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CHARACTERISTICS OF MOLTEN SALTS AND RECOMMENDATIONS FOR USE IN SOLAR POWER STATIONS

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Molten salts (MS) in the 580°C range could be used to store excess energy from solar power stations and possibly from nuclear or coal. The energy can be stored up to a week in large containers at elevated temperature to generate eight hours of electricity to be used at night or during peak demand hours. This helps to reduce the fluctuation experienced at thermal solar power stations due to weather conditions. Our research supported by Office of Naval Research (ONR), presents a survey of salts to be used in molten salt technology. The physical characteristics of these salts such as density, melting temperature, viscosity, electric conductivity, surface tension, thermal capacity and cost are discussed. Cost is extremely important given the large volumes of salt required for energy storage at a commercial power station. Formulas are presented showing the amount of salt needed per required megawatts of stored energy depending on the type of salt. The estimated cost and the size of tanks required and the operating temperatures are presented. Recommendations are made regarding the most efficient type of molten salt to use. Commercial thermal solar power stations have been constructed in the US and overseas mainly in Spain for which molten salt is being considered. A field of flat mirrors together with collection towers are used in some designs and parabolic troughs used in others.

Keywords: Commercial electric station, Energy storage, Energy production, Molten salt technology, Solar salts, Thermal solar power.

1 INTRODUCTION

Molten solar salts are a great and effective way to store excess solar energy for future use due to the vast heat storage capacities of solar salts. In order for the solar salts to effectively store heat, the salts must be contained. This is done by storing the solar salts in large insulated tanks in order to keep the molten salts in a closed system.

This project examines the current method of using insulated stainless steel cylindrical shells to store molten salt and presents a preliminary design of real life examples. In addition, this design solution is compared to alternative shell designs that are expected to be more efficient in reducing shell thicknesses and stainless steel using hybrid shell design and shapes other than cylindrical shells.

2 TYPES OF MOLTEN SALTS

There are various kinds of salts, all of which can be melted for use as a molten salt. This report will mostly focus on five salts: sodium nitrate, lithium nitrate, potassium nitrate, sodium chloride, and a mixture of 60% sodium nitrate and 40% potassium nitrate. These salts have been most prominently mentioned in the literature and are being used in experimental thermal sun storage facilities since they are cost effective (Janz 1967). Other salts that can be used in these applications, both alone and in mixture form, include calcium nitrate, potassium chloride, and lithium chloride (Janz 1967).

3 PHYSICAL PROPERTIES OF MOLTEN SALTS

The first aspect of solar salts that must be considered are there physical properties, including melting point, density, viscosity, surface tension, heat capacity and electrical conductance. The density of these solar salts directly affect the loading exhibited by the storage tanks and any piping used. The melting point reflects an approximation of the temperatures these storage tanks will experience, which can be used to determine thermal expansion, ultimate strength and thickness along with heat shielding requirements of the tanks. The viscosity determines the resistance of the molten salt while flowing through any pipes used. Surface tension is the measure of force a liquid exerts on a surface by interacting with the surface. Lastly, the electrical conductance determines the salt's ability to conduct electricity. Table 1 compares the densities and melting points of these various salts.

Table 1. Physical properties of solar salts (Haynes 2012a, Janz *et al.* 1972).

Compound or Mixture	Melting Point (°C)	Density at MP (g/cm3)
Sodium Nitrate – $NaNO_3$	306.5	1.900
Lithium Nitrate – $LiNO_3$	253.0	1.781
Potassium Nitrate – KNO_3	334.0	1.865
Sodium Chloride – NaCl	800.7	1.556
60 % $NaNO_3$ / 40 % KNO_3	225 (approximate)	1.870 (at 625 K)

Comparing the melting points, the 60% sodium nitrate and 40% potassium nitrate mixture has the lowest melting point with an approximate melting point of 225°C (Janz *et al.* 1972). The next lowest melting point is lithium nitrate at 253°C (Haynes 2012a). On the other side of the spectrum, sodium chloride (basic table salt) has the highest melting point considered at 800.7°C (Haynes 2012a). The melting point of a salt is an important consideration for solar salt applications, which means that based on melting point, the best salt, for our applications is the 60% sodium nitrate and 40% potassium nitrate mixture since it has the lowest melting point considered while sodium chloride is the worst salt considered since it has the highest melting point.

Comparing the densities of these salts, the salt with the lowest density considered is sodium chloride with a density of 1.556 g/cm3 (Haynes 2012a). The salt with the next lowest density is lithium nitrate with a density of 1.781 g/cm3 (Haynes 2012a). At the other end, the salt with the highest density considered is sodium nitrate with a density of 1.900 g/cm3 (Haynes 2012a). Unlike melting point, density is not as important of a consideration, especially since the relative difference in densities between these salts is small.

