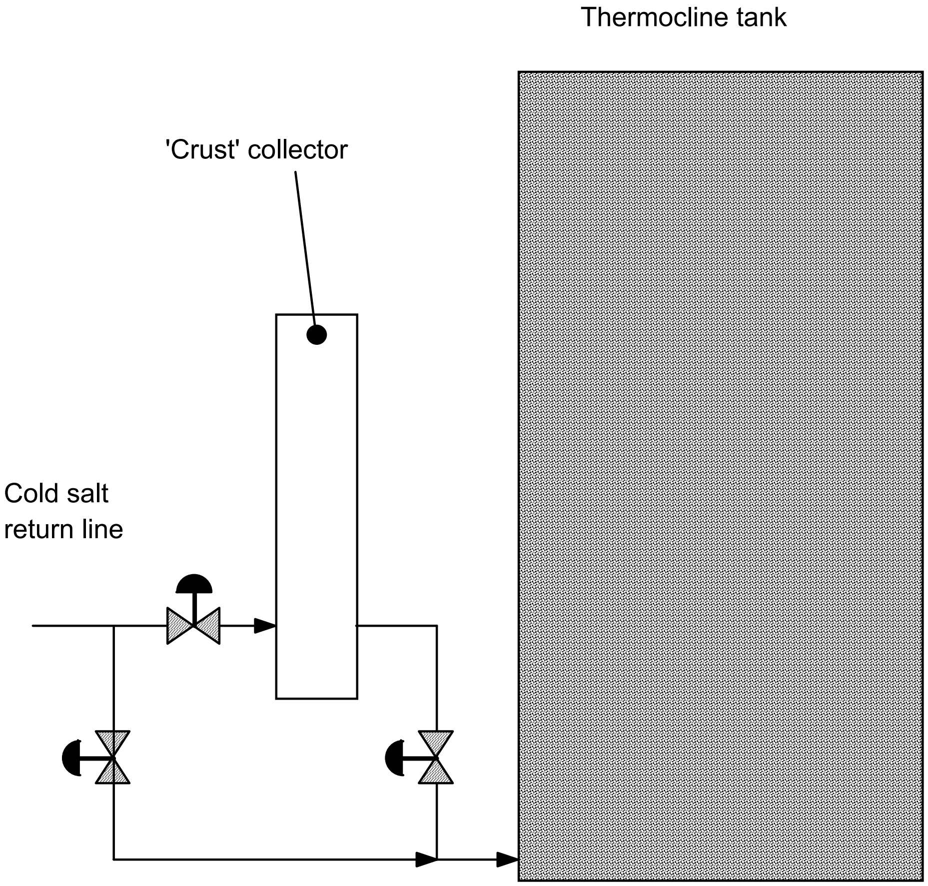


Figure 1. Schematic of collector and thermocline tank

Figure 2 shows a possible design in a bit more detail. A baffle in the vessel causes the returning cold salt to flow past the cooled collector. The collector is a hairpin dip-leg made from steel pipe. Cooling could be provided by air flow. Only the temperature of the salt in the boundary layer of the metal surface needs to be sub-cooled, not the entire flow. The collection rate would be slow, but continuous as long as flow is maintained, similar to forming a stalactite. To ensure that crystallization occurs at the bend in the dip-leg, a double-wall pipe could be used to insulate the up/downcomers and a single wall section for the bend.

An important aspect of the collector tank is that the seal at the flange must be leak-free and must be able to be resealed multiple times.

The design and efficiency of this unit depends on a number of factors: the solubility curve, heat transfer properties in the boundary layer, fluid flow characteristics, adherence of the solid deposit to the dip-leg, etc.. The mechanical design will depend on the layout of the tank and other factors not yet considered. This device is intended to supplement an approach that minimizes the amount of CO_2 in the cover gas of the salt tank (as noted above).

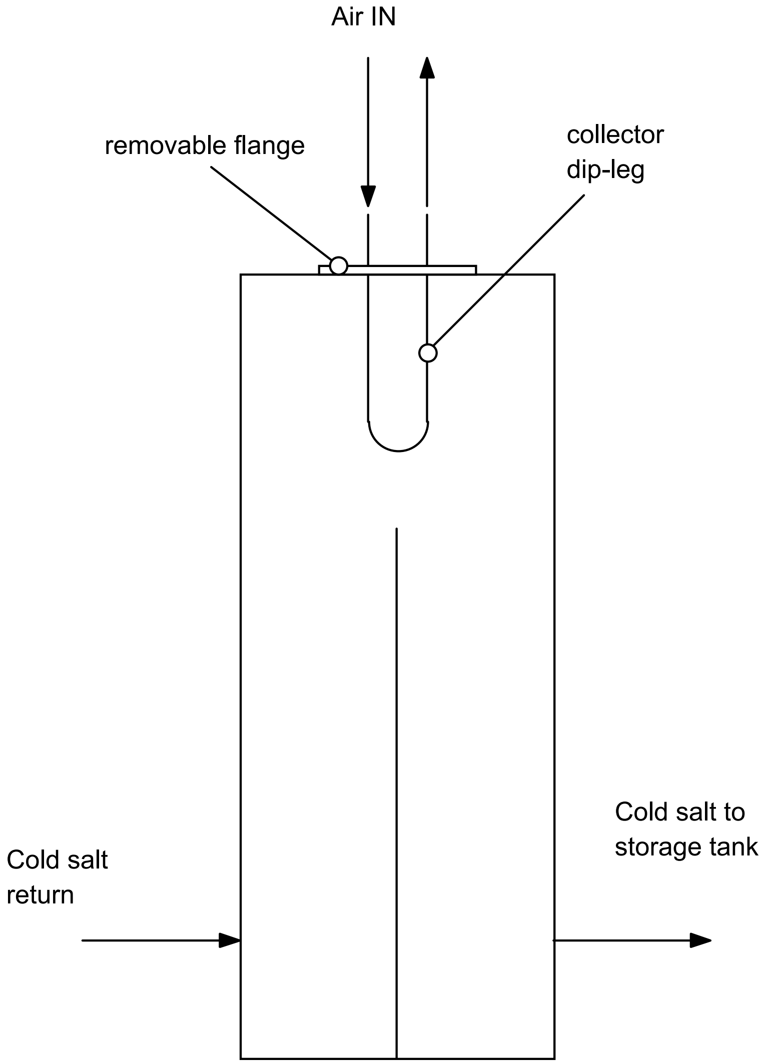


Figure 2. Detail of a possible layout of the carbonate collector vessel.

Additional Characterization Needed

This experimental program raised concerns regarding characterization of HitecXL ternary nitrate salts in the large-scale power plant environment. In the long run, more comprehensive studies are required to better characterize, understand, and specify the ternary molten nitrate salt formulation recommended for commercial use. Additional studies are recommended to evaluate ternary molten salt freeze/thaw behavior and other engineering and thermal properties. Finally, engineering studies are needed for handling large quantities of these salts during initial plant startup and during daily load changes. These studies should address such factors as maintaining minimum system temperatures to avoid freezing and salt disassociation; chemical treatment or CO_2 getter systems to control $CaCO_3$ scaling; measuring physical properties (density, viscosity, heat capacity, thermal conductivity); characterizing and understanding molten salt viscosity, pumpability, and pump costs; maintaining adequate or continuous field flow and mixing; and optimizing use of heat trace in critical areas (and the related parasitic costs).

