**Advanced Molten Salt for Solar Thermal Power Generation with Supercritical Steam Turbines**

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## Part 1. Results of the Phase I Project

Halotechnics is developing a novel molten salt heat transfer and thermal storage material that will enable the use of state of the art supercritical steam turbines in solar thermal power plants. This material, named Saltstream 700, targets a melting point of 200 °C and a maximum operating temperature of 700 °C (shown in Figure 1). This broad operating range is currently unavailable with any commercially feasible material in the marketplace. Halotechnics has screened over 2000 unique salt mixtures during the course of a successful six month NSF SBIR Phase I program, including mixtures of chloride, carbonate, and sulfate salts. We have discovered several salt systems with promising eutectic melting points near 250 °C and stability limits exceeding 700 °C. We have filed two patents based upon this work [1], [2].

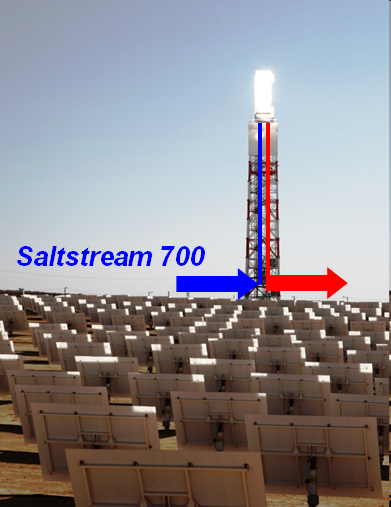


Figure : Target properties of the advanced heat transfer fluid.

We believe that the sun is the ultimate source of energy. It is imperative that we reduce our usage of natural gas and especially coal to address pressing societal concerns – climate change and environmental degradation, energy security and price volatility. Solar thermal power, a compelling source of renewable electricity at large scale, represents a possible solution to fossil fuel use. With further technological advances, solar thermal power will become cheaper than natural gas or coal and able to provide electricity day and night. This Phase I award has allowed Halotechnics to develop technology bringing the nation closer to achieving this vision.

Halotechnics has applied combinatorial chemistry techniques, originally developed for pharmaceutical applications, to a new field: solar thermal materials. This transformative research benefits from the large body of knowledge developed for over 15 years in combinatorial chemistry and uses this know-how to address the pressing problem of renewable power generation.

There were two overall goals of the Phase I program: 1) to screen novel mixtures of salts and discover eutectic (low melting point) mixtures and 2) gain an understanding of the thermal decomposition of salts of interest (high maximum temperature). These two goals together expanded the operating range of the molten salt heat transfer fluids. Based upon the results of this work we have down-selected to the most favorable molten salt mixtures that achieve the technical objectives. Chloride based salt mixtures are the leading candidates for further development. They exhibited the lowest melting point eutectics that we discovered in Phase I and were stable at high temperature. Even at temperatures up to 900 °C, it appears that the dominant mass loss with a chloride based melt is simple evaporation due to a low but non-zero vapor pressure. We observed some decomposition to oxides at high temperature with carbonate and sulfate based mixtures.

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Since completing Phase I in June 2011, Halotechnics has identified a pathway to further reduce the melting point and cost of the proof of concept salt mixtures discovered during the initial R&D program. By modifying the composition we have identified a low cost mixture with a melting point at 230 °C. Halotechnics is now proposing a Phase II project to continue this work and complete the commercialization of Saltstream 700.

## Part 2. Phase II Technical Objectives

*2.1 Technical Objectives*

Halotechnics has engaged leading solar thermal technology developers and asked them what they need to meet their technology roadmap milestones. There is a clear focus on achieving supercritical steam conditions (620 °C or higher) in the next generation of solar thermal power plants, thereby achieving gross turbine efficiencies approaching 50% and significantly reducing the levelized cost of electricity [3]. This higher operating temperature would have the additional benefit of slashing thermal energy storage costs by making more effective use of the molten salt storage media. In order to achieve 620 °C steam, heat exchanger constraints require approximately 650 °C bulk salt temperatures. This in turn means that film temperatures in the solar receiver (the hottest point in the salt system) would be approaching 700 °C [4].

In order to make the goal of supercritical plants a commercial reality the target properties of the heat transfer and thermal storage fluid are as follows:

* Thermal stability as a liquid to at least 700 °C
* Melting point near 200 °C
* Low cost salt components available in bulk quantities
* Vapor pressure less than 1 bar at 700 °C
* Chemical compatibility with high temperature steel or nickel alloys

Currently available molten salt materials as shown in Figure 1 are not capable of achieving the target properties. Solar salt is a mixture of sodium nitrate and potassium nitrate, used in the current generation of solar thermal power plants. It is not capable of operating above 600 °C because it thermally decomposes. FLiNaK is a mixture of fluoride salts developed for nuclear applications. Its melting point is 454 °C, too high to be practical for thermal storage [5].

Halotechnics has identified a promising mixture which could satisfy the technical objectives with further development. This mixture is a binary eutectic chloride salt that melts at 230 °C and is chemically stable to 700 °C as shown by preliminary experimental work done in our laboratory. This mixture represents a compelling proof of concept fluid that will be further optimized during the course of Phase II in order to achieve the technical objectives stated above.

*2.2 Approach: Transformative Research Using Combinatorial Materials Science*

The research activities proposed for Phase II utilize combinatorial chemistry techniques to screen up to thousands of candidate salts for suitable thermophysical and economic properties. The most promising candidates will undergo rigorous corrosion testing with common structural materials, as well as flowing heat transfer tests in a pumped test loop with thermal cycling.

This project will leverage technology used in the metal heat treating industry, with decades of experience in handling high temperature molten salt. Salt baths for austempering and martempering of steel are commonly used with chloride salts at temperatures exceeding 900 °C. The efforts will focus primarily on chloride based salt mixtures, with mixed anion compositions of chloride-sulfate and chloride-carbonate as a secondary effort. Nitrate salts are not sufficiently stable at 700 °C and will not be considered as candidates in this program.

