SANDIA REPORT

SAND88-8686 Unlimica Release Printed July 1988

Chemical and Engineering Factors Affecting Solar Central Receiver Applications of Ternary Molten Salts

Submitted to American Institute of Chemical Engineering National Meeting Proceedings

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Prepared by Sandia National Laboratories Albuquerque, New Mexico 87185 and Livermore, California 94551 for the United States Department of Energy under Contract DE-ACO4-76DP00789

TOTAL PAGES: 33

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SAND88-8686 Unlimited Distribution Printed July 1988

CHEMICAL AND ENGINEERING FACTORS AFFECTING SOLAR CENTRAL RECEIVER APPLICATIONS OF TERNARY MOLTEN SALTS

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ABSTRACT

We have investigated the feasibility of using molten salt mixtures that melt at relatively low temperatures (120°C to 180°C), which consist of a sodium/potassium nitrate mixture with added lithium or calcium nitrate, as working fluids in solar thermal energy systems. The chemical stability of these ternary mixtures at high temperature, a key unknown property, was determined experimentally. Ternary salt mixtures are somewhat less stable than the binary mixture currently used, but appear to be usable at maximum temperatures of 460°C to 550°C, depending on composition. The implications of the properties of ternary salt mixtures in the engineering design of solar central receivers, especially concerning operating temperature range, efficiency, and subsystem component costs, were determined for selected compositions.

SOLAR THERMAL TECHNOLOGY FOREWORD

The research and development described in this document were conducted within the U. S. Department of Energy's (DOE) Solar Thermal Technology Program. The goal of the Solar Thermal Technology Program is to advance the engineering and scientific understanding of solar thermal technology, and to establish the technology base from which private industry can develop solar thermal power production options for introduction into the competitive energy market.

Solar thermal technology concentrates solar radiation by means of tracking mirrors or lenses onto a receiver where the solar energy is absorbed as heat and converted into electricity or incorporated into products as process heat. The two primary solar thermal technologies. central receivers and distributed receivers, employ various point and linefocus optics to concentrate sunlight. Current central receiver systems use fields of heliostats (two-axis tracking mirrors) to focus the sun's radiant energy onto a single tower-mounted receiver. Parabolic dishes up to 17 meters in diameter track the sun in two axes and use mirrors or Fresnel lenses to focus radiant energy onto a receiver. Troughs and bowls are linefocus tracking reflectors that concentrate sunlight onto receiver tubes along their focal lines. Concentrating collector modules can be used alone or in a multi-module system. The concentrated radiant energy absorbed by the solar thermal receiver is transported to the conversion process by a circulating working fluid. Receiver temperatures range from 100°C in lowtemperature troughs to over 1500mC in dish and central receiver systems.

The Solar Thermal Technology Program is directing efforts to advance and improve promising system concepts through the research and development of solar thermal materials, components, and subsystems, and the testing and performance evaluation of subsystems and systems. These efforts are carried out through the technical direction of DOE and its network of national laboratories who work with private industry. Together they have established a comprehensive, goal directed program to improve performance and provide technically proven options for eventual incorporation into the Nation's energy supply.

To be successful in contributing to an adequate national energy supply at reasonable cost, solar thermal energy must eventually be economically competitive with a variety of other energy sources. Components and system-level performance targets have been developed as quantitative program goals. The performance targets are used in planning research and development activities, measuring progress, assessing alternative technology options, and making optimal component developments. These targets will be pursued vigorously to ensure a successful program.

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EXECUTIVE SUMMARY

The molten salt currently used as a working fluid in solar central receiver (SCR) systems for electric power production is a mixture of sodium nitrate (60 wt.%) and potassium nitrate (40 wt.%). Since this salt melts at a temperature near 240°C, all components in contact with it (except the solar-heated receiver panels) must be heat-traced to avoid freezing the salt or severe thermal shock. A working fluid with a lower melting point (preferably below 150°C) would allow heat-trace requirements to be reduced or, for larger components, eliminated. Furthermore, if the working temperature range could be extended to lower temperatures, improved receiver thermal efficiency and decreased component costs could lower the levelized cost of energy.

