Proceedings World Geothermal Congress 2023
Beijing, China, October, 2023

Heat Exchange and Durability Performance of Ni-P-PTFE Coatings in Geothermal Heat Exchanger Boiling Environment

Sigrun Nanna Karlsdóttir, Halldór Pálsson, Gifty Oppong Boakye, and Adolph Jr. Bravo

Faculty of Computer Science, Industrial and Mechanical Engineering, University of Iceland, Hjardarhagi 2-6, Reykjavik Iceland

snk@hi.is, halldorp@hi.is, gob13@hi.is, ajm10@hi.is

Keywords: coatings, corrosion testing, ORC heat exchanger, geothermal utilization

ABSTRACT

In utilization of geothermal energy, the materials used for geothermal power plant equipment often experience corrosion and scaling due to the chemistry of the geothermal fluid and elevated temperatures in the equipment. For low-medium temperature geothermal areas (below 150-180°C) Organic Rankine cycle (ORC)- heat-exchangers (HE) are often needed for the geothermal power plants for the electricity production and increased efficiency. Carbon steel materials are commonly used for the pipes and plates of heat exchangers due to good heat transfer properties the down-side is their poor anti-scaling and -corrosion properties. To overcome this corrosion-resistant alloys such as various stainless steels with less favorable heat transfer properties but better anti-scaling and -corrosion properties have been used. In the research project GeoHex different coatings were developed to enhance scaling and corrosion resistance and heat transfer performance. These coatings were tested in an experimental ORC heat-exchanger (HE) test equipment (test rig) designed to evaluate the anti-scaling and -corrosion properties and heat transfer properties in boiling heat transfer experiments. The coatings developed were designed for two different conditions for the ORC-HE; for the brine side and the working fluid side. These included Ni-P-PTFE composite coating that were tested in the ORC-HE at RT to 80°C on the brine side and two different amorphous coatings on the working fluid side. The microstructure and chemical composition of the coatings were analyzed before and after the tests with Scanning Electron Microscope and X-Ray Energy Dispersive Spectroscopy to evaluate the durability of the coatings. The morphology and hydrophobic properties (wettability) were also examined with roughness and water contact angle (WCA) measurements. The coatings were observed to increase the WCA in most of the coatings, however, higher angles were measured after the LT test influenced by the morphology of the coatings after the exposure. The results showed that the Ni-P-PTFE coatings had relatively good corrosion resistance and were highly hydrophobic and increased heat transfer compared to the bare carbon steel substrate. Thus the Ni-P-PTFE coating was concluded to be promising for application in ORC-HE environment.

1. INTRODUCTION

The proper selection of heat exchangers is crucial to the longevity and sustainability of geothermal power plants. When choosing a material for a specific environment, factors such as cost and material reliability should be considered. High temperature and high pressure geothermal heat exchanger applications typically use high-performance materials like austenitic stainless steel, Ni and Ti alloys (e.g., UNS S31254, UNS N06625, and UNS R50400) [1,2,3]. However, these materials can be expensive, so they are not used as frequently as UNS S31600 and S30400 steels of lower corrosion resistance [1,4], which are two of the most extensively used and researched materials in geothermal environments. Utilizing geothermal fluids to generate power or heating for district systems can be difficult for metal alloys due to dissolved species and gases in the fluid, leading to corrosion and scaling issues, which depend on the geothermal fluid's pH, salinity, and composition (e.g., where CO_2 and H_2S is present) [5]. Organic Rankine Cycle (ORC) geothermal power plants are an alternative option for fields with temperatures below 200 °C [1,6]. However, a study by Ravier [6] reported corrosion issues of a carbon steel heat exchanger system operating at relatively low reinjection temperatures between 70°C to 40°C.

