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1 2	High temperature corrosion behaviour on molten nitrate salt-based nanofluids for CSP plants
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12	
13	Abstract
14	Recently, a number of theoretical and experimental studies have been performed to
15	understand the effect of nanoparticles on thermal properties and heat transfer performance
16	but there is a lack regarding their corrosion properties. In this work, an extended corrosion
17	characterization (at central tower plant storage temperature (565°C)) has been carried out
18	in two different grades of solar salt (industrial and refined purity) doped with the addition
19	of 1 wt% Al ₂ O ₃ nanoparticles or 1 wt% SiO ₂ nanoparticles. Corrosion rates were
20	determined in commercial stainless steel commonly used in CSP technology (347SS) by
21	gravimetric tests, measuring the weight gain during 1000 hours, identifying the corrosion
22	products by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The
23	lowest corrosion rate (0.007 mm/year) was obtained in the refined solar salt with the
24	addition of 1 wt% Al ₂ O ₃ nanoparticles. A protective layer was formed in the steel-salt
25	interphase, identified through XRD as Al ₂ O ₃ .
26	Additionally, hematite (Fe ₂ O ₃) and magnetite (Fe ₃ O ₄) were obtained as unprotective
27	corrosion products throughout the test carried out with or without nanoparticles. In
28	addition, the presence of impurities on the salts generated some stable compounds, as
29	magnesium ferrite (MgFe ₂ O ₄).
30	
31	Keywords: Nanoparticles; molten salts; corrosion; Concentrated Solar Power
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34 List of nomenclatures:

- 35 | CSP: Concentrated Solar Power
- 36 SEM: Scanning Electron Microscopy
- 37 XRD: X-ray diffraction
- 38 TES: Thermal Energy Storage
- 39 LCOE: Levelized Cost of Electricity
- 40 RSS: Refined Solar Salt
- 41 ISS: Industrial Solar Salt
- 42 ANP: Alumina Nanoparticle
- 43 | SiNP: Silica Nanoparticle

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44 | EDX: Energy Dispersive X-Ray

1. Introduction

Concentrating Solar Power (CSP) technology captures and stores the sun's energy in the 46 form of heat, using materials that are low cost and stable for decades. Today's most 47 advanced CSP systems are towers integrated with two-tank molten-salt TES, delivering 48 thermal energy at 565 °C for integration with conventional steam-Rankine power cycles 49 50 [1]. This design has lowered the cost of CSP electricity by approximately 50% over the prior generation of parabolic trough systems. However, the decrease in cost of CSP 51 52 technologies has not kept pace with the falling cost of solar photovoltaic systems and further research is needed. High-temperature molten salt has been commonly used as an 53 54 effective working fluid for CSP systems, increasing electrical efficiency and reducing the Levelized Cost of Electricity (LCOE). However, the high freezing point of the Solar Salt 55 56 (221 °C) may result in its solidification on a cloudy day or at night. In this direction, the 57 design of multicomponent mixtures by the addition of alkali/alkaline earth nitrates could extend the working temperature range of thermal energy storage [2, 3] but an 58 enhancement in the thermal conductivity and heat capacity at storage temperatures must 59 be necessary for a successful development of this technology. 60

In this direction, high temperature nanofluids have received great attention over the last decade due to their increased specific heat compared to the base fluids [4, 5]. In the last years, several researches have been performed to understand the effect of nanoparticles on thermal properties and heat transfer performance [6-10]. These researches have been focused on Thermal Energy Storage (TES) materials (molten salts) commonly used in