Several techniques for reducing the freezing point of molten salt working fluids are possible. They include use of ternary nitrate salt mixtures, addition of high concentrations of sodium nitrite (such as in Hitec, a tradename of DuPont) and hydration of the salt (a technique limited to receiver startup and shutdown). The first option has not been extensively explored and is the focus of this report.

Ternary mixtures of NaNO₃ and KNO₃ with other alkali or alkaline earth nitrates have much lower melting points than the present SCR salt mixture. For example, the eutectic of LiNO₃, NaNO₃ and KN₃ (30:18:53, wt.%) melts at 120°C, while a 30:24:46 (wt.%) mixture of Ca(NO₃)₂, NaNO₃ and KNO₃ melts at approximately 160°C. Calcium nitrate has the added advantage of low cost, while lithium nitrate is more expensive than the present SCR salt.

A key question regarding the properties of ternary salt mixtures is whether their chemical stability at high temperature is sufficient to obtain a useful working temperature range. We have determined the extent of decomposition of several ternary nitrate mixtures of Ca/Na/K/NO₃ and Li/Na/K/NO₃ in the presence of air. We observed that stability of these mixtures depends on decomposition reactions involving nitrite, rather than the initial reaction of nitrate decomposing to nitrite. From an engineering viewpoint, the maximum usable temperature is limited by the formation of insoluble or corrosive oxide decomposition products. Although the hightemperature chemical stability of molten mixtures of Na/K/NO₃ was reduced somewhat by adding either calcium nitrate or lithium nitrate, the ternary mixtures appear to be usable at relatively high temperatures. Ca/Na/K/NO₃ mixtures can be used to at least 460°C to 500°C (comparable or slightly greater than Hitec), while Li/Na/K/NO₃ salts appear usable up to at least 500°C to perhaps 550°C

The impact of using ternary molten salt mixtures on the levelized energy cost of an SCR has been calculated. The viscosity of the salts and their cost have a system impact of less than $\pm 3\%$. The effects of variation in temperature range, however, can be substantial. It appears that extending the operating temperature range 100°C lower (to 185°C) could reduce LEC by up to 6%, as well as offer benefits in heat-tracing and cold component durability. Decreasing both the upper and lower operating temperatures by 100°C could offer a small advantage (about 1%) for cheaper salts containing calcium nitrate.

The results of this study indicate that significant advantages in costs and operational convenience may be realizable using ternary salts that melt at low temperatures as working fluids in SCRs. However, many practical questions must be addressed before they are applied to SCR electric power systems. Two areas offer significant economic incentive to warrant consideration for further development of this aspect of SCR technology. First, an accurate determination of the cost of lithium nitrate, when produced in large quantities, should be made since this salt offers the greatest engineering advantages. The feasibility of using regeneration techniques to extend the maximum useful temperature of less expensive selts, such as Hitec or calcium nitrate mixtures, should also be evaluated.

CHEMICAL AND ENGINEERING FACTORS AFFECTING SOLAR CENTRAL RECEIVER

APPLICATIONS OF TERNARY MOLTEN SALTS

INTRODUCTION

The working fluid of a solar central receiver (SCR) power plant determines many of the characteristics of the plant since this fluid performs the key function of collecting and storing solar energy. These characteristics include the operating temperature range, which determines potential applications, and the design of plant support systems, such as pumping and heat-tracing requirements. In addition, storage capabilities, for coupling the non-steady solar energy source to the application and for optimizing time-of-day usage of the collected energy, depend strongly on fluid properties.

Selection of the working fluid has been a major concern since the SCR concept was first investigated. Various gases, liquids, and solids have been considered depending on the desired operating conditions and end-use application [1]. Liquids (e.g., water, liquid metals, molter salts) offer convenience and good heat transport characteristics, although their operating temperature ranges are limited. Vaporization or chemical instability generally limits the upper operating temperature, while freezing at lower temperatures can necessitate the cost and complexity of heattracing. Recent studies have shown molten nitrate salts and liquid sodium to be particularly suitable for use in SCR systems, operating in the 280-600°C range, coupled to Rankine-cycle electric power generation systems (EPGS) [1]. Based on cost and safety considerations, the Central Receiver Utility Studies (CRUS) [2] selected a molten nitrate salt (NaNO₃KNO₃, 60:40, wt.%), herein referred to as solar nitrate salt, as the best working fluid.

