**Halotechnics response to action items**

Action items from the Panel:

1.  The key innovative aspect to the proposed project is the use of a kind of “combinatorial chemistry” approach to developing new eutectic salts from a wide range of possible compositions.  Can you explain how much of this approach is new to this particular proposal?  Has the company already used this approach to develop similar material systems before?  If so, what is the novelty specific in this particular R&D project?

We believe that our previous work with discovering eutectic salts is an asset to the current proposal, since it validates the methodology we are proposing for discovering new thermal materials. The discovery of novel materials with the target properties is a high-risk endeavor that requires powerful techniques and know-how in order to maximize its chance of success.

An approach similar to that described in this proposal was used once before in a program to develop a nitrate-based heat transfer fluid. This program is currently underway at Halotechnics, funded by the DOE grant referenced in the proposal. The novelty of our NSF proposal lies primarily in the new target materials, which are carbonate, sulfate, or chloride based salt mixtures, rather than in the methodology of how to discover them. These materials are chemically very different from nitrate salts (higher melting point, varying reactivity, etc.) and new handling protocols will have to be developed to adapt our materials discovery workflow to their properties. We will also need to modify our melting point apparatus to operate at higher temperatures. We have some experience with these materials as trace additives to nitrate salts as part of the DOE program but we are now proposing to use them as the majority component in the salt mixtures, significantly changing the handling and measurement requirements.

2.  Can you give greater detail on what separates this proposed NSF SBIR project from the already-funded DOE effort, other than changes in some of the target material specifications?  Put another way, can you give an argument why this effort, at just $150,000, will be able to come up with new and improved materials versus the much larger $1.5 million DOE effort?  Please be specific and quantitative if possible.

The primary difference between our current DOE program and the proposed NSF SBIR program is the target material properties and the candidate material systems we have identified to achieve these targets. The methodology, experimental hardware, and data analytics will be very similar for both programs, although the materials for the NSF SBIR program will require higher temperature melting point measurements and unique handling protocols. The high temperature decomposition mechanics will also differ significantly with the proposed materials for the NSF SBIR program, although we intend to use the same apparatus (TGA) to quantify this behavior.

We believe that we can leverage previous work from the DOE program to focus on additional high-impact materials with a smaller NSF SBIR grant of $150,000. While we believe scientifically and commercially significant results can be achieved in Phase I, we view our NSF Phase I proposal as the first portion of a larger research program, to be followed by Phase IB and Phase II applications (assuming each phase is successful). We have granted current third party investors in Halotechnics an option to invest next year when their funds would be matched in a Phase IB program. Assuming a successful SBIR Phase I, Phase IB, and Phase II would result in an NSF SBIR program totaling $740,000 which is closer in size to the DOE program.

The DOE program is a three year effort, including the development of a materials discovery workflow and primary screening program (Phase 1), a secondary screening program (Phase 2), and finally a field testing program (Phase 3). Each phase is funded with $500,000. Halotechnics has completed Phase 1 of this program and is approximately 25% complete with Phase 2. Much of the infrastructure, including the software tools for experiment design, automation, and data analytics has been developed under this grant. The experimental hardware is also largely complete. This previous work can be leveraged for the proposed NSF SBIR program to allow significant work to be accomplished with less funding by requiring less time and staffing costs to develop the methodology and apparatus for materials discovery. For example, the DOE program required 6 months of method and workflow development before discovery could begin. We are proposing a shorter 3 month period for method and workflow developing before discovery begins.

3.  Is there any material specification or property that separates salts appropriate for trough applications versus those for central receiver applications, other than the operating temperature range?

The operating range is the primary difference, but viscosity requirements also differ between trough and central receiver plants. Viscosity is of a lesser concern with central receivers since there is less piping to pump the salts through. In a central receiver plant, the salt piping is confined to the tower and thermal storage systems at the tower’s base. In a tough plant however, there are many kilometers of pipes distributed in a field which must carry the molten salt to collect the heat from the receivers. For this reason the parasitic pumping losses in a trough plant are significantly higher than in a central receiver plant. The pumping losses increase with a higher viscosity salt, making this property a higher concern for trough applications.

Candidate salts for both central receiver and trough applications have similar constraints on materials compatibility and corrosion, long term stability, and cost.

Action items from the Program Director:

1.  The specific materials systems to be explored in this effort are very unclear, as is the scientific motivation behind these choices.  Please elaborate.  Also, is there a difference in the materials phase space to be explored and what was the thinking that led to the choice of this new phase space?