Materials development. Halotechnics has developed world class experimental techniques, software tools, and data handling capabilities for combinatorial chemistry R&D. We have successfully used our techniques to screen over 14,000 unique materials to date and to develop our patent-pending heat transfer fluids. Halotechnics will conduct a high throughput materials discovery program to rapidly screen unique mixtures of inorganic salts and to optimize the properties of Saltstream 700. We will leverage “eutectic” or low-melting behavior, which produces dramatic reductions in the melting point when salt components are combined in the right proportions in a mixture. We have assembled a high throughput workflow consisting of our proprietary software driving custom scientific apparatus capable of mixing and screening the melting point of over 100 samples every day. We have the capability to measure additional thermophysical properties of interest, such as heat capacity, heat of fusion, viscosity, and thermal stability.

Corrosion mechanisms. A key consideration for a commercially viable heat transfer and thermal storage fluid is its compatibility with common structural alloys. Halotechnics will undertake a fundamental study of the corrosion mechanisms of our Saltstream 700 candidates with common stainless steel and nickel-based alloys. Corrosion testing will be performed in two segments: short-term screening experiments and long-term evaluation tests with durations up to 3000 hours. Both types of corrosion tests will be performed using the Halotechnics MCAT system (Multichannel Corrosion Analysis Tool). Corrosion experiments will use sealed crucibles to control the atmosphere in contact with molten salt during corrosion testing. The alloy specimens from the corrosion tests will be evaluated by standard methods of gravimetric analysis (mass changes) and metallographic examination of cross-section images.

Flow testing. Halotechnics is developing a prototype 700 °C thermal storage system funded by a separate National Renewable Energy Laboratory (NREL) subcontract. This system will be constructed at a laboratory scale complete with molten salt pumps, a two tank design with a hot tank at 700 °C and a cold tank at 300 °C, a radiative furnace for heat input, and a heat sink. The NREL funded test loop will provide a flexible platform for flow corrosion testing, startup and shutdown procedures, freeze recovery, and heat transfer coefficient measurement. Once successful at laboratory scale we intend to scale up the design for pilot testing before full scale commercial deployment.

The proposed program is 24 months in duration, divided into two 12 month sections. See Figure 2 for a timeline showing the tasks and technical milestones.

**Milestone 1:** Approximately five candidate salt mixtures to be subsequently tested in Year 2. The melting point of each must be less than 200 °C (250 °C allowable). Each must be thermally stable up to at least 700 °C (650 °C allowable). Each must be low cost and with vapor pressure less than 1 bar at 700 °C.

**Milestone 2:** At least one candidate salt mixture and data verifying its compatibility with steel or nickel alloys. Complete data of flow testing at laboratory scale sufficient to justify scaling up to pilot testing.

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|  | **Year 1** | | | | **Year 2** | | | |
| **Task / Milestone** | **Q1** | **Q2** | **Q3** | **Q4** | **Q5** | **Q6** | **Q7** | **Q8** |
| 1. Workflow development |  |  |  |  |  |  |  |  |
| 2. High throughput screening and optimization |  |  |  |  |  |  |  |  |
| Milestone 1: Optimized salt candidates |  |  |  |  |  |  |  |  |
| 3. Corrosion assessment and mitigation |  |  |  |  |  |  |  |  |
| 4. Flow testing |  |  |  |  |  |  |  |  |
| Milestone 2: Flow test performance data |  |  |  |  |  |  |  |  |

Figure : Phase II project timeline.

* 1. *Work Plan*

**Task 1: Workflow development**

Halotechnics has developed comprehensive experimental techniques, software tools, and data handling capabilities for combinatorial chemistry R&D. We have successfully used our techniques for a variety of applications in developing patent-pending heat transfer fluids [6]. Figure 3 shows the high throughput workflow we will utilize for rapidly screening up to thousands of candidate salt mixtures for desirable properties and narrow the candidates down to one optimal material. Each stage is labeled with the approximate number of experiments to be performed. The workflow acts as a sieve and screens a large number of candidate materials, eliminating the majority at each stage and reducing the number of experiments necessary at the subsequent stage.



Figure : Screening workflow for advanced molten salt.

Mixture design and formulation: Halotechnics has developed custom software capable of rapidly designing a set of combinatorial salt mixture experiments in a desired region of interest in high dimensional phase space. Each desired set of experiments will be fed into the high throughput experimental workflow for subsequent formulation. The salt mixtures will be dispensed in powder form with the automated powder dispensing robot at Halotechnics (MTM Powdernium, Symyx Technologies, Santa Clara, CA). Salt mixtures will be dispensed onto a glass plate with 96 separate wells. The mixtures will be melted and homogenized in a furnace at 400 °C for 12 hours, then cooled and stored in a dry box for subsequent melting point screening. Throughput: 96+ samples per day.

Melting point: After mixing, the samples will be tested using the Parallel Melting Point Workstation (PMP) from Symyx Technologies. The PMP allows the melting point for each mixture in the 96 well plate to be measured simultaneously. The PMP is capable of operation up to 315 °C which is sufficiently hot to measure salt mixtures in the vicinity of the proposed baseline salt mixture (see Task 2). The PMP heats the plate at a controlled rate and uses an optical method to record the temperature at which each mixture transitions from opaque to clear. This transition corresponds to the liquidus temperature, which is defined as the temperature during heating at which the last remaining solid phase melts and becomes liquid. The results of the melting test will be used in iterative library designs to find the eutectic mixture of a given system of component salts. In this manner we will rapidly measure the melting point of up to thousands of unique mixtures in search of optimal properties. Throughput: 96+ samples per day.