In order to understand the potential impacts of the working fluids on SCR systems, we briefly review how a central receiver system works. Figure 1 is a simplified schematic of an SCR system using solar nitrate salt. Salt from the cold (285°C) storage tank is circulated through the receiver, where it is heated to 565°C by focused solar energy reflected from the field of heliostats (sun-tracking mirrors). The hot salt is stored in another storage tank, from which it is pumped to a steam generation system (SGS) to raise steam for the EPGS turbines when needed. The salt then returns to the cold tank to begin the cycle anew.

The desired properties of the molten salt working fluid include thermal stability over the working temperature range, a low melting point, compatibility with materials and low cost. These factors impact SCR systems as follows:



Figure 1. Solar Central Receiver System Schematic

i) The thermal stability of the molten salt generally limits the maximum system temperature. This maximum directly affects the operating temperature of the EPGS and thus its efficiency.

ii) The melting point of solar nitrate salt $(240^{\circ}C)$ is high enough to require trace-heating of all components to prevent freezing and thermal shock during startup. The trace-heating at this temperature must be electrical, implying reliability limitations and parasitic energy consumption. If the melting point could be lowered substantially (say to $(150^{\circ}C)$, trace-heating could probably be eliminated for large lines and tanks and could be accomplished inexpensively with pressurized hot water or steam on remaining lines.

iii) A broad working temperature range (maximum vs. melting point) improves efficiency since the inventory of salt and pumping requirements are decreased for a given energy capacity.

iv) At high temperatures, chemical decomposition of nitrate and nitrite salts can result in production of corrosive solutes (alkali oxides) which attack containment materials. Currently, Alloy 800 and 300-series stainless steels are used for all hot salt components, while carbon steels are used for cold components. Decomposition of solar nitrate salt above 600°C sets the upper temperature limit for stainless alloys in this salt.

v) The cost of the working fluid obviously has a major impact on optimizing system design. High salt costs, for example, offset the advantages of large storage systems in increasing the value of power delivered. The salts we are studying here range in cost from below that of solar nitrate salt to substantially higher.

Solar nitrate salt is currently recognized as the best compromise between performance and cost and has been used in large-scale engineering demonstrations of SCRs [3]. The properties of this mixture have been characterized by an extensive research program and the results were reviewed in detail elsewhere [4]. Although numerous surveys of molten salts for solar thermal energy applications have been conducted [5-7], few realistic alternatives to solar nitrate salt are evident in these compilations. The characteristics of several possible substitutes are discussed below, including a few identified by this study.

Hitec (a tradename of DuPont), a mixture of alkali nitrates and nitrites consisting of $NaNO_2-NaNO_3-KNO_3$ (40:7:53, wt.%), m.p. 141^OC, has been used industrially as a heat transfer fluid for many years. This mixture was recently used in an SCR in France [8], although at a much lower maximum temperature (450^OC) than systems using solar nitrate salt. Disadvantages associated with the high concentration of nitrite include chemical instability and somewhat higher cost. Contact with air oxidizes nitrite to nitrate and raises the melting point, thereby requiring a hermetically-sealed system. Even in a sealed system, alkali oxides are formed at high temperature, which will aggravate corrosion. Recent development of side-stream regeneration systems for industrial purposes allows Hitec to be used at temperatures up to 540°C for short periods by reversing the decomposition reactions [9]. The cost effectiveness of regeneration systems for SCRs has not yet been determined, however.

A convenient approach to producing an improved working fluid would be to add a constituent to solar nitrate salt that depresses the melting point significantly without compromising its properties. Metallic nitrates are likely choices because of their miscibility and potential stability contact with air. Inspection of published phase diagrams revealed that ternary mixtures of NaNO, and KNO, with several alkali and alkaline earth nitrates have quite low melting points. The eutectic of LiNO, NaNO, and KNO₃ (30:18:53, wt.%) melts at 120° C, while a mixture of Ca(Å), NaNO₃ and KNO₃ (30:24:46, wt.%) melts at about 160° C [10]. Other metallic nitrates are either unlikely to be stable [11] or are not available in large quantities. Lithium-containing nitrate mixtures have been mentioned as possible working fluids for thermal energy storage [6], while calcium-containing mixtures do not appear to have been previously considered. The available data concerning these ternary salt mixtures are not adequate for realistic engineering appraisals of SCR systems. In particular, thermal stability has not been determined. Although the behavior of the pure salts indicates that mixtures are unlikely to be as stable as solar nitrate salt, the behavior of ternary mixtures, which are primarily sodium and potassium nitrate, cannot be predicted.