Polymer materials, composites, and anti-scale/hydrophobic coatings are examples of technological materials that can improve component functionality and cost efficiency [7,8]. One of the main drawbacks of using coatings in geothermal conditions is the possibility of corrosion at the coating-substrate interface [9]. At this interface, imperfections and a loss of anti-adhesion lead the underlying substrate to corrode quickly [10]. Another important effect of coatings is their effect on heat transfer through convection behavior when in contact with fluids undergoing heating, cooling or phase change. This can potentially lead to improvements in heat transfer, or reduction, since the coatings can alter the surface contact properties and roughness.

The goal of this study is to understand how hydrophobic coatings and nanocomposite materials behave in a simulated boiling ORC geothermal heat exchanger. Ni-P based nanocomposite coating (with PTFE nano particles) that aim to provide thinner layers with the were tested, evaluated and compared to commonly used carbon steel and stainless steel (UNS S30400). The coatings were tested in an experimental ORC heat-exchanger (HE) test equipment (test rig) designed to evaluate the anti-scaling and -corrosion properties and heat transfer properties in boiling heat transfer experiments.

2. MATERIALS AND METHODS

Substrate and coated plates were tested in an Organic Rankine Cycle (ORC) heat exchange rig to evaluate heat exchange properties and durability for commercial-scale application.

2.1 Rig and testing conditions

Boiling heat transfer testing was done in an ORC rig designed and constructed within the GeoHex project. It operates in a fully closed loop setup, with a brine-side heater and a working fluid-side cooler (condenser) undergoing phase change. A schematic of the rig is shown in Figure 1. R134a (UN3159) was used as the working fluid (WF) on the phase change side. For the brine, tap water was used in place of mineral-rich geothermal brine to avoid scaling in sensitive parts of the rig, such as the metering ports and valves. Measured parameters from the rig, which are used in heat transfer calculations, are summarized in Table 1.

Table 1. Measured values in the ORC rig

Property	Unit	Range
Temperature	°C	20-80
Pressure	bar	0-9
Flow rate	$Lmin^{-1}$	0-3.2

Short-term tests to evaluate heat flux and overall heat transfer coefficients were conducted over eight hours per test, herein called a short-time test (ST). During the test, the pressure of the working fluid was set constant at 7 bar. The brine flow rate was also kept constant at 3.1 $Lmin^{-1}$. The only parameter adjusted during the measurement period is the inlet temperature of brine. For each selected (and controlled) value of the inlet temperature, the outlet temperature was allowed to reach a steady state to exclude any transient effects on the heat transfer performance. This was done in steps of 4°C, where it took between 10 and 30 minutes to reach steady state for each inlet temperature change. This process resulted in 12 to 14 different steady-state conditions for each sample, making it possible to estimate the heat transfer performance for several temperature differences and heat transfer values.

Long-term tests (LT) were also conducted over 200 hours to simulate longer exposure of the plates to the geothermal brine. Like the short-term tests, the R134a pressure and the brine flow rate were kept constant and only the brine inlet temperature was adjusted during the tests. The primary purpose of the long-term tests was to evaluate possible variations in durability of the coating, i.e., damages such as adhesion defects and corrosion.

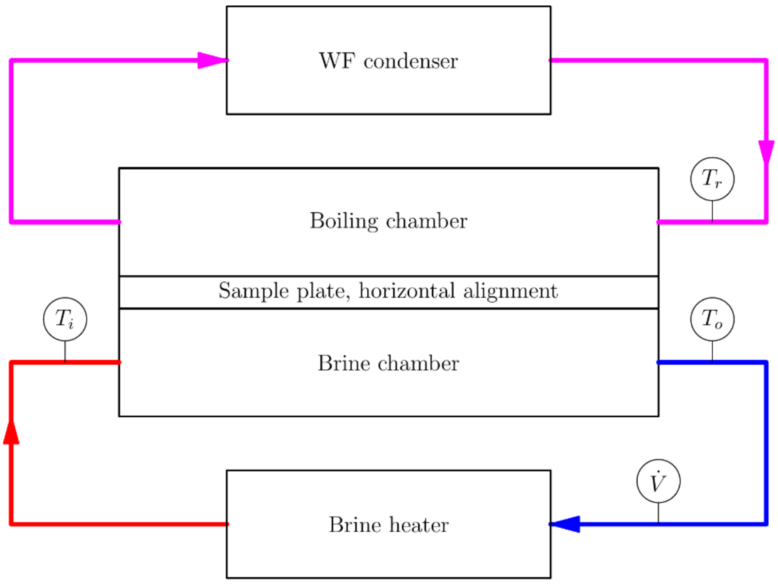

Figure 1. Schematic of the design of the ORC rig and position of the coated sample, being exposed to the WF on on-side and the simulated brine on the other side.

