THE APPLICATION OF MOLTEN SALTS TO SOLAR LARGE POWER SYSTEMS*

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Abstract

Various solar thermal power concepts in which the end product is electricity (for utility use) are described. It is shown that molten nitrate salts are leading candidates for the heat transfer and thermal energy storage fluids. Selected research problems and current results are described concerning the decomposition and corrosion characteristics of nitrate salts.

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Introduction

Molten salts have been used for many years in the chemicals and metals industries. Common applications include removing heat from exothermic reactors and providing heat to processing equipment such as evaporators and concentrators (1). They have also found widespread use as a bath medium for the heat treatment of metals (2). Recently interest in molten salts has heightened because of their proposed use in solar energy systems (3) and the purpose of this paper is to review the application of salts to such systems.

Various solar energy concepts in which molten salts may be used as the fluid for heat transfer and thermal energy storage will be reviewed. Fluid requirements and conditions of operation will be discussed and it will be shown that molten nitrate salts are leading candidates. Several examples of current research and current technical problems will be given.

Solar Energy Systems

This paper concerns the solar large power concept where the end product is electric power. The four components of the system, shown in Figure 1, are the heliostat, the receiver, the thermal energy storage system, and the electric generation system. Solar energy is incident on a field of heliostats, computer driven mirror reflectors, and is focused onto a central receiver. There the energy is absorbed by a heat transfer fluid which is then diverted to the thermal energy storage system. The storage system serves two purposes, to extend the time of operation beyond which there is adequate solar insolation, and to buffer the electrical generation equipment from the thermal cycles inherent in a solar energy source. By means of a secondary water/steam heat transfer loop, the thermal energy storage system is used to convert water to superheated steam which is then used to drive the electric generating turbines of a steam Rankine cycle. As an alternative path for the heat transfer fluid from the receiver, the energy may be used directly to generate electricity. In this case a secondary heat exchange loop is of course necessary to generate the steam if the primary heat transfer is not water/steam.

There are numerous variations of the concept illustrated in Figure 1. One option is to have a system of dispersed point focusing collectors, each collector having its own small receiver situated at its focal point. Line focus systems have also been proposed in which the solar energy is focussed along a line. A central receiver line focus system consists of a field of heliostats all directing solar energy to the same linear receiver. Another variation is the dispersed line focus system comprised of many different collectors each with its own linear receiver.
There is a need for fluids to serve as the heat transfer and energy storage media in all of the systems discussed above, and it is for this purpose that molten salts have been proposed.

Fluid Requirements and Selection

Fluid Requirements

Regardless of the system design and configuration, the requirements of the heat transfer and energy storage fluids are essentially the same. Fluid temperatures range from 350-600°C and the fluid must be thermally stable, non-corrosive, and possess suitable thermal properties in this temperature range. Fluid flow rates will reach values of 3-3.3 m/s through receiver tubes. While the intrinsic behavior of the fluid is probably not altered by flow rate, the corrosion processes may be affected. Parts of the system will be thermally cycled; there will be diurnal cycling upon which shorter term transients will be impressed due to such things as cloud coverage. While the fluid properties will probably not be strongly affected by cycling, the fluid/containment material interaction may be. For example, protective oxide scales may be breached upon thermal cycling. The fluid/containment material interaction may also be affected by the mechanical state of the alloy. Thermal transients discussed above cause thermal stresses which may accelerate crack growth mechanisms. Stresses may also develop as a result of the combined effects of thermal gradients (due to asymmetric heat fluxes and one sided receiver tube heating) and constrained motion. The synergistic effects of thermal, mechanical, and chemical environments must be considered in the fluids selection process.

There are several other considerations which greatly influence system and hardware designs and are as important as the operational requirements discussed above. The fluid should be non-reactive with air in order to eliminate the need to design, operate and maintain an air-tight leak-proof system. Similarly, fluids with a high vapor pressure are undesirable because of the costs associated with a high pressure containment system. Because large quantities of fluid are required for thermal energy storage, the fluid must be inexpensive, and readily available in abundant quantities.