In this paper, we investigated the feasibility of using ternary molten salt mixtures as alternatives to solar nitrate salt in an SCR system. We were particularly interested in the chemical stability and costs of ternary mixtures with significantly lower melting points than solar nitrate salt. The necessary chemical stability data regarding ternary mixtures of alkali and/or alkaline earth nitrates were obtained experimentally. We then analyzed potential impacts of these alternative working fluids on SCR electric power systems.

METHODOLOGY

Experiments were performed to determine the extent of decomposition (with respect to nitrite and oxide ions) of ternary salt mixtures at equilibrium in oxygen-saturated melts. Experiments with Ca/Na/K/NO2 mixtures were conducted in air to examine conditions relevant to molten salt storage tanks vented to the atmosphere. Experiments with Li/Na/K/NO2 mixtures were conducted in oxygen, simulating storage tanks with CO2 scrubbers, since atmospheric CO, can react with the melts to form carbonates. The ternary nitrate mixtures were prepared from reagent grade salts without further purification. Calcium nitrate tetrahydrate was used as a source of calcium nitrate, while all other salts were nominally anhydrous. Melts were allowed to equilibrate for a prolonged period of time at various temperatures and samples were then analyzed in aqueous solution for decomposition products by titremetric methods. The aggregate amount of oxide ions formed is reported since all types of oxide ion species are converted to hydroxide by water. The details of the experimental procedures have been reported elsewhere [12].

The engineering analysis of the effect of the properties and costs of various salt dixtures on the performance of a central receiver plant was conducted using the CRUS design as a baseline. For a given system, the sizes and thermal ratings of the varicus components are determined to maximize the return to the investors. This involves maximizing profits by minimizing the capital and operating costs of energy production while maximizing th value of the product. Jenerally, this means more than simply minimizing the levelized ost of energy (LEC), since, for example, the cost of energy might be lowest with very little thermal storage. However, increasing the amount of storage to allow power generation during times . day when the value c^{c} energy is highest might increase the return on investment. We assume that the value-related aspects of plant sizing are already optimized. Since we are making small changes in the overall plant, we then need to consider only the impact on LEC of changing the working fluid. For any given change in working fluid or operating conditions, a new optimization would ultimately be required to maximize the return on investment but is not necessary to understand the potential impacts on system performance.

RESULTS AND DISCUSSION

Chemical Stability of Alternate Molten Salts

The equilibrium chemistry of molten nitrate salts has been reviewed thoroughly elsewhere [11,13]. Metal nitrates decompose to yield nitrites and oxygen, according to Eq. 1.

(1)
$$MNO_3 = MNO_2 + 1/2 O_2$$
.

The equilibrium constant, K_1 , is given by

(2)
$$K_1 = (NO_2)(P_{0_2})^{1/2} / (NO_3),$$

where the molal (mol/kg) concentrations of the anions are substituted for activities. Nitrite may subsequently decompose to yield several oxide species by a number of reactions. It is the formation of these secondary decomposition products that limits the useful temperature range, since oxides generally have limited solubility in the melt, tend to aggravate corrosion, and can interact with atmospheric carbon dioxide to form carbonates (which also have limited solubility).

In this study, we characterized the decomposition behavior of ternary nitrate melts by the amounts of nitrite ion and various oxide ion species formed at equilibrium (in lithium-containing mixtures) or by the temperature at which insoluble phases were first observed (calciumcontaining mixtures). For the purposes of this report, we present those results that are necessary to evaluate the impact of molten salt mixtures on the cost-effectiveness of various SCR sub-systems. A detailed discussion of the chemistry of these ternary mixtures is available elsewhere [12].