2.2 Heat transfer performance evaluation

The total heat transfer in the rig experiments can be estimated on the brine side, based on measured inlet and outlet temperatures, flow and the density and specific heat of the brine. This is described in equation (1) as

$$q = \rho \, c_p \, \dot{V} \, (T_i - T_o) \tag{1}$$

where ρ denotes brine density, c_p is the specific heat, $\dot{V}$ is the volumetric flow and T is the temperature of the inlet and outlet, respectively. The heat transfer on the WF-side is governed by nucleus boiling at constant temperature and this phase change temperature is denoted by T_r. Thus, temperature difference in the process can be defined as

$$\Delta T_m = \frac{T_i - T_o}{\ln\left(\frac{T_i - T_r}{T_o - T_r}\right)} \tag{2}$$

Finally, the overall heat transfer coefficient U can be related to the heat transfer with equation (3)

$$q = UA\Delta T_m \tag{3}$$

where A denotes the heat transfer area which is 100 square centimeters in the experiments.

2.2 Materials

Three sets of sample plates coated with Ni-P-PTFE composite coating on the brine side and with two different coatings; Nanoporous TiO_2 and Fe-doped TiO_2/Al_2O_3 on the working fluid side were tested using the ORC heat exchanger. Bare carbon steel substrate plates were also tested for comparison with coated samples. The sets of sample plates tested are summarized in Table 2. For each set, two samples were subjected to the short-term (8h) test while one sample was tested long-term (200h).

Table 2. List of samples tested

Sample sets/names	Brine-side coating	WF-side coating
Substrate: Carbon steel (S275JR)	Uncoated	Uncoated
NiP-1: Nanoporous-NiP	Ni-P-PTFE	Nanoporous TiO_2
NiP-2: FeDoped-NiP	Ni-P-PTFE	Fe-doped TiO_2/Al_2O_3

The short-term tested samples were used in evaluating the heat flux improvement of the Ni-P-PTFE coating in comparison to the uncoated substrate plates. In evaluating the durability of the coating, data collected from the long-term (LT), short-term (ST), and uncoated samples were compared.

2.3 Material characterization for durability analysis

Material characterization of the coated and uncoated samples were obtained before and after exposure to the simulated geothermal brine environment. Surface morphology and elemental composition were analyzed using scanning electron microscopy (FE-SEM, Zeiss Supra 25®) equipped with an EDS -Oxford Instrument®. DataPhysics® OCA - Series device was used to measure the wet contact angle (WCA) and assess the wettability of the plates before and after testing. A Solarius® SD-V100-3219 3D optical profilometer was used to measure surface roughness and assess topographical changes due to brine exposure.

3. RESULTS

3.1 Heat flux and heat transfer coefficient

Two main heat transfer characteristics parameters are compared in the study, the heat flux through a unit area (q_w) and the overall heat transfer coefficient (U). Note that in both cases the parameters include effects of the substrate conductivity as well as the convection properties of both brine and working fluid.

Figure 2 shows results for the coated samples, compared to an uncoated substrate. The coated surfaces show significant improvement in heat transfer, except from the second sample with Fe-doped surface coating which shows more erratic behavior for temperature differences below 25°C. It can also be noted that after reaching a critical heat flux with temperature difference above 35°C, the performance is slightly worse than for the uncoated samples.