Fluid Selection

Typical classes of fluids proposed for heat transfer and energy storage are oils, water/steam, molten salt, and liquid metal (3). The Barstow pilot plant (4) design calls for water/steam as the heat transfer fluid and a mixture of oil and rocks as the energy storage medium. Costs can be saved in second generation (after Barstow) solar thermal power systems if the same fluid is used for heat...
transfer and energy storage. This requires a liquid with a lower vapor pressure over a large temperature range (350 to 600°C). Molten salt and liquid metal satisfy that criterion. Sodium has an extensive data base from which to draw information and has been used as a heat transfer fluid at high temperatures in nuclear reactor applications. However, sodium is expensive and requires elaborate safety precautions. For this reason, molten salt appeared to have potential cost savings. But which salt?

There are, of course, numerous salts and salt mixtures that could potentially be used in a solar thermal power system. However, after screening the possibilities and excluding such things as lithium salts (too expensive), sulfates and phosphates (too corrosive), and carbonates and fluorides (melting points too high) one is left with such common materials as nitrates, chlorides, and bromides of the alkali metals and alkaline earths to choose from. After more careful scrutiny chlorides and bromides can be excluded because of melting points and cost. Based on this rather straightforward reasoning alkali metal nitrates appear to have the best chance of the salts considered for success in a solar thermal power system.

The merits and shortcomings associated with each class of fluid are listed in Table I. In preparing Table I the comments pertaining to molten salt are made assuming the chemical composition to be drawsalt, an equimolar mixture of NaN\(_2\)O and KNO\(_3\). From this table it is clear that no class of fluid materials is obviously superior to the others.

In order to determine the most attractive fluid for use in a central receiver system one should take a plant design using the fluid in question, and conduct a cost analysis. The most important criterion is the cost of energy, and the projected energy cost should be the key constituent in determining the most attractive class of fluid material. Recent cost studies have been carried out (5) and the details of the studies are outside of the scope of this paper. Suffice it to say the potential for the lowest cost energy system resides with using nitrate salt for heat transfer and energy storage.

**Salt Composition**

The nitrate/nitrite salts of sodium and potassium are of greatest interest because of suitable temperature ranges of liquid formation, nonreactivity to air, and low cost. The salt composition most prominently used in industry is the three component mixture of 40% NaN\(_2\)O-53% KNO\(_3\)-7% NaN\(_3\) by weight. This mixture is marketed by Coastal Chemicals under the trade name HITEC and by Park Chemical under the name Partherm 290. It is known that the nitrite constituent is not stable at high temperatures, and if heated in air to the
| Fluid                  | Advantages                                      | Disadvantages                                      |
|-----------------------|------------------------------------------------|---------------------------------------------------|
| Water/Steam           | - Extensive user experience                     | - High pressure containment                        |
|                       | - Direct coupling of receiver to power generation system | - Sealed system                                    |
|                       |                                                  | - Low gas phase heat transfer coefficient          |
|                       |                                                  | - Low gas phase energy density                     |
| Liquid Metal (Na)     | - Extensive data base                            | - High materials costs                             |
|                       | - Low vapor pressure                             | - Sealed system                                    |
|                       | - Excellent thermal properties                   | - Fire hazard                                      |
| Molten Salt (nitrates)| - Inexpensive chemicals                         | - Minimal user experience at peak operating conditions |
|                       | - High energy transfer density                   | - Thermal stability and corrosion issues unresolved|
|                       | - Low vapor pressure                             |                                                  |
|                       | - Excellent thermal properties                   |                                                  |
|                       | - Open system design                             |                                                  |
| Oil                   | - Relatively non-corrosive                       | - Extensive decomposition at higher temperatures   |
temperatures of interest for solar power applications the nitrite readily converts to nitrate. Therefore, compositions of interest for solar power systems lie along the NaNO$_3$-KNO$_3$ binary.

Drawsalt is nominally an equimolar mixture of NaNO$_3$ and KNO$_3$ at the eutectic composition. Drawsalt is marketed by several companies including Park Chemical as Mixture AL-2. Due to cost considerations it is desirable to use NaNO$_3$ rich off-eutectic compositions; the NaNO$_3$ constituent is less expensive than KNO$_3$. NaNO$_3$ rich binary mixtures are marketed commercially by Park Chemical in the form of Partherm 430, a 60% NaNO$_3$-40% KNO$_3$ by weight mixture. While many of the solar projects have adopted the Partherm 430 composition as baseline, the choice of fluid is not restricted to current market items as tailormade compositions could easily be prepared. Nevertheless, it is clear that the greatest promise for a viable fluid is a NaNO$_3$-KNO$_3$ mixture, rich in the NaNO$_3$ constituent.

