A REVIEW OF THE CHEMICAL AND PHYSICAL PROPERTIES OF MOLTEN ALKALI NITRATE SALTS AND THEIR EFFECT ON MATERIALS USED FOR SOLAR CENTRAL RECEIVERS

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ABSTRACT

Sandia National Laboratories, Livermore (SNLL), has been responsible for developing thermal energy collection and storage technologies for solar central receiver (SCR) applications as the lead laboratory designated by the U. S. Department of Energy. The focus of one of these efforts has been the evaluation of the properties of a mixture of sodium nitrate and potassium nitrate as a single-phase working fluid for SCR systems. This paper summarizes the results of a comprehensive research program that was established by SNLL to address issues relevant to the use of molten nitrates at temperatures up to 600°C. It was concluded that molten nitrate salt is technically feasible as a working fluid for advanced SCR and offers a number of advantages compared to alternative fluids.

Introduction

The selection of a molten salt, consisting of a mixture of sodium nitrate and potassium nitrate, as a heat transfer fluid for high-temperature solar central receivers (SCR) was initially derived from a systematic screening process which identified several favorable characteristics, such as a low melting point (222°C), the availability of large quantities at low cost, and the minimal hazards associated with its use [1,2]. Low cost is particularly important if the fluid is to serve as the thermal energy storage media as well as the receiver coolant [3]. Although molten nitrate salts have been used extensively for heat transfer in industrial processes [4] and compilations of some of their properties are available [5], the maximum temperature intended for SCR systems is 600°C, which is significantly higher than previous applications. For this reason, a research program was undertaken to establish a data base describing the properties of a molten mixture of NaN0₃ and KNO₃ over the complete range of temperatures relevant to advanced SCRs.

The majority of the research efforts were conducted at SNLL, although several industrial, university, and national laboratories participated as well. The program included studies of chemical stability, physical properties, corrosion of metallic materials, environmental effects on the mechanical properties of alloys, and compatibility of non-metallic materials with the molten salt. A comprehensive group of studies has been completed and this review...
summarizes those research activities and the results obtained. The technical issues which motivated the studies in each area are described and their impact on engineering concerns are discussed. This review includes results obtained during the operation of large-scale demonstration experiments.

Chemical Properties

The important issues concerning the chemical properties of molten nitrate salt mixtures were choosing the composition, verifying chemical stability at high temperature, determining the effects of cover gas composition and atmospheric contamination on the melt and assessing any hazards which might arise when using molten salt in an SCR.

The liquidus line in the phase diagram reported in a previous study does not indicate a eutectic, but rather a broad band of low-melting mixtures surrounding the minimum melting point of 222°C at 50 NaNO₃-50 KNO₃ (mol. %, 46-54 wt. %) [5]. The phase diagram was re-examined using differential scanning calorimetry (DSC) and its important features were confirmed [6]. The data suggested that a mixture enriched in NaNO₃ relative to KNO₃ would be desirable since the significant reduction in cost would easily offset the disadvantages of a slightly increased melting point. The composition 44 NaNO₃-56 KNO₃ (mol. %, 60-40 wt. %), which melts at 238°C, was chosen for advanced SCR applications and was successfully used in several engineering projects [7-9].

A key consideration in qualifying this molten salt mixture for long-term use was chemical stability, since molten nitrate salts may undergo a variety of reactions depending on the temperature and the composition of the cover gas. The primary reaction is the decomposition of nitrate to nitrite and oxygen.

\[ \text{NO}_3^- = \text{NO}_2^- + 1/2 \text{O}_2 \]  

Experimental investigations of the equilibrium of reaction (1), at temperatures up to 600°C, determined the equilibrium constant [10,11] and the enthalpy change (23.03 Kcal/mol [10]). Figure 1 compares the equilibrium constant of the mixed salt, as a function of temperature, with published results for the pure components. The concentration of nitrite in melts in equilibrium with air is about 3 wt.% at 565°C and 7% at 600°C. The equilibrium data have been used to calculate the amount of nitrite expected to form in either open or closed systems covered with a variety of gases [11]. It was concluded that air at atmospheric pressure is more than adequate to minimize nitrite formation.