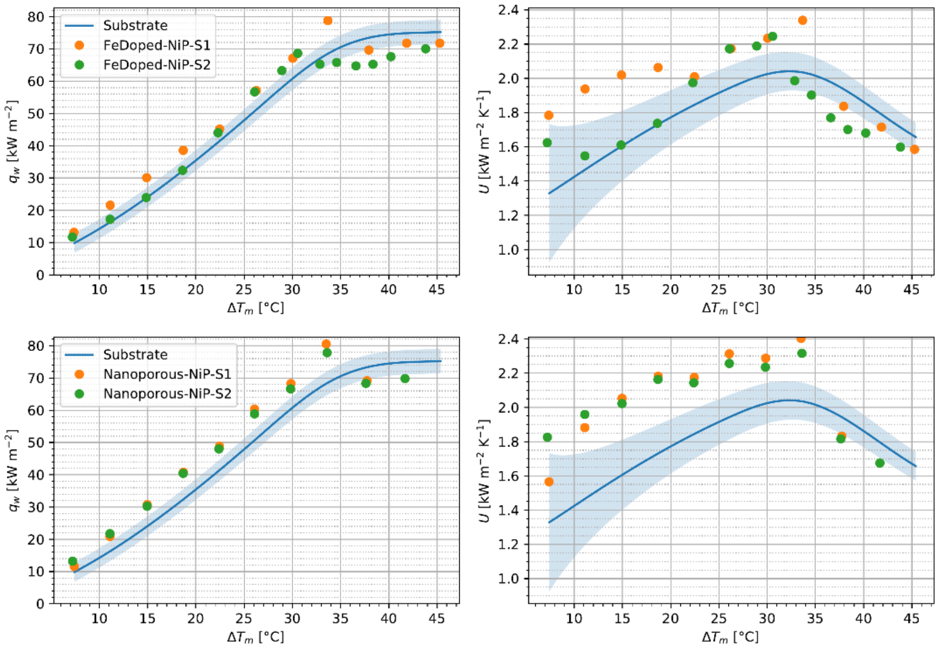

Figure 3. Heat flux (left) and overall heat transfer coefficient (right) with Ni-P-PTFE on the brine side and Fe-doped (top) and Nanoporous (bottom) on the WF-side. A confidence interval for the results of uncoated S275JR samples is shown as a shaded band.

There is not a clear difference between the results for the two WF-side coatings when they are compared directly, which coincides with results on stainless steel substrates which are not documented here. This indicates that the improvement in heat transfer is mainly due to the Ni-P-PTFE coating on the brine side which is in line with the fact that the convection on the brine side has a greater effect on the overall heat transfer when temperature difference increases and the nucleus boiling on the WF side becomes stronger. The improvement here is around 15% at the maximum values of *U*, and well above the 95% confidence limit.

3.2 Durability analysis

<u>Visual Inspection</u>

Photographs of the carbon steel substrate and coated samples before and after testing are shown in Table 3. The carbon steel substrate showed changes in the surface after exposure to geothermal brine with a greater degree of orange and brown discoloration in the long-term tested sample. Deposits and surface features were observed on the carbon steel such as the formation of holes and the deposition of orange substances indicating corrosion products. The baffled flow pattern of the brine inside the rig is evident on the surface of the plates.

Table 3. Photographs of samples before and after rig testing showing surface changes after exposure to brine.

	Untested	**Short-term (8 h)**	**Long-term (200 h)**
Substrate (CS_275JR)			
Ni-P-PTFE (Nanoporous -WF)			
Ni-P-PTFE (Fe-doped -WF)			

Surface changes were also observed in the Ni-P-PTFE coated samples after exposure to brine. This can be seen in the photographs shown in Table 3. For the untested coated sample spots of scale-like deposits were present on the surface. Fewer of these deposits remained after the short-term test and none after the long-term test, indicating that the exposure to the simulated brine affected these deposits, potentially removing part of them. Discoloration was also observed in the Ni-P-PTFE coated samples with few small spots that had the resemblance of holes. These features were marked and analyzed further by using SEM/EDS for microstructural and chemical composition analysis.

