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,*}

^aPolytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA

^bDepartment of Physics, Faculty of Science, University of Jaffna, Jaffna 40 000, Sri Lanka

^cDepartment of Aerospace and Mechanical Engineering, University of Arizona, Tucson, AZ 85721, USA

^dDepartment of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721, USA

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% ZnCl₂ 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 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.

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

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

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 microns 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 $\text{Ca}(\text{NO}_3)_2$ 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 *et al.* [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 *et al.* [16], on two different stainless steels (types AISI 304 and 430) and low-Cr (~2%) alloy steel (T22). It has been found that the alloy T22 underwent greatest mass gain as expected for a low Cr content steel, whereas alloys 304 and 430 showed almost zero gain/loss of mass with immersion time up to 2000 hours.

Li *et al.* [17] have studied the corrosion behavior of NaCl-KCl (1:1 mol%) molten-salt mixture on Fe-Cr, Fe-Al and Ni-Al alloys at 670 °C and found that Al and Ni helped to increase the corrosion resistance, whereas Cr had some detrimental effects. Corrosion behavior of some

nickel containing alloys in molten LiCl-KCl salt mixture was investigated in a recent work [18] and the results showed better corrosion resistance for Inconel 600 and Inconel 690 alloys than that of Inconel 625 and alloy 800H at high temperatures. Abramov *et al.* [19] have done a spectro-electrochemical study of stainless steel corrosion in NaCl-KCl melt and found out that the major corrosion products of steel are iron, manganese and chromium species.

In the present study, a molten-salt HTF was developed from a ternary mixture of NaCl-KCl-ZnCl₂ (13.4:33.7:52.9 mol%), and its vapor pressure and corrosivity towards nickel- and iron-based alloys were investigated at various temperatures up to 800 °C by electrochemical and traditional immersion methods. The ternary salt mixture is found to be stable at temperatures well above 800 °C exhibiting a vapor pressure of 0.7 atm at 800 °C. It is very interesting to note that Hastelloy C-276 (nickel based alloy) in the ternary salt mixture was found through immersion testing to exhibit an exceptionally low corrosion rate of 10 microns per year in the absence of air at 800 °C.

2. Experimental

2.1 Materials

The NaCl, KCl and ZnCl₂ salts (Alfa Aesar, Ward Hill, MA, USA) were used for preparing the ternary eutectic mixture with a melting point of 204 °C [20,21] for a composition of 13.4, 33.7 and 52.9 mol% of these salts, respectively. All the salts were stored in inert atmosphere or under vacuum before loading into the furnace to avoid absorption of moisture from air. The reference electrode for the electrochemical method was fabricated using silver (99.95 %) and silver chloride (99.9 %) powders (Strem Chemicals, Inc. Newburyport, MA, USA). Hastelloy types C-276 (thickness: 0.4 mm) and C-22 (thickness: 0.6 mm) (Haynes International Inc., Kokomo, IN,

USA [22], and the stainless steel SS-304 (thickness: 0.6 mm) (Stainless Supply, NC, USA) [23] were used for evaluating corrosion behavior both by electrochemical and immersion methods in salt #1, NaCl-KCl-ZnCl₂ (13.4:33.7:52.9 mol%). Table 1 shows the elemental composition of the Hastelloys and stainless steel alloys.

2.2 Vapor Pressure Measurement

Vapor pressure of the ternary eutectic mixture, NaCl-KCl-ZnCl₂ (13.4-33.7-52.9 mol. %) was measured at various temperatures using a set-up shown in Fig.1a. The set-up includes a quartz test cell, a quartz sleeved thermocouple, a condenser and a pressure gauge along with access to a vacuum pump. The test cell was vacuumed to remove the air before the salt was heated up. Vapor pressure values were automatically recorded at 10 degree temperature steps using LabView software. The set-up was calibrated by measuring the vapor pressure for ZnCl₂ salt at different temperatures and comparing the results with the data reported in the literature [24]. The sample weight was about 100 g for every measurement.

