Applied Energy 159 (2015) 206–213

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Vapor pressure and corrosivity of ternary metal-chloride molten-salt based heat transfer fluids for use in concentrating solar power systems

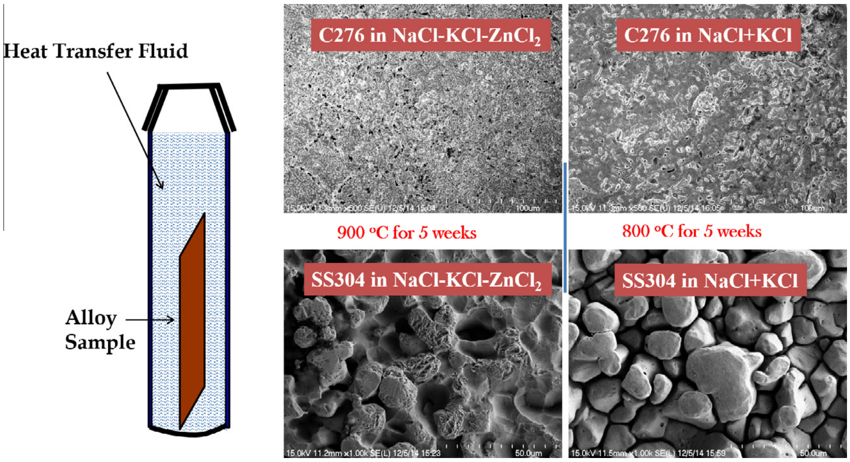
K. Vignarooban [a,b], Xinhai Xu [a], K. Wang [c], E.E. Molina [c], P. Li [c], D. Gervasio [d], A.M. Kannan [a,*]

[a] *Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA*
[b] *Department of Physics, Faculty of Science, University of Jaffna, Jaffna 40000, Sri Lanka*
[c] *Department of Aerospace and Mechanical Engineering, University of Arizona, Tucson, AZ 85721, USA*
[d] *Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA*

HIGHLIGHTS

- Applicability of NaCl–KCl–$ZnCl_2$ salts for CSP applications is evaluated.
- Corrosion rates are estimated by electrochemical and immersion methods.
- Hastelloys show corrosion rates of <10 μm/year at 800 °C under anaerobic conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 24 August 2015
Accepted 31 August 2015

Keywords:
Chloride eutectic molten salts
High temperature corrosion
Vapor pressure
Potentiodynamic polarization
Immersion test
Corrosion rate

ABSTRACT

Higher operating temperatures increase efficiency of the concentrating solar power plants but promote faster corrosion of the pipes and vessels made of Hastelloy or stainless steel materials for the molten-salt mixtures. Hastelloys C-276 and C-22 and stainless steel 304 coupons evaluated in the present study in a eutectic molten salt consisting of 13.4 mol% NaCl, 33.7 mol% KCl and 52.9 mol% $ZnCl_2$ showed substantially lower corrosion rates in the absence versus presence of air from 200 to 800 °C as determined by electrochemical and gravimetric methods. In the presence of air, the corrosion rate for the Hastelloy C-276 in the molten salt was found to diminish with immersion time and converges around ~50 μm per year after 4 weeks of immersion at 500 °C, which is close to the value ~40 μm per year obtained using the electrochemical method at 500 °C. For anaerobic corrosion rate estimation, the corrosivity of an alloy sample was examined by immersing in molten salt inside a sealed quartz container without any contact with air, which is possible because the vapor pressure of the eutectic molten salt is only about 0.7 atm at 800 °C. The corrosion rate of the Hastelloy C-276 was only 10 μm per year in the molten salt in the absence of air at 800 °C, which is extremely low compared to 500 μm per year in conducting corrosion studies in the presence of air at 800 °C. The Hastelloy coupons after immersion testing in the absence of air have then been examined also by SEM, and the images did not show any

---

[*] Corresponding author. Tel.: +1 (480) 727 1102; fax: +1 (480) 727 1549.
E-mail address: amk@asu.edu (A.M. Kannan).

http://dx.doi.org/10.1016/j.apenergy.2015.08.131

significant changes in the surface. This behavior indicates that, from a corrosion standpoint, the eutectic molten salt in the absence of air is suitable as a heat transfer fluid in Hastelloy C-276 pipes and containers up to 800 °C.

1. Introduction

Concentrating solar power (CSP) is emerging as one of the important technologies as a clean and renewable energy system for potential base load applications. Even though the CSP related research and development was evident from early 90s, the number of publications jumped to >700 every year after 2010 indicating the recent interest and financial support from various agencies [1]. Accordingly, most of the commercial installations have been made during this decade particularly in Spain and the United States, with respectively about 58% and 40% of the total 1220 MW global installed CSP capacity [2]. The International Energy Agency has set a target of >1000 GW global CSP installations by 2050 and the European Union (EU), from the perspective of environmental protection, sets a target of 80–95% reduction of EU greenhouse gas emissions by 2050 compared to that in 1990, encouraging the installation of CSP systems [3,4].

Among various CSP technologies, parabolic trough collector type occupies more than 82% of the global CSP installations. However, the most recent CSP installations in the United States, including the world's largest CSP plant – Ivanpah Solar Power Tower (Ivanpah Dry Lake, CA) commissioned in 2014, are the solar power tower (SPT) systems [5]. The main reason for the present trend of installing SPT systems is the potential enhancement in efficiency of heat into electricity conversion. The only disadvantage of SPT is that the initial installation cost is relatively high compared to other CSP technologies. CSP systems are based on a simple operating principle; solar irradiation is concentrated by using programmed mirrors (*heliostats*) onto a receiver, where the heat is collected by a thermal energy carrier called heat transfer fluid (HTF).