Thermochemical equilibrium calculations were used to predict the behavior of nitrate melts over a wide range of conditions. The thermodynamic model included reactions of nitrate and nitrite which yield alkali oxides and gases, such as oxygen, nitrogen and NO. The result of these studies was the construction of the phase stability diagram of the Na-O-N system at various temperatures [12]. The study determined that the concentration of oxide ions was negligible at SCR.
temperatures, but increased rapidly above 600°C. This is an important finding because oxide ions are known to be very corrosive (a later section discusses rapid corrosion above 600°C). A comparison of the oxide ion concentrations measured in equilibrium melts with predictions of the thermodynamic calculations suggested that oxide ions behave non-ideally in nitrate melts [13].

The stability of the melt with respect to the major constituents of air is an obvious benefit for an SCR system. However, a concern that atmospheric carbon dioxide and water vapor might cause the salt to deteriorate during long-term use was also addressed. The interactions of CO₂ and H₂O with nitrate melts were studied using electrochemical and chemical techniques [14]. It was found that CO₂ can cause minor chemical changes by reacting to form carbonate. Although DSC studies showed that the solubilities of alkali carbonates in the nitrate salt were large [1], the carbonates of metallic impurities might precipitate in the coolest sections of heat exchangers. However, problems related to carbonate precipitation are not expected because the availability of CO₂ is very limited. The solubility of water vapor was found to be completely reversible up to 600°C and no hydrolysis was observed [14]. Procedures are available for removing anionic contaminants, such as nitrite and carbonate, if needed [11,15]. No adverse effects on the molten salt were observed during approximately 1000 hours of testing of a one-megawatt SCR electric power generating system at the Central Receiver Test Facility in Albuquerque, NM [9].

Two reports were prepared which discuss loading, operating and maintaining SCR systems that contain large quantities of salt [15,16]. Hazards management related to the use of molten nitrate salt has also been discussed, although in an SCR the necessary precautions are those associated with any hot fluid, since oxidizable materials will not be present [15,16]. A comprehensive review of the hazards associated with molten salts has been published by Allen and Janz [17].

Physical Properties

A knowledge of the physical properties of the working fluid in a SCR is essential for design calculations involving heat transfer and fluid flow in such components as receivers, heat exchangers, pumps, and thermal energy storage subsystems. Although data on most of the important properties (for example, viscosity, density, thermal conductivity and heat capacity) are available in the literature for single alkali nitrate salts [5], the properties of the SCR mixture were not available over the operating temperature range. Experimental measurements of these properties were made at temperatures which significantly extended the range of existing data. The measured values are presented in Figure 2.

Viscosity, density and surface tension (not shown) were determined from 250°C to 600°C using a single apparatus [18]. Viscosity decreased from about 5 gm/cm/sec at 250°C to 1 at 600°C, while density decreased moderately with temperature and was nominally 1.8 gm/cm³. These data
agree with literature values at lower temperatures where comparisons can be made. Thermal conductivity was found to be weakly dependent on temperature from 250°C to 400°C and the measured values were nominally 0.5 W m⁻¹ K⁻¹ [19]. Minor additions of NaNO₂ and/or Na₂CO₃ to the melt had a negligible effect. The heat capacity of the molten mixture was determined by differential scanning calorimetry and found to be about 140 J K⁻¹ mol⁻¹ [20,21]. Difficulty in containing the salt in the thermal conductivity and heat capacity apparatus limited the accessible temperature range. The equations expressing the temperature dependence of each property are available in the above references.

**Corrosion of Metallic Materials**

It was necessary to resolve two issues before selecting suitable alloys and metals for containment of the molten salt. These were the corrosion rates at operational temperatures and the solubility of metallic oxides in the molten salt. Although the corrosion behavior of various metals and alloys has been reported previously, the data have been derived from short-term tests and were not considered adequate for engineering design. The concern with regard to solubility behavior was that dissolved corrosion products might precipitate in the coldest parts of the flow system and foul or plug them, a phenomena called thermal-gradient mass transfer.

