Final Scientific Report

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Deep Eutectic Salt Formulations Suitable as Advanced Heat Transfer Fluids

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I. Executive Summary:

Concentrating solar power (CSP) facilities are comprised of many miles of fluid-filled pipes arranged in large grids with reflective mirrors used to capture radiation from the sun. Solar radiation heats the fluid which is used to produce steam necessary to power large electricity generation turbines. Currently, organic, oil-based fluid in the pipes has a maximum temperature threshold of 400 °C, allowing for the production of electricity at approximately 15 cents per kilowatt hour. The DOE hopes to foster the development of an advanced heat transfer fluid that can operate within higher temperature ranges. The new heat transfer fluid, when used with other advanced technologies, could significantly decrease solar electricity cost. Lower costs would make solar thermal electricity competitive with gas and coal and would offer a clean, renewable source of energy.

Molten salts exhibit many desirable heat transfer qualities within the range of the project objectives. Halotechnics developed advanced heat transfer fluids (HTFs) for application in solar thermal power generation. This project focused on complex mixtures of inorganic salts that exhibited a high thermal stability, a low melting point, and other favorable characteristics. A high-throughput combinatorial research and development program was conducted in order to achieve the project objective. Over 19,000 candidate formulations were screened. The workflow developed to screen various chemical systems to discover salt formulations led to mixtures suitable for use as HTFs in both parabolic trough and heliostat CSP plants. Furthermore, salt mixtures which will not interfere with fertilizer based nitrates were discovered. In addition for use in CSP, the discovered salt mixtures can be applied to electricity storage, heat treatment of alloys and other industrial processes.

II. Comparison of the actual accomplishments with the goals and objectives of the project

Over the course of the project, Halotechnics developed three unique sets of salt based mixtures which can be used as HTFs for either parabolic trough or heliostat CSP solar power plants.

To develop a mixture suitable for parabolic troughs, Halotechnics targeted a salt formulation with the following characteristics

- Thermal stability as a liquid to about 500°C,
- Vapor pressure of about 5 atmosphere to about 500°C,
- Freezing point less than 80°C,
- Specific gravity in the range of 0.7-1.7 to about 500°C,
- Heat capacity in the range of 2-5 J/g/K to about 500°C,
- Viscosity of about 1 centipoise to about 500°C,
- Chemical compatibility with common stainless steels.

5,130 unique mixtures were screened and evaluated using the workflow described below. Halotechnics developed and patented a salt mixture which melts at 65 °C and is stable to 500 °C. No further characterization was done. Table 1 lists the composition of this mixture by mole %.

Li^+ (mol %)	Na^+ (mol %)	K^+ (mol %)	Ca^{+2} (mol %)	Cs^+ (mol %)	NO_3^- (mol %)
15	10	30	15	30	100

Table 1

In addition, Halotechnics developed salt based mixtures which would be suitable for heliostat power plants. The mixtures were developed to meet the following specifications:

- Melting point less than 238 °C (248 °C maximum)
- Thermal stability as a liquid to about 565°C (550°C minimum)
- Heat capacity in the range of 2-5 J/g/K (1 J/g/K minimum, no maximum) to about 500°C
- Raw materials cost 20% less than 60/40 solar salt (10% minimum)

6,599 mixtures were screened using the workflow described below. Numerous salt mixtures which met the melting point and thermal stability specifications were developed. Five mixtures which were reported in a patent are listed in Table 2. Cost reductions were estimated using real quotes of industrial grade material. Heat capacities of the two most promising mixtures were measured.