Appendix C - Isothermal Testing Schedule and Data Sheet

Schedule **Date:**

Time	Zone 1	Salt Sample ID	Zone 2	Salt Sample ID
Initial Samples	August 1	1-0-A, B, C	August 2	2-0-A, B, C
Month 1	September 3	1-1-A, B, C	September 4	2-1-A, B, C
Month 2	October 1	1-2-A, B, C	October 2	2-2-A, B, C
Month 3	October 31	1-3-A, B, C	November 1	2-3-A, B, C
Month 4	December 2	1-4-A, B, C	December 3	2-4-A, B, C
Month 5	January 2	1-5-A, B, C	January 3	2-5-A, B, C
Month 6	February 3	1-6-A, B, C	February 4	2-6-A, B, C
Month 7	March 3	1-7-A, B, C	March 4	2-7-A, B, C
Month 8	April 1	1-8-A, B, C	April 2	2-8-A, B, C
Month 9	May 1	1-9-A, B, C	May 2	2-9-A, B, C
Month 10	June 2	1-10-A, B, C	June 3	2-10-A, B, C
Month 11	July 1	1-11-A, B, C	July2	2-11-A, B, C
Month 12	August 1	1-12-A, B, C	August 1	2-12-A, B, C

Procedure

1. In the isothermal testing logbook, note the condition of the salt in the pot and take salt sample adequate for 3 split bottles, labeled on the cap as noted above. If chemical analysis support is setup, deliver samples (and update separate sample tracking log).
2. Remove the 3 rock/sand sample baskets, draining as much of the molten salt as possible before removal from the pot. Flush baskets to remove as much exterior salt as possible. Allow to cool.
3. Carefully remove rock/sand samples and initially wash with tap water to remove as much salt as possible. Note which sample containers hold which samples (for re-loading in #8).
4. With demineralized water, flush and soak 3 separate rock/sand samples to remove all salt deposits that are easily removable.
5. After cleaning, dry samples at 80C for 1 hour in portable oven.
6. Take pictures similar to those taken of the initial samples. In the logbook, note condition of rock/sand samples and any observations relative to the original (control) materials.
7. Carefully weigh and log below:

Samples	Zone 1 (450C) Weights	Zone 2 (500C) Weights
Rock alone – kg		
Sand alone – kg		
Rock and sand Rock (kg):		
Sand (kg):		

8. Re-install rock/sand samples in their original containers.
9. Carefully re-install sample baskets in the isothermal test pots.
10. Note date and time of completion in the logbook, along with any operational notes.

Appendix D - Thermal Cycling Test Schedule and Data Sheet

Schedule **Date:**

	Est. Date	Salt Sample ID
Initial Sample	August 26	TC-0 A, B, C (287 and 450)
400 cycles	September 12	TC-4-A,B (450C)
1000 cycles	October 8	C-10-A,B; H-10-A,B
2500 cycles	December 11	C-25-A,B; H-25-A,B
5000 cycles	March 31, 2003	C-50-A,B; H-25-A,B
7500 cycles	July 16, 2003	C-75-A,B; H-75-A,B
10,000 cycles	October 30, 2003	C-100-A,B; H-100-A,B

Procedure

1. At the completion of a cycle, temporarily shut down the system, including displacer, watchdog, bubblers, and data acquisition. If not already done, backup data and purge data files if appropriate.
2. Maintain salt temperature in the hot and cold tanks (Zones 1, 7, and 8 as needed), and Zones 2 and 6 piping heat trace.
3. Close hot and cold tank isolation valves.
4. Thaw the drain freeze plug and, when ready with pans, remove the drain cap, open the drain valve slowly, and drain salt from test chamber. Try to only capture fines in one pan, bulk of salt in another.
5. Remove insulation from the tank flange and drain line.
6. Shut down heat trace for Zones 3, 4, and 5 on the test chamber.
7. Obtain salt samples and label as noted above (provide additional labels if needed).
8. When drained and there appear to be no isolation valve leaks, open the test chamber flange and pull the flange and weight rod clear for observation and sampling.
9. Carefully remove the top screen and controlled rock/sand samples.
10. With demin water, thoroughly wash rock and sand, then dry at 80°C for 1 hour.
11. Take pictures similar to those taken of the initial samples. In the logbook, note condition of the rock/sand samples and any observations relative to the original control materials.
12. Carefully weigh and log below:

Samples	Test Chamber Weights
Rock alone – kg	
Sand alone – kg	

13. Re-install rock/sand in the test chamber. Either thoroughly clean the sample screen, or install a new screen.
14. Close the test chamber flange, re-insulate, re-cap the drain, and close the drain valve.
15. Re-energize heat trace for Zones 3, 4, and 5.
16. Carefully re-open isolation valves, cold side first, and then hot side to vent and fill.
17. Carefully add frozen drained salt to the cold tank (remove displacer), and add any makeup necessary to replenish to correct levels in the tanks. Re-install displacer.
18. Resume cycle system operation when components and control system are re-established.

Appendix E - Summaries and Details of Startup and Operational History

Isothermal Test

Given the relatively simple test apparatus and setup, the operational experience with the isothermal tests was routine and almost without incident for the 12-month test duration. The Chromalox controllers were visually monitored on a daily basis to ensure setpoint temperatures were maintained. Each month, a portion of a day was devoted to temporarily removing, washing, drying, weighing, and photographing – and then re-inserting – the rock and sand samples, and taking salt samples from both sample and control pots for both test temperatures. Observations and sample weights were recorded in a test logbook. Salt samples were analyzed off-site at another SNL facility, and the results recorded and plotted in an Excel spreadsheet.

Zones 1 and 2 contained the rock and sand samples in molten salt at 450°C and 500°C, respectively. The team established "control" pots without samples at the same temperatures, Zones 4 and 5, on September 3, 2002, thus lagging the sample pots by approximately one month (due to salt procurement delays). Because of supply limitations, half the quantity of salt was melted in the control pots. This resulted in an identical molten mixture, but also a doubling of the effective surface-volume ratio in these pots as compared to the Zones 1 and 2 pots containing the samples.

On April 15, 2003, a brief power outage occurred while all site personnel were engaged in unrelated testing. Approximately 36 hours later, test personnel noted that three of the four zone controllers had tripped, requiring manual reset (the fourth controller remained locked in while calling for heating, so was not affected). Zones 2, 4, and 5 froze; Zones 4 and 5 were restored and ramped back to test conditions. The band heaters on Zone 2 were damaged, requiring a total rebuild, including new heaters and insulation. Despite design efforts to prevent it, molten salt had wicked by a direct pathway and caused corrosion around the heaters. By April 21 (following a weekend in the frozen state), Zone 2 was fully restored to test conditions.

On June 8, 2003, another brief power outage occurred that affected Zones 1 and 4 (both at 450°C). Both zones froze, but were restored quickly (this time, no band heater failures occurred). At that time, another watchdog circuit was installed to immediately page test personnel should another power outage occur. No further operational concerns occurred after those events.

Thermal Cycling Test

Early in the testing process, a fair amount of time was spent making slight adjustments in hot and cold tank set points and other heat trace in order to achieve the desired hot and cold soak temperatures of 450°C and about 285°C. On the cold side, desired conditions were achieved early and remained stable.

A small controlled sample of rock and sand contained in wire mesh (identical to that at the top and bottom of the chamber) was installed midway between the two bottom thermocouples and two top thermocouples (TCs) that are immersed in the rock/sand. To a small extent, the wire tended to alternately conduct (or "wick") heat both out of and into the test chamber as the wall temperature cycled and hot/cold salt flow occurred.