With respect to the nitrate-nitrite reaction, the ternary mixtures behaved quite similarly to the binary solar salt mixture. The values of the equilibrium constants, K_1 , for Eq. 1 are plotted in Figure 2 for a range of concentrations of $Ca(NO_3)_2$ and $LiNO_3$. A value of $K_1 = 0.01$ corresponds to the formation of 0.2 molal nitrite in the melt or approximately 2 wt.%. Lithium-containing mixtures had K_1 values approximately equal to solar nitrate salt, except for a slight decrease at low LiNO₃ concentration. Calcium-containing mixtures displayed slightly lower values of K_1 than the binary, although the effect of $Ca(NO_3)_2$ concentration was negligible over the range studied.



Figure 2. Arrhenius plot of the equilibrium constants for the nitrate/nitrite/oxygen reaction in molten mixtures of alkali and alkaline earth nitrates

High-temperature decomposition of calcium-containing ternary salts was manifested by the irreversible formation of a solid phase. The temperature at which this phase appeared was only resolved approximately since equilibrium measurements were performed at increments of $20-25^{\circ}C$. The temperature at which the insoluble material formed decreased as the concentration of Ca(NO₃)₂ increased, as shown in Table 1. The solid phase was identified as calcium carbonate by x-ray diffraction analysis and represents the product of the reaction of the carbon dio ide in air with oxide ions formed by decomposition of nitrite. Excluding CO₂ from the melt, by scrubbing it from the air in a salt storage tank, would raise the maximum temperature somewhat, but the formation of CaO, another compound with low solubility, would still limit the upper temperature.

Melts containing lithium nitrate remained homogeneous liquids at higher temperatures than calcium nitrate-containing ternary mixtures. This was due to the greater inherent stability of lithium-containing mixtures, as well as the absence of CO_2 from the cover gas in experiments with LiNO₃, which prevented carbonates from forming. Lithium-containing ternary salts produced soluble oxide ion species, whose concentration was very sensitive to the amount of LiNO₃ in the mixtures. Figure 3 shows how the total oxide concentration varies with LiNO₃ content at the three temperatures studied.

Limited solubility of oxide species in lithium-containing ternary melts at low temperature may limit the useful maximum temperature. However, lacking these data at present, we have ten tively estimated the upper temperature limit of these melts from corrosion considerations. Previous studies conducted in a lithium-containing ternary salt at 600° C imply that the corrosion rates of Incoloy 800 and 316 SS will be moderate at 550° C, despite the presence of some oxide [14]. We also note that by minimizing the amount of LiNO₃ used, and accepting a slightly higher melting point, the oxide concentration can be reduced to a fraction of that of the eutectic ternary mixture (Fig. 3).

Given the observations of the high-temperature stability of these salt mixtures, we have made preliminary estimates of their maximum useful temperatures. These estimates are summarized in Table 1, which also lists the melting points of the mixtures. The highest working temperature was obtained for a ternary mixture containing lithium nitrate, which also had the lowest melting point. Calcium nitrate-containing mixtures rival the properties of Hitec salt, but fall below the maximum temperatures currently achieved with solar nitrate salt. The following section considers the

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Figure 3. The total oxide ion content of ternary molten salt mixtures of Li/Na/K/nitrates

TA	BI	E	1

Temperature	Stabilit	y of	Ternary	Mo	lten	Salt	Mixtures
-------------	----------	------	---------	----	------	------	----------

	Melting	Upper	Solid Phase
Composition	Point	Limit	Observed
(wt.%)	(°C)	(°C)	(°C)
Ca(NO3)2:Na:K:NO3			
16:34:50	190	500	515 (a)
30:24:46	160	480	504 (a)
42:15:43	140	460	481 (a)
Li:Na:K:NO3			
12:18:70	200	550 (b)	
20:28:52	150	550 (b)	
27:33:40	160	550 (b)	
30:18:52	120	550 (b)	
NaNO ₂ :Na:K:NO ₃ (Hitec)			
40:7:53	141	450 (c)	
			•

(a) The insoluble phase was primarily CaCO₃.
(b) In the absence of atmospheric CO₂.
(c) Based on References 8 and 9.

impact of the properties of these salts on the sub-systems that comprise an SCR power generating system.

