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## MOLTEN NITRATE SALT DEVELOPMENT FOR THERMAL ENERGY STORAGE IN PARABOLIC TROUGH SOLAR POWER SYSTEMS

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### ABSTRACT

Thermal energy storage can enhance the utility of parabolic trough solar power plants by providing the ability to match electrical output to peak demand periods. An important component of thermal energy storage system optimization is selecting the working fluid used as the storage media and/or heat transfer fluid. Large quantities of the working fluid are required for power plants at the scale of 100-MW, so maximizing heat transfer fluid performance while minimizing material cost is important. This paper reports recent developments of multi-component molten salt formulations consisting of common alkali nitrate and alkaline earth nitrate salts that have advantageous properties for applications as heat transfer fluids in parabolic trough systems. A primary disadvantage of molten salt heat transfer fluids is relatively high freeze-onset temperature compared to organic heat transfer oil. Experimental results are reported for formulations of inorganic molten salt mixtures that display freeze-onset temperatures below 100°C. In addition to phase-change behavior, several properties of these molten salts that significantly affect their suitability as thermal energy storage fluids were evaluated, including chemical stability and viscosity. These alternative molten salts have demonstrated chemical stability in the presence of air up to approximately 500°C in laboratory testing and display chemical equilibrium behavior similar to Solar Salt. The capability to operate at temperatures up to 500°C may allow an increase in maximum temperature operating capability vs. organic fluids in existing trough systems and will enable increased power cycle efficiency. Experimental measurements of viscosity were performed from near the freeze-onset temperature to about 200°C. Viscosities can exceed 100 cP at the lowest

temperature but are less than 10 cP in the primary temperature range at which the mixtures would be used in a thermal energy storage system. Quantitative cost figures of constituent salts and blends are not currently available, although, these molten salt mixtures are expected to be inexpensive compared to synthetic organic heat transfer fluids. Experiments are in progress to confirm that the corrosion behavior of readily available alloys is satisfactory for long-term use.

### 1. INTRODUCTION

When combined with thermal energy storage (TES), a solar parabolic trough electrical power plant has the important ability to dispatch electrical output to match peak demand periods. An important component of TES system optimization is the choice of heat transfer fluids used in the TES system and/or the solar field. Very large quantities (millions of kilograms) of heat transfer fluid are required for energy storage in 100-MW to 200-MW power plants and entail high capital investment costs, so minimizing that cost while maximizing the heat transfer fluid performance is paramount.

The current generation of commercial parabolic trough plants uses a mixture of organic compounds, diphenyl oxide and biphenyl oxide, as the heat transport fluid in the collector field. This synthetic oil currently offers the best combination of low freezing point (12°C) and upper temperature limit (393°C) among available heat transfer fluids. However, the characteristics of this fluid have essentially set a floor on the leveled energy costs for two reasons. First, the peak allowable fluid temperature effectively limits live and reheat

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steam temperatures to about 370°C, which limits the gross efficiency of the Rankine cycle. The efficiency limit sets a minimum value for the required collector area per MWe of plant rating. Second, commercial solar projects can often reduce the levelized cost of energy through the addition of a thermal storage system. The storage system, in conjunction with a larger collector field, increases the annual capacity factor and distributes the operation and maintenance costs over a larger number of megawatt-hours. However, a direct thermal storage system using organic oil as the storage medium is generally considered to be too expensive.

Current commercial projects must rely on an indirect storage system, in which thermal energy from the field is transferred to a second fluid for storage.[1] An indirect system entails performance penalties due to the temperature drops associated with the transfer of energy between the collector loop and storage as well as the cost of collection-to-storage heat exchangers. To improve upon the temperature and pressure limitations of a synthetic oil, a molten salt can be adopted as the heat storage fluid. These inorganic fluids offer several favorable characteristics, including upper temperature limits in the range of 500°C, lower unit cost, vapor pressures of only a few Pascals and satisfactory physical properties. The fluid properties allow two important advancements in the technology. The Rankine cycle efficiency improves, which reduces the collector area required per MWe of plant rating and the combination of low fluid cost and low vapor pressure allows the heat transport fluid to be used directly as the thermal storage medium. The elimination of the oil-to-nitrate salt heat exchangers also reduces the unit storage system costs. Such a direct system would benefit greatly from a redesigned parabolic trough system, such as the Supertrough described by Kolb and Diver.[2]

