SUITABILITY OF THIN CERAMIC COATINGS TOWARDS SCALE REDUCTION IN HEAT EXCHANGERS

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ABSTRACT

Scaling of heat exchangers (HE) in the chemical industry, district heating, oil and gas, power plants, etc. results in a loss of performance which leads to production stops for cleaning and therefore increased operation costs. One approach to mitigate fouling is to alter the properties of the metal heat exchanger surface by applying a coating. For a coating to be successful in any heat exchanger application it needs to have a good adhesion to the metal but also to keep the heat transfer through the metal plates as unaltered as possible. This requires a thin coating with a relatively good thermal conductivity. In this study a new ceramic coating is tested and it is shown that these requirements can be met. Initial tests with this coating in hard water were performed and the ability of the coating to minimize calcium carbonate nucleation/deposition and the ease of cleaning was assessed. The results showed that the coating led to a reduction in the amount of scaling and a lower adhesion of the crystals to the coated plate.

Keywords: scaling, plate heat exchangers, brazed heat exchangers, cleaning, calcium carbonate

INTRODUCTION

Scaling is the unwanted precipitation of crystals formed in a flowing medium as well as the direct crystallization at the solid surface. The most common forms of scale are calcium carbonate and calcium sulfate. These salts have an inverted temperature solubility meaning that they will precipitate above a certain temperature (around 60°C). Other factors like pH, water hardness, flow rate, pressure, etc. will also influence the crystallization process. Scaling occurs in diverse industries like pulp and paper, oil production, power plants and cooling water processes (Yang, 1999; Keysar et. al., 1994; Alahmad, 2008; Cho et.al., 2003; Muller-Steinhagen, 2000; The U.S. Department of Energy, 1998). Calcium carbonate scaling will lead to an increased pressure drop and a reduced heat transfer due to the hard insulating layer that builds-up at the metal surface (thermal conductivity of 2,9 W/m k (Muller-Steinhagen, 2000). In extreme cases the scale layer will be so thick that the result is a clogged heat exchanger impossible to regenerate with an acidic cleaning in place (CIP). There are several approaches to mitigate scaling, like promoting turbulence (increasing the shear stress) and the use of chemical or physical additives that interfere with the crystal formation (The U.S. Department of Energy, 1998; Tijing, 2011). Another approach is to modify the steel surface by making it unattractive to the strong crystal adhesion. For the last years, Alfa Laval has been focusing on the latter strategy, i.e modifying the surface of the heat exchanger by applying a thin coating (Santos, 2013, 2015a). Contrary to a shell and tube heat exchanger, a compact plate heat exchange is made of thin and corrugated plates to increase the surface area and induce turbulence in the flowing medium. As a consequence, plate heat exchangers are very efficient in transferring heat even though their compact size. On the other hand this will add extra requirements to any coating that is intended for plate heat exchangers, mainly its thickness, which needs to be relatively low (< 10 or 20 µm depending on the application), thermal conductivity and adhesion to the substrate. A new ceramic coating with a thickness < 1 µm and thermal conductivity of around 2 W/m K was tested in a scaling rig.

In the majority of the studies, scaling is achieved by mixing aqueous solutions of two soluble salts, $NaCO_3$ and $CaCl_2$ (Keysar et. al., 1994; Alahmad, 2008; Tijing, 2011; Cheong et. al., 2013). This leads to a fast crystallization resulting in large amounts of $CaCO_3$ crystals. In contrast, scaling in industrial applications occurs much slower. For ex., in pulp mills the $CaCO_3$ layer formed on the metal surface builds up with a rate of around 0.5 mm per month (Markham and Bryce, 1980). In this study scaling was achieved by heating hard tap water in order to simulate industrial conditions better.

EXPERIMENTAL

Surface treatment

The NANOmel surface treatment was done by SiOx Aps. The silicon-based NANOmel coating is done using a liquid precursor that is applied using a wet chemical process, followed by a thermal curing step. The resulting coating is a purely inorganic silicon oxide. Two different versions of the coating were tested, here denoted by version 1 and version 2.