2.3 Corrosion Rate Measurement

2.3.1. Electrochemical method

Potentiodynamic polarization studies were conducted for the Hastelloys or stainless steel samples (working electrodes) in NaCl-KCl-ZnCl₂ (13.4:33.7:52.9 mol%) at 250, 500 and 800 °C in air using a quartz cell (see Fig.1b), fabricated at the Technical Glass Products (www.technicalglass.com, Painesville, OH). As seen in Fig. 1b, the test set-up has provision to hold the working, counter and reference electrodes in the molten-salt mixture. A quartz tube terminating with a quartz frit (pore size ~ 20-30 μm) and filled with homogenous mixture of equal amounts of Ag and AgCl powders was used as the reference electrode, whose potential is

approximately 0.20 volt versus the standard hydrogen electrode (SHE). As shown in Fig.1b, the electrochemical cell accommodates a working electrode of either Hastelloy C-276 or C-22 or Stainless Steel 304 along with counter and reference electrodes for conducting potentiodynamic polarization scans of the working electrode using a computer controlled potentiostat (PARSTAT-2273 Advanced Electrochemical System). The working electrode was scanned at 0.2 mV.s^{-1} starting from -30 to +30 mV from the open circuit potential of the working electrode versus Ag/AgCl reference electrode. The working and counter electrodes were identical metal alloys and the geometric areas were 2.6 and 8 cm^2 , respectively. In order to eliminate any mixed potentials in the three electrode system, the counter electrode material was the same alloy used as the working electrode in every measurement. All the tests were repeated 5 times and the variation was within 5 %. The CR values were calculated from the corrosion currents using the formula derived from the Faraday's Law, as given by ASTM Standards G59 and G102 [25]:

$$CR \text{ (in } \mu\text{m per year)} = K_1[(i_{corr}EW)/\rho] \quad (1)$$

where $K_1 = 3.27$ in $\mu\text{m.g.}\mu\text{A}^{-1}.\text{cm}^{-1}.\text{yr}^{-1}$, i_{corr} is the corrosion current density in $\mu\text{A.cm}^{-2}$, EW and ρ are the equivalent weight and density (g.cm^{-3}) of the alloy sample, respectively. More detailed information about the experimental set-up, reference electrode etc. is available in an earlier publication in Solar Energy [26].

2.3.2 Immersion method

Weight loss for the metal alloy coupons was monitored by immersion method in 13.4 mol% NaCl, 33.7 mol% KCl and 52.9 mol% ZnCl_2 molten salt at various temperatures in the presence and absence of atmospheric air. The metal alloy coupons were prepared before and after the immersion tests as per ASTM standards. Before each test, the alloy coupons were first washed

with DI water. After drying in air they were polished by 600 SiC paper and then rinsed in DI water and acetone. After the immersion tests, the alloy coupons were sonicated in DI water for 15 min followed by a 15 min sonication in 5.55 wt.% HCl and another 15 min sonication in DI water. Then the mass of the metal coupons were weighed and weight loss values were obtained. Six different coupons of the Hastelloy C-276 were immersed in the molten salt of 50 g mass at 500 °C in six different quartz test cells in the presence of air (Fig. 1c) and the weight loss was measured for each coupon (effective surface area ~ 4 cm²) that has a different duration of immersion (sample 1 for one week, sample 2 for two weeks, and so forth). To conduct immersion tests in the absence of air (Fig. 1d), Hastelloys C-276, C-22 and Stainless Steel 304 were immersed in the molten salt at 400 and 800 °C. All the tests were repeated 5 times and the variation was within 5 %. CR values were calculated from the weight loss values by using the following formula, assuming uniform dissolution:

$$CR \text{ (in } \mu\text{m per year)} = (365)10^4 \left[\frac{WL}{(\rho AT)} \right] \quad (2)$$

where WL is the weight loss in gram, ρ is density (g.cm⁻³) of the alloy, A is the total immersed area in cm², and T is the immersion duration in days. All the data were collected by conducting three trials for each sample and the average CR values were calculated for comparison.

The Hastelloys C-276, C-22 and stainless steel SS-304 coupons (5 samples for each experiment) were also immersed for 5 weeks in the ternary salts mixture (NaCl-KCl-ZnCl₂ 13.4:33.7:52.9 mol%) at 900 °C and in the binary salts mixture (NaCl-KCl 50-50 mol%) at 800 °C in sealed quartz cells for corrosion rate estimation. The surface morphology of the alloy samples before and after immersion studies were examined by JEOL JSM-5900LV Scanning Electron Microscope.