<u>Microstructural and Chemical composition analysis</u>

SEM images of the untested (Fig 1a) and long-term tested (Fig 1b-1c) carbon steel substrates are shown in Figure 2. The discoloration observed visually corresponded to widespread deposition on the surface. Chemical maps indicate the deposits are Fe-O rich corrosion products. Cracking and pitting are also observed in areas with more intense deposition as shown in Fig 2d. These results show corrosion damage of the carbon steel substrate after exposure to the geothermal brine.

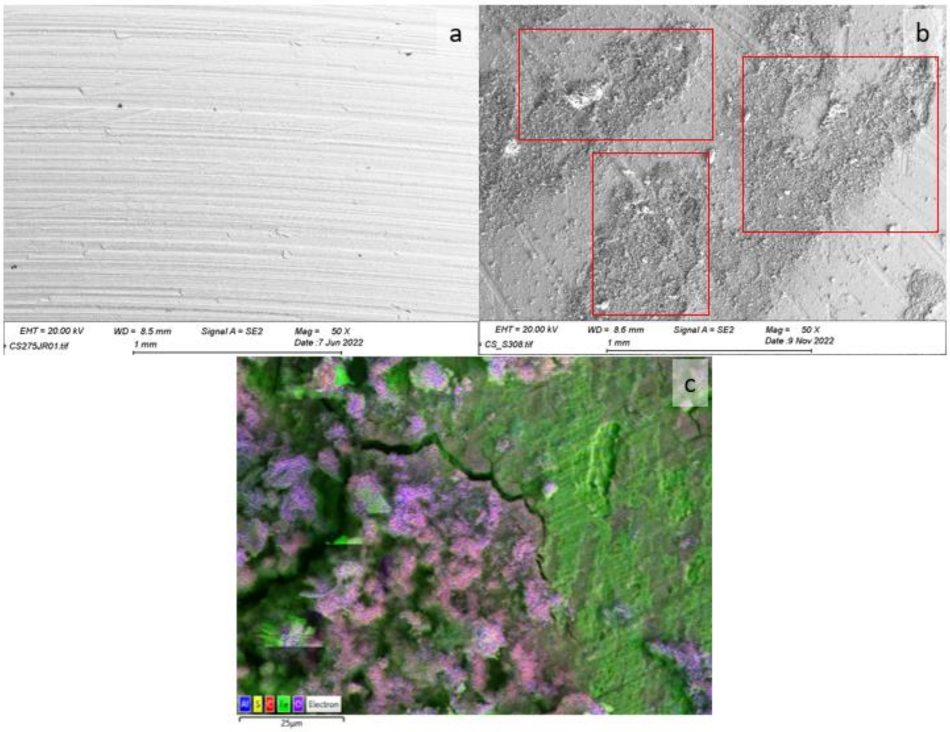

Figure 2. SEM images and chemical analyses of carbon steel substrate before (a) and after (b) rig test, and chemical (elemental) maps of the surface at higher magnification showing corrosion products and cracks (c).

The brown spots observed in the untested coated sample in Table 3 for the Ni-P-PTFE coatings correspond to carbon- and fluorine-rich areas based on the EDS analyses (see Figure 3a). This is possibly due to non-dispersion and agglomeration of PTFE particles (C_2F_4) in the coating which become visible at the surface. In other areas no brown spots were visible and SEM/EDS analysis of those areas showed good dispersion of the PTFE nanoparticles. The agglomeration of PTFE was likely due to the coating process and only visible at the surface of the plates. These were removed after exposure to the geothermal brine, with none observed in the long-term tested plates.

Although the long-term tested samples were generally smoother, some smaller dark spots were still observed visually. In the SEM analysis these spots corresponded to relatively large holes with deposition of material inside as shown in Figure 3b. Similar holes were also present in the untested samples (see Fig. 3a), implying these were present before testing and were not caused by exposure to brine. Some oxidation products were detected inside a hole in the long term (LT) tested sample, see Fig. 3b, which indicates that some corrosion reactions occurred.