On the hot side, achieving the desired hot soak temperature was slightly more difficult. Due to system losses, the team initially had to raise the temperature in the hot tank to near 460°C in order to get temperatures in the test chamber that bounded the desired 450°C during the 15-minute hot soak time. Compared to the cold soak, there appeared to be a bit more of the wicking action from the controlled sample basket. And during the course of the hot soak, the test chamber temperatures ramped up slightly. During the first 350 cycles, the upper chamber temperatures ranged from about 446° to 453°C during the soak, and the lower TCs ranged from about 442°C to about 446°C. As it was undesirable to raise the hot tank temperature above 460°C due to concerns about the upper chemical stability limit of the molten salt, the temperature response was deemed adequate.

There were a few minor problems to address early in testing. The control card (a relay) for the lower hot tank TC became erratic (though it did not affect any of the system controls) and required a short planned outage of only a few minutes to change out. A few enhancements to the control system display were made. At 327 cycles, the compressor tripped (motor overloads did their job) due to low oil. That was detected within less than 2 cycles, rapidly repaired, and thermal cycling was resumed. A pressure switch was installed to automatically trip the watchdog circuit and page test personnel should air be lost again.

Effort was spent to establish the hot and cold fill (charge) times. It was desirable to achieve the fastest times possible (to shorten the overall length of the test), yet allow adequate time for heat transfer and to minimize impact of mixing in the hot and cold tanks. The best times ranged from the low 15-minute duration to low 16-minutes. Early in testing, it was discovered that too fast is not good. As noted during the startup phase, the hydraulic system oil (low volume, low flow, high viscosity) was very sensitive to ambient temperature changes. The solar tower test location is not insulated and has relatively course climate control. With very cool, wet weather, the stroke times increased (significantly beyond those set in the control system, such that charging was still occurring while the system was in the soak interval). A number of options were considered, including insulating, heat tracing the hydraulic components, better ambient control, etc.. As an interim measure, lamps were installed near the system to keep it warm. That proved too much, with the opposite affect. Displacement time dramatically dropped, charging the system too fast, not allowing heat transfer to occur and thermal stability to be achieved, and particularly hitting the hot tank with cold salt that did not mix well.

The bottom line: the cycle was disturbed, and it was difficult to stabilize hot tank temperature and also achieve optimal hot soak temperatures. Since the system was sensitive to these kinds of changes, the lamps were abandoned. The hot tank was manually bubbled, the hot tank temperature set point was slightly increased, and the hot tank bubbler intervals were adjusted accordingly. With those changes, hot and cold charge times went back to normal.

As noted earlier, the team had to maintain the hot salt at 460°C to achieve desired test chamber conditions during the hot soak. Following the charging upset just discussed, the set points on heat trace were temporarily ramped up 2°C to continue to achieve hot soak goals, yielding bulk hot tank salt temperatures around 463°C. This was very near or above the understood upper temperature for chemical stability of this salt. At about 400 cycles, minor adjustments were made to heat trace circuits that lowered the salt temperature in the hot tank and achieved a higher, flatter profile during the hot soak that nicely bounded the target 450°C. The cold soak was slightly high (in the range of 288°C to 298°C) after the charging upset, but was returned to normal following adjustments.

Routine operation after each 1000-cycle interval was to grab hot tank and cold tank salt samples for analysis and trend plotting. The only significant system trips occurred very near midnight October 14, 2002 due to an unresolved trip and shutdown of the LabVIEW application, and on January 2, 2003 due to another LabVIEW trip related to how the application handles and stores historical data. Test personnel responded to the watchdog circuit page and restarted the system with about an eight-hour delay required to restore tank conditions before resuming thermal cycling.

Appendix F - Filler Material Analytical Details

Sample Preparations and Instruments Used

Test personnel delivered a number of samples of thermocline filler materials, reaction products, and system parts to lab personnel for analyses. The samples include the following.

- Quartzite rock control (no salt exposure)
- Silica sand control (no salt exposure)
- Zone 1 (450°C) rock – 1 year exposure
- Zone 1 (450°C) sand – 1 year exposure
- Zone 2 (500°C) rock – 1 year exposure
- Zone 2 (500°C) sand – 1 year exposure
- Rock – 10,000 thermal cycles
- Sand – 10,000 thermal cycles
- Collected fines and other degradation/reaction products

The original request, made before the tests were finished, was for documentation of any changes or degradation that might have occurred to the surfaces of the various starting and exposed filler materials. Additional analyses were requested after the discovery of unexpected reaction and degradation products.

Lab personnel examined the exterior morphology of the sand and gravel. Samples of the various materials were placed on SEM stubs (small holders that look like blunt tacks) with electrically conductive, double-sticky tape specifically designed for SEM applications. Because the samples are not electrically conductive, they were coated with a thin layer of gold/palladium in a vacuum evaporation device. This coating is necessitated by the need to bleed off the electrons that the instruments beam onto the samples. If left alone, the electrons will build up a static charge on the sample, repel the electron beam, and thereby obviate any possibility of analyses. The primary instrument for this exterior analysis was the JEOL (Japan Electron Optics Laboratory) 5900LV SEM which uses the JEOL Control User Interface version 3.13 software on a Microsoft Windows 98 operating system. A ThermoNORAN Vantage system with the Vista version 2.3 software on a Microsoft Windows NT 4.00.1381 operating system controls the energy dispersive spectra (EDS) system which was operated at 20 KeV.

Other lab personnel in the Sandia metallography lab prepared cross-sections of the various sand and gravel samples. The samples were encased in epoxy plugs, ground down to a suitable region of the grains with silicon carbide, and the surfaces polished with diamond. Unfortunately, lab staff were not aware about the possibility of soluble material in the rinds that formed around the exposed grains, so water was used, as usual, when grinding, polishing, and cleaning the samples. Personnel also completed a final polish with colloidal silica which was noted in the actual examinations.

Lab personnel then examined the cross-sections via SEM. A conductive coating was applied to the samples but carbon was used to simplify EDS analyses. Analyses were performed on the cross-sections with a Hitachi S4500 Field Emission Gun Scanning Electron Microscope (FEG-SEM) operated at 15 KeV. Commercial Princeton Gamma-Tech hardware and software were used for image acquisition and elemental EDS analysis.

Besides interpreting the data collected by other members of the team, lead laboratory staff examined some of the samples with a JEOL (Japan Electron Optics Laboratory) JXA – 8600 Superprobe, an electron microprobe x-ray analyzer. This instrument was operated with hardware and software developed by Tracor Northern (now Thermo Electron Corporation) and improved by technical staff from Sandia National Laboratories.

Secondary Electron Microscopy and Electron Microprobe Analyses of Thermocline Control Sand

Summary

The control samples show sand grains composed mainly of quartz with a few grains of microcline and traces of other minerals. SEM analyses of the grain surfaces and cross-sections show cracks, pits, and other features consistent with their high-energy origin. Internal cracks will provide weaknesses that will enhance physical degradation and pathways for the intrusion of molten salt.

Observations

The control samples were examined to determine the morphology, surface textures, internal structure, chemistry, mineralogy, and contamination inherent to the normal starting material. Visually, the sand samples look like normal, very coarse sand. Most of the grains are white to almost clear with a frosted surface and moderate translucency. A few of the grains are pale pink and more opaque. Rare and random dark spots in these first two materials indicate the presence of some other minor species.

SEM photos of the sand surfaces show a well-rounded morphology with myriads of fine cracks, pits, and spall scars (Fig. 1 and 2). The spall scars appear smooth compared to the rest of the grain. The pits and cracks appear at a number of scale sizes and most appear random. A few cracks are circular or oval such as the one located between the two parts of the legend at the bottom left corner of Figure 2.