Na^+ (mol %)	K^+ (mol %)	SO_4^{-2} (mol %)	Cl^- (mol %)	NO_3^- (mol %)	MP (°C) (DSC)	C_p (300 °C) (J/K·g)	Est. Cost Reduction
65.11%	34.89%	0.00%	4.20%	95.80%	237	not measured	2.84%
64.98%	35.02%	2.10%	1.93%	95.97%	235	not measured	3.07%
65.42%	34.58%	2.18%	4.45%	93.37%	231	1.52	4.81%
60.17%	39.83%	0.00%	6.11%	93.89%	216	not measured	1.42%
71.20%	28.80%	1.60%	0.00%	96.40%	246	1.51	5.35%

Table 2

Furthermore, Halotechnics developed salt based mixtures which were not based off of alkali nitrates critical to the food chain. Ten (five minimum) candidate formulations were to be developed to meet the following criteria:

- Melting point: 250 °C or below
- Maximum temperature: 550 °C or above
- Composition: Eliminate potassium nitrate and sodium nitrate from mixture

7,529 mixtures were screened which would either eliminate KNO_3 or eliminate both $NaNO_3$ and KNO_3 from the resultant mixture using the workflow described below. Fourteen mixtures were developed which eliminate KNO_3 and five mixtures were developed which eliminated both $NaNO_3$ and KNO_3. The five mixtures which eliminated both $NaNO_3$ and KNO_3 were reported in a patent and are listed in Table 3.

Zn^{+2} (mole %)	K^+ (mole %)	Na^+ (mole %)	SO_4^{-2} (mole %)	Cl^- (mole %)	MP (°C) (DSC)
63.50%	24.30%	12.30%	2.10%	97.90%	255
64.50%	9.80%	25.70%	3.00%	97.00%	241
64.00%	11.00%	25.00%	4.10%	95.90%	234
62.00%	38.00%	0.00%	2.00%	98.00%	239
43.60%	33.60%	22.80%	0.00%	100.00%	257

Table 3

The salt mixtures listed in Table 3 were further characterized. One salt mixture was to be chosen which would meet the following criteria:

- Heat capacity: Within 5% of the value for Solar Salt at any given temperature.
- Density: Within 5% of the value for solar salt at any given temperature.
- Viscosity: Within 5% of the viscosity of solar salt at any given temperature.
- Cost: The cost per kg is less than the cost per kg of solar salt
- Chemical corrosion rate for carbon steel, 316 stainless, 347 stainless, Inconel 620, and Hastelloy 230 alloys is less than the chemical corrosion rate with solar salt
- Long-term thermal stability at 550 °C or above

The thermophysical properties of the salt mixtures were fully characterized and reported. The heat capacities of the mixtures were roughly 55% to 60% less than the heat capacity of Solar Salt. The densities were roughly 15% - 20% greater than the density of Solar Salt. The viscosities were significantly greater than the viscosity of Solar Salt. In general, the corrosion rate of the mixtures on stainless steel 316, stainless steel 347, Inconel 625 and Hastelloy 230 was similar or significantly less than the corrosion rates for Solar Salt. The thermal stability of these mixtures at 600 °C under a static environment was comparable to that of Solar Salt.

The mixture which was had the most favorable properties has the following composition:

- $ZnCl_2$: 76.8% by weight
- NaCl: 6.3% by weight
- KCl: 7.3% by weight
- Na_2SO_4: 8.3% by weight

The properties are listed below.

- Melting Point = 233.8 ± 1.9 °C
- Heat Capacity (300 °C) = 0.946 ± 0.034 J/K·g

- Density (300 °C) = 2.48 g/cm^3
- Viscosity (500 °C) = 5.95 cP
- Thermal Stability: 1.17% wt loss over 250 hours at 600 °C
- Corrosion Rate:

Alloy	Corr Rate @600 °C (mil/yr)
316L	24 ± 7
347H	50 ± 3
HA230	22 ± 1
I-625	22 ± 3

- Est. Cost = $2.17/kg

III. Summary of Project Activities :

Phase 1: Develop fluids with MP ≤ 80 °C for parobolic troughs	**Phase 2:** Develop lower cost fluids for solar towers	**Phase 3:** Develop fluids which exclude nitrates used in fertilizers	**Phase 4:** Characterize properties of non fertilizer based fluids