Concentrated Solar Power (CSP) plants and a majority of the works [10-12] showed that 66 67 the specific heat of nano-salt was increased. The percentage of addition (used in this work, 1wt.%) is based on the excellent thermal transfer obtained by several authors with the 68 same nanofluids [5]. Many efforts have been required to carry out the research work 69 published up to date due to the lack of standards for the preparation, the measurement and 70 the evaluation of the results, as well as to approach the understanding of the behaviour of 71 the composite at the nano-scale [13]. Therefore, the fact of having the nanoparticles well-72 dispersed rather than agglomerated is one of the objective in this technology since it will 73 74 cause fluidity issues or higher corrosion behavior. Well-dispersed nanoparticles essentially result in an increased surface to volume ratio, which can lead to enhanced 75 76 thermal conductivity, a transport-related property. Jo et al.[4] conclude that a compressed liquid creates a layer adjacent to the interface with the solid and the specific heat capacity 77 78 enhancement in a nanomaterial can result from an increased interface area between the surrounding liquid and the nanoparticles improving the specific heat capacity of 79 80 nanomaterials.

- Different authors [14-17] have evaluated the effect of the impurities in the convencional molten salts proposed as thermal energy storage material concluding that impurities tend to drive corrosion. However, there is not information in the literature regarding the corrosive effect in molten salt based nanofluids. The corrosive evaluation of these improved molten salts must be studied since nanoparticles are solid in the mixture, being potential candidates to promote erosion/corrosion in CSP pipelines.
- This is one of the main factors to take into account in the corrosion test performed during 1000 hours. The aim of this paper is the corrosive evaluation of two grades of solar salt (SQM, Refined (RSS) and Industrial (ISS) grades) with the most common addition of Al₂O₃ and SiO₂ nanoparticles found in the literature (1wt.%), at 565 °C in contact with 347SS.

2. Materials and methods

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96 97 The saline nitrates used in the research were NaNO₃ and KNO₃ (SQM grades RSS and ISS). Two Solar Salts (60:40 wt. of NaNO₃:KNO₃) of different purity were prepared: the refined grade, RSS (SQM, NaNO₃≥99.5 wt.%; SQM, KNO₃≥99.6 wt.%) and the industrial grade, ISS (SQM, NaNO₃≥98.0 wt.%; SQM, KNO₃≥95.0 wt.%). Two types of ceramic nanoparticles were selected, Al₂O₃ nanoparticles

98	(ANPs) and SiO ₂ nanoparticles (SiNPs). ANPs were purchased from Kawaken
99	Chemicals as an industrial water-based nanofluid, Alumisol 10A, containing fiber-
100	shaped boehmite nanoparticles (L=50 nm, ϕ =10 nm) at 10 wt% according to the
101	manufacturer. The boehmite (aluminium oxyhydroxide, AlOOH) is a precursor of
102	the γ -Al ₂ O ₃ . On the other side, a dispersion of colloidal silica at 30 wt%, Ludox SM-
103	30, from Sigma-Aldrich was used as a source of spherical SiNPs.
104	Four nanofluids were produced with these materials, including 1 wt.% of each
105	nanoparticle in combination with each of the salts RSS and ISS. Once the synthesis
106	process involving nanoparticles addition was arranged (addition procedure was
107	explained in a previous paper [18]), the mixed formulations were sealed inside a dry
108	box with desiccants. The steel analyzed in the saline medium was an austenitic
109	stainless steel (347SS, 2%Mn/11%Ni/18%Cr) commonly proposed as container
110	material in CSP plants.
111	The dimensions of the steel samples used in the gravimetric corrosion tests were 20
112	$\text{mm}\times 10~\text{mm}\times 2~\text{mm}.$ A grinding process was performed using silicon carbide (SiC)
113	P1000 abrasive paper with a (SiC grit size: $18.3\ \mu m$). This treatment produces a
114	homogeneous surface in the sample and promotes delamination of the possible
115	oxides and the small imperfections where corrosion could be located. The samples
116	were subsequently washed with acetone in an ultrasound bath to eliminate any
117	remaining dirt. The dimensions of each sample were measured using an electronic
118	caliber (± 0.01mg), and each sample was weighed using an analytical balance
119	(Mettler Toledo) with a 0.00001 g responsiveness. Subsequently, the samples were
120	placed into alumina crucibles (Fig 1) with the saline mixture and then heated in a
121	resistance furnace at 565 °C.