Coating properties

Water contact angles were measured by the static sessile drop method, using a Ramé-Hart Instrument Co. goniometer. Contact angles were measured on coated planar 2B steel test samples, as the geometry of the HE plates did not allow for precise direct measurements. A Taylor Hobson Pneumo profilometer (Form Talysurf Series 2 50i) was employed to measure the arithmetic mean surface roughness on both the ridges (top of the chevron pattern) and the valleys of the plates. The water contact angle and arithmetic mean surface roughness are presented in Table 1.

Table 1. Water contact angle (ϴ) and arithmetic mean surface roughness (Ra) on the uncoated and coated plates.

Plate	Θ_{water} (°)	Ra (µm)	
		Ridge	Valley
Uncoated	66 ± 6	0.70	0.11
Version 1	45 ± 1	0.35	0.09
Version 2	85 ± 1	0.42	0.07

Focused Ion Beam (FIB) milling

The coatings investigated in this study are hard and brittle and artefacts from mechanical preparation (such as cracks) were observed after the metallurgical preparation of cross-sections. Hence, coating cross-sections were solely prepared by FIB cross-sectioning on a FEI Helios NanoLAB 600 SEM. The microscope was fitted with a Ga^+ ion source and a gas injection system for the injection of precursor gas for e.g. CVD Pt deposition. The ion source was generally operated with an accelerating voltage of 30 kV for milling. Moreover, to prevent ion beam damage in the vicinity of the site of interest, a double layer (electron beam CVD followed by ion beam CVD) of Pt was deposited prior to milling. A schematic drawing of the FIB-SEM setup is shown in Figure 1. For cross-sectioning the sample was tilted to 52 °, yielding a FIB direction perpendicular to the specimen surface. Cross-sectional images were taken under 52 ° tilt to the electron beam, leading to a vertical compression of the images.

The coatings had an average thickness of 400 nm.

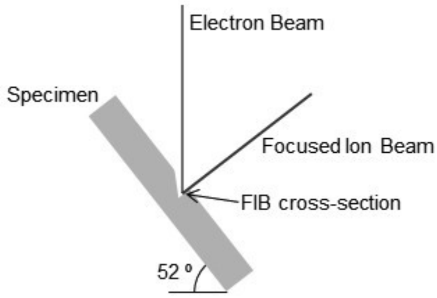

Fig.1 Schematic drawing of FIB cross-sectioning.

Imaging and scaling composition

Scanning electron microscope images were recorded using a Hitachi TM3030 Plus table top microscope, operated at 15 kV. EDS analysis was performed in the SEM, using a Quantax 70 system.

Experimental set-up

The scaling test was run with a total of four M3 plate heat exchangers (PHE) with 8 stainless steel 316L plates (16 × 42 cm). Two of these PHEs were installed with coated plates (version 1 and 2) and the other two with uncoated plates. The units were operated with hard tap water until they clogged or up to a period of 6 days. A schematic diagram of the test set-up is shown in Fig. 2. The tap water enters the test heat exchanger at a flow rate set at 2 L/min and is heated up to 87°C by circulating water at 98°C in the adjacent channel. The flow rate is recorded during the test. The cold water pump power (PR) is recorded (in watts); the pressure (P) is monitored manually (low pressure, 0.4 – 0.6 bar, in cold water line indicates no obstructions to the flow, it reaches 2.2 bar in a blocked line); the cold water outlet temperature (set at 87°C) is used to control the opening of the valve (V) and adjust the hot water flow to maintain this set temperature. The scaling test was run with one PHE at a time. The PHEs were running intermittently for 15 min and then 15 min without flow. A heat recovery PHE is used to recover some of the energy back to the hot line and a copper brazed (CB) HE is used before disposal of the water into the drain to reduce its temperature to below 50°C. Additionally, the coating was also applied and tested on CB HE in a similar manner, since they are the standard in district heating applications.

