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Evaluation of corrosion resistance of A516 Steel in a molten nitrate salt mixture using a pilot plant facility for application in CSP plants

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A B S T R A C T

This paper evaluates the corrosion of A516 carbon steel in the binary Solar Salt (60 wt% $NaNO_3$/40 wt% KNO_3) by dynamic immersion test at 500 ℃. To this end, a novel patented experimental facility enabling dynamic degradation tests of materials in contact with molten mediums was developed and used. Experimental results showed greater corrosion rates and thicker oxide layers in samples subjected to dynamic tests than the static ones. The dynamic test facility allows the simulation of (such as flux, thermocycling, etc.) of a CSP plant. The patented experimental pilot plant is a great step forward in learning about the physicochemical properties and behaviour of molten salts and also behaviour of substrates in contact with them under realistic working conditions.

1. Introduction

In recent years the demand for energy has dramatically increased, with renewable energy being encouraged because of its known advantages [1]. The easy integration of concentrated solar power (CSP) with thermal energy storage (TES) makes CSP commercially more attractive than other renewables energies because of its high feasibility and efficiency [2]. Solar thermal plants, which concentrate the Sun's energy to produce steam and electricity, often use molten salt mixtures as a heat transfer fluid (HTF) and/or as a thermal energy storage (TES) medium [3]. Currently the best industrial compound for use in TES is an alkali metal nitrate mixture composed of 60 wt% $NaNO_3$/40 wt% KNO_3 (commonly called Solar Salt) [4]. This mixture melts at 223 ℃ and is thermally stable until about 530 ℃, offering high density, low vapour pressure, moderate specific heat, low chemical reactivity and low cost [5,6].

Corrosion behaviour of materials is a very important issue for molten salts and CSP plants [7]. In 1985 Slusser et al. performed one of the first studies on corrosion in CSP by molten salts [8]. In this study, they worked on corrosion behaviour by nitrate-nitrite salts on both nickel-based and iron-based alloys. In the last few years, many authors have performed a large number of corrosion degradation studies on steels and other alloys in molten salts [9–12]. Among the numerous steels and alloys, some researches have tested corrosion of carbon steels in contact with this storage fluid [13–16]. Goods et al. [14] evaluated isothermal corrosion of carbon steel in mixtures of $NaNO_3$ and KNO_3. They found very low corrosion rates and magnetite was the

main corrosion product. Fernandez et al. [16] studied the corrosive effects of 40 wt% $NaNO_2$/7 wt% $NaNO_3$/53 wt% KNO_3 at 390 ℃ on a carbon steel (A516). Their study revealed a good resistance of A516 steel under this corrosive environment, and they identified a layer 2.66 μm thick composed mainly of magnetite and hematite. On the other hand, some other authors have studied the behaviour of A516 in the Solar Salt at various temperatures [17–19]. Bradshaw et al. [17] studied the effect of chloride content which exists in the binary salt on its corrosive behaviour in contact with A516 carbon steel at 400 ℃ and 450 ℃, since chloride is a very common impurity in this salt. Ruiz-Cabañas et al. [18] studied the behaviour of A516 gr70 carbon steel immersed in a real solar plant in operation. The results are totally representative of real corrosion in molten salt tanks in commercial CSP plants.

All of the above mentioned authors carried out their studies by static immersion tests, these conditions being less realistic than the extreme conditions found in a CSP plant. Parameters such as dynamic flow in contact with the substrate, oxidizing gas atmosphere, and thermal cycling can influence corrosion behaviour [20], and to the best of our knowledge no systematic dynamic studies in easy to manipulate and reliable facilities with molten salts exist. Thus, the aim of this work was to evaluate corrosion of A516 carbon steel in salt mixture of 60 wt % $NaNO_3$ and 40 wt% KNO_3 in dynamic conditions at 500 ℃. In addition, dynamic results were compared to static results in order to evaluate the effect of flowing salt.

Even though the maximum working temperature of A516 is 427 ℃ (established by ASME code), 500 ℃ was selected as test temperature in

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Table 1
Chemical composition of carbon steel A516 (wt%).

Alloy	C	Si	Mn	P	S	Cr	Mo	Nb	N	Fe
A516	0.15	0.30	1.45	0.02	0.015	0.2	0.06	0,01	0.26	Bal.

this research in order to lead the steel to the limit of its mechanical resistance. This experimentation is the first step forward a new research line where A516 will be coated in order to improve its mechanical properties. The results presented in this paper will be the comparison base for following research stages.

2. Experimental procedure

2.1. Material

2.1.1. Substrate

The corrosion tests were performed on commercial A516 carbon steel with the composition shown in Table 1. Specimens were manufactured with nominal dimensions of 20×10×2 mm and the surface was prepared by sanding with silicon carbide (SiC) abrasive paper.

2.1.2. Preparation and characterization of the salt mixture

The alkali metal nitrates that were used as the corrosive agent in this work were $NaNO_3$ and KNO_3 (Panreac®). Some properties of interest and the impurity content of these salts are shown in Table 2. The composition in weight percentage of the alkali metal nitrate mixture used was of 60 wt% $NaNO_3$/40 wt% KNO_3 and it was prepared on the basis of the industrially used Solar Salt composition.

