



Materials selection for thermal energy storage systems in parabolic trough collector solar facilities using high chloride content nitrate salts



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ABSTRACT

The increasing role of concentrated solar power (CSP) within the renewable energy portfolio is attributed to the possibility of integrating thermal energy storage (TES) systems. Then, CSP technology has become one of the most interesting clean options to deliver dispatchable power on demand. Nowadays, commercial facilities use high quality solar salts (60%:40% NaNO₃ and KNO₃ by weight) as storage medium due to the attractive properties of this fluid to be applied under CSP operation conditions. Taking into account that CSP installations are designed with really large TES systems containing tens of thousands of tons, the use of lower quality nitrates salts would reduce the molten salts inventory cost and finally the investment cost of the CSP storage systems at commercial scale. The most important drawback of selecting low quality nitrates salts for high temperature CSP applications is the corrosion impact produced by impurities. Accordingly, chlorides have been identified in the state of the art as the impurity with higher effect over corrosion. This work is focused on A516 Gr70 carbon steel corrosion performance evaluation under high-chlorides content nitrates salts (1.2% and 3% by weight) at 400 °C. In addition, the feasibility of using the proposed low purity mixtures with current CSP facilities materials selection is analyzed. Results reported within this study show the critical effect of chloride content over corrosion mechanism producing lack of adherence between base metal and oxides layers in addition to corrosion products delamination and internal cracking. Then, the use of A516 Gr70 carbon steel is rejected for a long term design under solar salts containing chlorides content in the range 1.2–3% by weight being necessary a higher corrosion resistant materials selection. An improved materials selection focused on higher corrosion resistance alloys is discussed.

1. Introduction

Nowadays, low carbon economy policies are increasingly strict and demanding to change current trends in energy supply which are unsustainable from economic, environmental and social point of view. Accordingly, there is a worldwide pressing need for the development of advanced energy technologies in order to address the global challenges of clean energy, climate change and sustainable development [1,2]. Therefore, renewable energies become in crucial players within this new scenario being the concentrated solar power (CSP) one of the most interesting clean energy alternative [3,4]. The increasing role of CSP technology has been associated to the possibility of integrating large scale thermal energy storage (TES) systems to adapt electricity production to daily energy demand [5–8]. TES systems based on

nitrate molten salts are currently available at commercial scale by using an inorganic mixture composed by 60% NaNO₃ and 40% KNO₃ by weight, the so-called solar salts. Solar salts meet requirements such as high thermal stability, high energy density, and low vapor pressure, among others, to be considered as appropriate thermal energy storage medium for CSP facilities [9–13].

One of the most important drawbacks inherent to solar salts is the corrosiveness associated to this fluid at high temperature. The molten nitrate salts in combination with the metallic components (storage tanks, piping, heat exchangers, valves, among others) of solar power plants constitute a corrosive system with the molten salt acting as an electrolyte. Although metal alloys corrosion mechanisms are well known in numerous aqueous electrolytes, lack of knowledge has been detected regarding corrosion mechanisms of metals under solar salts

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operation conditions in CSP plants. The use of inappropriate materials selection could result in the deterioration of the alloy properties compromising its validity for the final application for which they were designed. Corrosion mechanisms in molten salts are highly influenced by the oxygen ions present in the corrosive environment. Accordingly, pO^{2-} defines the oxide ion activity being a direct function of the metal corrosion in the medium. E- pO^{2-} diagrams are commonly used as an alternative to Pourbaix diagrams to analyze the performance of metals in contact with molten salts at high temperature [14]. Molten salts corrosion mechanism is driven by two main stages. Firstly, an alloy oxidation phenomenon is produced generating the corresponding oxides layers depending on the alloying elements of the metal and molten salts nature. Subsequently, molten salt produces a fluxing action over the protective oxide layers deteriorating it by dissolution. Therefore, the transference of oxidizing species through the metal and the metal ions into the molten salt is favored initiating accelerated attack [15].