Heat capacity: The heat capacity is a critical property for a thermal storage material; a higher heat capacity means less material is needed to store a given amount of thermal energy. We will use a differential scanning calorimeter (DSC) to accurately measure the heat capacity of the hits resulting from PMP screening. Halotechnics has received funding under a separate ARPA-E program to purchase a top of the line DSC capable of operation up to 1500 °C (DSC 404 F1 Pegasus, NETZSCH Instruments, Burlington, MA). This instrument will be available for use on the proposed NSF program. The DSC can measure crucial thermal properties our proprietary materials, including melting point (albeit with relatively low throughput), heat capacity, and heat of fusion. With autosampling capability the DSC has the ability to screen sets of 20 samples automatically. Each heat capacity test takes approximately one hour. The DSC will also be used to verify the promising candidates resulting from PMP screening by measuring the melting point with high accuracy. For salt mixtures melting above 315 °C, Halotechnics will measure the melting point by DSC which is capable of very high temperature operation. Throughput: 20 samples per day.

Viscosity: A low viscosity is desired to reduce parasitic pumping losses in the solar thermal power plant. Halotechnics has received funding under a separate ARPA-E program to purchase a high temperature viscometer capable of measuring a wide range of viscosity up to 1600 °C (RSV-1600, Orton Instruments, Westerville, OH). The device uses a spindle immersed in the melt which is contained in a platinum crucible. The viscometer is designed for glass applications but will be modified to measure the lower expected viscosity of our molten salt mixtures. Throughput: 1-2 samples per day.

Thermal stability: The maximum operating temperature of salt candidates will be assessed by long term furnace tests using 500 g batches of the salt mixture. This relatively large sample size gives more realistic data on the chemical stability of the salt over time, since the surface area to volume ratio is closer to large scale batches. The chemical composition will be quantified before and after the test by standard methods to quantify any decomposition to oxide, carbonate, hydroxide, or other expected species.

Density: A high density is desirable in order to reduce the required size of pipes and tanks. This property can be calculated with sufficient accuracy. If higher accuracy is needed, a simple device with a furnace and balance can be constructed that measures the density with a buoyancy force method.

Thermal conductivity: A high thermal conductivity is desirable in order to reduce the heat exchanger size necessary to deliver a desired heat flow. This property is difficult to measure with high accuracy, especially at high temperatures where radiative effects dominate. Halotechnics will calculate the estimated thermal conductivity of salt mixture candidates, and will work with analytical labs to measure the property for a small number of promising candidates. NREL is also developing an instrument capable of high temperature thermal conductivity measurements. Halotechnics has a good relationship with NREL and may have access to the instrument for salt evaluation purposes.

Vapor pressure: The vapor pressure of the molten salt must be less than 1 bar at the maximum expected operating temperature, since higher pressures would require designing the storage tanks to be pressure vessels and would greatly increase the fabrication costs (due to thicker wall sections and more expensive welds). The vapor pressure can be estimated with sufficient accuracy by assuming a simple weighted mole fraction of the constituents of the salt mixture.

Equipment necessary to complete the high throughput workflow will be procured and set up at Halotechnics facilities. The methods necessary for sample preparation and accurate data acquisition will be developed. Experimental protocols will be developed to ensure consistent and reliable data handling.

*Key risks and recovery plan:* The majority of the equipment and methods for performing high throughput screening of molten salt materials have been developed and used at Halotechnics for other programs, so the risk of not achieving the desired workflow is low. In the event the molten glass viscometer proves impractical for use with molten salt, Halotechnics will use its current molten salt viscometer which has been successfully used to measure the behavior of molten salt up to 500 °C. The viscosity up to 700 °C can be extrapolated with reasonable accuracy.

**\* Task 2: High throughput screening and optimization \***

Phase I screened over 2000 unique salt mixtures and successfully discovered a novel eutectic chloride mixture, called E253, that melts at 253 °C and is stable to 700 °C. However, this mixture is too expensive to be commercially viable because it contains significant amounts of cesium chloride and lithium chloride. As mentioned above, Halotechnics has identified a promising baseline mixture from which to begin high throughput screening and optimization. This mixture is a binary eutectic of potassium chloride and zinc chloride, called E230 as shown in Figure 4 [7]. This mixture eliminates the expensive cesium and lithium in E253 and replaces them with zinc. By tonnage, zinc is the fourth most abundantly produced metal in the world [8].

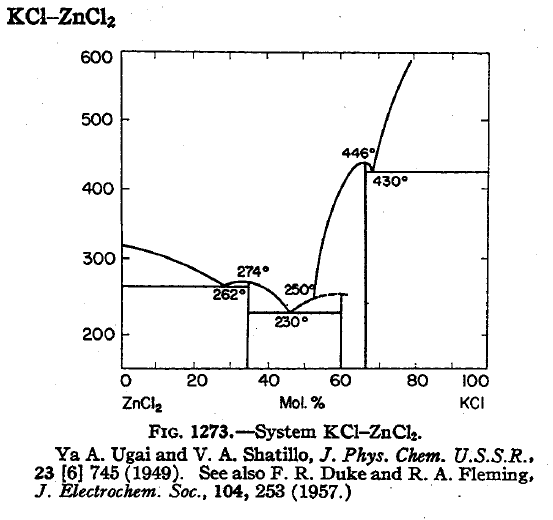


Figure : Phase diagram showing KCl-ZnCl2 eutectic at 230 °C (E230).

We have performed sufficient analysis on E230 to verify that as a proof of concept material, it appears suitable for heat transfer and thermal storage applications from 230 °C up to 700 °C. We have performed a long-term stability test by holding a sample of the salt in a furnace maintained at 700 °C for 56 hours. The chemical composition was analyzed with ion chromatography before and after the test. The melting point and heat of fusion were analyzed with DSC before and after the test. In both chemical composition and thermal properties the composition was unchanged to within experimental error. This result indicates that negligible decomposition occurred to oxides, hydroxides, or other components. The weight of the sample decreased by only 0.85%, indicating that the vapor pressure was low. Figure 5 shows a DSC test of E230. Table 1 shows other measured and estimated physical properties of E230.

From a melting point and stability perspective E230 is very favorable. However its properties must be improved in several areas:

Vapor pressure. Pure zinc chloride boils at 732 °C. At the target maximum temperature, mixtures containing high portions of zinc chloride are expected to have vapor pressures less than 1 bar. This is not an unreasonable vapor pressure to deal with from an engineering perspective, but in general the lower the vapor pressure the better. We expect that the most effective way to reduce the high temperature vapor pressure of the molten salt mixture is to reduce ZnCl2 content.