Sandia National Laboratories has evaluated alternative inorganic molten salts that are inexpensive relative to organic fluids, can be used at higher temperatures of 450°C to 500°C or more (increasing power cycle efficiency), and have virtually no vapor pressure within operating temperatures and are thus amenable to use in large TES tanks. The primary disadvantage of most molten salt formulations is relatively high freezing points that range from about 130°C to 230°C depending on composition as compared to about 13°C for organic fluids. As such, considerable care must be taken to ensure that salt heat transfer fluid does not freeze in the solar field or any other system piping. Despite these engineering issues, overall evaluations for this direct molten salt heat transfer fluid approach have been encouraging, with the main issue being the selection of a molten salt formulation with an acceptable freeze point as well as high temperature durability.

Several molten salt heat transfer fluids have been used for solar thermal systems. The binary Solar salt mixture was used at the 10 MWe Solar Two central receiver project in Barstow, California.[3] It will also be used in the indirect TES system for the Andasol plant in Spain.[4] Among the candidate mixtures, it has the highest thermal stability and the lowest cost, but also the highest melting point. Hitec HTS® has been used for decades in the heat treating industry. This salt is

thermally stable at temperatures up to 454°C, and may be used up to 538°C for short periods, although a nitrogen cover gas is required to prevent the slow conversion of the nitrite component to nitrate.[5] The currently available molten salt formulations do not provide an optimum combination of properties, freezing point, and cost that is needed for a replacement heat transfer fluid in parabolic trough solar fields. Therefore, the work summarized in this report sought to develop a heat transfer fluid that will better meet the needs of parabolic trough plants.

Table 1 compares the liquidus temperatures (liquid-solid phase transition temperature) of a number of molten nitrate salt mixtures. Inspection of published phase diagrams revealed that ternary mixtures of  $\text{NaNO}_3$  and  $\text{KNO}_3$  with several alkali and alkaline earth nitrates have quite low melting points. The eutectic of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  melts at 120°C, while a mixture of  $\text{Ca(NO}_3)_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  melts at about 133°C.[7] Several eutectic systems containing three constituents are liquids as low as 52°C. Unfortunately, melts containing ammonium nitrate decompose at a low temperature and those containing silver nitrate would be prohibitively expensive.

For mixtures of molten nitrate salts containing more than three constituents, no phase diagrams appear to exist that would identify those having lower liquidus temperatures than the mixtures listed in Table 1. A straightforward approach to identifying an improved heat transfer fluid would be to add constituents to solar nitrate salt that depress the melting point significantly without compromising its properties. Metallic nitrates are obvious choices because of their miscibility and potential stability in contact with air. The thermodynamic criteria for melting point depression by additions of a second constituent have been summarized by Stolen and Grande.[6] Constituents of systems whose phase diagrams that display eutectic behavior satisfy the thermodynamic criteria, while those that display peritectic behavior do not. Although the activity coefficients for all the mutual combinations of the alkali metal nitrates and alkaline earth nitrates are not available, it is reasonable to expect that such criteria will be satisfied by additions of calcium nitrate and lithium nitrate to sodium nitrate and potassium nitrate because all binary combinations of these nitrate salts display melting point depression, as well as eutectics, as do the ternary systems.[7]

In this paper, common-anion additions to  $\text{NaNO}_3$ - $\text{KNO}_3$  mixtures (binary Solar salt) were investigated as a means to identify low melting (low liquidus temperature) mixtures. The properties of multi-component molten nitrate salt mixtures were evaluated as alternative heat transfer and/or storage fluids for a parabolic trough system. Of particular interest were the chemical stability and viscosity of multi-component mixtures that display significantly lower melting points than Solar nitrate salt. The necessary chemical stability data regarding multi-component mixtures of alkali and/or alkaline earth nitrates were obtained experimentally.