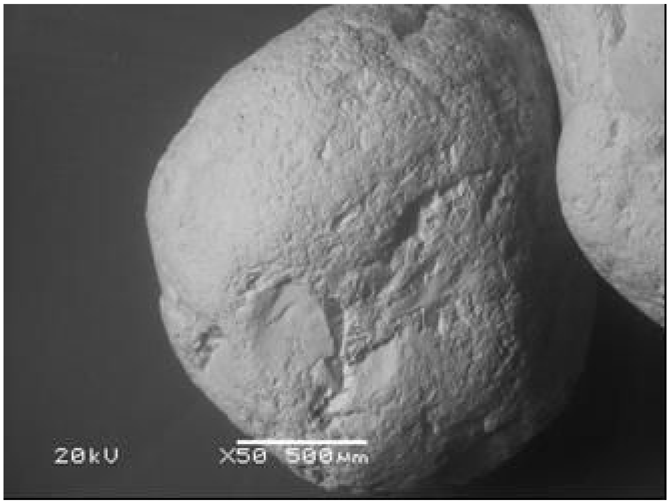


Figure 1. Low magnification SEM image of control sand grains showing a frosted (finely pitted and scratched) surface and spall scars. Spall scars are recognizable by their smooth surfaces.

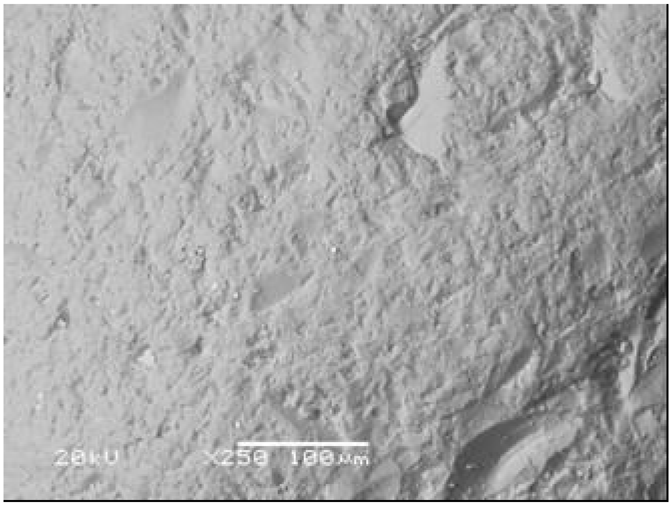


Figure 2. Medium magnification SEM image of a control sand grain showing a frosted (finely pitted and scratched) surface and spall scars. Spall scars are recognizable by their smooth surfaces. Small grains of debris are just barely noticeable. A percussion mark is located between the two parts of the legend.

Chemically, the grains are mostly silica (SiO_2) as is shown by the EDS spectrum of Figure 3. Some minor phases show up here and there, in almost every grain. Figure 4 reveals that the surface is replete with fine grains of material. Many of these are probably the same phase as the host grain but others, such as the bright grain in the center of the BSE, are obviously different. The EDS spectrum (Fig. 5) reveals this grain to be zirconium silicate. Most of the others are less exotic.

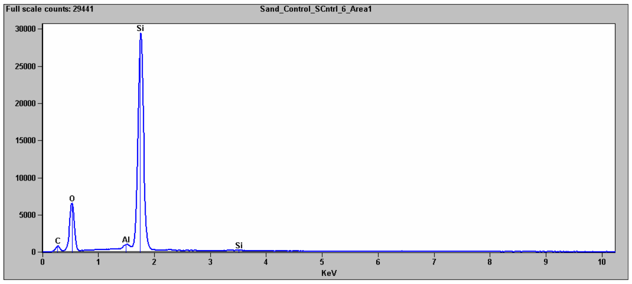


Figure 3. EDS spectrum of the surface of one of the grains. The major peaks are from silicon and oxygen indicating that the bulk of the material is silica. The minor peaks are from debris on the surface.

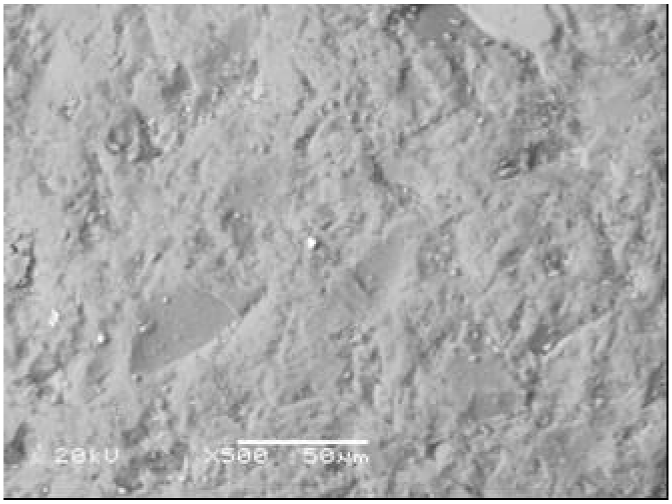


Figure 4. High magnification SEM image of a control sand grain showing a frosted (finely pitted and scratched) surface and spall scars. Spall scars are recognizable by their smooth surfaces. Small grains of debris are quite noticeable. The small bright grain in the center of the image is zirconium silicate. Others may be more silica and other common phases.

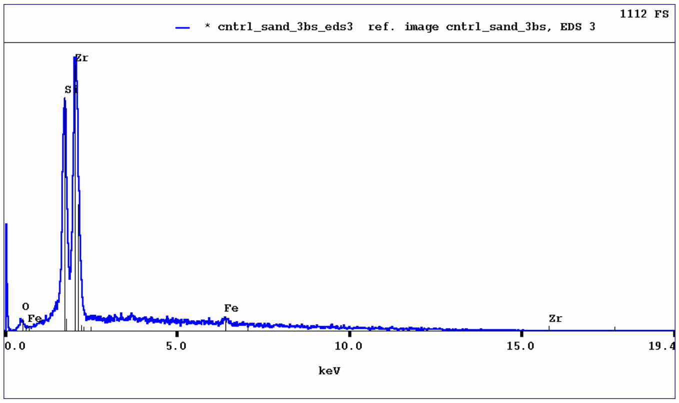


Figure 5. EDS spectrum of the bright grain in Figure 4. The major peaks are from zirconium, silicon, and oxygen indicating that this material is zirconium silicate.

Cross-sections of the control sand reveal that many, but not all, of the grains are quite homogeneous, chemically, and most exhibit internal cracks. Figures 6 & 7 show this quite well. In Fig. 6 the grains consist of one phase. The large grain on the left has a well-defined crack on its left side. In addition, lines of small pits on the right side define insipient cracks or grain boundaries that could become cracks that are too fine to be discerned at this magnification. Similar observations are made for Figure 7. In addition, this figure has a grain containing a couple of second phase particles. EDS spectra (Figs. 8 & 9) reveal that most of the grains are silica while the second phase is potassium aluminum silicate.

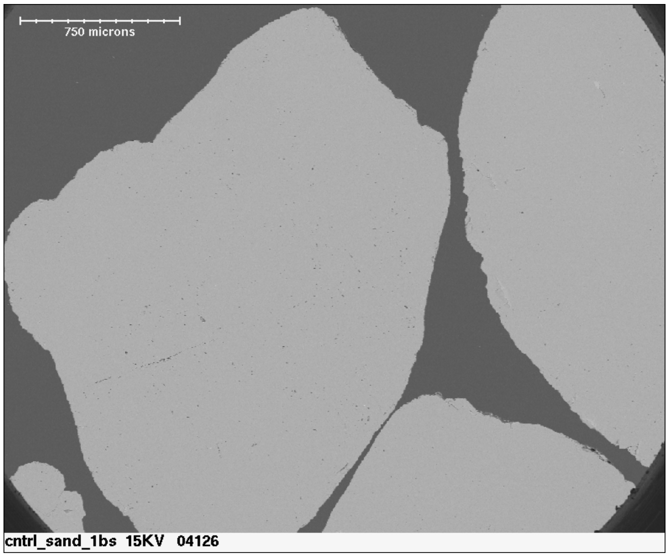


Figure 6. BSE image of cross-sectioned sand grains. All the grains in this view are single phase. A well-defined crack is visible on the left side of the left hand grain. Rows of small pits define the traces of smaller cracks or grain boundaries on the right side of the same grain.