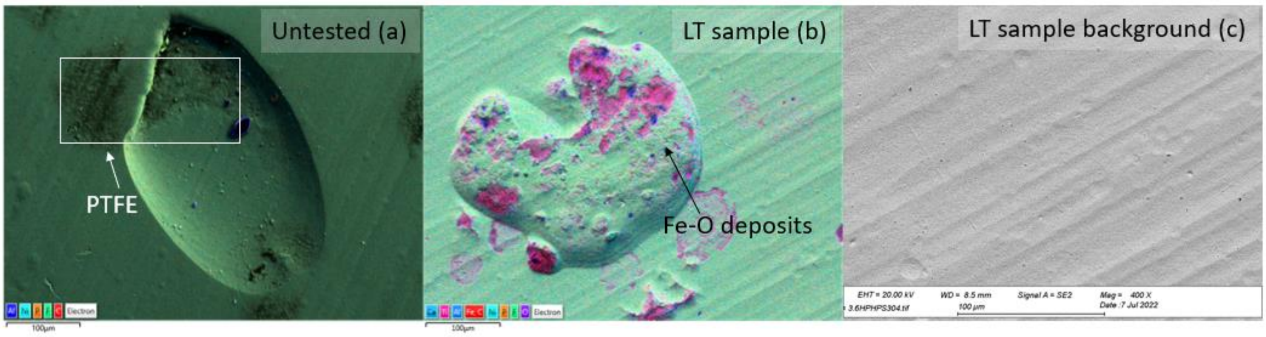

Figure 3. SEM images of holes found in the (a) untested and (b) tested samples, in comparison to (c) an area of the tested plate without defect.

Both sets of the Ni-P-PTFE coated plates indicate an increase in oxygen content with testing as summarized in Table 4 where results from chemical analyses of the untested, short-term (ST) tested, and long-term (LT) tested plates are compared. The most discolored area of the long-term tested sample corresponded to the highest oxygen content, indicating some oxidation occurring on the surface. Despite 5-6% weight fraction (wt%) of oxygen was measured on the surface, no deposition of oxides were visible on the surface and in some areas there was no concentration of oxygen detected. In this study the chemical analysis performed with the EDS equipment were qualitative not quantitative. The chemical analysis of the cross-section of the area with oxygen detected is shown in Figure 4. In the coating, the oxygen signal was weak and undetectable, indicating the oxygen previously measured from the exposed surface does not penetrate deep into the coating. The oxygen signal from the substrate was stronger as seen in the chemical map, which likely occurred during the process of cross-sectioning. Nevertheless, this indicates that the coating is only weakly oxidized. Results from these chemical analyses and comparing it with the chemical analyses of the tested carbon steel substrate demonstrates the protection of the Ni-P-PTFE coating against corrosion in this test environment.

Table 4. EDS chemical analyses of untested and tested Ni-P-PTFE coated samples, indicating increase in oxygen content with increased exposure to the brine. Elements given in wt%.

	Untested	NiP-1			NiP-2		
		ST	**LT**	**LT *(darkest area)***	**ST**	**LT**	**LT *(darkest area)***
C	6.8	9.2	8.9	9.5	7.5	10.8	11.3
F	4.3	7.2	6.7	6.7	5.4	6.7	7.5
P	8.6	8.1	8.2	8.0	8.7	7.3	7.3
Ni	79.3	74.5	72.3	70.7	76.8	70.8	68.1
O	**1.0**	**0.7**	**3.3**	**4.1**	**1.5**	**4.2**	**5.6**