## Experimental Methods

The molten salt mixtures were prepared from  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{LiNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ -tetrahydrate Reagent Grade salts (Sigma-Aldrich Co., St. Louis, MO). To melt small quantities of the nitrate mixtures for observations of solidification behavior and viscosity measurements, weighed amounts of the individual salts were loaded into high-purity alumina crucibles and were heated in small furnaces open to the atmosphere. The temperature was initially maintained at approximately  $150^\circ\text{C}$  to allow the water of hydration of the calcium nitrate constituent to evolve slowly. After visual indications of vapor evolution ceased, the melts were heated to  $350^\circ\text{C}$  to  $400^\circ\text{C}$ , periodically stirred, and maintained at an elevated temperature for at least one overnight period before cooling and subdividing for property determinations.

Chemical stability tests were performed by melting several kilograms of molten salt mixtures in stainless steel crucibles that were equipped with gas dispersion tubes. The melts were heated to successively higher temperatures, up to at least  $520^\circ\text{C}$ , and kept at each constant temperature for several days as dry air was bubbled through the melt. Salt samples were removed at each temperature increment for chemical analysis. The nitrite ( $\text{NO}_2^-$ ) concentration was assayed by Hach Analytical Method 8153 using a Hach Co. (Loveland, CO) DR2010 UV-VIS spectrometer.

The liquidus temperature, at which solidification begins, was determined for a range of multi-component molten nitrate salt compositions. Approximately 10 grams of the salt mixtures was placed in Pyrex test tubes which were housed in several recesses in a large aluminum block to dampen temperature fluctuations. The assembly was heated in an oven and temperatures were progressively lowered from about  $20^\circ\text{C}$  above the liquidus point until a small amount of a solid phase was observed in a particular tube. The corresponding liquid phase was sampled and analyzed to determine the cation ratios of the residual liquid. Each temperature stage was maintained for at least several days and typically for a week or longer at temperatures below  $100^\circ\text{C}$ . In some tests, an alumina chip was added to assure nucleation sites were present for solidification.

The viscosity of numerous molten salt mixtures were measured using a Brookfield DV-II+ viscometer (Brookfield Engineering, Middleboro, MA). The molten salt mixtures were contained in a stainless steel tube that was heated in a small furnace at constant temperature maintained by a Brookfield Thermosel controller. Viscosities were measured by increasing the temperature sequentially from a starting temperature about  $10^\circ\text{C}$  to  $20^\circ\text{C}$  above the liquidus to a maximum of approximately  $220^\circ\text{C}$ , then successively decreasing the temperature to re-determine values for repeatability. The molten salt was maintained at each temperature sufficiently long enough for a steady state to be attained and the viscosity to indicate a constant value. The viscometer configuration was limited to about 10 cP at the low end of measured values. However, despite the limited accuracy of low viscosity measurements, it was adequate to compare the effect of the constituents of the molten salt mixtures on viscosity.

## RESULTS AND DISCUSSION

### Liquidus Temperatures of Molten Salt Mixtures

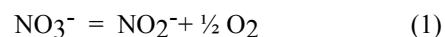
The most important property of the molten salt formulations is the liquidus temperature, at which a solid phase is formed by a particular composition. For binary mixtures of alkali metal nitrates and alkaline metal nitrates, the minimum liquidus temperature is typically a eutectic point. Ternary phase diagrams of molten nitrates are typically more complex than simple eutectic systems.[7] The phase behavior of multi-component mixtures of nitrate salts is likely to be even more complex, as well as difficult to represent graphically.

Mixtures of the four nitrate salts were identified that display liquidus temperatures less than  $100^\circ\text{C}$ . These quaternary mixtures are designated QA, QB and QC and correspond to the sodium nitrate constituent being present in relatively high, medium or low concentration. Precise specifications of these compositions cannot be given in this paper because the information is the subject of a patent application in preparation. Regardless, all of the constituent nitrate salts must be present in significant proportions to create a low-melting mixture based on those evaluated to date. Liquidus temperatures for several such mixtures are collected in Table 2 and are compared with published values for several binary and ternary nitrate mixtures.

The experimental determination of the minimum liquidus temperature and composition for the sodium-potassium-calcium-lithium nitrate system is not complete. Experiments continue to identify potentially lower-melting mixtures by extrapolating the existing data. Computational molecular dynamics methods are in progress to identify minimum liquidus compositions and provide directions within the four-dimensional composition space that indicates lower liquidus temperatures.