The motivation for our target materials systems is driven by the desired operating range of central receiver solar thermal plants. We have surveyed the scientific literature, including phase diagram compilations and academic publications, and have selected three materials systems with properties that are promising for the proposed operating range. These salts have high thermal stability but do not have currently known eutectic mixtures with low enough melting points to be viable. Information on ternary eutectics is available for these systems, but little or no information is available on quaternary and higher order systems. We intend to explore these high order combinatorial systems to discover new eutectic mixtures with lower melting points. The data generated by the proposed program will embody a rich database of high order phase diagrams, furthering scientific knowledge in the field of inorganic materials.

Carbonates Carbonates are low cost, stable, and typically non-corrosive. They have high melting points as pure substances (typically 700 to 900 °C) but readily form eutectic mixtures. The lithium, sodium, and potassium system we show in the proposal has a eutectic melting point of 394 °C. We will target carbonate salts made from the alkali metal and alkaline earth elements. Transition metal carbonates typically decompose at temperatures too low to be of interest for this proposal.

Sulfates Sulfates are generally lower cost than carbonates, stable, and non-corrosive. They have higher melting points as pure substances (typically 900 to 1100 °C) but do form known eutectic mixtures. The sodium, potassium, and zinc system we show in the proposal has a eutectic melting point of 384 °C. We will target sulfate salts made from the alkali metal and transition metal elements. Sulfates from alkaline earth elements have very high melting points (1400 to 1600 °C) which will likely prevent them from forming eutectics in the required temperature range.

Chlorides Chlorides are low cost and stable but do have corrosive tendencies with steel. It will be important to perform additional characterization of candidate salt mixtures consisting of chlorides to quantify their long term corrosion behavior with alloys of interest for central receiver applications. Chloride melting points for pure substances are typically 600 to 800 °C. The lithium, sodium, and potassium system we show in the proposal has a eutectic melting point of 332 °C. We will target chloride salts made from the alkali metal and alkaline earth elements. Rare earth chlorides may also be potential components. Transition metal chlorides typically decompose at temperatures too low to be of interest for this proposal.

See Table 1 for a list of candidate salt components. These salts were selected on a basis of promising melting point, sufficient thermal stability, and potential availability in large scales and low cost.

| **Group** | **Material name** | **Formula** | **Melting point (°C)** | **Boiling point (°C)** |
| --- | --- | --- | --- | --- |
| ***Carbonates*** | lithium carbonate | Li2CO3 | 723 | d. 1300 |
|  | sodium carbonate | Na2CO3 | 851 | 1600 |
|  | potassium carbonate | K2CO3 | 898 | d. |
|  | rubidium carbonate | Rb2CO3 | 837 |  |
|  | cesium carbonate | Cs2CO3 | 792 |  |
|  | calcium carbonate | CaCO3 | d. 825 |  |
|  | strontium carbonate | SrCO3 | 1497 | d. 1340 |
|  | barium carbonate | BaCO3 | 811 | d. 1300 |
| ***Sulfates*** | lithium sulfate | Li2SO4 | 860 | 1377 |
|  | sodium sulfate | Na2SO4 | 884 |  |
|  | potassium sulfate | K2SO4 | 1076 |  |
|  | rubidium sulfate | Rb2SO4 | 1050 |  |
|  | cesium sulfate | Cs2SO4 | 1005 |  |
|  | chromium (III) sulfate | Cr2(SO4)3 |  |  |
|  | manganese (II) sulfate | MnSO4 | 700 | d. 850 |
|  | iron (II) sulfate | FeSO4 |  |  |
|  | copper (II) sulfate | CuSO4 | d. 560 |  |
|  | zinc sulfate | ZnSO4 | d. 680 |  |
|  | zirconium (IV) sulfate | Zr(SO4)2 |  |  |
|  | aluminum sulfate | Al2(SO4)3 | d. 1040 |  |
| ***Chlorides*** | lithium chloride | LiCl | 614 | 1360 |
|  | sodium chloride | NaCl | 800 | 1413 |
|  | potassium chloride | KCl | 790 | 1500 |
|  | rubidium chloride | RbCl | 715 | 1390 |
|  | cesium chloride | CsCl | 645 | 1297 |
|  | magnesium chloride | MgCl2 | 714 | 1412 |
|  | calcium chloride | CaCl2 | 775 | 1936 |
|  | strontium chloride | SrCl2 | 874 | 1250 |
|  | barium chloride | BaCl2 | 960 | 1560 |
|  | lanthanum chloride | LaCl3 | 859 |  |
|  | cerium (III) chloride | CeCl3 | 817 |  |
|  | neodymium chloride | NdCl3 | 758 | 1600 |

Table 1: Candidate materials for combinatorial screening. (d. = decomposition)

Other salt types exist and will be investigated as alternatives to the three primary systems described above. Fluoride salts form eutectics but are typically more expensive and more corrosive than chloride salts. Bromide salts are also more expensive. Hydroxide salts are very reactive and corrosive but have been used for many years in industrial applications. Tungstates and molybdates are known to form eutectic mixtures but are generally more expensive and have limited data on eutectic behavior. Borates are cheap but have limited data on eutectic behavior.