Corrosion and mass transfer behavior were investigated using thermal convection loops, which operated at temperatures spanning the range of a SCR, 300°C to 600°C [22]. The alloys tested were Alloy 800, 304SS and 316SS. The rates of metal loss of these alloys were 5-12 micron/year at 600°C [23-26]. Measurements of metal losses by chemical descaling revealed that the majority of metal consumption was due to oxidation [26]. Chemical analyses of the salt in the loops established that chromium was soluble, whereas iron and nickel were negligibly soluble. The solubility of chromium, as chromate ion, in molten nitrates is quite large; accordingly, thermal-gradient mass transfer was not observed.

Corrosion data for a wide variety of alloys and metals were obtained from long-term experiments in isothermal crucibles. Materials for the complete range of operating temperature environments were tested, including stainless steels (austenitic and ferritic), chromium-molybdenum steels, carbon steel, aluminum diffusion-coated steels, nickel, aluminum and titanium. Representative results from these studies are summarized in Table 1. In general, alloys with at least 9% chromium were quite corrosion resistant up to 600°C [27]. A nickel-base alloy, IN600, was somewhat more corrosion resistant than Alloy 800, although it underwent internal oxidation, which the iron-base alloy did not. Cr-Mo steels with 1 to 5% Cr experienced metal loss rates as high as 100 micron/year over a restricted temperature range [28]. Aluminized Cr-Mo steels were very resistant at 600°C [29]. Similarly, aluminum was negligibly affected at 565°C. Titanium oxidized more rapidly than ferrous alloys, but formed an adherent surface oxide layer, while nickel experienced severe intergranular corrosion [30].
A better understanding of corrosion mechanisms was obtained by studies of the kinetics of oxidation and depletion in crucible tests. The rate laws for both processes in most Cr-containing alloys were parabolic up to 600°C [27,32]. At these temperatures, the corrosion products were spinels of iron and chromium and Fe₂O₃. Above 615°C, sodium ferrite was formed [31], corrosion rates increased markedly, and kinetics were observed that indicated the formation of a non-protective surface film [32], as shown by the plot of Cr depletion from Alloy 800 in Figure 3. The relatively rapid oxidation of Cr-Mo steels was associated with the formation of Fe₆₋₉ [29]. Electrochemical polarization studies of Alloy 800 confirmed the passivation of Alloy 800 in the melt [33] and the suppression of galvanic corrosion of Alloy 800/mild steel couples by surface films [1]. Some of the chemical and electrochemical factors relevant to corrosion in molten nitrites, including the inadvisability of cathodic protection, have been discussed by Smyrl [34].

Since the oxide scales on high-temperature alloys were very adherent, no thermal cycling tests were done. Examination of scale layers on the inside surface of Alloy 800 receiver tubes, that had operated for about 1000 hours in a cyclic solar radiation environment, revealed adherent oxides that grew somewhat faster than isothermally-grown scales [35]. Operation of a forced-convection loop did not reveal any obvious erosion damage to surface scales [11].

**Environmental Effects on the Mechanical Properties of Alloys**

The receiver tubes of SCRs present unusual problems in materials selection and design because of the stresses which arise from one-sided heating, as well as from the thermal cycling inherent in solar receiver operation [36]. A key concern was whether the molten salt, in conjunction with the thermomechanical environment, would promote cracking of alloys used for receiver tubes and other components or otherwise degrade their mechanical properties. The complexity of mechanical testing in a molten salt environment limited studies to the most favored alloys, Alloy 800, 316SS and HT-9 (receiver tubes) and 2-1/4Cr-1Mo steel (steam generator tubes).