Recent Developments

While it is comforting to have such an extensive amount of industrial experience backing up the use of nitrate salts, it is also important to realize there are some major differences between current industrial usage and intended solar applications. Industrial experience has generally been at temperatures lower than 600°C. Furthermore, many of the heat transfer applications are for constant operation isothermal reactors. Industrial uses are designed to avoid thermal and mechanical cycling, two conditions which will definitely be present in portions of solar power systems. Finally, 25-30 year lifetimes as desired for solar energy systems are not typical design goals for current industrial equipment. Because of these differences, many studies are being carried out to develop a better understanding of molten nitrate salt behavior. To date these studies have indicated no insurmountable problems. However, the data base needed for reliable lifetime predictions is far from complete. Several examples of current research to generate this data base are given below.

Thermal Decomposition

When heated the nitrate salts undergo numerous reactions (6-10). The nitrate ion may decompose to nitrite and oxygen and the nitrite ion may undergo subsequent decomposition to an oxide species with the release of N$_2$, O$_2$, and/or NO$_x$. Direct vaporization to complex nitrate gas species has also been proposed (11). The preponderance of information in the literature suggests the most important reaction to consider is

\[ \text{nitrate} + \text{nitrite} + \text{oxygen} \]
It is often proposed that this reaction alone is sufficient to represent the decomposition chemistry. In an operating system, the salt composition will attain a fixed nitrate to nitrite ratio as determined by the oxygen partial pressure. Once this composition is reached, further changes in the salt will not occur. The operational characteristics and the thermal properties of the salt will not be significantly affected by these composition changes.

Recent studies by Kramer (12) have shown, however, that there are conditions under which the nitrate/nitrite/oxygen reaction is not the most important; in fact, conditions have been found where this reaction does not appear to be operative. The decomposition of NaN$_3$ and KNO$_3$ into a vacuum has been studied by thermogravimetric and simultaneous evolved gas analysis techniques. The objectives were to determine the intrinsic decomposition processes and rates for the nitrate, i.e., the decomposition of the nitrate without recombination reactions due to interactions from gaseous species. The evolved gas species when heating to temperatures of less than 350°C were N$_2$ and NO. No evidence of O$_2$ was observed. Heating to higher temperatures also produced N$_2$ and NO species; however, after an induction period, O$_2$ was seen. The oxygen was clearly a less abundant species than N$_2$ and NO. It is emphasized that Kramer's studies were carried out at conditions quite different from those anticipated in solar power systems. Nevertheless, the results provide mechanistic insight into decomposition mechanisms which may be operative at higher temperatures and atmospheric pressures.

Corrosion

Nitrate salts are very strong oxidizers. In selecting alloys for containment a logical starting point is with alloys developed to withstand gaseous oxidizing environments. These alloys, for example stainless steel, withstand oxidation by the formation of passive protective oxides. The corrosion behavior of 316 stainless steel immersed in drawsalt is shown in Figure 2. It is seen that the rate of weight gain decreases with time, indicative of a corrosion process involving protective product layers.

Recent research carried out by Bradshaw (14) and Keiser et al. (15) have shown there are conditions under which deviations from protective oxide formation behavior are seen. As an example, preliminary results generated by Bradshaw (14) are shown in Figure 3 in which the weight changes of Incoloy 800 coupons suspended in a convection test loop with drawsalt as the fluid are shown. At the three temperatures studied there was an initial weight gain, caused by the formation of oxides on the sample coupons. With time all samples experienced weight losses. The weight loss was so significant at high temperatures that the net sample weight change was negative. The weight losses did not occur solely as a result of
oxide flaking and spalling. Microstructural analysis revealed that the oxide thickness increased steadily with time. A working hypothesis has been formulated in which the corrosion process is assumed to be comprised of several simultaneous processes, the formation of adherent oxide layers, and the selective dissolution of chromium from the alloy and the loss of oxide. Current studies are in progress to develop a complete qualitative and quantitative understanding of these processes. To put everything in proper perspective, it is noted that significant alloy depletion is observed only at temperatures greater than the anticipated operating temperatures in solar power plants. All studies to date suggest uniform corrosion will not be a detrimental problem in operating plants as long as the temperature is maintained at temperatures less than 600°C.