Figure 1. Alumina crucibles filled in with nanofluid (left) and alloy specimen immersed into the solid nanodoped-salt before the test (right).

Table 1: Impurity content in solar salts employed in this work

Impurity	RSS Solar Salt (wt%)	ISS Solar Salt (wt%)
Chloride	0.060	0.260
Perchlorate	0.064	0.247
Sulfate	0.011	0.146
Carbonate	0.010	0.009
Nitrite	<0.001	<0.001

Different technical grades of solar salt (refined and industrial) have been selected for the nanoparticles addition since the impurities present in the salt could have influence in the integration of these particles in the salt matrix. Static gravimetric measurements were performed after 200, 400, 600, 800 and 1000 hours of exposure at the testing temperature in the isothermal immersion test. After the samples were removed from the crucible, they were left to cool down slowly and subsequently washed out with warm distilled water to eliminate the salt in which they were immersed and they were dried and weighed. Five weight measurements were taken from each sample and between each measurement the samples were kept into dry box with desiccants. The average value of the weight obtained from the five measurements has been used for the analysis of the results. The formula (Eq. 1) to calculate the mass gain over time is:

$$\frac{\Delta m}{S_0} = \frac{m_f - m_i}{S_0} \qquad (Eq 1)$$

where m_i is the initial mass of the specimen, m_f is the mass of the same at time t and S_0 is the initial area of the specimen. Finally, the microstructural characterization has been carried out in a scanning electron microsopy (SEM, JEOL 6460LV with EDAX)), using EDS analysis in order to stablish the morphology as well as the corrosion mechanism. X-ray diffraction analysis (with a grazing angle of 0.5°) model X'Pert Pro/MRD from Panalytical was used for the corrosion components elucidation after 1000 hours of test.

3. Results

3.1. Corrosion of ISS and its nanofluids

The gravimetric weight gain that occurs on ISS is shown in figure 2, where the results obtained with the industrial grade solar salt (ISS) and its corresponding nanofluids (the ISS with 1%Al₂O₃, and the ISS with 1%SiO₂) can be compared.

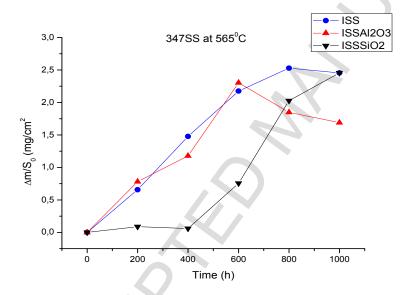


Figure 2: Gravimetric weight gain curve obtained in ISS and its nanofluids for 347SS at 565°C

At 600 hours of experiment, the corrosion produced by ISS + 1% Al₂O₃ was higher compared with the weight gain in the solar salt without nanoparticles. Beyond this point the corrosion rate is reduced, probably due to the sedimentation of the nanoparticles at the bottom of the crucible.

To explain this behavior, a micro-structural (surface and cross section) study of the SS347 was performed using scanning electron microscopy (SEM). Figure 3 shows the sample surface morphology of the steel after 800 hours of exposure to ISS + 1 %wt. Al₂O₃, as well as an analysis via Energy-Dispersive X-ray spectroscopy (EDX) of the particles

found on the surface. At the end of the test, a uniform sodium ferrite (Na₂FeO₄) scale was obtained.

Spectrum	0	Na	Fe		
Spectrum 1	40.28	32.59	27.13		
Spectrum 2	38.99	20.21	40.80		

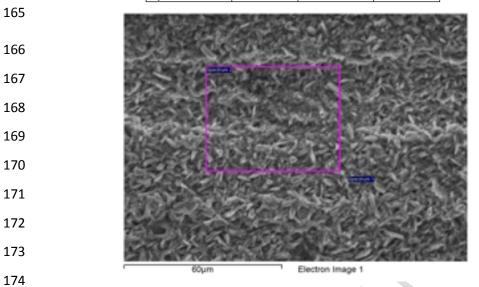


Figure 3: Detail of the 347SS specimen surface after 800 hours immersed into ISS+1%Al₂O₃ For the cross sectional study, SEM pictures have been obtained by backscattered electron microscopy.