Cost. An important aspect of a commercially viable heat transfer fluid is the cost of the raw materials used to produce it. Halotechnics has performed quantitative supply chain analysis to determine the logistics and price of the raw materials that will be used to formulate the heat transfer fluids under development. We have begun developing relationships with leading salt suppliers. We have developed custom software tools for calculating and optimizing the price of the salt mixtures. Zinc chloride is fairly low cost (approximately $1500 per metric ton [8]) and available in bulk quantities, but there are other salts that are even cheaper. Sodium chloride, common table salt, is one of the cheapest materials available at approximately $200 per ton. Many other salts are available with costs below $1000 per ton; these will be added to the mixture to reduce the overall cost. Halotechnics targets a raw materials cost less than $1000 per ton for the optimized salt mixture resulting from Phase II.

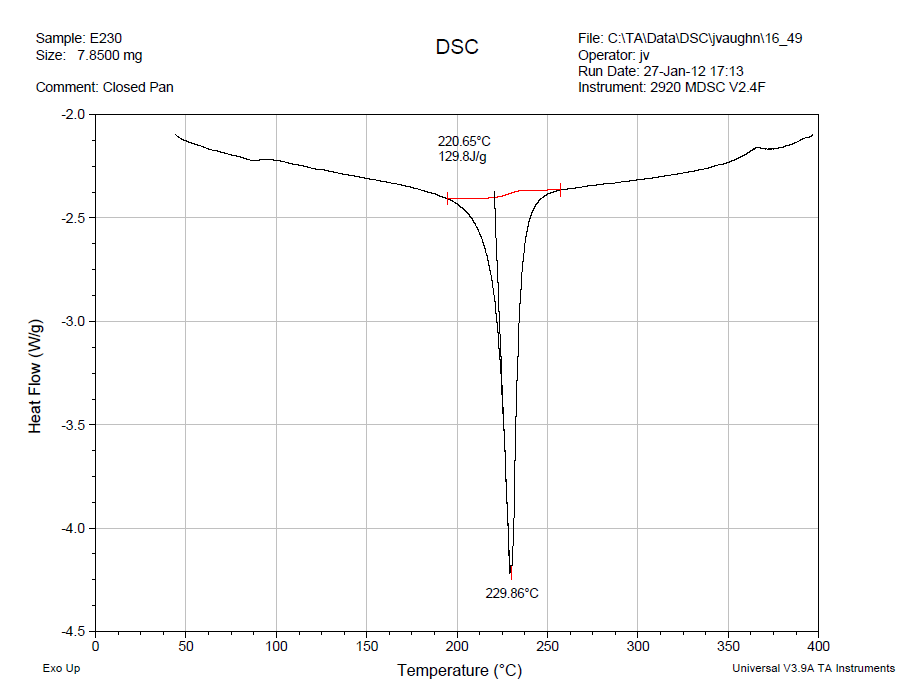


Figure : \* DSC test of E230 showing melting point and heat of fusion. \*

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| **Property** | **Value** | **Method** |
| Composition (by mole fraction) | 56% ZnCl2  44% KCl | Measured during synthesis |
| Composition (by weight percent) | 70% ZnCl2  30% KCl | Measured during synthesis |
| Melting point (liquidus) | 230 °C | DSC |
| Long term thermal stability at 700 °C | 0.85% wt. loss post dehydration. Insignificant change in chemical composition. | Furnace, 56 hrs. in air |
| Heat capacity | 0.95 J/g-K | DSC |
| Heat of fusion | 130 J/g | DSC |
| Viscosity | <10 cP @ 500 °C | Estimated from E253 data |
| Vapor pressure | 5.30x10-6 bar @ 300 °C  0.584 bar @ 700 °C | Estimated from mole fraction ZnCl2 and KCl |
| Density | ρ (300 ºC)=2090 kg/m3  ρ (700 ºC)=1860 kg/m3 | Estimated from mole fraction ZnCl2 and KCl |

Table : \* Physical properties of E230. \*

Halotechnics will conduct a high throughput materials discovery program to rapidly screen unique mixtures of inorganic salts and to optimize the properties of E230. Our technique to develop advanced low melting point materials involves selecting a simple two component baseline mixture and adding a third component to that baseline mixture, measuring the resulting properties, and searching the phase space until the ternary eutectic is found. We will continue this search with all feasible earth abundant components in three component mixtures. Then we will select the most promising components and begin the same process with four component (quaternary) mixtures to develop high order eutectics.

Based upon favorable data from our Phase I work regarding the low melting point and high thermal stability of chloride salts, we will focus primarily on these materials for Phase II. Mixed anion salt mixtures will be considered as a secondary focus. Carbonate and sulfate salts tend to form deep eutectics when mixed with chlorides as shown in Figure 6. Therefore low-cost carbonate and sulfate salts will be considered as secondary constituents in the Phase II salt mixtures.

We have performed a preliminary literature review and have identified a list of low cost salts that may improve the physical and economic properties when added to the E230 baseline. For example, the addition of sodium chloride reduces the melting point by approximately 30 °C. Other salts may have a similar effect: calcium chloride, manganese chloride, lead chloride, and others. We will first perform a complete literature review to assess the current knowledge with two or three component mixtures of the salts of interest. Next we will use FactSage thermochemical modeling software to predict eutectic compositions of chloride mixtures containing zinc chloride. FactSage is a fully integrated software package that specializes in predicting chemical properties from the world’s largest set of evaluated and optimized thermodynamics databases. Halotechnics has used thermodynamic modeling tools where appropriate to predict approximate liquidus temperatures and composition of high order eutectic mixtures. FactSage provides a flexible interface to generate liquidus projection phase diagrams and calculate eutectic properties in chloride salts. This modeling work will be limited to chloride salts only as the databases available for carbonate and sulfate salts are incomplete. FactSage modeling capabilities with zinc chloride containing mixtures is also rather limited, therefore the majority of our efforts will focus on experimental methods.