Slow strain rate tests and creep tests in the molten salt at 600°C established that neither environmentally-induced cracking nor significant acceleration of oxidation due to deformation occurred in Alloy 800 [37,38]. Figure 4 shows the insensitivity of the ductility of Alloy 800 to strain rate during prolonged immersion in the molten salt, as compared to air. Slow strain rate tests showed that the strength and ductility of 316SS were unaffected, but a measurable loss of the ductility of HT-9 was observed [39]. No significant reduction in lifetime was found during fatigue and creep-fatigue tests of Alloy 800 in molten salt at 650°C when compared to tests in air [40]. 2-1/4Cr-1Mo steel experienced a loss in ductility at temperatures up to 525°C, due to the acceleration of oxidation by deformation over a range of strain rates [41]. However, this does not preclude its use in heat exchangers at lower temperature.
Compatibility of Non-metallic Materials

Other compatibility questions which were investigated concerned the selection of non-metallic materials for several important functions, including fluid seals for valves, thrust bearings in pumps, and internal insulation and solid ballast for thermal energy storage.

A comprehensive study was conducted to evaluate materials for valve stem seals in flow control valves [42]. Compression packings were emphasized because this type of seal offers economic advantages in large valves. Below 300°C, good compatibility was observed with polytetrafluoroethylene (PTFE) and graphite. Other materials commonly used to fabricate packings for high temperature, including asbestos, borosilicate glass, aramid fiber and perfluoroelastomers, were not suitable. PTFE is not mechanically acceptable at higher temperature, and graphite began to oxidize rapidly above 400°C, as shown in the thermogravimetric analysis plot in Figure 5. Thus, valve designs must limit the temperature of the packing to 300°C.

Compatibility tests were conducted with a variety of ceramics. Silicon carbide, proposed as an thrust bearing in pumps, displayed good resistance to the molten salt, resulting in a corrosion rate of 7 micron/year at 565°C, due to dissolution of SiC as silica or silicate [30]. Boron nitride was relatively inert in the melt below 300°C [42], while dense alumina was unaffected up to 630°C [32]. Many refractory insulating materials were evaluated as internal insulation for large salt storage tanks, where wetting by the molten salt at 565°C would be necessary [43]. Dissolution of the silica phases in these materials caused unacceptable deterioration. Experiments were also conducted with materials which would be useful as inexpensive ballast for thermal energy storage. Taconite pellets (mainly iron oxide) were relatively stable in contact with the salt at 565°C, but granite was not [44].

Conclusions

A comprehensive data base on the properties of molten nitrate salts has been established that allows SCR systems to be designed with confidence in their performance. The data base includes information on the chemical and physical properties of molten mixtures of NaNCl and KNO₃ and the effects of the molten salt on many metallic and non-metallic materials commonly used in high-temperature applications.

Molten nitrate salt was shown to be chemically stable in air at temperatures up to 600°C, the upper design limit. Higher temperatures should be avoided because decomposition yields high concentrations of nitrite and alkali oxides. The effects of atmospheric CO₂ and H₂O on the melt appeared to be minimal as a practical matter. The important physical properties of the melt were determined and are available to designers. Although values of thermal conductivity and heat capacity at maximum temperatures would be desirable, extrapolations of available data are suitable for design purposes.
Materials are available to fabricate all the components needed for an SCR system. Good corrosion resistance was demonstrated by Alloy 800, 300-series stainless steels, and 9Cr-1Mo at 600°C during long-term tests. Corrosion rates of ferrous alloys increased rapidly at higher temperatures and these temperatures should be avoided. Chromium was slowly leached from some alloys by the salt, but thermal gradient mass transfer was not observed. The oxide layers on high-temperature alloys were adherent, although oxidation was somewhat faster during the thermal cycling experienced in receiver demonstration tests. Corrosion allowances of up to 100 micron/year may be necessary for 2-1/4Cr-1Mo at 460°C. The molten salt did not cause cracking of receiver tube alloys. Among non-metallic materials, graphite and PTFE were resistant at 300°C, but silica-containing refractories deteriorated at 565°C.

The fundamental conclusion of this research program is that the use of molten nitrate salts for energy collection, transfer and storage in SCR systems is technically feasible. This conclusion is supported by demonstrations in multi-megawatt receiver tests and electric power generation experiments.