Spectrum	0	Na	Si	K	Са	Cr	Mn	Fe	Ni
Spectrum 1	38.58	7.39	-	-	0.26	0.77	1.36	51.64	-
Spectrum 2	33.20	1.24	/ -/	0.23	-	2.05	1.42	61.40	0.47
Spectrum 3	28.72	1.49	0.80	0.26	-	4.40	1.71	61.74	0.88
Spectrum 4	19.85	0.72	1.02	-	-	28.00	1.59	38.64	10.19
Spectrum 5	14.83		0.71	-	-	20.06	1.35	46.82	16.23

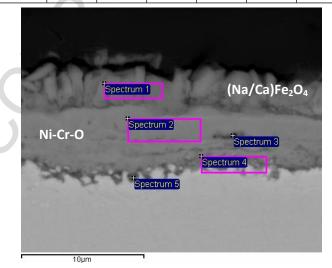


Figure 4: Detail of the cross-section of the 347SS specimen after 1000 hours immersed into $ISS+1\%Al_2O_3$

A protective layer composed by Ni-Cr-O has been detected in the steel surface and in the upper part an non protective layer composed by (Na/Ca)Fe₂O₄ was obtained, trough the following reactions:

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$$Na_2O + Fe_2O_3 \rightarrow Na_2Fe_2O_4$$
 (Reac. 1)
193 $CaO + Fe_2O_3 \rightarrow CaFe_2O_4$ (React. 2)

On the other hand, for ISS+1 wt.%SiO₂, the analysis of the surface shown in figure 5 presents a less compact corrosion layer, probably due to the Si content detected in the corrosion layer. This influence of the Si presence in corrosion layers was recently publish by Hamid et al. [19], concluding that 1 wt% Si additions could modify the steel surface interacting with the impurities present in the corrosive environment along with the alloying elements of the steel.

Spectrum	0	Na	Mg	Si	Са
Spectrum 1	64.69	35.31		-	-
Spectrum 2	64.29	8.15	-	-	27.56
Spectrum 3	45.89	27.72	9.12	17.27	-

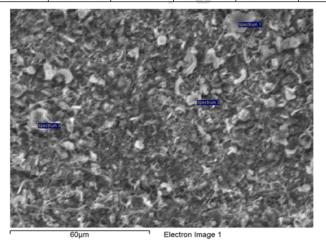


Figure 5: Superficial image of 347SS immersed during 800 hours in ISS+1 wt.% SiO₂

This silicon content was also detected in the cross sectional study at different levels through the corrosion layer. The composition of these products have been determined by XRD (table 2) and in this case, SiO₂ and Fe₂SiO₄ were identified in the steel and in the remaining salt after the corrosion test.

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Spectrum	0	Na	Mg	Si	K	Са	Cr	Mn	Fe	Ni
Spectrum 1	50.96					47.81			1.23	
Spectrum 2	32.71	0.94	0.41	0.42			8.27	1.62	52.67	2.96
Spectrum 3	35.32	2.08	1.61	0.42		7.45	3.50	1.52	36.80	11.29
Spectrum 4	35.15	4.66	3.54		0.34		0.59	1.02	54.70	
Spectrum 5	18.45		0.84	0.67		0.29	16.75	1.80	52.55	8.65
Spectrum 6				0.42			13.90	1.14	72.62	11.91

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Spectrum 4 Spectrum 1 (Na/Ca/Mg)Fe₂O₄ Spectrum 3

Figure 6: Cross sectional image of 347SS immersed during 1000 hours in ISS+1 wt.%SiO₂.