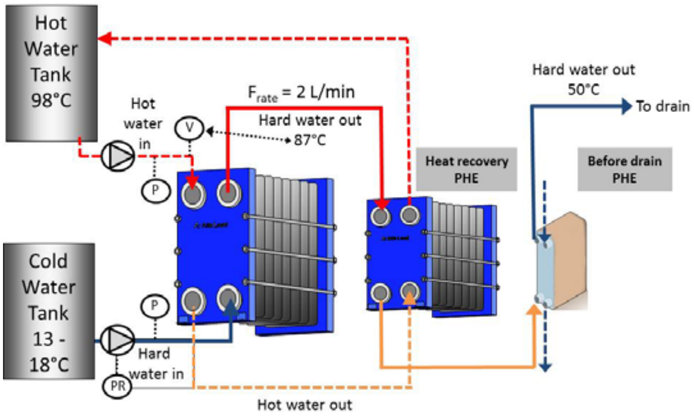

Fig. 2 Scaling set-up.

RESULTS

To estimate the scaling tendency of the water, the Ryznar index was calculated. A value of Ryznar index of 6 means water neutrality i.e. no calcium carbonate dissolution or scaling tendency. A value higher than 6 indicates calcium carbonate dissolution and a value lower than 6 indicates scaling tendency.

Table 2 shows the Ryznar index calculated at 87°C with the values from the water analysis supplied by the scaling lab. The tests were performed with two different water chemistries as can be seen in Table 2.

Table 2. Analysis of the water used in both scaling tests (performed by the scaling lab).

Total alkalinity HCO_3^- (mg/L)	Calcium (mg/L)	Conductivity (µS/cm)	pH	Ryznar Index[c]
330[a]	96	252	7.4	5.30
319[b]	212	856	7.5	4.61

[a]Water chemistry corresponding to the 1st test
[b]Water chemistry corresponding to the 2nd test
[c]Calculated at a temperature of 87°C

The development of scaling on the uncoated plates was monitored by the pump usage, the cold water flow rate and the valve position. From Fig. 3 a small increase in the pump power can be observed, indicating that there was a buildup of pressure in the system. After 6300 min the large increase in pump power points to a blockage in the system. In a similar way the flow rate of the cold water outlet decreased to 1.5 L/min at around the same time frame (Fig. 4). The corresponding data for the NANOmel version 1 coated plates is presented in Figs. 5 and 6. During the test of the coated unit a number of blockages occurred in the system which led to its shutdown for cleaning. The coated PHE was bypassed during the cleaning and therefore not in contact with the cleaning chemicals. Figs. 5 and 6 show the increases in the pump power and decreases in the flow rate due to the blockages. After the last cleaning the pump and flow rate were kept constant at the set values, meaning that no blockage occurred on the NANOmel version 1 coated PHE.

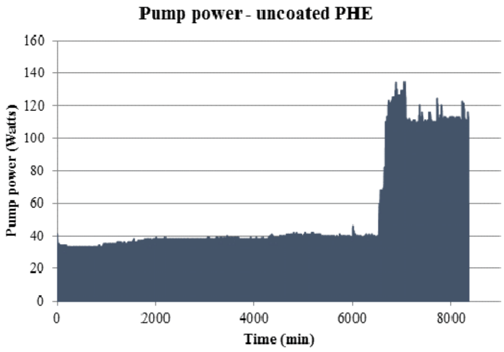

Fig. 3 Pump power (Watts) recorded for the uncoated PHE during the scaling test.

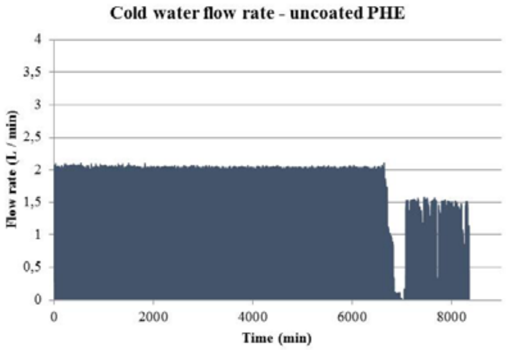

Fig. 4 Flow rate (L/min) recorded for the uncoated PHE during the scaling test.