3. Results and Discussion

Fig.2 (a-f) shows the potentiodynamic scans recorded for Hastelloy C-276 at 500 and 800 °C, Hastelloy C-22 at 250 and 500 °C and Stainless Steel 304 at 250 and 500 °C in 13.4 NaCl: 33.7 KCl: 52.9 ZnCl₂ molten salt in the presence of air. In order to ensure a steady state polarization and to avoid disturbing the surface properties on the alloy electrode surfaces, a slower scan rate (0.1- 0.3 mV s⁻¹) and a narrow polarizing voltage window ($\pm$ 30 mV range from the OCV) were used, as suggested by Zhang *et al.* [27]. The CR values estimated from the potentiodynamic scans are shown in Fig.3a as histograms for Hastelloys C-276, C-22 and Stainless Steel 304 alloys in the eutectic molten salt. As seen in Fig. 3a, Hastelloys C-276 and C-22 show almost identical CR values of 40 ± 5 μ m per year at 500 °C, whereas the SS-304 shows extremely high CR (380 ± 40 μ m per year) at 500 °C even though the CR value (20 ± 3 μ m per year) at 250 °C is significantly low. This is not too surprising as the reduction potential of nickel (-0.25 V vs SHE) is about 0.2 volts more noble than iron (-0.44 V vs SHE) [28]. So it is reasonable that the lower stability of SS-304 at elevated temperatures is due to the high iron content in SS-304 compared to that in the Hastelloys. This observation is in consistence with the commonly accepted contention that the nickel alloys are less corroded than iron alloys in chloride media [29]. The Hastelloy C-276 was most stable among the three alloys evaluated showing lowest CR at 500 °C. However, as shown in Fig.3a, the CR for the Hastelloy C-276 at 800 °C is relatively higher ($\sim 500 \pm 50$ μ m per year) compared to that of C-276 and C-22 at 500 °C.

Fig. 3b shows the CR values for Hastelloy C-276 in molten salt in the presence of air by monitoring the weight loss with immersion duration. As shown in Fig.3b, the CR values at 500 °C slowly reduces with immersion time and saturates at around 50 ± 5 μ m per year after 4 weeks

of immersion. This average value of 50 μm per year is relatively close to the value obtained from the potentiodynamic method (~ 40 μm per year). A similar CR behavior with immersion time has also been reported by Estill *et al.* [30] for Hastelloy C-22 immersed in a mixture of NaCl and KNO_3 at 100 $^\circ\text{C}$. According to Estill *et al.* [30], a protective Cr_2O_3 layer is usually formed on the surface of the chromium containing alloys leading to slowdown in the dissolution rate of underlying metal. Then the CR decreases as the exposure time to the corrosive medium increases. The variation of CR values with temperature for the Hastelloy C-276 in NaCl:KCl:ZnCl₂ (13.4-33.7-52.9 mol %) follows Arrhenius behavior with an activation energy estimated as $\sim 35 \text{ KJ.mol}^{-1}$, derived from the Arrhenius plot shown in Fig.4.

Alloys with chromium, which forms a protective Cr_2O_3 layer, are usually known as passivating metals. All three types of alloys studied in the present study namely, C-276, C-22 and SS-304 contain 16, 22 and 18 % chromium, respectively (see Table 1). In a previous weight loss study of molten-salt corrosion published by Slusser *et al.* [14] in 1985, it has been reported that, 15-20% chromium containing nickel alloys performed as the best corrosive resistant alloys in molten nitrate-nitrite salts at high temperatures, whereas iron alloys perform poorly even with substantial Cr content [31,32].

In order to validate the CR values obtained from potentiodynamic scans, immersion test was carried out for Hastelloy C-276. It is generally accepted that corrosion rates obtained from analysis of weight loss of metal with immersion time gives more accurate CR values compared to electrochemical methods [33,34]. The electrochemical method is still being used to estimate CR, as this is faster and non-destructive, whereas the immersion method is a time consuming testing process taking several weeks or even months to get measurable weight loss of the metal alloy coupons.