A non protective layer composed by (Na-Ca-Mg)Fe₂O₄ has been formed in the corrosion 227 layer, responsible of the higher gravimetric weight gain determined when the steel is immersed into ISS+1 wt.%SiO₂ as shown in figure 1. 228

It is important to highlight that the stability of the salts during the corrosion process showed an important reduction when SiO₂ nanoparticles are involved and the salt solidified two times during the corrosion test.

Yang et al. [20] reported that when molten nitrate salts come into contact with a containment substrate such as quartz or stainless steel at temperatures above 500°C, the release of nitrogen oxide could be foreseen due to the extensive reaction of NO₃- with SiO₂ or with Cr, respectively. The reactions included:

SiO₂ + 2NO₃
$$\leftrightarrow$$
 SiO₄²⁻ + 2NO₂ (Reac. 3)

and
$$Cr + 2NO_3 \leftrightarrow CrO_4^{2-} + 2NO$$
 (Reac. 4)

The results attained in our work revealed that the presence of the SiO₂ nanoparticles 238 promotes the decomposition of nitrate or nitrite to form silicates (Na₂SiO₃) and NO gas. 239

3.2. Corrosion of RSS and its nanofluids

In order to compare the corrosion behavior produced by a Solar Salt with a different impurity content (lower percentage of chloride), RSS provided by SQM has been studied. In this case, the gravimetric weight gain is lower compared to the previous case using ISS and there is not a clear correlation between the corrosion produced by the addition of nanoparticles to the RSS. The better corrosion behavior was obtained for RSS+1 wt.%Al₂O₃ showing a gravimetric weight gain around 0.5 mg/cm².

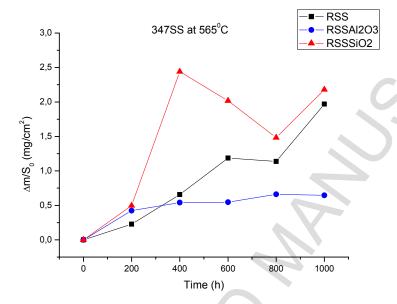


Figure 7: Gravimetric weight gain of the 347SS specimens immersed into the refined solar salt (RSS) and the corresponding nanofluids at 565°C

In this direction, it is important to highlight the morphology of the specimens surface immersed in RSS+1 wt.%Al₂O₃ (figure 7), showing needle-like structures containing Al. This structure, integrated in the steel matrix, increase the protection against the corrosion produced by molten salts.

Spectrum	С	0	Na	Mg	Са	Cr	Mn	Fe
Spectrum 1	12.84	40.40	5.98	1.73	4.49	1.14	0.89	32.53
Spectrum 2	9.89	33.31	9.59	1.59	3.07	1.13	3.34	38.09
Spectrum 3	7.99	36.09	4.93	2.85	4.80	1.18	2.08	40.08

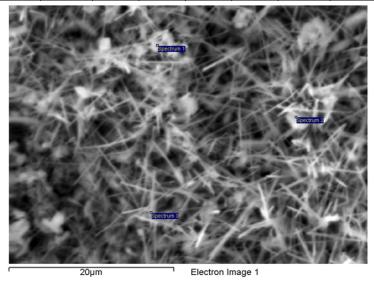


Figure 8: Detail of the surface morphology of a 347SS specimen immersed in RSS+1 wt.%Al₂O₃ for 800 hours.

Presently, there is no a clear explanation about the potential mechanism leading to the corrosion protection obtained by this needle-like aluminium oxide morphology.

An extended research will be carried out in the future to understand the fundamentals behind the better corrosion behaviour due to the Al_2O_3 nanoparticles. On the other hand, the formation of this corrosion-protective layer could reduce the heat capacity enhancement produced in the molten salt by the addition of the nanoparticles, which was indeed the main objective pursued in their development [11, 18]. If a synergic effect between the corrosion protection and the thermal properties could be attained, the key for an interesting increment of the efficiency and the cost reduction of this technology could have been found.