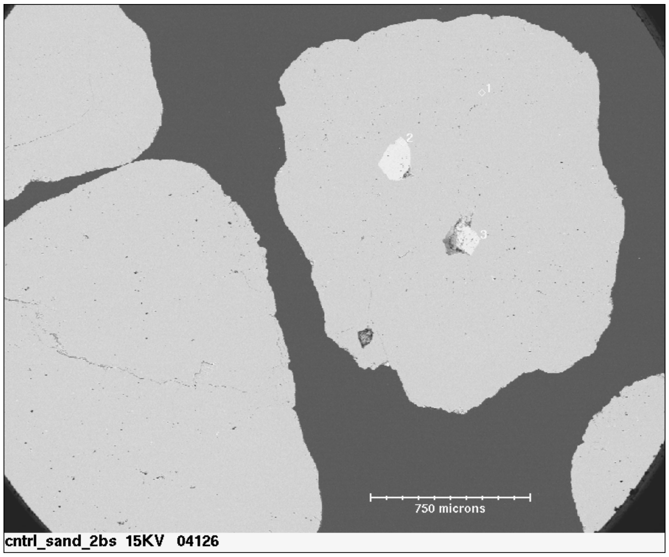


Figure 7. BSE image of cross-sectioned sand grains. One of the grains in this view has two phases. The second phase is a potassium aluminum silicate. Again a well-defined crack is visible on the left side of the left hand grain and rows of small pits define the traces of smaller cracks or grain boundaries in the same grain.

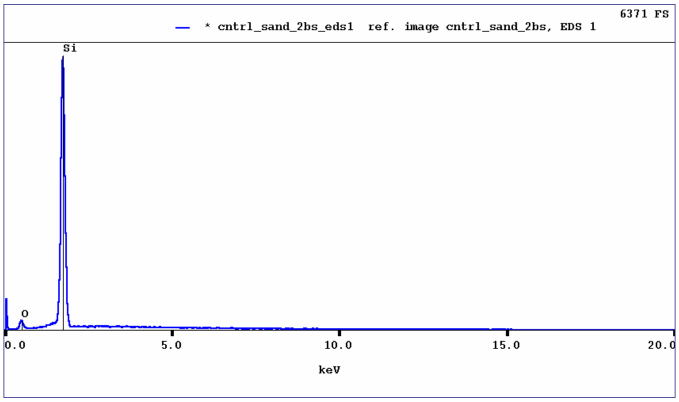


Figure 8. EDS spectrum of the majority phase in Figure 7. The major peaks are from silicon and oxygen indicating that this material is silica.

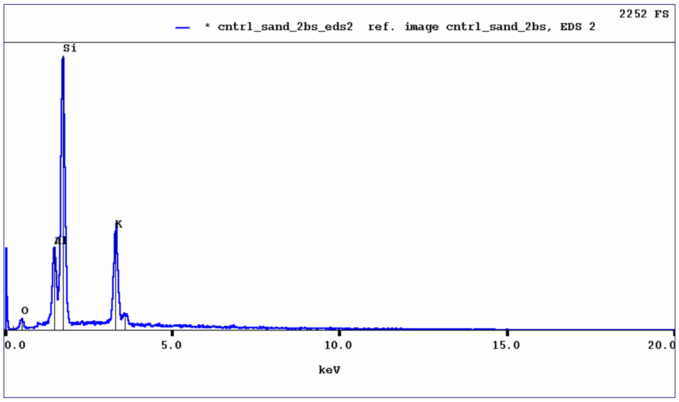


Figure 9. EDS spectrum of one of the bright grains in Figure 7. The major peaks are from potassium, aluminum, silicon, and oxygen indicating that this material is potassium aluminum silicate.

Not all of the grains are pure silica or even single phase. Figure 10 shows a complicated grain where silica is only a minor phase. The element maps of Figure 11 reveal that we have at least four phases are present. The main phase is potassium aluminum silicate. Silica grains, such as those in the lower right hand corner of the grain, are the next most abundant. The bright grains are rich in K, Fe, Al, Si, and O. The darkest grains are sodium aluminum silicates.

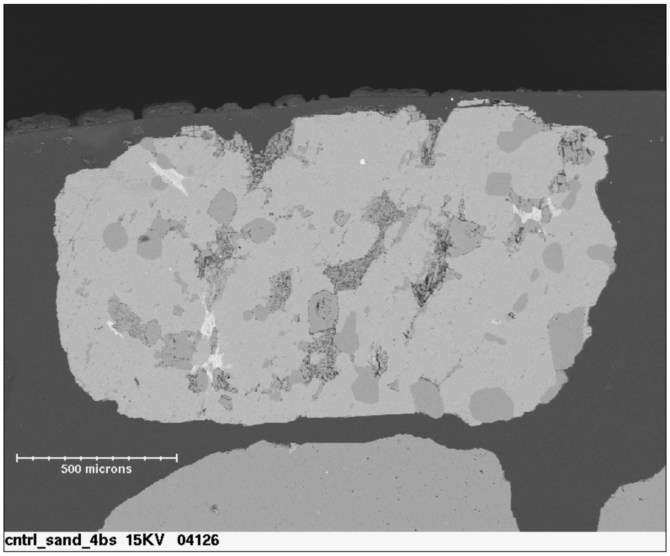


Figure 10. BSE image of a cross-sectioned, multi-phase sand grain. There are at least four major phases in this grain. The main phase is potassium aluminum silicate. Silica grains, such as those in the lower right hand corner of the grain, are the next most abundant. The bright grains are rich in K, Fe, Al, Si, and O. The darkest grains are sodium aluminum silicates.

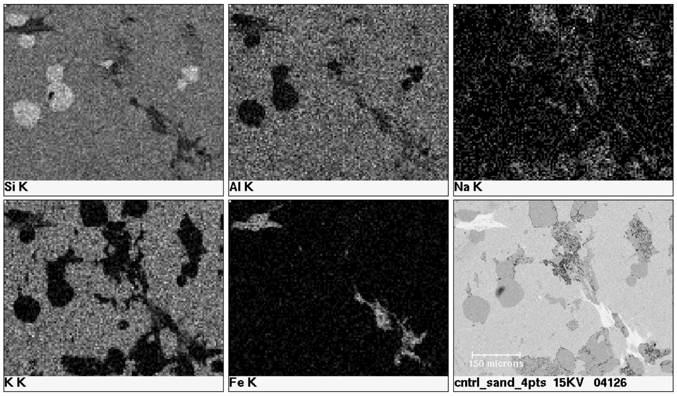


Figure 11. Element maps of part of the grain shown in Fig. 10. The maps show the distribution of the various elements and thus reveal four different chemical combinations (phases or minerals).