Table 2 compares the viscosities, surface tensions, and electrical conductance of various solar salts.

Table 2. Physical properties of solar salts at melting point (Janz 1967) (Janz *et al.* 1972).

Compound or Mixture	**Viscosity (mPa-s)**	**Surface Tension (mPa)**	**Electrical Conductance (S/cm)**
Sodium Nitrate – $NaNO_3$	3.038	116.35	0.9713
Lithium Nitrate – $LiNO_3$	7.469	115.51	0.3958
Potassium Nitrate – KNO_3	2.965	109.63	0.6324
Sodium Chloride – NaCl	1.459	116.36	0.8709
60 % $NaNO_3$ / 40 % KNO_3	3.172*	121.80 (at 510 K)	0.7448*

Note: Values with a single asterisk (*) have been extrapolated for the 60% $NaNO_3$ mix at 580 K

Comparing the viscosities, the salt with the lowest viscosity is sodium chloride with 1.459 mPa-s (Janz 1967). The next lowest salt is potassium nitrate with 2.965 mPa-s (Janz 1967). Conversely, the salt with the highest viscosity is lithium nitrate with 7.469 mPa-s (Janz 1967). In comparison with other physical properties, considered, viscosity is not the most important property to consider in comparing molten salts. However, it is a property of some importance as the viscosity compares the resistance exerted against the molten salts while flowing through a pipe, which is something the molten salts will have to do in the containment units.

Comparing the surface tension, the salt with the lowest surface tension is potassium nitrate with 109.63 mPa (Janz 1967). The next lowest salt is lithium nitrate with 115.51 mPa (Janz 1967). On the other side, the salt with the highest surface tension is the 60% sodium nitrate and 40% potassium nitrate mixture with 121.80 mPa (Janz *et al.* 1972). In comparison with other properties considered, surface tension is also not one of the most important properties to consider in comparing molten salts to be used in our applications. However, it is a property of some importance because it affects the tanks and piping of the containment units

Comparing the electrical conductance, the salt with the highest electrical conductance is sodium nitrate with 0.9713 S/cm (Janz 1967). The next highest salt is sodium chloride with 0.8709 S/cm (Janz 1967). On the other side, the salt with the lowest electrical conductance is lithium nitrate with 0.3958 S/cm (Janz 1967). Compared to the other physical and thermodynamic properties considered, electrical conductance is a minor consideration when comparing solar salts for energy storage applications.

4 THERMODYNAMIC PROPERTIES OF MOLTEN SALTS

Solar salts are known for their ability to store heat for long periods of time. The heat of fusion measures the required amount of heat needed to convert a substance from a solid state to a liquid state, or simply the amount of heat needed to melt a substance. The specific heat capacity measures a substance’s ability to store heat. Lastly, thermal conductivity measure a substance’s ability to conduct heat through said substance. All three properties considered are of major importance since these properties compare how the salts conduct and store heat. Table 3 compares the thermodynamic properties of solar salts.

Table 3. Thermodynamic properties of solar salts (Janz 1967) (Cornwell 1970) (Haynes 2012b) (Janz *et al.* 1979).

Compound or Mixture	Specific Heat Capacity (J/mol/K)	Thermal Conductivity (kW/mol/K)	Heat of Fusion (kJ/mol)
Sodium Nitrate – $NaNO_3$	131.8	5.66	15.50
Lithium Nitrate – $LiNO_3$	99.6	5.82	26.70
Potassium Nitrate – KNO_3	115.9	4.31	9.60
Sodium Chloride – NaCl	48.5	8.80	28.16
60 % $NaNO_3$ / 40 % KNO_3	167.4 (at 510 K)	3.80	13.77
Note: Since some values were given in calories in some sources, they were converted into joules for this table (1 cal = 4.184 J or 1 kcal = 4.184 kJ) (IUPAC n.d.).			

Comparing the specific heat capacity, the salt with the highest specific heat capacity is the 60% sodium nitrate and 40% potassium nitrate mixture with 167.4 J/mol/K (Janz *et al.* 1979). The next highest salt is sodium nitrate with 131.8 J/mol/K (Janz 1967). On the other side, the salt with the lowest specific heat capacity is sodium chloride with 48.5 J/mol/K (Janz 1967). Based on this comparison, the best salt to use for energy storage is the 60% sodium nitrate and 40% potassium nitrate mixture since it has the highest heat capacity considered while sodium chloride is the worst salt considered since it has the lowest heat capacity.