Impacts of Alternate Molten Salts on SCR Systems

Based on the experimental results, there appear to be a number of alternative salt mixtures with melting points from 120 to $160^{\circ}C$ (120 to $80^{\circ}C$ lower than solar nitrate salt) for use in SCR systems. Upper temperature limits for these salts vary from about $460^{\circ}C$ to nearly that of solar nitrate salt ($565^{\circ}C$). In the analyses that follow, we will determine the impact on LEC of two factors, operating temperature range and salt costs. We have considered three temperature ranges:

Case	Range (^O C)	Corresponding Molten Salt
Base	285-565	solar nitrate salt (current technology)
1	185-565	a low-melting salt stable at high temperature; e.g., 20% LiNO ₃ in solar nitrate salt or regenerated Hitec are possibilities
2	185-465	a low-melting salt stable at moderate temperature; e.g., 30% Ca(NO ₃) ₂ in solar nitrate salt and Hitec are examples

For each of the above cases, we have looked at the effects of salt cost for four salt mixtures, which are listed below in order of increasing cost.

salt-A - 30% calcium nitrate	(42:28:30, wt.% Na/K/Ca/NO ₃),
salt-B – solar nitrate salt	(60:40, wt.% Na/K/NO3),
salt-C - flitec	(7:53:40 vt.% Na/K/NO ₃ ,NaNO ₂),
salt-D - 20% lithium nitrate	(48:32:20, wt.% Na/K/Li/NO ₃).

Although all of the salt mixtures are obviously not applicable to all operating temperature ranges, we performed calculations for the entire matrix to be complete.

For a baseline case, we used a plant design taken from the recent CRUS, in which solar nitrate salt was the working fluid [2]. Relevant plant parameters and performance are summarized in Table 2 for this 100-MWe plant. All potential impacts of alternative working fluids are relative to TABLE 2

Design Parameters for a Solar Central Receiver Power Plant

Configuration	South-shifted surround field External cylinder receiver			
Receiver Rating	468 MW (thermal)			
Net Turbine Output	100 MW (electric)			
Storage Capacity Annual Electric	6 hours			
Generation Receiver Thermal	322 GWh			
Efficiency	88% (annual)			
EPGS Efficiency Salt Temperature	412			
Maximum	565 ⁰ C			
Minimum	285 ⁰ C			

this plant. We assumed that no major system design changes would be required and that the components could be fabricated from the same materials. These assumptions are valid to the extent that we limit the temperature range so that the chemical stability of the fluid is as good as current systems. Given these assumptions, the impact of the working fluid reduces to effects on receiver efficiency, EPGS efficiency, storage system costs, and pump parasitics. We will look at each factor individually, and then combine the results to consider the overall impact of each case.

Receiver thermal efficiency is a function of temperature, with losses occurring by convection and radiation. On an annual basis, the base case receiver efficiency is about 88%, with a 3% loss to convection and a 9% loss to radiation [2]. The other cases considered result in some lowering of the receiver temperature, and thus in some increase in annual produced energy. Convective losses are directly proportional to the difference between the surface temperature of the receiver and ambient temperature; a simplified calculation is accurate enough for our purposes here. We assumed that the average surface temperature could be approximated by averaging the inlet and outlet temperatures and adding a value $(30^{\circ}C)$ for the average temperature gradient across the receiver tube wall. The convective loss for the base case (3%) would change to 2.6% for case 1 and to 2.3% for case 2.

Radiative losses are proportional to the difference in the fourth power of the local absolute panel temperature and ambient temperature. Dividing the receiver into three temperature zones (lower, average, and upper), we estimated the loss from each and calculated the relative change in radiation loss for each case. The base case radiation loss (9%) becomes 7.8% for case 1 and 5.2% for case 2. Receiver losses and changes in annual energy are summarized in Table 3, Line 1. Net annual energy can increase 1.8% for case 1 and 5.1% for case 2.