### Chemical Stability of Molten Salts

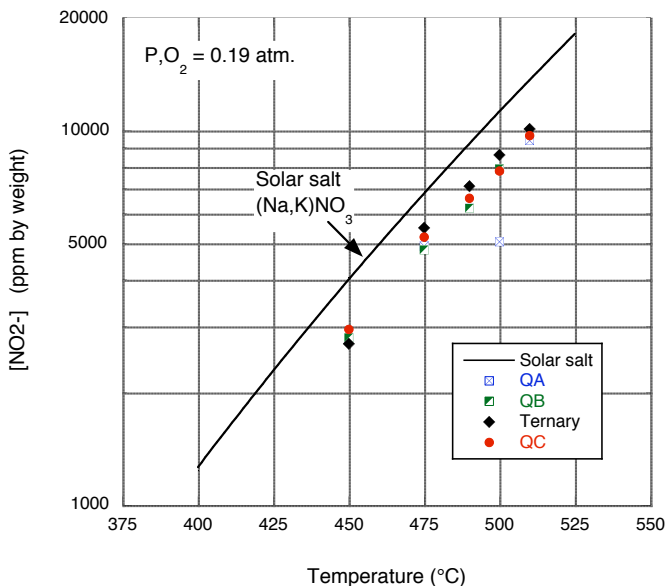
It is essential that low-melting molten salt mixtures be sufficiently stable at high temperature to realize any advantages in an solar thermal energy system. The primary aspects of molten nitrate salt chemistry that are relevant to solar thermal applications are the primary equilibrium chemistry and the reactions by which the molten salts interact with atmospheric gases such as carbon dioxide. The chemical equilibrium of the binary Solar salt mixture has been studied at high temperature and the mixture is quite stable up to  $600^\circ\text{C}$ . The primary reaction is the partial dissociation of nitrate ion ( $\text{NO}_3^-$ ) to nitrite ion ( $\text{NO}_2^-$ ) and oxygen, as shown by Equation 1. The shift from nitrate to nitrite occurs slowly and is limited by the partial pressure of oxygen in the atmosphere contacting the molten salt. The equilibrium constant for the nitrate dissociation reaction,  $K_1$ , is given by Equation 2, in which the molal concentrations of the anions and the partial pressure of oxygen represent the thermodynamic activities of the compounds.



$$K_1 = [\text{NO}_2^-] (\text{P}, \text{O}_2)^{1/2} / [\text{NO}_3^-] \quad (2)$$

Nissen and Meeker measured the equilibrium constant for an equimolar mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . [8] The equilibrium shift of the equimolar mixture results in 1.1 mol% (anion basis) nitrite at 500°C and 5.7 mol% at 600°C in contact with air. The nitrite shift behavior of ternary molten nitrate salts containing either calcium nitrate or lithium nitrate additions to binary mixtures of  $\text{NaNO}_3$  and  $\text{KNO}_3$  has been shown to follow Eqns. 1 and 2. The values of the equilibrium constant depend somewhat upon the particular composition of the mixture but are comparable to that of binary Solar Salt. [9]

The equilibrium concentrations of nitrite ion in several quaternary nitrate salt mixtures were measured between temperatures of 450°C and 510°C. The results are plotted in Figure 1 which shows ppm by weight of nitrite ion versus temperature in a semi-log format. The line indicates the behavior of binary Solar salt. The concentration of nitrite in the quaternary mixtures is somewhat less, but nevertheless comparable, to that calculated for the binary Solar salt at corresponding temperatures. The Na-K-Li nitrate eutectic mixture (shown as filled diamond symbols) was also studied and the results confirmed measurements made in an earlier study. [12] The chemical equilibrium data follow the same trend with temperature as Solar salt, which indicates that the enthalpy of the controlling chemical process is effectively the same, i.e., reaction (1).

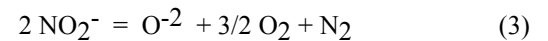


**Figure 1. Nitrite concentrations in quaternary molten nitrate salts at chemical equilibrium with air compared to binary Solar salt.**

Because the equilibrium concentration of nitrite is less than one percent at the proposed maximum operating temperatures of solar trough systems, molten salts which contain substantial concentrations of nitrite, such as Hitec HTS, must be protected from contact with air. Such contact gradually reverses reaction (1), thereby decreasing the nitrite level and consequently increasing the melting point. Low-melting molten salts

containing significant amounts of nitrite that may be identified by future experimental studies would require a system designed to minimize or avoid contact with air. Such systems are within the design envelope of a trough receiver system.