The alumina needles were also observed on the cross sections of the specimens, like that shown in figure 8. In this case a compact protective layer of spinel (FeCr₂O₄) formed on the steel surface, which leads to increase the corrosion resistance of the steel in contact

with the molten salt.

Spectrum	0	Na	Mg	Al	Si	Cl	К	Са	Cr	Mn	Fe	Ni
Spectrum 1	32.35	0.75	0.48					0.84	10.99	1.83	50.68	2.09
Spectrum 2	36.13	7.28	1.41	0.76		0.32		1.05	0.98	1.70	50.38	
Spectrum 3	32.76	0.59	0.58		0.37			0.54	11.16	1.96	51.48	0.55
Spectrum 4	29.06				0.81		0.36		29.69	2.22	34.50	3.36

Spectrum 2

, [†]Spectrum 3 Spectrum 4 **(FeCr₂O₄)**

Spectrum 1

Figure 9: Detail of the 347SS specimen cross-section immersed into ISS+1% Al_2O_3 for 1000 hours

According to the obtained gravimetric curve (figure 7), the steel immersed in the refined solar salt containing 1 wt.%SiO₂, presents irregularities on the mass increment. This behavior could be explained due to the spallation of the oxidic layer, as can be observed on the surface morphology of the specimen shown in figure 10.

Spectrum	0	Na	K	Са	Cr	Fe
Spectrum 1	30.71	13.78	-	-	4.74	50.76
Spectrum 2	34.34	24.77	0.79	2.24	-	37.86

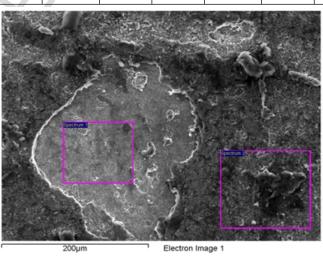


Figure 10: Detail of the 347SS specimen surface after immersed in RSS+1 wt.%SiO₂ for

(pink box on the right, in figure 10). The composition of the surface after spallation

310 800 hours

The EDX analysis of the surface after the oxide-spallation was carried out (pink box on the left, in figure 10), as well as the analysis of the oxide surface adhered to the specimen

314 (spectrum 1) presents a higher Cr content.

This is a protective layer, which was seen in the cross section of the specimen (figure 11) in the inner zone, close to the steel surface. In this case the thickness of the corrosion layer obtained was 12.13 microns at the end of the test, showing the higher weight gain according the gravimetric curve (figure 7).

Spectrum	0	Na	Si	Cr	Mn	Fe	Ni
Spectrum 1	35.50	7.07	0.57	0.96	0.86	55.05	-
Spectrum 2	29.12	-	0.56	6.15	1.28	59.22	3.66
Spectrum 3	19.78	-	0.68	30.35	1.74	31.07	16.37
Spectrum 4	32.24	-	1.14	14.90	1.99	47.12	2.61
Spectrum 5	17.70	-	0.71	28.50		35.72	17.37

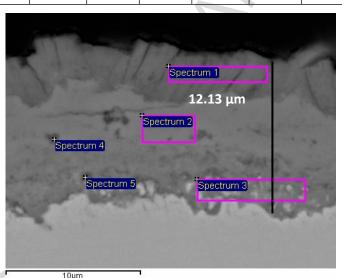


Figure 11: Detail of the 347SS specimen cross-section after immersed into ISS+1 wt.%SiO₂ for 1000 hours

XRD analysis were carried out after the corrosion test, both in the samples as well as in the salts in contact with them. Results are shown in table 2.