References

1. R. W. Carling, et al, "Molten Nitrate Salt Technology Development Status Report," SNLL, SAND80-8052, March 1981.
2. T. T. Bramlette, et al, "Survey of High Temperature Thermal Energy Storage," SNLL, SAND75-8063, March 1976.
3. J. D. Fish, et al, Chem. Eng. Prog., p. 48, Jan. 1983.
4. R. W. Carling and R. W. Mar, "Industrial Use of Molten Nitrate/Nitrite Salts," SNLL, SAND81-8020, December 1981.
5. G. J. Janz, et al, "Physical Properties Data Compilation Relevant to Energy Storage. Vol. II. Molten Salts," National Bureau of Standards, NSRDS-NBS 61, part II, April 1979.
6. C. M. Kramer and C. J. Wilson, "The Phase Diagram of NaNO₃-KNO₃", SNLL, SAND80-8052, April 1980.
7. "Advanced Central Receiver, Phase 2, Final Report", Martin-Marietta Corp., MCR-81-1707, Sandia Contract 18-6879C, Vol. 2, May 1981.
8. J. T. Holmes, Proc. 19th Intersociety Energy Conversion Engineering Conf., p. 1700, Amer. Nucl. Soc., 1984.
9. "Molten Salt Electric Experiment (MSEE) - Phase I", Martin-Marietta Corp., MCR-84-548-2, Sandia Contract 81-7469, Sept. 1984.
10. D. A. Nissen and D. E. Meeker, Inorg. Chem., 22, 716 (1983).
11. Op. cit., Ref. 7, Vol. 3 - Materials.
12. R. W. Mar and C. M. Kramer, Solar Energy Matls., 5, 71 (1981).
13. A. S. Nagelberg and R. W. Mar, "Thermochemistry of Nitrate Salts," SNLL, SAND81-8879, January 1982.
14. S. H. White and U. M. Twadoch, "A Study of the Interactions of Molten Sodium Nitrate-Potassium Nitrate 50 Mol % Mixture with Water Vapor and Carbon Dioxide in the Air," EIC Laboratories, Inc., Sandia Contract 20-2991, SAND80-8182, Sept. 1981.
15. L. C. Fiorucci and S. L. Goldstein, "Manufacture, Distribution, and Handling of Nitrate Salts for Solar Thermal Applications," Olin Corp., SNLL Contractor Report, SAND81-8186, November 1982.
16. "Design, Handling, Operation and Maintainence Procedures for Hitec Molten Salt", Badger Energy, Inc., SNLL Contractor Report, SAND80-8179, Jan. 1981.
17. C. B. Allen and G. J. Janz, J. Hazardous Matls., 4, 145 (1980).
18. D. A. Nissen, J. Chem. Eng. Data, 27, 269 (1982).
19. T. Foosnaes, et al., "Thermal Conductivity of Nitrate Mixtures," University of Trondheim (Norway), Sandia Contract 20-2992, 1982.
20. R. W. Carling, "Heat Capacities of NaNO₃, KNO₃, and (Na,K)NO₃," Proc. Third Intl. Symp. on Molten Salts, p. 385, The Electrochemical Society, 1981.
21. D. A. Nissen and R. W. Carling, "Viscous Flow and Structure in Alkali Metal Nitrates", SNLL, SAND82-8669, April, 1982.
22. W. S. Winters, R. W. Bradshaw and F. W. Hart, "Design and Operation of Thermal Convection Loops for Corrosion Testing in Molten NaNO₃-KNO₃," SAND80-8212, June, 1980.
23. R. W. Bradshaw, "Corrosion of 304SS by Molten NaNO₃-KNO₃ in a Thermal Convection Loop," SNLL, SAND80-8856, December 1980.
24. R. W. Bradshaw, "Thermal Convection Loop Corrosion Tests of 316SS and IN800 in Molten Nitrate Salts," SNLL, SAND81-8210, Feb. 1982.
25. P. F. Tortorelli and J. H. DeVan, "Thermal Convection Loop Study of the Corrosion of Fe-Ni-Cr Alloys by Molten NaNO₃-KNO₃," Oak Ridge National Laboratory, ORNL TM-8298, December 1982.
26. R. W. Bradshaw, "A Thermal Convection Loop Study of Corrosion of Alloy 800 in Molten NaNO₃-KNO₃," SNLL, SAND82-8911, January 1983.
27. R. W. Bradshaw, "Kinetics of Oxidation and Elemental Depletion of Austenitic and Ferritic Steels in Molten Nitrate Salt", SNLL, SAND87-8011, 1987.
28. R. W. Bradshaw, "Oxidation of Chromium-Molybdenum Steels by Molten Sodium Nitrate - Potassium Nitrate," SNLL, SAND87-8012, 1987.
29. R. W. Carling, R. W. Bradshaw, and R. W. Mar, J. Matl. Energy Sys., 4, 229 (1983).
30. R. W. Bradshaw, SNLL, unpublished data.
31. D. R. Boehme and R. W. Bradshaw, High Temp. Sci., 18, 39 (1984).
32. R. W. Bradshaw, "Oxidation and Chromium Depletion of Alloy 800 and 316SS in Molten NaNO₃-KNO₃ at Temperatures above 600°C," SNLL, SAND86-9009, Jan. 1987.
33. R. A. Osteryoung and H. Fernandez, "Corrosion of Alloys in Molten Nitrates", Univ. of Buffalo Foundation, SAND80-8181, Sept. 1982.
34. W. H. Smyrl, "Corrosion in Molten Salts Used for Solar Thermal Storage Applications", SMLA, SAND78-0246C, Dec. 1978.
35. J. J. Stephens, R. E. Semarge and R. W. Bradshaw, in Microbeam Analysis-1986, A. D. Romig and W. F. Chambers, eds., Microbeam Analysis Society, 1986.
36. R. W. Mar and J. C. Swearengen, Solar Energy Matls., 3, 37 (1981).
37. S. H. Goods, J. Matl. Energy Sys., 3, 43 (1981).
38. S. H. Goods, J. Matl. Energy Sys., 5, 28 (1983).
39. S. H. Goods, High Temperature Corrosion in Energy Systems, p. 643, M. F. Rothman, ed., The Metallurgical Society, 1985.
40. J. L. Kaae, "Final Report on Low-Cycle Fatigue and Creep-Fatigue Testing of Salt-Filled Alloy 800 Specimens," General Atomic Co., Sandia Contract 82-8182, May 1982.
41. S. H. Goods, Metall. Trans. A, 16, 1031 (1985).
Table 1. Corrosion rates of selected alloys and metals in molten NaNO₃-KNO₃.