Nitrite ions, as well as nitrate ions, may decompose at sufficiently high temperature to yield several types of oxide ion species, e.g., oxide, peroxide and superoxide. [10] A generalized decomposition reaction of nitrite is given by Eqn. 3, in which oxide ion formation is accompanied by evolution of nitrogen oxides. Carbon dioxide in the atmosphere has a marked effect on the concentrations of oxide ion species in nitrate melts. [11] Carbon dioxide in air will convert oxide ions to carbonate, according to Equation 4.

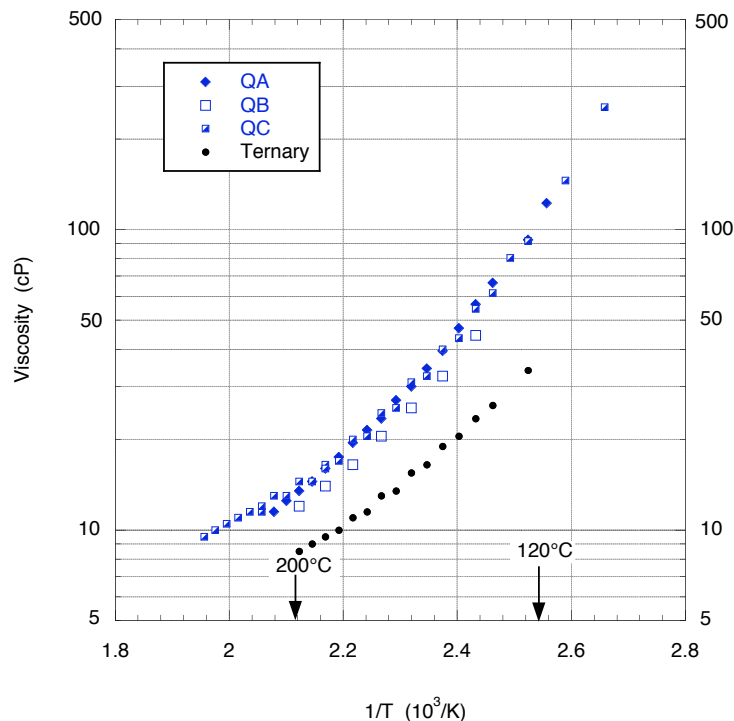


The solubility of carbonate ion in binary Solar salt is approximately 5 mol% near the eutectic point. [7] Such a high solubility presents little concern for a heat transfer and storage system because an extremely long time would be required to absorb enough  $\text{CO}_2$  from the atmosphere to saturate a large mass of molten salt. However, no phase diagrams are available for multi-component systems to indicate the solubility of carbonate. Solubility of carbonate appears to be significantly less in multi-component nitrate mixtures containing calcium nitrate. A solid phase was observed at high temperature in molten ternary mixtures of  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ , at temperatures from 500°C to about 540°C, depending on the proportion of calcium nitrate present. These melts were contacted for several days with air by a bubbler to enhance the interaction of the molten salt with carbon dioxide. [12] Chemical analysis of salt samples identified the presence of carbonate ions. The concentration of dissolved carbonate ions increased with temperature but saturation levels were not determined.

An important consequence of decomposition reactions with regard to using a molten nitrate salt mixture as a heat transfer fluid is that insoluble products may form, which tend to plug valves, pipes and heat transfer surfaces. Another effect is that the soluble oxide ions aggravate corrosion at high temperatures. The use of nitrate molten salts for heat transfer or storage at high temperature is limited by reactions (3) and (4). Observations regarding the appearance of a solid phase in multi-component molten salt mixtures are collected in Table 3. The quaternary mixtures gave visible indications of solid phases after several days at 520°C accompanied by  $\text{CO}_2$  bubbling. This material was a small fraction of the melt and was not amenable to sampling in the experimental apparatus used. In contrast, the ternary Li-Na-K-nitrate melt did not demonstrate any solid phases after similar periods at 540°C, which agrees with behavior reported in previous experiments. [12] It appears that the quaternary nitrate mixtures are chemically stable at temperatures of nominally 500°C. The chemical stability is being further evaluated during prolonged testing.