Fig.5 shows the vapor pressure values for NaCl-KCl-ZnCl₂ (13.4-33.7-52.9 mol. %) ternary molten salt at various temperatures up to 950 °C for three trials. As seen in the Fig. 5, the vapor pressure increases slowly when the temperature is increased from 200 to 800 °C (~ 0.7 atm). There is a significant increase in vapor pressure above 800 °C. At 850 °C, vapor pressure is ~ 1.0 atm, the safety limit accepted by the CSP society. There are almost no reports available in the literature on vapor pressure of these ternary or even binary chloride mixtures. In 2014, Ye *et al.* [35] have studied the vapor pressure of a eutectic salt mixture, Na₂CO₃-NaCl, using transpiration method based on Dalton's law of partial pressure. They reported a vapor pressure value of 0.0005 atm at 800 °C, which is much less than the value obtained for the ternary chloride molten-salt mixture at the same temperature in the present study.

As the vapor pressure is found to be only about 0.7 atm at 800 °C for NaCl-KCl-ZnCl₂ ternary molten-salt mixture, it was decided to conduct the weight loss corrosion experiments by immersion method for the Hastelloy C-276 up to 800 °C by sealing the test cells to ensure the absence of oxygen or moisture, as shown in Fig. 1d. Once a small amount of corrosion occurs in the sealed vessel, the alloy coupons and salt are essentially in an anaerobic environment. The corrosion rates in this type of cell are virtually anaerobic corrosion rates. Fig.6 shows anaerobic CR values estimated from the weight loss values through the traditional immersion method for two weeks for Hastelloys (C-276 and C-22) and SS-304 coupons at 400 and 800 °C. CR value from the immersion method for the Hastelloy C-276 at 500 °C in the presence of air is also given in Fig.6 for comparison.

As seen in Fig.6, the CR values are relatively low for the Hastelloy samples compared to that of the SS-304. Very specifically, the Hastelloy C-276 showed less than 10 ± 2 μm per year at 800 °C. This encouraging observation is a strong evidence that the atmospheric air plays a big role in

inducing the corrosion in the molten-salt/alloy systems. Even though the CR values are low for all the alloys from the sealed immersion experiments, the Hastelloy C-276 exhibits the best stability in the NaCl-KCl-ZnCl₂ (13.4:33.7:52.9 mol%) up to 800 °C compared to the other two alloy samples. The low corrosion rate of the chromium-containing alloys, like Hastelloy C-276 and C-22 in the NaCl-KCl-ZnCl₂ molten salt could be due to the formation of multiple complex chloride structures (K-Zn or Na-Zn) from the covalent (ZnCl₂) and ionic (NaCl and KCl) salts.

The corrosion rate values for Hastelloys C-276, C-22 and stainless steel SS-304 coupons by immersing them in the ternary and binary salts mixtures were also estimated. The results showed corrosion rates of 10 ± 3 , 10 ± 3 and 150 ± 20 $\mu\text{m}/\text{year}$ for C-276, C-22 and SS-304 in the ternary salts mixture, respectively at 900 °C. Whereas for C-276, C-22 and SS-304 in the binary salts mixture, the corrosion rates were 450 ± 30 , 250 ± 28 and 500 ± 30 $\mu\text{m}/\text{year}$, respectively. Fig.7 shows the SEM morphology of the three alloy coupons along with their fresh samples for comparison. The lines in Fig. 7(g) were the surface finish from the fresh sample. For C-276 and C-22 immersed in the ternary salts mixture, very evenly distributed corrosion products on the surfaces of the coupons are observed in Fig. 7(b) and (e). No obvious crack is observed in Fig. 7(e) for C-22, but tiny dark pores exist on the surface of C-276 as shown in Fig. 7(b). However, the surfaces of C-276 and C-22 immersed in the binary salts mixture showed significant change as shown in Fig. 7(c) and (f). Higher corrosion in SS-304 is evident from Fig. 7(h) and (i). Both the images show slagging morphology on the surfaces suggesting the formation of porous multi-layer corrosion products. Fig. 8(a) and (b) show these features more clearly at a higher magnification for Hastelloys C-276 and C-22. Similar slagging morphology has also been reported by Liu *et al.* [36] for C-22 coated by KCl and NaCl mixtures. Surfaces of SS-304 immersed in the ternary and binary salts mixtures are shown in Fig. 7(h), (i), and Fig. 8(c),

respectively. They indicate that the particle-phase products exist in both salt environments. Obviously the ternary eutectic salt do not leave any significant amount of free chloride to react with Cr metal and hence a low driving force to leach out Cr^{3+} from the alloy.