Conclusions

The control sand is mainly composed of quartz (SiO_2) grains but microcline ($NaAlSi_3O_8$) and other phases are evident. EDS analyses of the surface and interior of the grains show them to be rich in silicon and oxygen and quartz is the most common mineral of this composition. Minor contamination, especially on the surface, is to be expected. The carbon showing on the spectra is probably due to contamination by de-polymerization of the vacuum oils, due to beam generated heat, in the imperfect vacuum of the instruments. The second most common phase in the sand is microcline, one polymorph of potassium feldspar. Figures 10 & 11 detail the chemistry of a microcline grain and a variety of included phases. These include albite feldspar ($NaAlSi_3O_8$) and biotite (an iron-bearing mica). In addition to complete, large grains of microcline, tiny grains contaminate the surfaces of the quartz grains. A thorough search of the sand grains would reveal quite a few more exotic but expectable phases such as the zircon ($ZrSiO_4$) detailed in Figures 4 & 5. All of the phases detected in the sand are typical from sands derived from granitic rocks. The presence of large grains of microcline, etc. is indicative of young sand. Sands that experience more weathering and erosion would be “cleaner” but would also be much finer in size.

The highly rounded shape, pits, cracks, and spall scars are what one should expect from very coarse sand because it forms in high-energy environments such as fast moving streams or surf-pounded shorelines near granitic highlands. The circular feature mentioned above (Figure 2) is the surface expression of a percussion crack formed by something smashing into the grain. In three dimensions, this would look like the frustum of a cone. All of this damage to the grain surfaces is of technical interest because it indicates that such damage has been carried into the grain interiors as is shown in Figures 6 & 7. This damage sets the stage for physical degradation of the sand as well as chemical intrusion of molten salt into the grain interiors.

Secondary Electron Microscopy and Electron Microprobe Analyses of Sand Exposed to Molten Salts

Summary

All of the sand samples that have been exposed to the molten salt show evidence of physical degradation, intrusion of molten salts, chemical reaction and surficial contamination. The physical damage is mainly splitting of flakes near the grain surfaces and scalloping of the surface. The scalloping is thought to be a combination of both physical and chemical attack. Intrusion of molten salts occurs along pre-existing cracks, some of which may have been widened during testing. A suite of calcium-rich species has formed on the surfaces of the grains. Some of these are carbonates and others are dicalcium silicates. Most of the calcium carbonate is obviously calcite but other polymorphs may be present. The formation of dicalcium silicate indicates that some silica has been dissolved from the quartz grains.

Observations

Samples of sand grains exposed to molten salt were examined to determine what, if any changes have occurred. While the gross morphology hasn't changed much, the surface textures, chemistry, and mineralogy are all changed as a consequence of contamination and/or reaction of the sand grains with the molten salts.

Visually, the sand samples from all parts of the experiment look normal, very coarse sand in their gross morphology but their translucency is much reduced from the control samples and their surface textures are fuzzy.

SEM photos of the sand surfaces show the same well-rounded morphology as before but the myriads of fine cracks, pits, and spall scars are completely hidden beneath coatings (Fig. 1). High magnification SEM images reveal a number of euhedral (well-formed) crystalline morphologies present indicating that a number of new phases have formed (Fig. 2 & 3). The morphologies present include plates, acicular prisms (needles), thicker prisms, laths, and rhombohedra (six faced form, all of the faces are of the same rhombus or "diamond" shape).

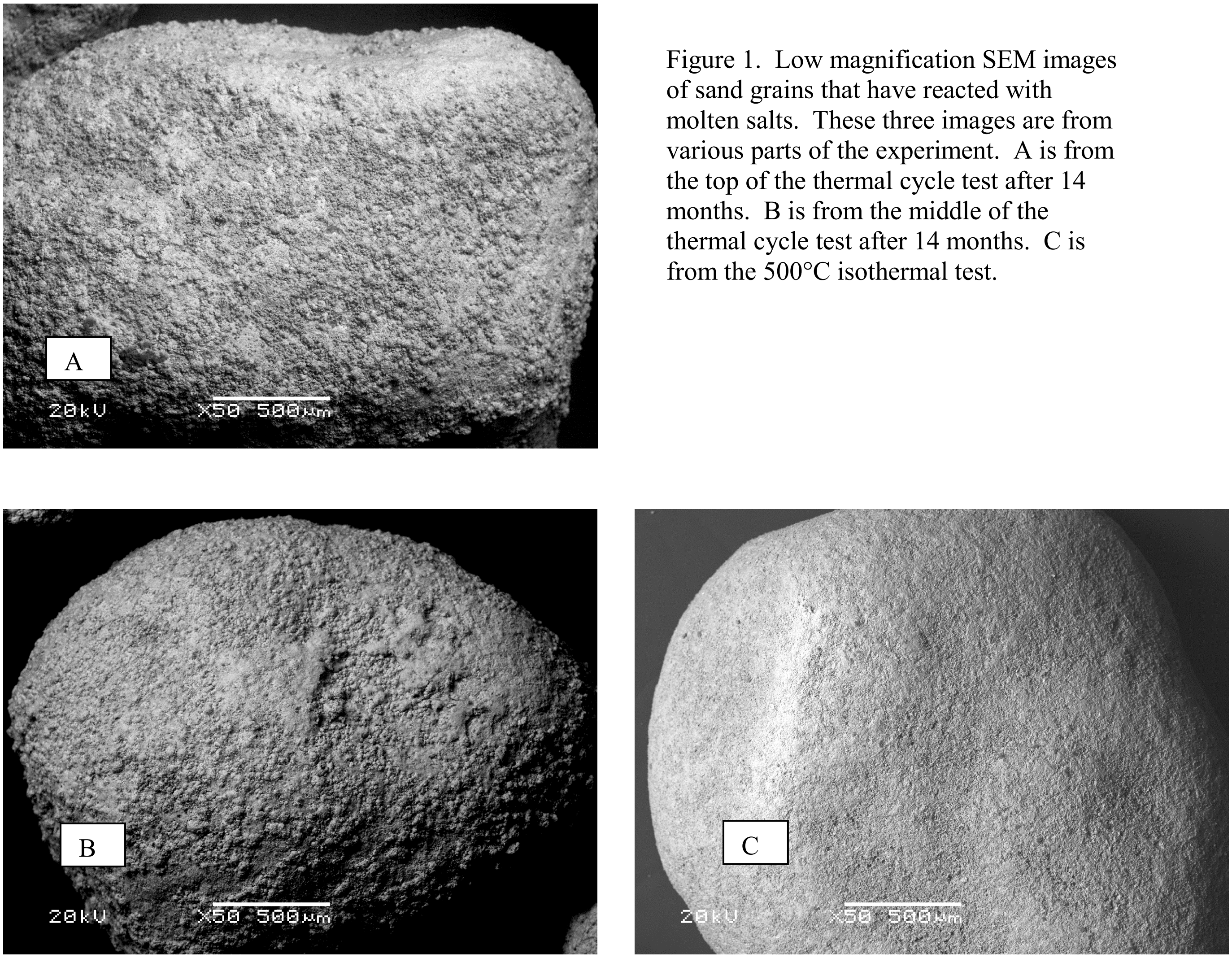
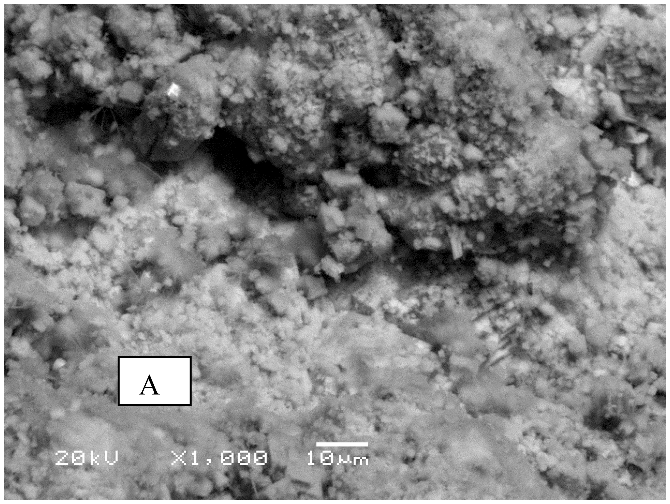
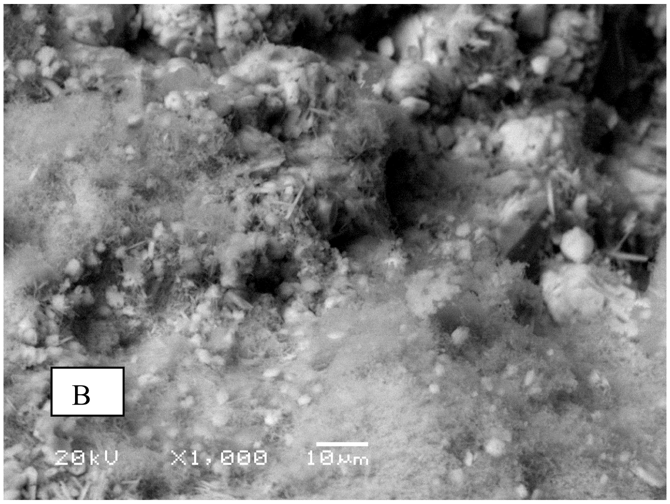
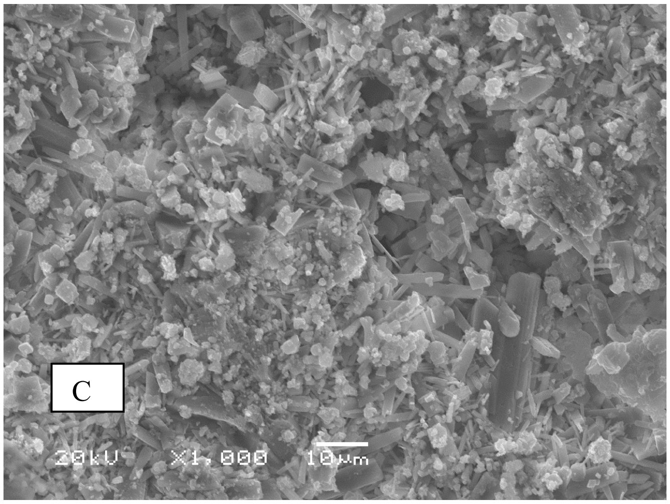