Comparing the thermal conductivity, the salt with the highest thermal conductivity is sodium chloride with 8.80 kW/mol/K (Cornwell 1970). The next highest salt is lithium nitrate with 5.82 kW/mol/K (Cornwell 1970). On the other side, the salt with the lowest thermal conductivity is the 60% sodium nitrate and 40% potassium nitrate mixture with 3.80 kW/mol/K (Cornwell 1970).

Comparing the heat of fusion, the salt with the lowest heat of fusion is potassium nitrate with 9.60 kJ/mol (Haynes 2012b). The next lowest salt is the 60% sodium nitrate and 40% potassium nitrate mixture with 13.77 kJ/mol (Janz *et al.* 1979). On the other side, the salt with the highest heat of fusion is sodium chloride with 28.16 kJ/mol (Haynes 2012b). Based on the comparison of salt characteristics presented in Table 1.3, the 60%/40% sodium/potassium nitrates present, for now the most interesting option for molten salt energy storage. However other options will be considered, such as, the addition of Nano silica to the salt mix in order to improve its specific heat capacity by 30% or more.

5 COST OF SOLAR SALTS

Ultimately, compared to the other considered salts, the most promising solar salt to use, so far, in molten salt energy storage, is the 60% Sodium Nitrate and 40% Potassium Nitrate mixture since it compares favorably against other salts in terms of thermodynamic and heating properties, which are the primary factors to consider for use as a solar salt.

However, when considering the use of solar salts, one must consider the costs of various types of salts. Table 4 compares the 60% sodium nitrate and 40% potassium nitrate mixture to various other solar salt substitutes that are available in the marketplace.

Table 4. Costs of solar salts (Kearney *et al.* 2001).

Compound or Mixture	ΔT (°C)	Cost of Salts ($/kg)	Cost of Power ($/kWH)
Hitec XL in 59% Water (42:15:43 Ca:Na:K)	200	1.43	18.20
	200	3.49 (w/o H_2O)	18.20
Hitec (7:53 Na:K: Nitrate, 40 Na Nitrate)	200	0.93	10.70
Solar Salt (60:40 Na:K Nitrate)	200	0.49	5.80
Calcium Nitrate Mixture Dewatered (42:15:43 Ca:Na:K Mixture)	200	1.19	15.20
	150	1.19	20.10
	100	1.19	30.00
Therminal VP-1 (Diphenyl Biphenyl Oxide)	3.96	100.00	57.50

The solar salt mixture (60% NaNO3 – 40% KNO3) is both the least expensive in terms of cost to purchase, which is 49 cents per kilogram, and the costs per kilowatt-hour of power generated, which is $5.80 per kilowatt-hour (IUPAC n.d.). The next best priced mixture in both aspects is the Hitec mixture, which costs 93 cents per kilogram to purchase and has a power cost of kilowatt-hour of $10.70 (IUPAC n.d.). In addition, the mixture the most expensive in both aspects is the Therminal VP-1, which costs $100 per kilogram to purchase and has a power cost of $57.50 per kilowatt-hour (IUPAC n.d.).

6 CORROSION FROM MOLTEN SALTS

In addition to being able to hold large quantities of heat, molten salts can be corrosive. Table 5 shows corrosion properties of stainless steel exposed to various molten salts.

Table 5. Corrosion properties of stainless steel using molten salts (Sohal *et al.* 2010).

Compound or Mixture	Temp (°C)	Corrosion Rate (mm/y)	
		SS 304	SS 316
Sodium Chloride – NaCl	845	7.2	7.2
Hitec Salt	538	0.21	<0.03
	430	------	0.007
	505	------	0.008
	550	------	0.074

The sodium chloride at a temperature of 845°C corrodes both types of stainless steel at 7.2 millimeters per year (Sohal *et al.* 2010). At 538°C, the Hitec Salt corrodes through SS 304 steel at 0.21 millimeters per year, and through the SS 316 steel at less than 0.03 millimeters per year (Sohal *et al.* 2010). In addition, the Hitec Salt corrodes through SS 316 steel 0.007 millimeters per year at 430°C, 0.008 millimeters per year at 505°C, and 0.074 millimeters per year at 550°C (Sohal *et al.* 2010).

7 CONCLUSION

A survey of molten solar salts for use in energy storage shells is presented, to provide electric generation stations with power for eight hours. Tables are shown providing the characteristics of various molten salts to be used in thermal solar energy stations.

Recommendations for the selection of an economical molten salt compound is made using various characteristics, including thermal capacity, availability, melting temperature, and the cost of salts.

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