4. Conclusions

The corrosion rates of Hastelloys C-276 and C-22 and stainless steel 304 in molten chloride salt (13.4mol% NaCl: 33.7mol% KCl: 52.9 mol% ZnCl_2) at 800 °C dramatically diminish when the alloy and the salt are isolated from air. This suggests that when the molten chloride salts are used as heat transfer fluids in CSP applications, these alloys (C-276, C-22 and SS-304) can be used as the container and piping alloys, if the molten salts are anaerobic. Based on the lower corrosion rate values observed from this study, the most likely alloy for containing and piping the molten salt heat transfer fluid is a Hastelloy C-276. The surface morphology of the alloy coupons after the immersion studies for 5 weeks clearly highlights the stability of the Hastelloy coupons compared to SS-304. The present study is highly encouraging for the Hastelloys with exceptionally lower corrosion rates in the ternary eutectic molten salt in the absence of air, up to 800 °C for CSP applications.

Acknowledgement

The Authors would like to thank the DOE MURI grant (Award # DE-EE00059) for the financial support.

- [1] Xu X, Vignarooban K, Xu B, Hsu K, Kannan AM. Prospects and problems of concentrating solar power technologies for power generation in the desert regions. *Renew Sust Energy Rev* 2015; under review.
- [2] Garcia IL, Alvarez JL, Blanco D. Performance model for parabolic trough solar thermal power plants with thermal storage: Comparison to operating plant data. *Solar Energy* 2011; 85: 2443-2460.
- [3] International Energy Agency. *Technology Roadmap-Concentrating Solar Power*. 2010.
- [4] European Commission. *A roadmap for moving to a competitive low carbon economy in 2050*. 2011.
- [5] Zhang HL, Baeyens J, Degreve J, Caceres G. Concentrated solar power plants: review and design methodology. *Renew Sust Energ Rev* 2013; 22: 466-481.
- [6] Pacio J, Wetzel T. Assessment of liquid metal technology status and research paths for their use as efficient heat transfer fluids in solar central receiver systems. *Solar Energy* 2013;93:11-22.
- [7] Cordaro JG, Rubin NC, Bradshaw RW. Multicomponent Molten Salt Mixtures Based on Nitrate/Nitrite Anions. *Journal of Solar Energy Engineering-Transactions of the Asme* 2011;133:011014.
- [8] Fernandez AG, Cortes M, Fuentealba E, Perez FJ. Corrosion Properties of a Ternary Nitrate/Nitrite Molten Salt in Concentrated Solar Technology. *Renew Energy* 2015;80:177-183.
- [9] Fernandez AG, Ushak S, Galleguillos H, Perez FJ. Thermal Characterization of an Innovative mixture for Energy Storage in CSP Plants. *Solar Energy Materials and Solar Cells* 2015;132:172-177.