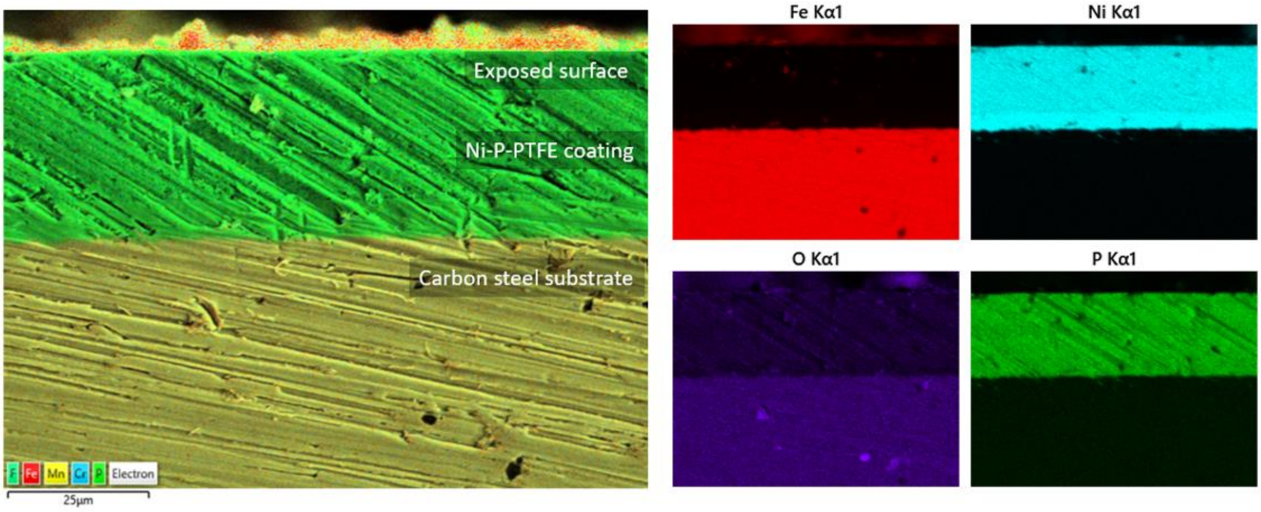

Figure 4. SEM and EDS maps of the cross-section of the area with most discoloration on the Ni-P LT tested specimen.

The WCA and surface roughness measurements of the coatings are summarized in Table 5. The WCA of the coated samples was higher than the substrate, demonstrating how the coating enhances the hydrophobicity of the surface. Furthermore, the WCA of the long-term tested samples were higher compared to the untested and short-term tested samples, suggesting the oxidized surface provided higher hydrophobicity. The measured surface roughness of the coated samples was lower compared to the carbon steel substrate, suggesting that the coating fills the surface features of the substrate resulting in a smoother and more even surface. There was no significant change in the roughness of the two sets of coatings after the long-term test, which supports the observed lack of features developed.

Table 5. WCA and surface roughness of the two sets of Ni-P-PTFE samples

	WCA (^{0})			Roughness, Ra (μm)			Key observations
Material	**Untested**	**ST**	**LT**	**Untested**	**ST**	**LT**	
Substrate: CS-275JR	80	97	99	0.81	0.44	2.50	1) Discoloration after testing 2) Increase in roughness due to formation of corrosion products
NiP-1 coating	103	102	107	0.81	0.38	0.34	1) Increase in oxygen 2) Increase in WCA with coating and testing;
NiP-2 coating	103	102	108	0.81	0.30	0.36	
Nano-porous coating	N/A	N/A	N/A	8.37	6.87	9.30	1) Water droplets collapsing upon contact with surface
Fe-doped coating	N/A	N/A	N/A	*	5.13	3.70	

N/A: the WCA value could not be measured because the water droplets were immediately adsorbed by the surface. *: measurement not available because of non-availability samples untested.

4. CONCLUSIONS

The Ni-P-PTFE coatings showed good corrosion protection and durability after testing in the brine side, i.e., preventing the carbon steel substrate to pitting corrosion of the surface as observed for non-coated sample. Only minor oxide formation was observed on the surface and no cracking or peeling of the coating. For the working-fluid side the nano-porous and the Fe-doped coatings perform quite good based on surface roughness and microscopic analysis. Both the nano-porous and the Fe-doped coatings show high hydrophilicity based on the WCA measurements; water droplets are immediately adsorbed by the surface which is what the intention was with using these coatings on the WF side.