## Viscosity of Molten Salts

The physical properties of heat transfer fluids, viscosity, density, heat capacity and thermal conductivity, are needed to perform engineering design calculations of trough collector and storage systems. Viscosity is particularly important because it strongly influences pumping costs in a distributed system with extended piping runs, such as a trough receiver plant. The viscosity of a number of molten salt mixtures were measured to determine the effects of the various constituents. Figure 2 presents an Arrhenius plot of viscosity measurements for the same quaternary molten salt mixtures that were discussed in the preceding section on chemical stability. This plot also contains data for the Li-Na-K-nitrate eutectic, which freezes at 120°C, for comparison.



**Figure 2. Viscosity of quaternary molten nitrate salts compared to the ternary lithium-sodium-potassium nitrate salt.**

Calcium nitrate additions to the multi-component molten salts significantly increase the viscosity. This result has been reported previously for binary mixtures of calcium nitrate and potassium nitrate.[13] The viscosity near the liquidus temperature was approximately 200 cP, which is not an unreasonable value for handling in a TES system. The viscosity at temperatures in the median range of normal operation of a trough system, e.g., 300°C, is approximately 5-6 cP and is 2-3 cP at 400°C, as determined by extrapolating the data from the measurable temperature range. Melts that contain appreciable calcium nitrate also display curvature in an Arrhenius plot in contrast to the linear slope of the calcium-

free ternary melt. Such behavior has been reported and discussed by Rhodes and colleagues.[13]

The experimental results generally agree with published studies to the extent that the compositions of the molten salts can be compared within their respective liquid-phase temperature ranges. Calcium nitrate-containing molten salts tend to form glassy, viscous melts near the freezing temperature while lithium nitrate appears to have a minor effect on the viscosity of mixtures. Further development studies will determine how to adjust the proportions of the constituents of a quaternary molten salt to minimize the low-temperature viscosity, while optimizing other fluid properties and cost.

## Cost of constituents

Cost data for commodity quantities of the individual nitrate constituents have been difficult to establish. Commodity prices in general have become quite volatile in the global economy and have tended to increase substantially. However, the relative cost of the constituents is expected to follow the ranking, according to cation, calcium < sodium < potassium < lithium.[14] This ranking is the same as that determined a number of years ago by a study of ternary molten nitrate salts for solar central receiver systems.[15] A recent study estimated the price of binary Solar Salt was to be 0.50 \$/kg and that of a ternary nitrate eutectic mixture containing calcium nitrate to be 0.90 \$/kg.[16] In comparison, the unit price of organic heat transfer oils is approximately \$3-4 per kilogram.[16] Thus, synthetic organic heat transfer fluids are relatively expensive, as storage media, and the cost of a low-melting mixture of nitrate salts very likely will be significantly less.

The most costly constituent of the multi-component mixtures under development is lithium nitrate. Lithium salts are available in commodity amounts primarily as lithium carbonate, rather than the nitrate. This suggests that lithium nitrate may be more economical to prepare in large quantities by converting from lithium carbonate with nitric acid.[15] This conversion process could be accomplished at the solar power plant site. The price of lithium carbonate reportedly doubled in the past year due to demand as a precursor for lithium batteries.[17] After conversion, the cost of lithium nitrate is estimated to be about 3.5 \$/kg.

The costs of the constituent nitrate salts will be very important to determine as these costs strongly influence the strategy of blending the constituents of molten salt mixtures to achieve the optimal mix of properties versus cost. Although calcium nitrate is the lowest cost constituent, it produces mixtures that have relatively high viscosity. In addition, the effect on thermal stability of mixtures is such that calcium nitrate is the least favored constituent. Lithium nitrate is the most expensive constituent but reduces the liquidus temperature, does not increase viscosity significantly and has only a modest effect of reducing the maximum useable temperature of a molten salt mixture, as discussed above. Regardless, the relative costs of the constituents are likely to remain in the sequence given above and thus blending strategy will obviously be to

minimize the use of  $\text{LiNO}_3$  while optimizing chemical stability and the physical properties of the mixture.