- [10] Sang L, Cai M, Zhao Y, Ren N, Wu Y, Burda C. Mixed Metal Carbonates/hydroxides for Concentrating Solar Power Analyzed with DSC and XRD. *Solar Energy Materials and Solar Cells* 2015;140:167-173.
- [11] Vignarooban K., Xu X, Arvay A, Hsu K, Kannan AM. Heat Transfer Fluids for Concentrating Solar Power Systems - A Review. *Applied Energy* 2015;146:383-396.
- [12] Liu M, Belusko M, Tay NHS, Bruno F. Impact of the heat transfer fluid in a flat plate phase change thermal storage unit for concentrated solar tower plants. *Solar Energy* 2014;101:220-31.
- [13] High Operating Temperature Fluids Funding Opportunity Announcement, # DE-FOA-0000567: Multidisciplinary University Research Initiative (MURI) of the US Department of Energy. 2012.
- [14] Slusser J, Titcomb J, Heffelfinger M, Dunbobbin B. Corrosion in Molten Nitrate-Nitrite Salts. *J Met* 1985;37:24-7.
- [15] Goods S, Bradshaw R. Corrosion of stainless steels and carbon steel by molten mixtures of commercial nitrate salts. *Journal of Materials Engineering and Performance* 2004;13:78-87.
- [16] Fernandez AG, Rey A, Lasanta I, Mato S, Brady MP, Perez FJ. Corrosion of alumina-forming austenitic steel in molten nitrate salts by gravimetric analysis and impedance spectroscopy. *Materials and Corrosion-Werkstoffe Und Korrosion* 2014;65:267-75.
- [17] Li YS, Spiegel M, Shimada S. Corrosion behavior of various model alloys with NaCl-KCl coating. *Mater Chem Phys* 2005; 93: 217-223.
- [18] Shankar AR, Kanagasundar A, Mudali UK. Corrosion of nickel-containing alloys in molten LiCl-KCl medium, *Corrosion Science Section, NACE Int* 2012; 69: 48-57.

- [19] Abramov AV, Polovov IB, Volkovich VA, Rebrin OI, Griffiths TR, May I, Kinoshita H. Spectroelectrochemical study of stainless steel corrosion in NaCl-KCl melt, ECS Transactions 2010; 33(7): 277-285.
- [20] Li PW, Chan CL, Hao Q, Deymier PA, Muralidharan K, Gervasio DF et al. Halide and Oxy-halide Eutectic Systems for High Performance High Temperature Heat Transfer Fluids, SunShot Concentrating Solar Power Program Review, April 2013, pp. 85-86.
- [21] Bale CW, Belisle E, Chartrand P, Decterov SA, Eriksson G, Hack K et al. FactSage thermochemical software and databases - recent developments. Calphad-Computer Coupling of Phase Diagrams and Thermochemistry 2009;33:295-311.
- [22] Corrosion Resistant Alloys, Haynes International Inc., Retrieved on Jan 15, 2015 from <http://www.haynesintl.com/CRAAlloys.htm>.
- [23] Chemical Information: 304 Stainless Steel Sheets, Stainless Supply Inc., Retrieved on Jan 15, 2015 from <https://www.stainlesssupply.com/order-metal-online/docs/g1c1045s1ss0p0/304-stainless-steel-sheet-4-finish.htm>.
- [24] Keneshea FJ, Cubicciotti D. Vapor Pressures of Zinc Chloride and Zinc Bromide and Their Gaseous Dimerization. J Chem Phys 1964;40 (1):191-9.
- [25] ASTM International, Volume 03.02, Standards G 5, G 48, G 59, G 61 and G 102 (ASTM International, 2003: West Conshohocken, PA).
- [26] Vignarooban K, Pugazhendhi P, Tucker C, Gervasio D, Kannan AM. Corrosion Resistance of Hastelloys in Molten Metal-Chloride Heat Transfer Fluids for Concentrating Solar Power Applications. Solar Energy 2014;103:62-9.

- [27] Zhang XL, Jiang ZH, Yao ZP, Song Y, Wu ZD. Effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density. *Corros Sci* 2009;51:581-7.
- [28] DOE Fundamentals Handbook of Chemistry. In: Anonymous Volume 1, DOE HDBK-1015/1.93, Ch. 2, p.4 January 1993: US Department of Energy Public Release.
- [29] Shankar AR, Kanagasundar A, Mudali UK. Corrosion of Nickel-Containing Alloys in Molten LiCl-KCl Medium. *Corrosion* 2013;69.
- [30] Estill JC, Hust GA, King KJ, Rebak RB. Corrosion rate of alloy 22 as a function of immersion time. *TMS Letters* 2005;2 (1):13-4.
- [31] Sorell G. The role of chlorine in high temperature corrosion in waste-to-energy plants. *Materials at High Temperatures* 1997;14:207-20.
- [32] Michel G, Berthod P, Mathieu S, Vilasi M, Steinmetz P. Chromium deposition on cobalt-based alloys by pack-cementation and behavior of the coated alloys in high temperature oxidation. *The Open Corrosion Journal* 2011;4:27-33.
- [33] Wang LL, Martin S.I., Rebak RB. Methods to calculate corrosion rates for alloy 22 from polarization resistance experiments, *Proceedings of ASME Pressure Vessels and Piping Division Conference*, July 23-27, 2006, Vancouver, BC, Canada.
- [34] Zou Y, Wang J, Zheng YY. Electrochemical techniques for determining corrosion rate of rusted steel in seawater. *Corros Sci* 2011;53:208-16.
- [35] Ye L, Tang C, Chen Y, Yang S, Tang M. The thermal physical properties and stability of the eutectic composition in a Na₂CO₃-NaCl binary system. *Thermochim Acta* 2014; 596: 14-20.