| Alloy       | Temp. (°C) | Corrosion rate (microns/year) | Reference |
|-------------|------------|--------------------------------|-----------|
| Alloy 800   | 565        | 5                              | 24,25     |
|             | 600        | 6-10                           | 25,26     |
|             | 630        | 75                             | 32        |
| 316SS       | 600        | 7-10                           | 24,25     |
|             | 630        | 106                            | 32        |
| 304SS       | 600        | 12                             | 23,27     |
| IN600       | 600        | 24                             | 30        |
|             | 630        | 60                             | 30        |
| 12Cr steel  | 600        | 22                             | 27        |
| 9Cr1Mo      | 550        | 6                              | 28        |
|             | 600        | 23                             | 27        |
| 2-1/4Cr1Mo  | 460        | 101                            | 28        |
|             | 500        | 26                             | 28        |
| carbon steel| 460        | 120                            | 30        |
| nickel      | 565        | >500                           | 30        |
| titanium    | 565        | 40                             | 30        |
| aluminum    | 565        | <4                             | 30        |
| aluminized Cr-Mo steel | 600 | <4                             | 29        |
Figure 1. Arrhenius plot of the equilibrium constants for the decomposition of an equimolar mixture of NaNO₃ and KNO₃ and the pure salts.

Figure 2. Experimental values of viscosity, density, thermal conductivity and heat capacity of a molten nitrate salt mixture at temperatures up to 600°C.

Figure 3. Kinetics of the loss of soluble chromium oxidation products from Alloy 800 immersed in the molten salt.
Figure 4. The effect of strain rate on the ductility of Alloy 800 exposed to molten nitrate salt at 600°C.
   a) total elongation (strain to fracture)
   b) reduction in area (R.A.)

Figure 5. Thermogravimetric analysis of the oxidation of graphite by molten nitrate salt.