HTF is one of the most important components for overall performance and efficiency of the CSP system. Since large amount of HTF is required to operate a CSP plant, it is necessary to minimize the cost of HTF while maximizing CSP performance. Besides transferring heat from the receiver to steam generator, hot HTF can also be stored in an insulated tank for power generation when sunlight is not available. Desired characteristics of a HTF include; low melting point, high boiling point and thermal stability, low vapor pressure (<1 atm) at high temperatures, low corrosion with metal alloys used to contain the HTF, low viscosity, high thermal conductivity, high heat capacity for energy storage, and low cost [6,7].

Very recently, several research reports have been published on different HTFs and their corrosion characteristics with piping/container materials. For example, Fernandez et al. [8] have studied the corrosion effects of a ternary nitrate/nitrite molten salt mixture with piping/container alloys such as T22 steel, which showed a corrosion layer of 6.05 μm with a protective layer formed inside the material. The same group has also showed the improved physico-chemical properties of quaternary mixture of $NaNO_3$, KNO_3, $LiNO_3$ and $Ca(NO_3)_2$ compared to that of traditional *'Solar Salt'* [9]. In 2015, Sang et al. [10] have investigated thermal and structural properties of $Li_2CO_3–Na_2CO_3–K_2CO_3$ molten salt mixture incorporated with hydroxides of lithium, potassium or calcium by using DSC and XRD, respectively. Lower melting points with excellent reproducibility were found when 10 wt.% LiOH or KOH was added into 40 Li_2CO_3–20 Na_2CO_3–40 K_2CO_3 (wt.%). Our recent review in the Applied Energy in 2015 compared various types of HTFs used in CSP systems including the corrosion issues along with the other important physico-chemical properties [11].

In today's commercial CSP systems, the eutectic molten-salts used are the binary mixture of 60% $NaNO_3$ and 40% KNO_3 (known as '*Solar Salt*') and ternary mixture of 53% KNO_3, 40% $NaNO_2$ and 7% $NaNO_3$ (known as '*Hitec*') [7, 12]. However, the '*Solar salt*' and '*Hitec*' are stable only up to 585 and 535 °C, respectively [12]. Hence, there is a need for developing HTFs with lower melting point (<250 °C) and higher boiling point (>1000 °C). It could also be noted that the limited worldwide reserves of nitrate salts is a major limitation for the CSP development. The IEA's target of 630 GWe of CSP installations by 2050 would require 30 times the current mine production of nitrate/nitrite salts from Chile and Peru. Therefore, less expensive and earth abundant HTFs with stability up to 800 °C or even higher temperatures are needed for CSP systems [13]. In this context, molten chloride eutectic salt systems are proposed as commercially viable HTFs.

Ionic metal chloride salts, such as NaCl and KCl are abundant in nature and boil at temperatures higher than 1400 °C. When a high melting (∼800 °C) cubic ionic chloride (NaCl or KCl) is mixed with a low melting (∼200 °C) tetrahedral covalent chloride ($ZnCl_2$), a eutectic mixture is formed with a low melting point (∼200 °C) and is stabilized by complexation between the ionic and transitional metal chlorides at high temperatures (>800 °C). Corrosion of container and piping alloys is a major problem in the CSP systems. Molten-salts are the most promising HTF candidates at high temperatures up to 800 °C for improving the efficiency in the CSP system, but, the corrosion issues are more significant with the molten-salts compared to other HTFs. The corrosion issues of piping/container alloys in contact with eutectic mixtures of $ZnCl_2$, NaCl and KCl based HTFs and the vapor pressure of these HTFs are evaluated in this study.

Vapor pressure of the eutectic molten salt and the stability of metal alloy piping/container materials are two very important issues for viable HTFs for CSP applications at elevated temperatures (up to 800 °C). There are very limited reports in the literature on vapor pressure of molten metal chloride salts and corrosion behavior of Hastelloys (C-276, C-22) and stainless steel (SS-304); these are the alloys typically used for piping/container in CSP systems. While the currently selected metal chlorides have relatively low cost compared to nitrates and nitrites, because of the abundant natural reserves of chlorides, the corrosion rate (CR) of metal alloys in chlorides is still not clear and needs to be explored.

Although, there are no reports available on corrosion issues of alloys in contact with these ternary chloride salt mixtures, there are several reports available on corrosion issues of binary nitrate/nitrite and binary chloride salt mixtures. In one of the earliest work performed in 1985, Slusser et al. [14] have studied the corrosion behavior of nickel and iron based alloys in contact with '*Solar Salt*'. They reported that the nickel alloys with 15–20% chromium content showed best corrosion resistance, whereas iron alloys with low or almost zero nickel content exhibited poor corrosion resistance at high temperatures. Goods and Bradshaw [15] have reported a corrosion rate value of 6–15 μm per year at 570 °C for two different stainless steels (SS-304 and SS-316) and 5 μm per year at 316 °C for a carbon steel (A36), in contact with *'Solar Salt'*. Using gravimetric immersion method, corrosion issues caused by Solar Salt at 390 and 550 °C have been studied by Fernandez