[36] Liu S, Liu Z, Wang Y, Tang J. A comparative study on the high temperature corrosion of TP347H stainless steel, C22 alloy and laser-cladding C22 coating in molten chloride salts. Corrosion Science 2014; 83: 396-408.

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 2e

Figure 2f

Figure 3a

Figure 3b

Figure 4

Figure 5

Figure 6

Figure Captions:

1. Schematic of test setups used for (a) vapor pressure measurements, (b) corrosion rate measurement by potentiodynamic method, (c) and (d) corrosion rate measurement by immersion method, with and without the presence of air, respectively.
2. Potentiodynamic polarization scans for (a) C-276 at 250 °C, (b) C-276 at 500 °C, (c) C-22 at 250 °C, (d) C-22 at 500 °C, (e) SS-304 at 250 °C and (f) SS-304 at 500 °C in 13.4 NaCl: 33.7 KCl: 52.9 ZnCl₂ molten salt in air at a scan rate of 0.2 mV s⁻¹.
3. Corrosion rate values in 13.4 NaCl: 33.7 KCl: 52.9 ZnCl₂ molten salt measured from (a) potentiodynamic method for C-276, C-22 and SS-304 alloys at two different temperatures and (b) immersion method for C-276 alloy at six different immersion durations (1 day, 2 days, 3 days and so on) at 500 °C.
4. Arrhenius plot of corrosion rates for C-276 alloy in 13.4 NaCl: 33.7 KCl: 52.9 ZnCl₂ molten salt at various temperatures using potentiodynamic method.
5. Vapor pressures as a function of temperature for NaCl-KCl-ZnCl₂ (13.4-33.7-52.9 mol %) eutectic molten-salt mixture.
6. Corrosion rate values from immersion method for C-276, C-22 and SS-304 alloys in 13.4 NaCl: 33.7 KCl: 52.9 ZnCl₂ molten salt at 400 and 800 °C in the absence of air.
7. Scanning electron micrographs for alloy coupons: (a) to (c) for C-276: a (fresh), b (900 °C in salt #1), c (800 °C in NaCl-KCl), (d) to (f) for C-22: d (fresh), e (900 °C in salt #1), f (800 °C in NaCl-KCl), and (g) to (i) for SS304: g (fresh), h (900 °C in salt #1), i (800 °C in NaCl-KCl). Salt #1 is NaCl-KCl-ZnCl₂ (13.4-33.7-52.9 mol%).
8. Scanning electron micrographs of (a) Hastelloy C-276, (b) C-22 and (c) SS-304 coupons after immersion tests at 800 °C for 5 weeks in NaCl-KCl binary salts mixture.

Figure 7

Figure 8

Table 1: Composition of Hastelloys C-276, C-22 and Stainless Steel SS-304 [13-14].

Hastelloy Type	Composition (wt. %)								
	Ni	Co	Cr	Mo	W	Fe	Mn	Si	C
C-276	57	1 [*]	16	16	4	5	1 [*]	0.08 [*]	0.01 [*]
C-22	56	2.5 [*]	22	13	3	3	0.5 [*]	0.08 [*]	0.01 [*]
SS-304	10	-	18	-	-	69	2	1	0.08 [*]

*Maximum

Heat Transfer Fluid

900 °C for 5 weeks

800 °C for 5 weeks