There is a possibility that mixed anion salt mixtures will also be useful to achieve the goals of this project. Halotechnics has experience in the behavior of mixed salt systems and the general compatibility of different salt types. For example, carbonates and sulfates are typically miscible and form eutectic mixtures.

You mention that one primary difference between the DOE proposal and this project is the materials systems (the DOE is nitrate salts).  However it seems that the DOE proposal document, while focusing on nitrates, also mentions a number of other systems.  Has the DOE work performed to date been exclusively on nitrates?  Can you certify that there’s no overlap in the DOE proposal’s materials systems and those chosen for NSF?

While we did work with some of the same materials in our DOE program as in the proposed NSF program, I can certify that there is no overlap in the materials systems due to the differing baseline mixtures and target material properties. If both programs achieve their goals, they will result in entirely distinct materials systems.

The strategy with the DOE program was to begin with a baseline mixture of three nitrate salts (lithium, sodium, potassium nitrate, with a eutectic melting point of 120 °C). We would add one additional component and search the phase space to find any new eutectic combination, then we would move on to the next additive and perform another search. After testing all feasible single additives, we began exploring higher order systems with two additives to the baseline, then three. We discovered a novel mixture with a melting point below 65 °C, which we are currently patenting. As a part of the DOE program we tested many nitrate and nitrite salts, hydroxides, fluorides, as well as some carbonate, sulfate, and chloride salts as additives. However, all our work under the DOE program was with nitrate/nitrite majority mixtures, the other salts we tested as additives were typically less than 10% of the total mixture. The additives are not soluble at higher levels at the DOE target melting point of 80 °C.

We intend to discover novel mixtures under the proposed NSF program with melting points at 200 °C. For this program our new baseline will be (using the carbonates as an example) lithium, sodium, and potassium carbonate, with a eutectic melting point of 394 °C. This baseline has a much higher melting point than what we worked with in the DOE program, and new eutectics we discover will be majority carbonate (or sulfate or chloride) with possible minority additives from other salt types. Nitrates however will not be a focus of the program because they are typically not stable up to 700 °C.

2.  Can you give the details behind the spin-off of Halotechnics from Symyx?  What were the terms of the spin-off?  What is Symyx’s current involvement in Halotechnics’ management/operations, if any?  How is the equity of Halotechnics distributed?

Symyx management made a strategic decision to exit all research operations at the end of 2009. Justin Raade had been leading the DOE eutectic salt research program as PI for one year at Symyx. He founded Halotechnics to spin out from Symyx and continue the R&D and commercialization of the nitrate salt-based materials his research was focused on. Several co-workers from Symyx joined Dr. Raade at Halotechnics, including Thomas Roark who will be involved with the proposed project. Symyx agreed to transfer the remaining portion of the grant (2 years and a total of $1 million) to Halotechnics. Symyx further agreed to assign all intellectual property related to thermal materials to Halotechnics. Halotechnics acquired the scientific software, laboratory equipment, and supplies necessary to continue the work from Symyx. In exchange for these items Symyx retained an ownership of 19% of Halotechnics.

3.  No materials and supplies are budgeted for the Phase I project.  Please explain.

Materials and supplies purchased by Halotechnics are typically used for all research programs, both externally funded and internal. For this reason they are allocated as indirect costs. For example, one pound of laboratory grade carbonate salt will be used for a variety of experiments over the course of several months, including melting point, thermal stability, and other tests. It is inevitably used on a variety of projects and cannot be budgeted as a direct cost.

We do not anticipate purchasing any major equipment to achieve the objectives of the proposed Phase I program.

4.  The proposal’s facilities and equipment section lists that the target move-in date for the company to acquire lab space is June 2009.  Please clarify and provide updated status on this.

We moved into our current facilities on June 28, 2010. Halotechnics is headquartered at the state of the art life science research facility, Emerystation North, located at 5980 Horton St. Suite 450, Emeryville, California, 94608. Completed in 2001, this facility is home to a variety of life science and biotech tenants including Halotechnics. We have leased approximately 1200 square feet of office and laboratory space.