EPGS efficiency is a function of the peak temperature of the turbine working fluid (steam). Assuming the steam generator design can be adjusted to give similar performance at the lower temperatures (i.e., 438°C steam from a 465°C salt vs. 538°C steam for the 565°C salt case), EPGS efficiency will fall from the 41% of the base case to about 39.5% for the lower temperature cases for commercially available turbines [15]. This will result in a 3.7% decrease in annual energy for case 2, as shown in Table 3, Line 2.

Storage costs depend on the working temperature range, which affects the storage system size and the salt costs. Neglecting changes in heat

TABLE 3 Summary of Impacts on Levelized Energy Cost (LEC) of Costs and Properties of Selected Molten Salt Mixtures

		· ·		Base	Case 1	Case 2
		Tezperature Range	min.	285	185	185
		(°C)	max.	565	565	465
<u>Line</u> (1)	Impact o	of Receiver Temperature Annual Efficiency	on			
		Annual Radiative Los	s	9.0%	7.8%	5.2%
		Annual Convective Lo	SS	3.0%	2.6%	2.3%
		Total Annual Thermal	Loss	12.0%	10.4%	7.5%
	Net	Annual Additional Ene	rgy	0.0%	1.82	5.1%
(2)	Impact o	of Upper Salt Temperatu EPGS Efficiency	re on	0.02	0.02	-3.7%
(3)	Relative	e Storage System Size		100.0%	74.0%	100.0%
(4)	Impact of on LEC	of Salt Cost and Temp. I from Storage System Co.	Range sts			
			Cost			
		Solt A 30% Coloium	$\frac{(3)(g)}{0.62}$	0 044	3 744	0.97
		Salt R . Solar Nitrato	0.02	-0.04^	-3.2%*	-0.0%
		$Salt_C = Hiteo$	0.75	0.04	2.04=	0.67
		Salt-D - 20% Lithium	1.18	3.1%	-0.3%	3.1%
(5)	Impact o Reqd. Fl	of Temp-Avgd. Viscosity ow on LEC from Pump Pa	and rasitics			
		Temp-Avgd. Viscosity	(mPa.s) correctio	1.78	2.70	3.25
			factor			
		Salt-A - 30% Calcium	1.2	0.2%*	-1.4%*	0.8%
		Salt-B - Solar Nitrate	1.0	0.0%	-1.5%*	0.6%*
		Salt-C - Hitec	1.0	0.0%	-1.5%#	0.6%
		Salt-D - 20% Lithium	1.0	0.02	-1.5%	0.6%
(6)	0verall	Impact on LEC				
		Salt-A - 30% Calcium		-0.6%*	-6.2%*	-1.3%
		Salt-B - Solar Nitrate		0.0%	-5.8%*	-0.7%*
		Salt-C - Hitec		0.6%#	-5.4%#	-0.1%
		Salt-D - 20% Lithium		3.1%	-3.6%	2.4%

* Hypothetical case, not a practical use of this salt.
Hitec would require regeneration at this temperature range.

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capacity (which are probably small for the salts considered here), storage system size is inversely proportional to the temperature range, meaning the base case storage size will decrease by 26% for case 1, while remaining the same for case 2 (Table 3, line 3). Since the storage system accounts for about 10% of the plant costs, the LEC will decrease by 2.6% in case 1, while remaining unchanged for case 2.

In considering salt costs, we assumed salt prices (per kg) of 0.62for the 30 wt.% calcium nitrate mixture (A), 0.73 for solar nitrate salt (B), 0.82 for Hitec (C) and 1.18 for the 20 wt.% lithium nitrate mixture (D). The last price (D) assumes that lithium nitrate could be obtained for 3.00/kg by large-scale production from Li₂CO₃. Since salt inventory accounts for half of the storage system cost in the base case (which in turn is 10% of the system cost), overall LEC impacts can be calculated by applying changes in salt costs to 5% of the LEC. Storage size and salt cost can impact the LEC by roughly $\pm 3\%$ as shown by the results summarized in Table 3, Line 4. Obviously, moving toward cheaper salt (calcium nitrate in this case) and using a wider operating temperature range decreases costs, and vice versa.