Figure 1. Low magnification SEM images of sand grains that have reacted with molten salts. These three images are from various parts of the experiment. A is from the top of the thermal cycle test after 14 months. B is from the middle of the thermal cycle test after 14 months. C is from the 500°C isothermal test.

Figure 2. High magnification SEM images of sand grains that have reacted with molten salts. These three images are from various parts of the experiment. A is from the top of the thermal cycle test after 14 months. B is from the middle of the thermal cycle test after 14 months. C is from the 500°C isothermal test. These images reveal euhedral crystals of various morphologies.







EDS spectra of a moderate sized area of the sand grain surfaces show them to be rich in calcium, silicon, and oxygen as is shown by the EDS spectrum of Figure 3. Some minor elements show up here and there. Figure 4 reveals that the surface is coated with a number of different phases. Figure 5 is an EDS spectrum from spot 4 on Figure 4. The high peaks for calcium, oxygen, and carbon indicate this euhedral crystal to be calcium carbonate. Figure 6 is an EDS spectrum from spot 1 on Figure 4. This less well-developed crystal contains oxygen, silicon, and lots of calcium so it is a form of calcium silicate. Because the calcium peak is much more intense than the silicon, it is probably a dicalcium silicate. To prove this, x-ray diffraction analyses showed that the coatings on several different samples are rich in calcite and gamma dicalcium silicate. This is a high temperature form of the material.

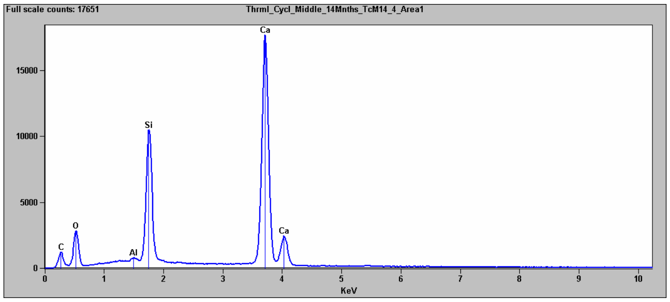


Figure 3. EDS spectrum of an area on the surface of a sand grain from the middle of the thermal cycling test. EDS spectra taken from sand grains in all of the various parts of the system are virtually identical.

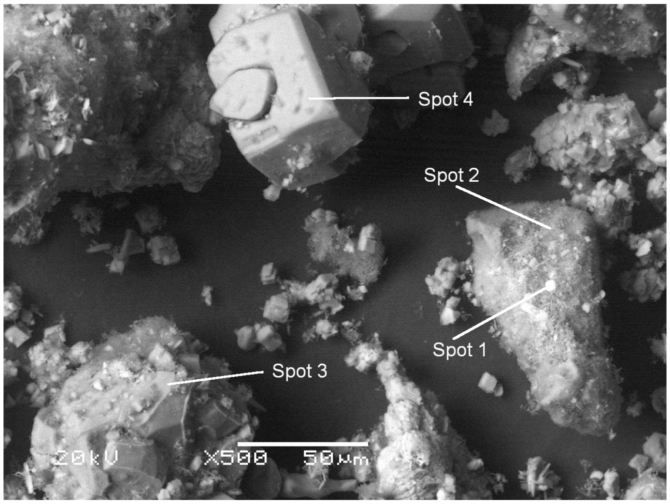


Figure 4. High magnification BSE image of a sand grain from the middle of the thermal cycle test showing a number of crystals. The EDS spectrum from spot four (Fig. 5) shows this euhedral crystal to be composed of calcium, oxygen, and carbon. Spot one is a dicalcium silicate crystal.

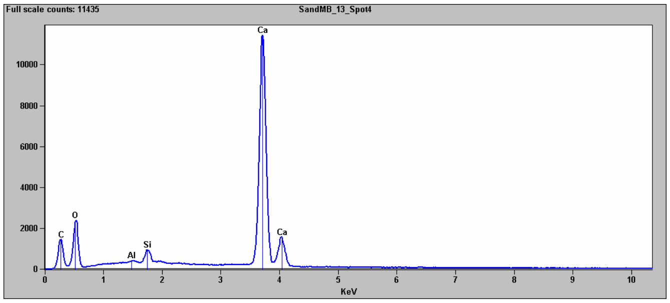


Figure 5. EDS spectrum of the euhedral crystal labeled spot 4 in Figure 4. The major peaks are from calcium, oxygen, and carbon indicating that this material is calcium carbonate.

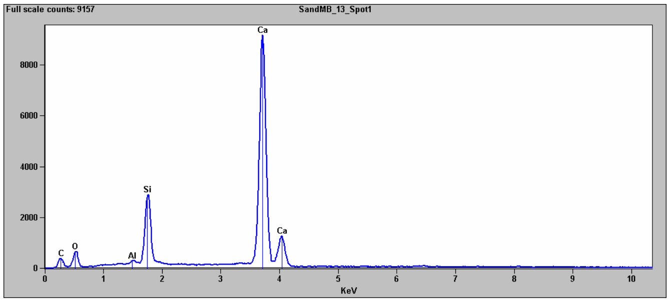


Figure 6. EDS spectrum of the crystal labeled spot 1 in Figure 4. The major peaks are from calcium, silicon, and oxygen indicating that this material is one form of calcium silicate. The intense calcium peak suggests this may be a dicalcium silicate.