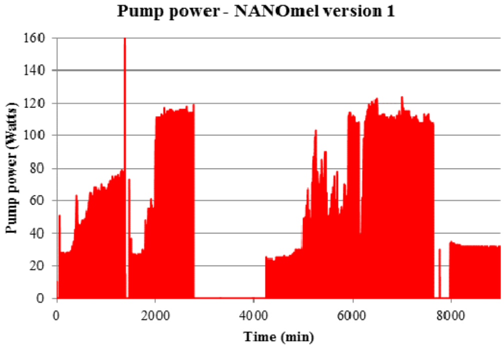

Fig. 5 Pump power (Watts) recorded for the NANOmel version 1 coated PHE during the scaling test.

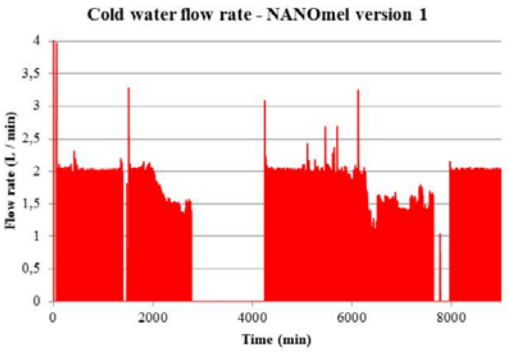

Fig. 6 Flow rate (L/min) recorded for the NANOmel version 1 coated PHE during the scaling test.

The position of the valve on the hot water side during the scaling test can be used to compare the performance of both PHEs. The valve monitors the cold water outlet temperature (set at 87°C) and adjusts the flow in the hot water line so that this temperature is maintained. It starts at 100% open and adjust the degree of opening to around 40% over the 15 minute run time. As scaling develops on the plates, the valve needs to remain open for longer time, and the final adjusted position for each 15 minute run increases until it reaches a point where the valve is open 100% for the entire 15 minute run. Fig. 6 shows the hot valve position, during the whole period of the scaling test, for the uncoated and NANOmel version 1 coated PHE. Even though the curve for the coated PHE shows disruptions, due to the above mentioned blockages, its superior performance compared to the uncoated PHE is clearly seen. While for the uncoated PHE the valve slowly shifted to higher values, indicating the need of supplying extra heat to the cold water, for the NANOmel version 1 coated PHE the valve kept its initial position the whole operation time. The latter reflects a lower amount of scaling on the coated plates and therefore a lower hindrance to the heat transfer.

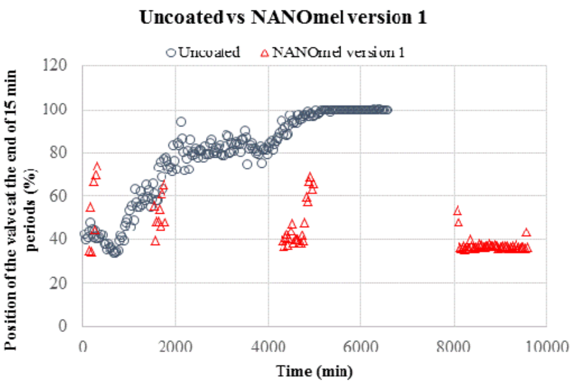

Fig. 7 Comparison of the position of the hot water valve at the end of the 15 minute run, during the whole scaling test, for the uncoated and NANOmel version 1 coated plates.

At the end of the scaling test the uncoated and NANOmel version 1 coated PHEs were disassembled to allow for analysis of the internal fouling distribution formed on each channel (Fig. 8). The visual appearance and amount of the scaling is shown in Fig. 8. As mentioned the scaling test was also carried out with copper brazed units, one uncoated and one NANOmel version 1 coated, and the visual appearance was analysed with the help of a boroscope (Fig. 9). The effect the coating had on preventing scaling in both unit types is evident. The scaling was drastically reduced on the coated units. While on the uncoated plates the scaling covers nearly the entire surface with a coherent layer, the scaling on the coated plates has a powdery appearance and is sparingly spread on the surface. The uneven scaling distribution on the uncoated plate (more on the bottom compared to the top of the plate) is related to the temperature. The hard water enters from the top and is heated up along the plate surface exiting on the bottom. After the scaling test the HE plates were characterized using scanning electron microscopy (SEM). On the uncoated plates, scale formation shows a tendency to initiate at the grain boundaries of the 2B steel substrate (Fig. 10). On version 1 coated plates, the grain boundaries are masked by the coating, and scaling formation proceeds in a random way. The scaling products were analysed using EDS, and contained primarily oxygen (62 atom-%), calcium (17 atom-%), and carbon (18 atom-%). The atomic ratio of 1:1:3 (Ca:C:O) indicates that the scaling product is calcium carbonate, $CaCO_3$. This was verified for the scaling products on both the coated, and the uncoated plates.