The extent to which the mechanical state of an alloy affects the corrosion behavior is as yet undetermined. Preliminary results generated by Goods (16) are shown in Figure 4, in which the oxide corrosion products formed on Incoloy 800 tubes under several different conditions are shown. Figure 4a shows the oxide formed while the alloy is held in drawsalt at 650°C for 550 hours while being strained to a maximum strain of 10%. The amount of oxide formed can be contrasted with that shown in Figure 4b, where the same alloy was heated in the identical salt for the same period of time at the same temperature, only without being strained. It is clear the amount of oxide had increased when strained. To complete the comparison, Figure 4c shows the amount of oxide formed when exposed to air. Comparing Figure 4b and 4c shows the nitrate salt environment to be a much more aggressive oxidizer than air. The experiments used to generate the results shown in Figure 4 are clearly an overtest of solar conditions, as the metal parts in an actual system will not experience 10% total strain and will not reach temperatures exceeding 600°C. Currently, long term experiments are underway to evaluate the corrosion processes taking place under realistic conditions, including stress and thermal cycling.

Summary

Various concepts have been proposed for the generation of electric power from solar energy. Such systems require the focusing of solar energy, and point focus and line focus designs have been proposed. As an additional design option, central receiver or dispersed receiver configurations are possible. Regardless of the specific system design, fluids are needed for heat transfer and thermal energy storage. It has been shown that molten nitrate salts are the most attractive choice for use as a fluid. The greatest interest lies with NaN₃-KNO₃ mixtures of compositions on the NaN₃ rich sides of the equimolar eutectic. Numerous research activities are being carried out to further the development of solar large power
systems using nitrate salts. While it is too early to predict the
future of such systems, it is clear the impetus exists for developing
a better understanding of nitrate salt behavior. Recent results
concerning decomposition and corrosion characteristics have been
described above.

REFERENCES

1. B. W. Watt and D. H. Kerridge, Chem. in Britain, 15, 78 (1979).
2. R. W. Foreman, "Heat-Treatment of Industrial Materials in Molten
Salt" presented at the Third Int'l Symp. on Molten Salts, 158th
Electrochemical Soc. Mtg. Hollywood, Fla., October 8, 1980.
3. T. N. Tallerico, "A Description and Assessment of Large Solar
Power Systems Technology," Sandia Laboratories Report #SAND79-
8015, August, 1979.
4. A. C. Skinrood, Solar Age, 24, June, 1978.
5. K. W. Battleson, P. De Laquil III, J. D. Fish, H. F. Norris, and
J. J. Iannucci, "1980 Solar Central Receiver Technology Evalua-
tion," Sandia Laboratories Report SAND80-8235, October, 1980.
6. R. F. Bartholemew, J. Phys. Chem. 70, 3442 (1966).
7. E. S. Freeman, J. Phys. Chem. 60, 1487 (1958).
8. E. S. Freeman, J. Am. Chem. Soc. 79, 838 (1957).
9. G. D. Sirotkin, Russ. J. Inorg. Chem. 4, 1180 (1959).
10. B. D. Bond and P. W. M. Jacob, J. Chem. Soc. A, 1265 (1966).
11. A. Buchler and J. L. Stauffer, J. Phys. Chem. 70, 4092 (1966).
12. C. M. Kramer (Sandia National Laboratories, Livermore, CA
94550) private communication.
13. T. R. Tracey, "Conceptual Design of Advanced Central Receiver
Power System, Phase I" Martin Marietta final report for DOE
contract EG-77-C-03-1724.
14. R. W. Bradshaw (Sandia National Laboratories, Livermore, CA
94550) private communication.
15. J. R. Keiser, J. H. deVan, E. J. Lawrence, J. Nucl. Mat. 85, 294
(1979).
16. S. H. Goods (Sandia National Laboratories, Livermore, CA 94550)
private communication.
Figure 1. A schematic illustration of a solar central receiver system for the generation of electricity.

Figure 2. The corrosion behavior of 316 stainless steel coupons immersed in Partherm 430 (60% NaNO₃-40% KNO₃ by weight) (13).
Figure 3. The corrosion behavior of Incoloy 800 samples suspended in a thermal convection loop with a Partherm 430 working fluid (14).
Figure 4. Oxide corrosion products found on Incoloy 800 tubes exposed at 650°C for 550 hours: (A) in contact with Partherm 430 and strained to 10%, (B) in contact with Partherm 430 and undeformed, (c) in contact with air and undeformed.