### Corrosion properties

Molten nitrate Solar Salt (binary mixture of  $\text{NaNO}_3$  and  $\text{KNO}_3$ ) is not aggressive with regard to corrosion of a variety of metals and alloys, including stainless steels and other ferrous alloys.[18] The addition of calcium nitrate or lithium nitrate to such molten salts is not expected to aggravate the corrosiveness of the melt because the chemical properties of the melts do not appear to change significantly, as discussed above. However, no published reports were identified concerning corrosion in multi-component molten nitrates. To fully evaluate the properties of such melts, corrosion tests are being conducted with several stainless steels (316L, 304, 321, 347) and alloy steels (9Cr-1Mo, 2 ¼ Cr-1Mo) that could be used to construct molten salt systems. These tests are being performed using two of the multi-component mixtures at 500°C and will expose alloy samples for several thousand hours. The results will be reported at the conference.

### SUMMARY

A range of quaternary molten salt compositions, based on solar nitrate salt, has been identified that displays much lower liquidus temperatures and that may be useful as heat transfer fluids for solar thermal energy systems. These molten salt mixtures contain calcium nitrate and lithium nitrate to depress the melting point of a salt mixture based on sodium nitrate and potassium nitrate. The working temperature ranges of these mixtures were established experimentally and the viscosity was measured at the low temperature range of these molten salts. At the limiting maximum temperature, instability was manifested by the appearance of solid phases. However, it appears to be feasible to use these quaternary mixtures at maximum temperatures of 500°C. Although viscosity is considerably higher than binary Solar salt, it does not preclude using the molten salts at a low temperature. Cost estimates are qualitative at this point, although these molten salt mixtures are expected to be relatively inexpensive compared to organic heat transfer fluids, thus making them amenable for use in large-scale thermal energy storage systems. Experimental studies are currently in progress to fully evaluate and optimize the physical and chemical properties of these molten nitrate salts.

### ACKNOWLEDGEMENTS

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### REFERENCES

1. U. Herrmann and D. W. Kearney, *J. Solar Energy Engg.*, **124**, 145 (2002).
2. G. J. Kolb and R. B. Diver, "Conceptual Design of an Advanced Trough Utilizing a Molten Salt Working Fluid", *SolarPACES 2008*, Las Vegas, NV, Mar. 3-7, 2008.
3. "Final Test and Evaluation Results from the Solar Two Project", J. E. Pacheco, Editor, Sandia National Laboratories SAND2002-0120, January 2002.
4. <http://www.solarpaces.org/Tasks/Task1/ANDASOL.HTM>
5. Badger Energy Corp., "Design, Handling, Operation and Maintenance Procedures for Hitec Molten Salt", Sandia National Laboratories Contractor report, SAND81-8179, January 1981.
6. *Chemical Thermodynamics of Materials*, S. Stolen and T. Grande, John Wiley and Sons, Ltd., West Sussex, UK, pp. 106-109, 2004.
7. *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins and H. F. McMordie, Editors, Vols. I and II, American Ceramic Society, 1964.
8. D. A. Nissen and D. E. Meeker, *Inorg. Chem.*, **22**, 716 (1983).
9. R. W. Bradshaw and D. E. Meeker, *Solar Energy Materials*, **21** (1), 51-60 (1990).
10. B. W. Hatt, in *Molten Salt Technology*, D. G. Lovering, Editor, Plenum Press, p. 438ff, 1982.
11. J. Jordan, W. B. McCarthy and P. G. Zambonin, in *Molten Salts*, G. Mamantov, Editor, Academic Press, p. 575ff (1969).
12. R. W. Bradshaw and D. E. Meeker, "Chemical Equilibria of Molten Ternary Nitrate Salt Mixtures", Sandia National Laboratories, SAND88-8845, May 1989.
13. E. Rhodes, W. E. Smith and A. R. Ubbelohde, *Proc. Roy. Soc. London, Series A*, **285** (1401), 263-274 (1965).
14. A. Hoshi, D. R. Mills, A. Bittar, T. S. Saitoh, *Solar Energy*, **79**, 3332 (2005).
15. R. W. Bradshaw and C. E. Tyner, "Chemical and Engineering Factors Affecting Solar Central Receiver Applications of Ternary Molten Salts", Sandia National Laboratories, SAND88-8686, July 1988.
16. B. Kelly, H. Price, D. Brosseau and D. Kearney, "Adopting Nitrate/Nitrite Salt Mixtures as the Heat Transport Fluid in Parabolic Trough Power Plants," *Proceedings Energy Sustainability 2007*, ES2007-36172, A.S.M.E., Long Beach, CA, June 27-30, 2007.
17. <http://www.moneyweek.com/file/32991/two-ways-to-play-the-lithium-boom.html>, Aug. 1, 2007
18. R. W. Bradshaw and S. H. Goods, "Corrosion of Alloys and Metals by Molten Nitrates", in *High Temperature Corrosion in Molten Salts*, C. A. C. Sequiera, Editor, Trans Tech Publications, Zurich, Switzerland, 2003, ISBN 0-87849-917-2.