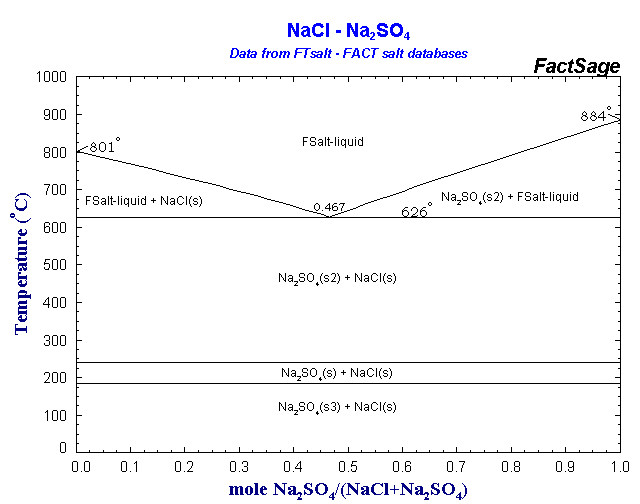
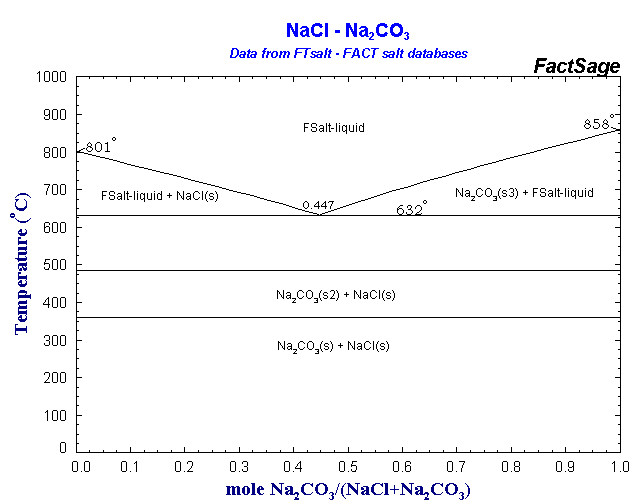


Figure : Binary phase diagrams showing eutectic behavior with NaCl-Na2CO3 and NaCl-Na2SO4. (images courtesy of FactSage).

Halotechnics will use the workflow developed in Task 1 to systematically screen the melting point of ternary mixtures based on E230 with one additional component. The most promising components that had the biggest melting point reduction from 230 °C will then be combined to explore the quaternary phase space based upon E230. In this manner we have the ability to explore high order mixtures, including five components (quinary) and more. See Table 2 for the materials palette we will draw from as candidate salt mixture components. We are confident that we can optimize the properties of our advanced molten salt and develop a high order mixture with a melting point near 200 °C at a lower cost and lower vapor pressure.

*Key risks and recovery plan:* There is a risk that no salt materials tested in Phase II will conform to the project objectives. For example, there may be a family of salt mixtures with low melting points but high vapor pressure. The risk from this possibility is likely low since we have obtained preliminary data showing candidate salt materials with favorable properties. This risk will be reduced by the throughput and flexibility of the workflow. If a system of salts is not generating candidates that meet the criteria, the search may be expanded to include more components or salts of a different variety.

**\* Task 3: Corrosion assessment and mitigation \***

It is imperative to gain an understanding of the dominant corrosion mechanisms affecting structural materials at the desired operating temperature. The purpose of corrosion testing is to demonstrate that suitable alloys are available to construct a durable engineering system using the molten salt mixtures discovered by Halotechnics combinatorial chemistry technology as described above. Our corrosion testing approach is based on the fundamental chemistry of molten chlorides and molten chloride-sulfate mixtures.

Corrosion-resistant alloys typically from a thin oxide layer at high temperature which significantly slows further oxidation [9]. However, molten chloride salts can dissolve this layer and allow further oxidation and deeper penetration of the affected surface. Furthermore, absorbed water in ZnCl2 is recognized as a significant source of moisture when preparing molten chloride mixtures, raising concerns about the formation of corrosive reaction products at high temperatures. For this reason, molten chloride salts constitute a potentially corrosive media depending to a significant extent upon the level of oxygen and water contamination of the melt. In this task we will develop methodologies to seal out or remove these impurities.

Corrosion of high-temperature alloys in molten chloride salts usually causes oxidation of alloying elements to form soluble products, as shown in the simplified illustration in Figure 7. The extraction of alloying elements can occur in the bulk alloy or at grain boundaries, as shown in the cross-section. A chloride-sulfate melt includes by definition a high proportion of oxygen containing anions, which represents an additional challenge in assessing and mitigating its corrosion behavior.

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| **Group** | **Material name** | **Formula** |
| ***Chlorides*** | sodium chloride | NaCl |
|  | potassium chloride | KCl |
|  | magnesium chloride | MgCl2 |
|  | calcium chloride | CaCl2 |
|  | strontium chloride | SrCl2 |
|  | barium chloride | BaCl2 |
|  | manganese chloride | MnCl2 |
|  | iron (II) chloride | FeCl2 |
|  | copper (II) chloride | CuCl2 |
|  | zinc chloride | ZnCl2 |
|  | lead (II) chloride | PbCl2 |
| ***Sulfates*** | sodium sulfate | Na2SO4 |
|  | potassium sulfate | K2SO4 |
|  | manganese (II) sulfate | MnSO4 |
|  | iron (II) sulfate | FeSO4 |
|  | copper (II) sulfate | CuSO4 |
|  | zinc sulfate | ZnSO4 |
|  | aluminum sulfate | Al2(SO4)3 |
|  | lead (II) sulfate | PbSO4 |
| ***Carbonates*** | sodium carbonate | Na2CO3 |
|  | potassium carbonate | K2CO3 |
|  | calcium carbonate | CaCO3 |
|  | strontium carbonate | SrCO3 |
|  | barium carbonate | BaCO3 |

Table : \* Materials palette. \*

The corrosion experiments proposed for Phase II will provide information lacking in literature reports with regard to the effect of impurities in the molten chloride salts and preparatory methods to minimize corrosion due to such impurities. Molten alkali chlorides containing significant proportions of zinc chloride are expected to present the same primary corrosion environment as alkali chlorides alone as well as the additional mechanism of displacement reactions between zinc ions and thermodynamically active alloying elements, such as chromium. An example of such a displacement reaction is Zn++ + Cr (alloyed) = Cr++ + Zn (metallic), which would result in extraction of alloying elements into the molten salt.