2.2. Corrosion study of the substrates

2.2.1. Dynamic corrosion test

The samples tested using isothermal dynamic immersion were analysed via gravimetric measurements. The previously cleaned specimens were introduced in a sample holder within the facility in contact with the salt mixture. Fig. 1 shows a sketch of the equipment. The equipment, patented under the reference code ES2534850B2 [21], enables degradation tests of materials in contact with molten mediums to be performed, remaining possible the simulation of a thermocycling process and the maintenance of stable conditions during whole study. As shown in Fig. 1, the equipment is made up of a tank (1) containing the melt (3) and heated by a regulated control loop (8) that acts on a heat transmission medium. The design has an adjustable impulsion system (2) and a modular testing chamber (5) with a system to hold (4) samples to be tested. The equipment also includes an auxiliary circuit (7) for gases including a stock of one or various gases (6). Finally, it has an online flanged port (9) for the possible insertion of complementary auxiliary experimental systems such as online corrosion monitoring sensors [10]. Thus, the described equipment assures a continuous circulation of the molten salt on the specimens under study, maintaining the selected temperature over the entire test. It should be underlined that samples are tested inside a chamber of alumina which avoids the contact between samples and the material which the device is made of. Furthermore, the material of the experimental device is stainless steel AISI 321 which is a material currently used in CSP plants and has

Table 2
Properties of $NaNO_3$ and KNO_3.

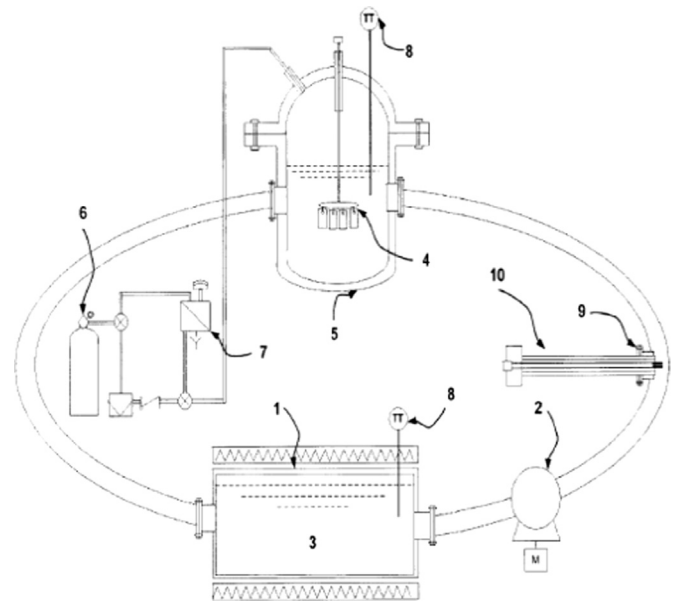| Salt	Melting point, °C	Decomposition point, °C	Impurity content, ppm	
			Cl^-	SO_4^{2-}
$NaNO_3$	308	380	175	11
KNO_3	334	400	148	418

Fig. 1. Sketch of the dynamic equipment [18].

shown an excellent behaviour [22]. These two materials ensure that there are no additional corrosion phenomena during the whole test.

The dynamic test was carried out at 500 °C. This temperature was measured constantly during the whole test. The velocity of test was set to 0.2 m s^{-1}. This velocity was selected on the basis of the flow velocity which is given in areas near to pipe bends and valves in the current CSP plants (0.2–0.5 m s^{-1}), which are areas where high levels of corrosion are found. On the other hand, the samples were placed into the facility so that the flow was parallel to them. That allows us to simulate the most common angle attack of the salt flow in CSP plants when the salt circulates through steel tubes. Once the test was completed (100 h), the tested specimens were analysed.

After removing the samples from the equipment they were cooled slowly in warm distilled water in order to eliminate the salt in which they had been immersed. They were then dried and weighed, average taken from five values of their weights. The formula (Eq. (1)) used to calculate the average weight variation over time is:

$$\frac{\Delta m}{S_0} = \frac{m_i - m_f}{S_0} \tag{1}$$

where m_i is the initial mass of the specimen, m_f is the mass of the sample at the selected time and S_0 is the initial area of the specimen.

2.2.2. Static corrosion test

The isothermal static immersion test was also analysed via gravimetric measurements. Firstly, cleaned specimens were placed in alumina crucibles and fully immersed in the molten mixture to give a melt depth of about 3.5 cm. The crucibles together with the solid salt mixture were then set inside an electrical tube furnace (Carbolite®) to reach the required temperature, which was measured constantly during the test. As in the dynamic corrosion test, the temperature selected was 500 °C in order to compare the results obtained in both tests. The tested specimens were analysed at 100 h. Two specimens were removed from the salt mixture for examination and analysis at the selected times.

As after the dynamic test, once the samples were removed from the oven, they were cooled, dried and weighed. Then the average weight variation over time was calculated using the above mentioned Eq. (1).

2.2.3. Characterization of the samples

The previously tested specimens were characterized by Scanning