**Table 1. Comparison of liquidus temperatures of various molten nitrate salt mixtures. Compositions are given as mol%, cation basis. Temperature data were obtained from Phase Diagrams for Ceramists published by American Ceramic Society/NIST.**

| Na   | K    | Ca   | Li   | NH4  | Other                  | Liquidus Temp. | Notes   |
|------|------|------|------|------|------------------------|----------------|---|
| mol% | mol% | mol% | mol% | mol% | mol%                   | °C             |   |
| 50   | 50   |      |      |      |                        | 221            | Na-K-NO <sub>3</sub> eutectic                                 |
| 66   | 34   |      |      |      |                        | 238            | Binary Solar Salt   |
| 7    | 44   |      |      |      | 49 NaNO <sub>2</sub>   | 141            | Hitec® HTS  |
| 21   | 49   | 30   |      |      |                        | 133            | Ca-Na-K-NO <sub>3</sub> eutectic                              |
| 18   | 52   |      | 30   |      |                        | 120            | Li-Na-K-NO <sub>3</sub> eutectic                              |
|      | 58   | 11   | 31   |      |                        | 117            | Ca-Li-K-NO <sub>3</sub> eutectic                              |
|      | 19.3 |      | 29.4 | 51.3 |                        | 92             | Poor thermal stability due to NH <sub>4</sub> NO <sub>3</sub> |
|      | 20.7 |      |      | 60.2 | 19.1 AgNO <sub>3</sub> | 52             | Lowest melting mixture identified in literature               |

**Table 2. Liquidus temperatures of multi-component molten nitrate salt mixtures. Compositions are given as mol%, cation basis.**

| Na   | K    | Ca   | Li   | Liquidus Temp. | Notes                            |
|------|------|------|------|----------------|----------------------------------|
| mol% | mol% | mol% | mol% | °C             |                                  |
| 50   | 50   |      |      | 221            | Na-K-NO <sub>3</sub> eutectic    |
| 21   | 49   | 30   |      | 133            | Ca-Na-K-NO <sub>3</sub> eutectic |
| 18   | 52   |      | 30   | 120            | Li-Na-K-NO <sub>3</sub> eutectic |
|      | 58   | 11   | 31   | 117            | Ca-Li-K-NO <sub>3</sub> eutectic |
| High | +    | +    | +    | < 95           | QA                               |
| Med. | +    | +    | +    | < 95           | QB                               |
| Low  | +    | +    | +    | < 95           | QC                               |

**Table 3. Approximate thermal stability limits of selected molten nitrate and nitrate-nitrite salt mixtures. Compositions are given as mol%, cation basis. The temperature values refer to melts in contact with air except for Hitec®.**

| Na   | K    | Ca   | Li   | Other                | Maximum Temp. | Notes                                |
|------|------|------|------|----------------------|---------------|--------------------------------------|
| mol% | mol% | mol% | mol% | mol%                 | °C            |                                      |
| 66   | 34   |      |      |                      | 600           | Binary Solar Salt (60-40, by weight) |
| 7    | 44   |      |      | 49 NaNO <sub>2</sub> | 450 to 538    | Hitec® HTS (Nitrogen cover gas)      |
| 18   | 45   |      | 37   |                      | 550           | Reference 15                         |
| 30   | 50   | 20   |      |                      | 505           | Reference 15                         |
| 20   | 50   | 30   |      |                      | 480           | Reference 15                         |
| High | +    | +    | +    |                      | ~ 520         | QA                                   |
| Med. | +    | +    | +    |                      | ~ 520         | QB                                   |
| Low  | +    | +    | +    |                      | ~ 520         | QC                                   |
| 18   | 45   |      | 37   |                      | > 540         | Li-Na-K-Nitrate eutectic             |