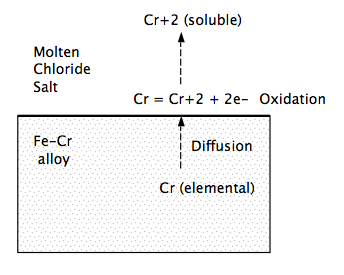
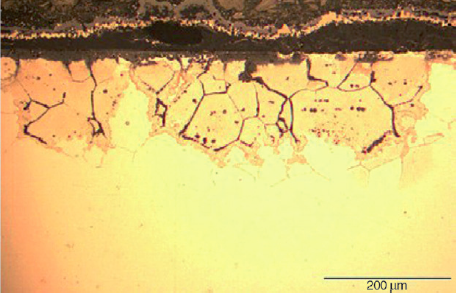
 

Figure : Simplified schematic of alloy corrosion in molten chlorides. (a) Bulk alloy corrosion. (b) Corrosion at grain boundaries (cross section of metal sample).

Corrosion experiments will also be conducted in the group of molten salts based on mixtures of sulfates and chlorides. These mixtures are recognized as causing ‘hot corrosion’ in combustion environments [10]. However, the key difference between general hot corrosion (as reported extensively in the literature) and the application of Halotechnics-developed sulfate-chloride mixtures is that the former operate in contact with excess air while thermal storage systems are most likely to be engineered to exclude air. The anaerobic condition of a thermal storage system will likely change the corrosion mechanism to some degree.

Alloy selection. The alloys selected for corrosion testing are listed in Table 3 along with their elemental compositions. The alloys include iron-based alloys (stainless steels, RA330) and nickel-based alloys designed for high temperature oxidation resistance as this group is expected to have the mechanical properties necessary to build thermal energy storage systems operating at 700 °C. Although the iron-based alloys may be more susceptible to corrosion than high-nickel alloys, they have been included because of the interest of solar thermal power system designers in using such materials and because the corrosion mitigation techniques that are also the subject of these tests may provide adequate corrosion resistance. We recognize that these selections are not inclusive of alloys that could be useful. Rather, the alloys were chosen to enable us to determine the effects of typical alloying elements, such as chromium (several), aluminum (e.g., Haynes 214), silicon (e.g., RA330), tungsten (e.g., Haynes 230), and molybdenum (e.g., IN625). This will allow us to establish a basis for choosing an optimal alloy according to availability and fabricability, or to survey additional candidates.

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| **Alloy** | **Ni** | **Cr** | **Fe** | **Mo** | **Si** | **Al** | **C** | **Other** |
| Inconel 625 | 58 | 23 | 5 | 10 |  | 0.4 | <0.10 | Nb+Ta 4.1 |
| RA330 | 37 | 18 | 42 |  | 1.5 | - - | 0.08 | Cu 1 |
| Haynes 230 | 61 | 22 | 1.3 | 1.3 | 0.4 | 0.3 | 0.11 | W 14.1 |
| Haynes 214 | 77 | 16 | 3 | -- | 0.2 | 4.5 | 0.05 | B,Y 0.01 |
| Haynes 556 | 20 | 22 | 35 | 3 | 0.4 |  | <0.10 | Co 18,W 2.5 |
| Alloy 800H | 30-35 | 19-23 | 40 |  |  | < 0.6 | <0.08 | Ti 0.60 max |
| 316 SS | 10-14 | 16-18 | 68 | 2-3 |  |  | <0.08 |  |
| 316Ti SS | 10-14 | 16-18 | 68 | 2-3 |  |  | <0.08 | Ti 5x%C |
| 321 SS | 9-12 | 17-19 | 69 |  |  |  | <0.08 | Ti 5x%C |

Table : Elemental compositions (weight %) of alloys for molten salt corrosion testing at 700 °C.

Isothermal corrosion testing. Corrosion testing will be performed in two segments, short-term screening experiments and long-term evaluation tests. The short-term screening experiments will be used to screen a relatively broad range of alloys and assess various methods to mitigate corrosion. The long-term evaluation tests will extend testing of those alloys that are the most corrosion resistant in concert with the most advantageous melt preparation methods and/or corrosion inhibitors. Short-term tests will be conducted for <100 hours, while long-term tests will last up to 3000 hours. Corrosion tests will be conducted at 700 °C in molten salts consisting solely of chlorides and in sulfate-chloride mixtures as various formulations are identified by the molten salt development activity described above.

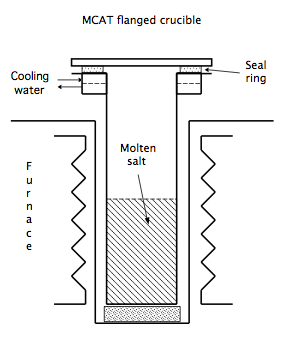
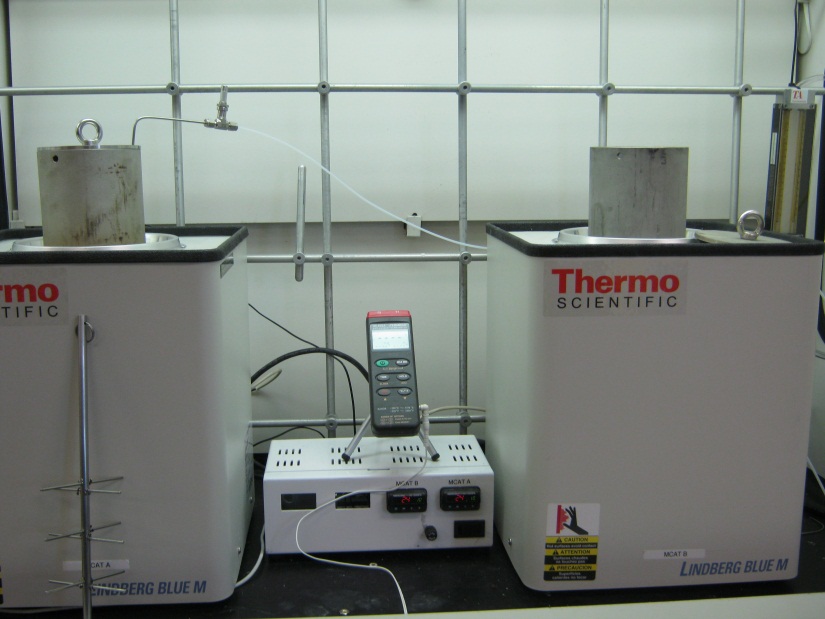