The Nanoporous-NiP (NiP-1) coating combination sample showed increased heat transfer compared to other coatings and the bare carbon steel substrate. There was though some drop in the heat transfer coefficient for one of the LT test as shown in Figure 2. From the material characterization it is possible that this is due to some decrease in heat transfer ability of the coating due to the formation of oxides on the surface after the long-term test. In general, the heat transfer results indicate a 15% increase in U, and a similar increase in the mean heat flux. The analysis showed that the NiP coatings performed best out of the coating materials tested within the GeoHex project in this experimental test equipment simulating ORC HE boiling environment for increasing lifetime of carbon steel substrate material and heat transfer properties.

5. ACKNOWLEDGEMENTS

This work is part of the Geo-Hex project ‘‘Developing advanced material with anti-scaling and anti-corrosion properties for cost-efficient and enhanced heat exchanger performance for geothermal applications’’. This project has received funding from European Union’s Horizon 2020 programme under grant agreement 851917. The authors would also like to acknowledge the resources and collaborative efforts provided by the consortium of the Geo-Hex project especially the TWI Ltd. and the University of Leicester that provided the coated samples.

REFERENCES

[1] S. Davíðsdóttir, B.G. Gunnarsson, K.B. Kristjánsson, B.A. Ledésert, D.I. Ólafsson, Study of corrosion resistance properties of heat exchanger metals in two different geothermal environments, Geosciences (Switzerland). 11 (2021) 1–23

[2] S.N. Karlsdottir, K.R. Ragnarsdottir, I.O. Thorbjornsson, A. Einarsson, Corrosion testing in superheated geothermal steam in Iceland, Geothermics. 53 (2015) 281–290

[3] A.I. Thorhallsson, A. Stefansson, D. Kovalov, S.N. Karlsdottir, Corrosion testing of materials in simulated superheated geothermal environment, Corros Sci. 168 (2020).

[4] N. Mundhenk, P. Huttenloch, T. Kohl, H. Steger, R. Zorn, Metal corrosion in geothermal brine environments of the Upper Rhine graben - Laboratory and on-site studies, Geothermics. 46 (2013) 14–21

[5] S.N. Karlsdóttir, Corrosion, Scaling and Material Selection in Geothermal Power Production, in: Comprehensive Renewable Energy, Elsevier Ltd, 2012: pp. 241–259.

[6] Ravier, O. Seibel, A.S. Pratiwi, J. Mouchot, A. Genter, K. Ragna Ragnarsdóttir, X. Sengelen, Towards an optimized operation of the EGS Soultz-sous-Forêts power plant (Upper Rhine Graben, France), in: European Geothermal Congress, European Geothermal Congress 2019 Den Haag, 2019: pp. 11–14.

[7] N. Mundhenk, J. Scheiber, R. Zorn, P. Huttenloch, A. Genter, T. Kohl, Corrosion and Scaling in the Geothermal Cycle of Soultz-sous-Forêts (France), in: Corrosion 2014/NACE International, OnePetro, San Antonio, Texas, 2014.

[8] A. Covelo, C. Menchaca, M. Flores, P.R. Rojas, M. Hernandez-Gallegos, E.M. Meza, R. Jaimes-Ramírez, J. Uruchurtu, Hydrophobic Coatings for Corrosion Control of Aluminum Heat Exchangers, in: C. Giudice, G. Canosa (Eds.), New Technologies in Protective Coatings, InTech, 2017.

[9] G. Oppong Boakye, E.O. Straume, D. Kovalov, S.N. Karlsdottir, Wear-reducing nickel-phosphorus and graphene oxide-based composite coatings: Microstructure and corrosion behavior in high temperature geothermal environment, Corros. Sci. 209 (2022) 110809.

[10] J. Scheiber, G. Ravier, N. Cuenot, A. Genter, In-Situ Material and Corrosion Studies at the Soultz-sous-Forêts (France) EGS Site, World Geothermal Congress 2015. (2015) 8.