Regarding nitrate salts corrosion, the corrosive effect is inherent to the nitrate-nitrite equilibrium of these fluids at a given temperature. Once reduction reaction from nitrate to nitrite is produced, the anionic oxidation of the alloy is carried out in the corrosive medium via the following reactions (iron is taken as an example):



The aggressiveness of nitrate baths could be enhanced by the formation of peroxide and superoxide ions in the medium by the following chemistry [16–18]:



Impurities associated to typical $NaNO_3$ and KNO_3 grades used in solar applications such as chlorides, sulfates, carbonates, and nitrites, among others, could enhance the aggressiveness of solar salts over metallic materials. Accordingly, nitrates salts used for CSP applications are high quality $NaNO_3$ and KNO_3 grades containing low amount of impurities which increase the final cost of the storage medium (Table 1). Current CSP plants installations are designed with huge TES systems with thousands of molten salts tons, being the Solana Generation Station the plant with the larger molten salt inventory at commercial scale (125,000 metric tons of solar salts) [19]. Then, molten salt inventory cost is a very important item in the overall TES cost of a CSP plant. TES energy costs are shown in Fig. 1 for a 50 MW oil parabolic trough collector (PTC) installation with storage capacity from 1 h to 15 h. Molten salts cost is in the range of 23–48% of the total energy cost depending on installed storage capacity [10]. Taking into account that achieving fully dispatchable CSP plants is the objective of this type of facilities, molten salts inventory is one of the most important parameter for TES costs reduction.

Costs associated to current nitrate salts used in CSP TES systems are highly influenced by the final purity provided by the supplier. Then,

Table 1.
Typical compositions of commercial $NaNO_3$ and KNO_3 for solar applications.

Purity/Impurities	$NaNO_3$	KNO_3
Purity (%wt)	98–99.5	99.3–99.6
Chloride (%wt)	0.1–0.6	0.1–0.2
Sulfate (%wt)	0.10–0.50	0.05–0.5
Carbonate (%wt)	0.10	0.02–0.1
Nitrite (%wt)	0.02	0.02
Magnesium (%wt)	0.02–0.1	0.01–0.05

the use of nitrate salts with higher impurity levels would reduce the cost of molten salts inventory and, therefore, the investment cost of the storage systems. The most important drawback of selecting low quality nitrates salts for high temperature CSP applications is the chloride content increasing (main impurity in industrial grades) which has been identified in the state of the art as the impurity with higher impact over corrosion. Chlorides increase molten salts aggressiveness over carbon steels and low alloyed steels due to the formation of chlorine (Cl_2) [20]. Once chlorine has been produced by de combination of chlorides ions, diffusion processes through oxides layer are produced. Chlorine reacts with the steel alloying elements to form metal chlorides at the steel/oxides layer interface (iron is taken as an example in chemical Reactions (6) to (9)). Metal chlorides vapor pressure is relatively high at the interface and the evaporation of these species is produced (7). Then, metal chlorides diffuse back through the alloy oxides layers cracks and pores produced in the corrosion products of the steel. Finally, metal chlorides are oxidized to metal oxides as magnetite and hematite (8) and (9). Attending to chemical Reactions (8) and (9), chlorine is again produced being this specie available to start the process described previously (chemical Reactions (6) to (9)).



Several authors reported interesting results about the influence of chloride content in the corrosion performance of carbon steel showing a dependency between corrosion rates and chlorides content [21–24]. However, these results are associated to short corrosion tests which would be insufficient for a detailed evaluation of corrosion mechanism or longer thermal-corrosive treatments analyzing the effect of chloride content up to 1% by weight. Then, lack of knowledge has been detected about long term corrosion tests with nitrates salts containing chloride percentages higher than 1% by weight which would analyze the effect of low purity salts over metallic materials used in CSP facilities. Moreover, although the negative impact of chlorides over corrosion phenomena such as crevice corrosion and stress corrosion cracking (SCC) has been reported for different corrosive fluids [25–28], results associated to high chloride content nitrate salts have not been identified in the state of the art.

This paper is focused on the feasibility of using high-chlorides content nitrates salts as storage medium in PTC CSP installations. Then, corrosion performance of A516 Gr70 carbon steel under nitrates salts mixtures with different chlorides content levels was evaluated at 400 °C (maximum design temperature of the storage system in PTC facilities). Experimental tests performed in this study complete previous results reported by the authors over carbon steel corrosion performance exposed to solar salts containing typical impurity levels for CSP application in the TES-PS10 pilot plant [29]. Summarizing, laboratory tests within this study face the following purposes: (i) To identify the corrosion mechanism induced by nitrate salts with high chlorides content by a sensitivity analysis with 1.2% and 3% by weight, over A516 Gr70 carbon steel; (ii) To quantify A516 Gr70 corrosion rates, analyze the performance of welded joints and evaluate SCC and crevice corrosion susceptibility; (iii) To compare results obtained in this study with carbon steel corrosion performance in the TES-PS10 pilot plant [29]; (iv) To discuss the feasibility of using solar salts with higher impurity levels at commercial scale with the current materials selection of parabolic trough collectors CSP plants; and, finally (v) To evaluate a higher corrosion resistant materials selection for this application.

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