Molten salts exhibit many desirable heat transfer qualities within the range of the project objectives but typically have high melting points. Complex mixtures of inorganic salts were investigated to discover deep eutectic or low melting point formulations suitable as advanced heat transfer fluids. Eutectic mixtures of salts exhibit dramatic melting point reductions, but little experimental data exists for quaternary or higher order systems. Given the size of the phase space and the possibility of many unexplored salt systems made up of nitrates, nitrites, acetates, carbonates, chlorates, sulfates or other salts, it is likely there are undiscovered eutectic mixtures with melting points significantly below those already discovered and with sufficient thermal stability. In order to effectively map out the phase space in a reasonable amount of time, the power of high throughput combinatorial discovery tools (for fast materials synthesis and characterization) was combined with theoretical modeling and an efficient methodology for the design of experiments (to eliminate redundant or infeasible zones of the design space). Over 19,000 candidate formulations were screened. The overall discovery program workflow was divided into phases: a primary screen focused on melting point and thermal stability; a secondary screen focused on viscosity, vapor pressure, density, heat capacity, thermal conductivity, and materials compatibility; and finally a blend optimization program to further improve the performance characteristics of the most promising candidates from primary and secondary screening. The discovery program will focus on experimental methods to acquire data on the behavior of salt formulations and will utilize theoretical modeling techniques where advantageous.

Salt mixtures were formulated using automated robotic systems for both powder and liquid dispense. The powder dispense system is the MTM Powdernium from Symyx Technologies (Sunnyvale, California). This device measures each component as it is being dispensed and records the final weight with high accuracy. It can dispense many different components to many different mixtures. The liquid dispense system is the Synthesis Station Core Module from Symyx. Components are typically dispensed as powder, but some hygroscopic salts may be dispensed as an aqueous solution to avoid forming clumps when in powder form. The mixtures will be dispensed into a borosilicate glass plate containing 96 wells in an 8 by 12 array. Each mixture will have a total mass of 250 mg. The next step in the workflow is the mixing station (a high temperature muffle furnace) which removed any solvent from the mixture and homogenized the mixtures by raising the temperature sufficiently high to melt all components and soaking for at least 8 hours. Each component must be melted and well mixed in order for the mixture to be properly tested. After mixing, the melting points of the samples were analyzed using a modified version of 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. 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 were used in iterative library designs to find the eutectic mixture of a given system of component salts.

Differential scanning calorimeter was used to accurately measure melting point, heat of fusion and heat capacity. Its throughput is lower than the PMP so it was used primarily to verify PMP results when appropriate. Density was determined by measuring the buoyancy of a sinker of known density as a function of temperature in the fluid of interest. Viscosity was determined by measuring the torque required maintain a spindle of known geometry at a constant angular velocity as a function of temperature in the fluid of interest. Corrosion rates were determined by combining electrochemical impedance spectroscopy and linear polarization voltammetry.

The complete workflow is shown in Figure 1.