Cross-sections of sand exposed to molten salt document the coatings on the grain surfaces. Figure 7 shows this quite well. Unfortunately, most of the coating material was removed during sample preparation leaving a wide gap. This view shows crystals of calcium carbonate adhering to the epoxy mounting medium and the same material penetrating into the grain interior along pre-existing cracks. Figure 8 shows another grain which has retained quite a bit of material in the gap. The calcium carbonate crystals are again adhering to the epoxy mounting medium, there is an area of fine grained material with some bladed crystals, and an area of homogeneous, fine-grained material.

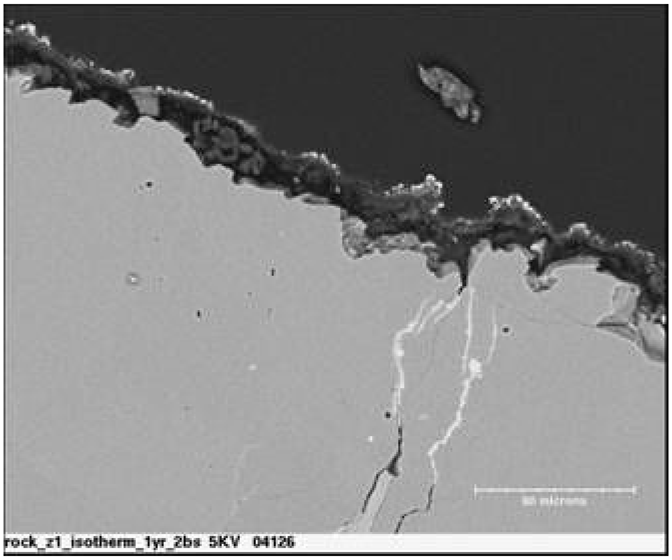


Figure 7. BSE image of a cross-sectioned sand grain surface from zone 1 of the isothermal test showing a thin line of calcium carbonate crystals adhering to the epoxy mounting medium and penetrating the grain along pre-existing cracks. This image shows that much of the coating has been removed during polishing.

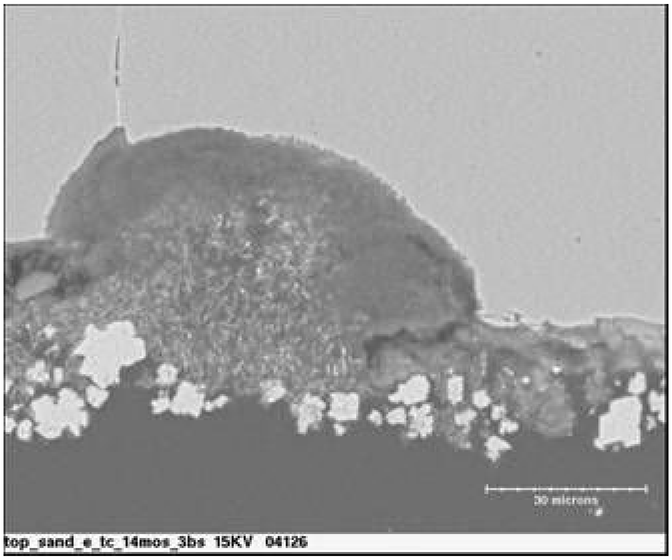


Figure 8. BSE image of another cross-sectioned sand grain surface showing the calcium carbonate crystals (looking like Lucky Charms), some retained inner coating material with blades of dicalcium silicate, and some polishing medium and debris packed into what was a gap.

Figure 9 shows a set of element maps of yet another grain that has retained some of its coating interior. The bladed crystals rich in calcium with some silicon are assumed to be dicalcium silicate. Note also that calcium carbonate has intruded along cracks into the grain interior. A minor amount of some potassium species has been trapped in the cracks by the calcium carbonate.

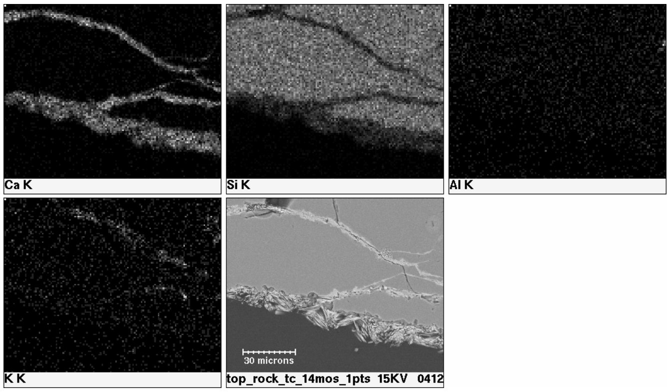


Figure 9. Back-scattered image and element maps of the surface of a cross-sectioned sand grain from the top of the cycle test. The bladed morphology and calcium and silicon content suggest these are dicalcium silicate. Note that calcium carbonate has intruded along cracks and several quartz chips are close to spalling off.

Figure 10 shows the cross-sectioned surface of a grain that has all of its coating removed during polishing. The scalloped and sculpted surface of the quartz grain has been obviously altered from its original texture. The material that partially fills the bottom of the gap is polishing medium plus sample debris.

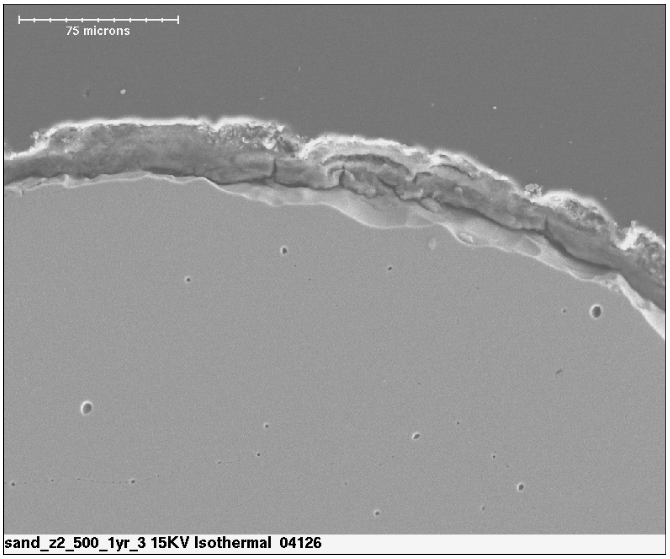


Figure 10. SEM image spectrum of the surface of a cross-sectioned sand grain from the isothermal test. The coating has been removed during polishing exposing the scalloped surface of the quartz grain.

Conclusions

All of the examined sand samples that were exposed to molten salt are all similar to one another and are covered with a coating of new crystalline phases. Lab personnel were able to identify calcite, a polymorph of calcium carbonate, and a polymorph of dicalcium silicate, the high temperature, gamma form (GCS). It is possible that other polymorphs of these two phases are present but this was not verified. It is unlikely that any other chemistries are present. It should be noted that although the calcite always forms well-developed rhombohedra, the GCS may occur in a wide variety of shapes. Prisms, blades, fibers, and needles are all possible crystal shapes for GCS and all of these were noted in the samples.

The presence of calcite can be explained by assuming contamination of the molten salt by air during sampling, etc. but the GCS requires that silica be dissolved from the quartz and other silicate grains. This can be verified to have occurred by noting the beautifully smooth scalloped surfaces exposed on the quartz grain in Figure 10.

Intrusion of molten salt into the interiors of the quartz grains is evidenced by the calcite that survived sample preparation. This and the formation of the coatings probably explains why the samples gained mass during the experiment even though some of the silica has been dissolved off the original surface of the quartz grains.

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