Figure : Multichannel Corrosion Analysis Tool for testing alloy and salt compatibility at 700 °C. (a) Photo of existing system. (b) Schematic showing flanged crucible modification.

Both types of corrosion tests will be performed using the Halotechnics MCAT (Multichannel Corrosion Analysis Tool) apparatus. Two of the four MCAT furnaces currently available are shown in Figure 8(a). Corrosion experiments will use modified crucibles that are mechanically sealed in order to control the atmosphere in contact with molten salt during corrosion testing as shown in Figure 8(b). We expect that sealing will be necessary to prevent oxygen and moisture from contaminating the melts and thereby aggravating corrosion. The alloy specimens from the corrosion tests will be evaluated by standard methods of gravimetric analysis (mass changes) and metallographic examination of cross-sectioned specimens. Samples of molten salt will be removed periodically and chemically analyzed to determine concentrations of dissolved alloying elements and alkaline species.

Corrosion tests will be conducted with groups of alloys rather than individually for greater efficiency. The specimens will be isolated by ceramic spacers to avoid galvanic effects possible in non-passivating electrolytes such as molten chlorides. Although we recognize the potential for galvanic corrosion, it is premature to include that phenomenon in the proposed tests until the general corrosion behavior of the alloy group has been determined and the design of a thermal storage system defines the materials for which galvanic corrosion might be a concern.

Corrosion inhibitor studies. The relatively corrosive nature of molten chloride salts may require supplementary methods to mitigate corrosion beyond simply minimizing absorption of oxygen-based impurities from the atmosphere in contact with the molten salt. We will adapt techniques used in the heat-treating industry in which molten chloride baths, necessarily exposed to the atmosphere, are ‘rectified’ by the addition of chemicals which react with soluble oxide contamination and thereby mitigate scaling and decarburization of metal work-pieces. Among such rectifiers are boric acid, for example, which scavenges oxygen from the melt to produce insoluble borates that can be removed by sedimentation. Other materials that have a very strong affinity for oxygen such as yttrium or zirconium (which form insoluble refractory oxides, locking up the oxygen and settling out as ultra-fine particles) may also be considered as candidate rectifiers. In addition to possible utility in chloride melts, rectifiers may reduce the solubility of oxidized alloying elements in sulfate-chloride molten salts by restricting the oxide ion activity. The parameters of exposure time and air contact are diametrically different for heat-treating (short duration in air) compared to a thermal storage system (long duration in inert gas) but the principles of controlling molten salt chemistry are generally the same.

Analytical techniques and necessary equipment. Metallographic examination of corrosion coupons will be performed by commercial laboratories that conform to the primary applicable ASTM standard, E3-11. Molten salt samples will be removed periodically during the course of corrosion tests and chemically analyzed for dissolved alloying elements and alkalinity. For tests in which inhibitors are added to the molten salts, analysis for the concentration of inhibitor will also be performed. Chemical analysis will be conducted primarily in-house at Halotechnics using aqueous solutions of sampled salts. The primary method of analysis will be standard methods of UV-VIS spectrophotometry that utilize various highly specific reagents which undergo a color change when reacted with the analyte of interest. Halotechnics will purchase a compact UV-VIS spectrophotometer that will fulfill most of the analytical needs foreseen (DR 3900 Benchtop Spectrophotometer, Hach Company, Loveland, Colorado).

The MCAT crucibles will be modified to add hermetic seals in order to control the atmosphere in contact with the molten salt mixtures thereby minimizing oxygen and moisture content. The seal configuration will consist of flanges and metal ring gaskets with a water cooling jacket to moderate the temperature of the seal. The existing stainless steel MCAT crucibles may experience corrosion due to the prolonged period during which the many tests will be conducted and the variable nature of the molten salt environments that are intrinsic to the testing program. Diffusion coatings of aluminum, silicon or combinations will be applied by pack-cementation (at a commercial vendor, e.g., Vaporkote or Chromalloy) to provide corrosion resistance of the crucibles.

*Key risks and recovery plan:* The basic risk of the corrosion testing effort is that no alloy among those in the proposed test matrix will display acceptable corrosion resistance to warrant constructing a thermal storage system. This risk is coupled with the possibility that the corrosion mitigation methods will not be sufficient to establish a viable alloy/molten salt combination within the experimental matrix that can be reasonably accomplished by the proposed effort.

The recovery path has several elements. First, expand the candidates for alloys by identifying alloys comparable to or exceeding the elemental composition of alloys that were determined to be most favorable in the test results. A survey of companies that develop high-temperature, corrosion-resistant alloys should be part of this effort to assure that no promising candidates were overlooked and to discover new alloys in development. Second, evaluate surface alloying methods such as pack cementation (aluminum, silicon) or tantalum surface alloying that would provide acceptable corrosion behavior, based on commercially-available methods for large-scale industrial applications. Third, conduct discussions with suppliers of rectifiers for heat-treating molten salts to identify additional candidates for testing or to collaborate in developing new formulations using Halotechnics combinatorial chemistry capability. Fourth, evaluate alternative de-oxidation techniques such as electrochemical reduction of oxygen contaminants.