Table 2: Corrosion products obtained by XRD in the steels tested and in the salt remaining

Molten salts	Nano	Steel	Corrosion	Corrosion products			
Monten saits	particle	Steel	Steel	Salt	(mm/year)		
	Al ₂ O ₃ (1 wt%)	347	MgFe ₂ O ₄ , Fe ₂ O ₃ , Fe ₃ O ₄ , Al ₂ O ₃	K ₂ Fe ₂ O ₄	0.007		
Solar Salt RSS Grade	SiO ₂ (1 wt%)	347	Fe ₃ O ₄ , Fe ₂ O ₃ , MgFe ₂ O ₄ , KCrO ₂	MgSiO ₄ , SiO ₂	0.022		
	-	347	MgFe ₂ O ₄ , Fe ₃ O ₄ , Fe ₂ O ₃	Na ₂ O	0.021		
	Al ₂ O ₃ (1 wt%)	347	MgFe ₂ O _{4,} MgAl ₂ O _{4,} Fe ₂ O ₃	Fe ₃ O ₄ , Al ₂ O ₃ , Ca ₂ Fe ₂ O ₅	0.019		
Solar Salt ISS Grade	SiO ₂ (1 wt%)	347	MgFe ₂ O ₄ , Fe ₃ O ₄ , MgO, SiO ₂ , Fe ₂ SiO ₄	SiO ₂ , Ca ₂ Fe ₂ O ₅	0.024		
	-	347	MgFe ₂ O ₄ , Fe ₃ O ₄ , MgO, MgCr ₂ O ₄	Fe ₂ O ₃ , MgFe ₂ O ₄	0.027		

The gravimetric corrosion rate was also included in the table 2. ISS mixture showed the higher corrosion rate due to the higher Cl content. The effect of nanoparticles does not seem to increase the corrosion rate obtained in the isothermal static study at 565°C. It has been found that Al₂O₃ nanoparticles present a better corrosion protection of the steel matrix when using RSS salts rather than using ISS salts. This effect could be interesting in order to design a protective methodology for the steels in contact with the salt since a superficial Al content has been detected. On the other hand, this corrosion-protective layer formed onto the steel reduces the content of the Al₂O₃ nanoparticles in the salt, whose main function is the enhancement of the thermal properties. Corrosion rates are in concordance with the results available in literature, regarding the immersion of 347SS in RSS. Kruizenga [21] reported a weight loss around 1.8 mg/cm² in same conditions at 1000 hours of test, which correspond to a corrosion rate of 0.02 mm/year.

356	4. Conclusions
357	The present work has carried out a corrosion study of a commercial stainless steel (347SS)
358	into nanofluids made of solar salt doped with 1%wt. of nanoparticles. The study
359	comprises tests with two different grades of solar salt (refined and industrial) and two
360	different types of nanoparticles, Silica and Alumina.
361	The results obtained in the corrosion study showed a higher corrosion rate using the
362	industrial solar salt grade, due to the higher chloride content, compared with the other
363	impurity grade (RSS) but the addition of nanoparticles do not increase the corrosion
364	behavior in the storage materials tested.
365	According with the results obtained, for RSS + 1wt% Al ₂ O ₃ , a protective layer was
366	obtained. This structure (composed mainly by Al ₂ O ₃) and integrated in the steel matrix,
367	increase the protection against the corrosion produced by molten salts.
368	One of the drawbacks detected in the nanofluid was a reduction of the viscosity in the salt
369	during the corrosion test, when SiO ₂ nanoparticles are involved. In this case, solidification
370	of the salt was produced during the test and the XRD analysis revealed the presence of
371	SiO ₂ and MgSiO ₄ , as main component in the salt remaining after the corrosion test.
372	The corrosive evaluation of these nanofluid showed that nanoparticles do not produce an
373	enhancement of the corrosion rate in static conditions. However, the corrosion should
374	also be tested in dynamic conditions since Al ₂ O ₃ /SiO ₂ are solid particles in the mixture,
375	being potential candidates to promote erosion/corrosion in CSP pipelines.
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381	Antofagasta.
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Highlights:

- ➤ Corrosion rates obtained during the experiments are similar using nanosalts or conventional nitrate molten salts.
- ➤ The knowledge acquired in corrosion using nanosalts can help to understand the corrosion issues associated with doped molten salts under operation in CSP plants.
- ➤ The use of molten salts doped with Al₂O₃ nanoparticles could increase the corrosion resistance in steels in contact with them