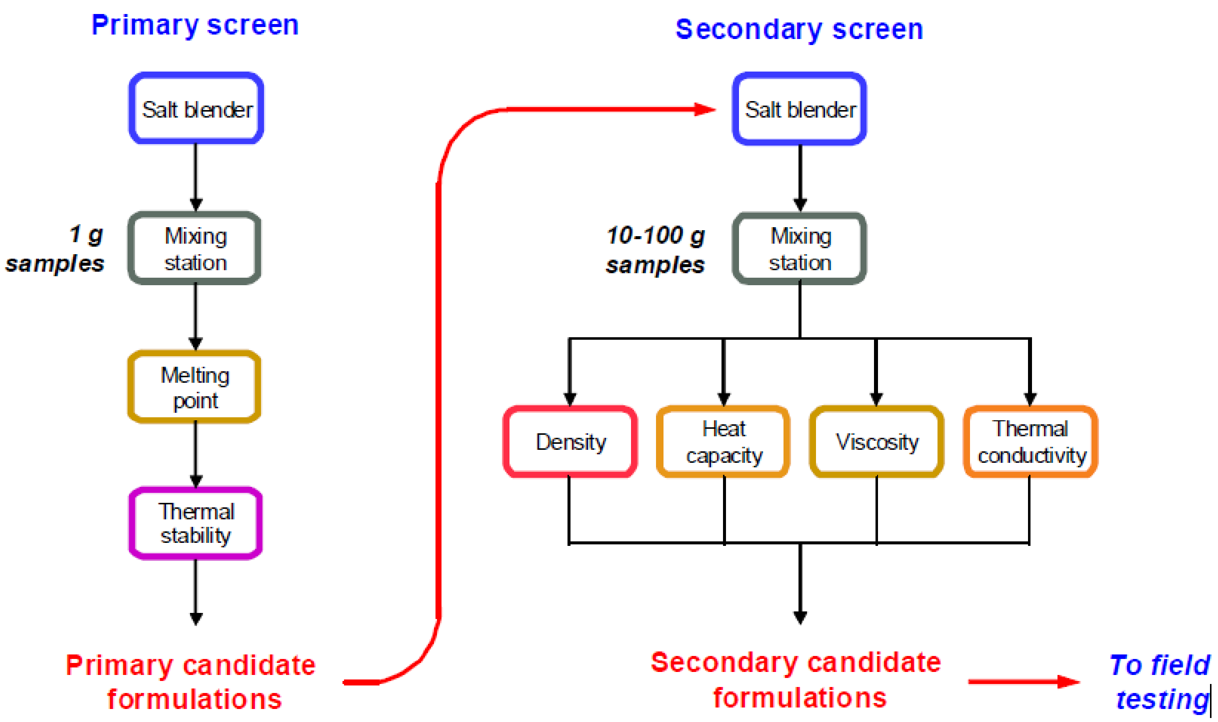

Figure 1

IV. Products and Publications developed under the award

1. Publications

<u>Archival Technical Journal Publications</u>
J. W. Raade and D. Padowitz, “Development of molten salt heat transfer fluid with low melting point and high thermal stability,” *Journal of Solar Energy Engineering*, vol. 133, issue 3, August 2011.

<u>Conference Publications</u>
J. W. Raade, D. Padowitz, and J. Vaughn, “Low melting point molten salt heat transfer fluid with reduced cost,” proc. 17th SolarPACES conference, Granada, Spain, 2011.

J. W. Raade and D. Padowitz, “Development of molten salt heat transfer fluid with low melting point and high thermal stability,” proc. 16th SolarPACES conference, Perpignan, France, 2010.

Conference Presentations (without full publication)

J. W. Raade, "The Promise of Thermal Storage: A vision of CSP displacing coal," presented on the panel "State of the art storage technology and its commercial applications" at the 5th CSP Summit conference, Las Vegas, Nevada, June 2011.

J. W. Raade, "The Promise of Molten Salt: A vision of CSP displacing coal," invited talk, CST Power conference, Scottsdale, Arizona, February 25, 2011.

2. Internet sites reflecting results
3. Networks or collaborations fostered

Collaboration

Jayaweera, Palitha, Tanzella, Francis, SRI International

4. Technologies/Techniques
5. Inventions/Patent Applications, licensing arrangements

Patents

J.W. Raade, D. Padowitz, Inorganic Salt Heat Transfer Fluid, USPTO 13/088,605

J. W. Raade, G. Hannah, T. Roark, J. Vaughn, Molten Salt Material for Heat Transfer and Thermal Energy Storage, USPTO 61/485,491

J. W. Raade, J. Vaughn, B. Elkin, Advanced Molten Salts for Solar Thermal Power Generation with Supercritical Steam Turbines, USPTO 61/592,859

J.W. Raade, T. Roark, J. Vaughn, B. Elkin, Low Melting Perchlorate and Nitrate Mixtures, USPTO 61/713,246

6. Other products such as databases, software, models

Publication of over 12,000 compositions screened under the program via a publicly searchable database at http://doe.halotechnics.com.