The operational cost of pump parasitics accounts for about 7% of the LEC of the base plant, roughly half of the total parasitic load at the design point [16]. Any increase in operating temperature range will tend to decrease pump parasitics since the same amount of fluid will hold more energy. Increases in viscosity (because of differing fluid properties or temperature ranges) will, of course, increase pump parasitics. Although we have no detailed information on the viscosities of the ternary mixtures, we expect the lithium-containing salt and Hitec to be about the same as solar nitrate salt and the calcium-containing salt to be about 20% more viscous. Table 3, line 5 summarizes the net impact of pump parasitics for each of the cases discussed. The temperature-averaged viscosities shown in Table 3 are for solar nitrate salt and are adjusted by a factor of 1.2 for 30% calcium nitrate (salt-A). The effect of decreasing temperature on viscosity is slightly outweighed by the improvements in operating temperature range in case 1.

The overall impacts on the LEC of using various molten salts were obtained by combining the effects of receiver efficiency, EPGS efficiency, storage system size and cost, and pumping parasitics. These impacts are summarized in Table 3, line 6. These results indicate that operating with an alternative salt in the current temperature range will have minimal impact on the LEC, while expanding the temperature range to lower temperatures would decrease the LEC 4-6%. This impact is significant and further investigation to verify our projected cost of lithium nitrate, or to determine the feasibility of regenerating less-stable salts such as calcium nitrate mixtures and Hitec, is warranted. In addition, using an inexpensive salt such as the 30% calcium nitrate mixture at a reduced temperature range (case 2) offers a slight LEC advantage (about 1%) and might be warranted given the factors discussed below.

There are a number of very important impacts of using salts that melt at low temperatures that cannot be easily quantified. The first involves materials issues in systems in which the operating temperature range is shifted lower by 100°C (case 2). All the systems examined would still require stainless steel alloys to operate above 400°C. However, the conditions imposed on the materials (particularly in the receiver) would be much less severe and offer significant potential for lifetime improvements. Cold-side components, operating well below 200°C, are likely to be more durable than the present components at 285°C. In addition, the possibility exists that components could be re-designed to reduce costs because of the less severe environment.

The second uncertain impact is heat-tracing. While simple in concept, heat-tracing involves a significant capital cost and parasitic energy loss. In addition, it has been a considerable problem in molten salt SCR testing due to various reliability problems, and it could affect system availability. While is it unlikely that an SCR system using any working fluid with a freezing point significantly above ambient could be operated without heat-tracing, reduction of the melting point (e.g., to 120°C or 160°C) could greatly reduce the need for it (particularly on large lines), while increasing the reliability of the heat-tracing still needed. In addition, using thermal (pressurized water or steam), instead of electrical, heat-tracing would reduce overall parasitic losses and mitigate reliability problems.

CONCLUSIONS

We have identified several ternary molten salt compositions, based on solar nitrate salt, that melt at much lower temperatures and that may be applicable to solar thermal energy systems. We established the working temperature ranges of these mixtures experimentally and determined the consequences of operating an SCR electric power system with salts having their characteristics, using a recently-prepared SCR design as a baseline. These molten salt mixtures, which employ lithium or calcium nitrate to depress the melting point of a salt mixture that is primarily sodium and potassium nitrate, demonstrated somewhat reduced chemical stability in contact with air at high temperatures, compared to solar nitrate salt. At the limiting temperature, instability was manifested by formation of corrosive, soluble decomposition products or the appearance of solid phases. However, it may be feasible to use these ternary mixtures at maximum temperatures of 460° C to 550° C, depending on composition. Mixtures containing lithium nitrate are particularly attractive because of the expanded operating temperature range obtainable.

The impacts of the characteristics of ternary molten salt mixtures, which have different working temperature ranges, physical properties (e.g. viscosity) and costs, on the levelized energy cost of electric power production have been calculated. The viscosity of the salts and their cost, within the estimates used here, have a system impact of less than 3%. The effects of variation in temperature range, however, can be substantial. It appears that extending the operating temperature range 100°C lower (to 185°C) would reduce the LEC by up to 6%, as well as provide benefits in heat-tracing and cold component durability. Decreasing both the upper and lower operating temperatures by 100°C could offer a small advantage (about 1%) for cheaper salts using calcium nitrate. Although numerous questions remain, significant advantages may be realizable in SCR electric power generating systems using salts that melt at low temperatures.

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