**Task 4: Flow testing**

Halotechnics has recently received a $1 million subcontract under the NREL SunShot Incubator program to develop a complete thermal energy storage system using the breakthrough Saltstream 700 candidate developed under the NSF funded program. This NREL funded system will be available for use as a molten salt test loop to vet materials developed under the NSF Phase II program.

The NREL test loop consists of molten salt pumps, insulated tanks, and related hardware necessary to pump, heat, store, and discharge the molten salt at 700 °C. A schematic of the test loop is shown in Figure 9. In place of a central receiver it uses a standard laboratory tube furnace to heat the molten salt as it flows through the pipes. In place of a steam generator it uses a radiator heat sink to discharge the thermal energy. The system uses a two-tank design with approximately 300 kg of molten salt, enough to store 30 kWh of thermal energy.

Once complete in Q4 2012, the NREL-funded thermal storage test loop will function as a flexible platform for subsequent testing and development under this program, including:

* startup/shutdown procedures
* freeze recovery techniques
* heat transfer coefficient measurement of molten salt
* flowing corrosion tests

Obtaining corrosion data under flowing conditions will more closely mimic the expected environment in full scale applications of Saltstream 700. Alloy specimens (witness coupons) will be attached to removable fixtures and inserted at locations corresponding to the highest temperature and the lowest temperature of the loop. The former (hot) location will allow corrosion to be monitored at its maximal rate and the latter (cold) location will enable us to determine if dissolved alloying elements are precipitating, should the respective concentrations exceed the saturation levels at the lowest temperature. This type of corrosion process is ordinarily referred to as thermal gradient mass transfer.



Figure : Schematic of prototype molten salt test loop.

The alloys tested in the ‘hot’ side will include the materials of construction of the loop, samples of the valve components, and candidates selected from among those studied in the MCAT corrosion tests described above. The ‘cold’ side collector will be a material that will not interfere with the identification of alloying element deposits, such as a ceramic. Samples of molten salt will be removed periodically during operation of the loop and analyzed for alloying elements and alkaline species by the same techniques as the MCAT tests.

The NSF and NREL programs at Halotechnics have strong synergies: the NSF grants fund materials science work to develop the novel fluid, and the NREL subcontract funds the engineering work to develop the thermal storage system using the novel fluid. There is no overlap in the work proposed for each program.

*2.4 Broader Impact*

Furthering science and engineering education.Funds from this award would be used to expand the Halotechnics Internship Program. Under this program, science and engineering students work as a paid intern at Halotechnics under the supervision of a senior member of staff. Students are assigned a research project that will complement the education they are pursuing and provide them a practical outlet of the skills they learn in a classroom environment. The students receive mentorship from their supervisor who provides one-on-one tutoring, guidance, and relevant technical advice. The nature of this relationship is by necessity one of mentorship especially early in the internship but is intended to transition to one of supervised independent research as the student acquires a working knowledge of their project field. A total of four students from UC Berkeley and Stanford University have participated in the Halotechnics Internship Program over the past two years. This Phase II award would expand the program with an additional 2-3 students. Typical project length is 3-6 months of full time work, with part time work possible during the academic year. Candidate interns are drawn from such majors as Chemistry, Materials Science and Engineering, Chemical Engineering, and related fields.

Impact on job creation. The funds from this award would allow Halotechnics to hire an additional full time chemist as well as 2-3 interns.

*2.5 Conclusion*

If successful this project will be both transformative and disruptive. We propose to use combinatorial chemistry methods to translate technology developed by the heat treating industry and use it to transform a new sector – solar thermal power. If successful, our technology will provide thermal energy storage at significantly lower cost and make solar generated electricity more competitive with fossil fuels.

## Part 3. Organizational Information

|  |  |  |
| --- | --- | --- |
| **Staff category** | **Full time employees** | **Part time employees** |
| Technical | 4 | 5 |
| Management | 2 | 0 |
| Administrative | 0 | 1 |
| Marketing | 0 | 1 |
| Manufacturing | 0 | 0 |
| *Total* | *6* | *7* |

Table : Staffing profile of Halotechnics.

|  |  |
| --- | --- |
| **Income type** | **2011** |
| Sales | $0 |
| Licensing | $0 |
| Contracts (R&D grants) | $650,000 |
| Research services | $60,000 |
| Other | $0 |
| *Total* | *$710,000* |

Table : \* Halotechnics, Inc. 2011 income statement. \*

We plan to grow to a total of 10-12 full time employees by Q2 2012. Key hires will be 2-3 experienced thermal/fluids engineers, a chemist, and an office manager.

*Key participants in Phase II:*

**Justin Raade, PhD (PI)** | CEO and Founder. Applied thermodynamics expert.

Dr. Raade will perform project management duties and oversee the technical efforts of the research.

**Darren Hickey** | Director of Engineering. 19 years of experience in thermal systems up to 1000 °C.

Mr. Hickey will lead the flow testing task with the laboratory scale flow system operating up to 700 °C.

**John Vaughn** | Analytical Chemist. 11 years of experience with inorganic chemical analytical methods.

Mr. Vaughn will be involved with designing and synthesizing salt mixtures and quantifying their physical and chemical properties.

**Robert Bradshaw, PhD** | Corrosion Chemistry Consultant. World leader in molten salt chemistry.

Dr. Robert Bradshaw will lead the corrosion test plan development. He will be involved in performing literature reviews, determining candidate alloys for corrosion testing, determining corrosion test conditions and hardware design, and reviewing the resulting data from corrosion testing.

## Part 4. Consultant and Subaward Agreements

Halotechnics will perform over 50% of the effort as defined by budget expenditures during Phase II.

Dr. Robert Bradshaw is a consultant to Halotechnics. See the Budget Justification for details of his consulting relationship.

There are no subawards planned for the proposed project.

## Part 5. Equivalent or Overlapping Proposals to Other Federal Agency

NONE.

Halotechnics has not submitted any equivalent or overlapping proposals to other federal agencies for the proposed work.