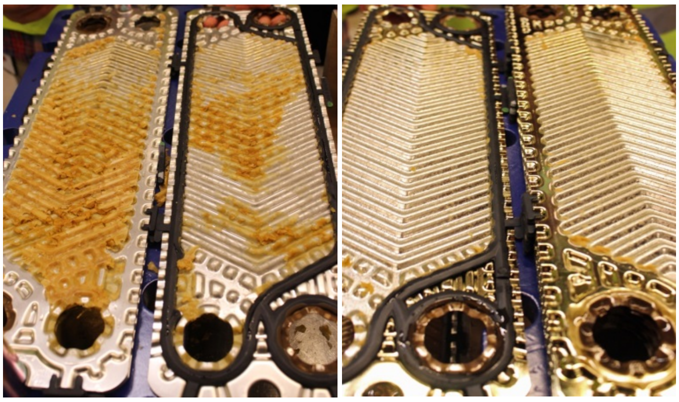

Fig. 8 Amount of scaling on the uncoated (left) and NANOmel version 1 coated (right) HE plate after the scaling test.

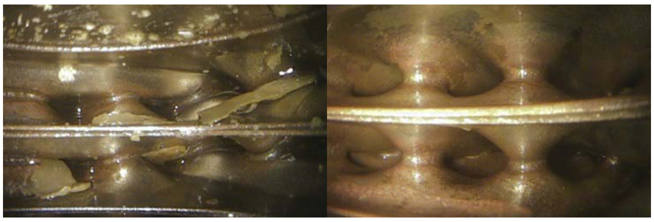

Fig. 9 Amount of scaling on the uncoated (left) and NANOmel version 1 coated (right) copper brazed HE after the scaling test.

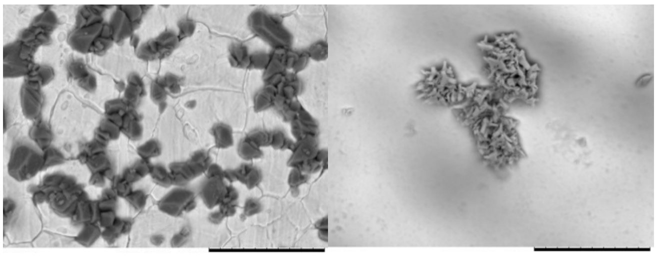

Fig. 10 Scale formation on a 2B steel surface (left); Scale formation on a NANOmel version 1coated surface (right). Scale bar is 30 µm.

The crystal structure of the calcium carbonate particles formed on both the uncoated and coated plates was investigated by SEM (Fig. 11). It can be seen that on both the uncoated and coated plate calcite crystals were formed.

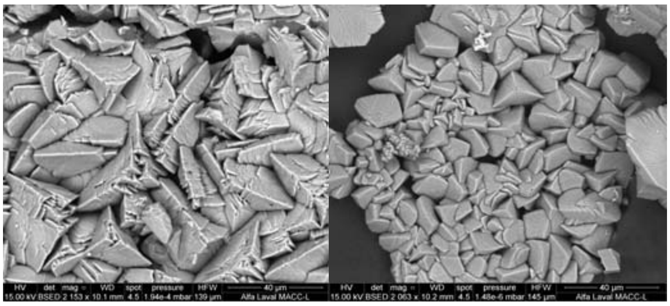

Fig. 11 Crystal structure of the scaling particles collected from the uncoated (left) and version 1 coated HE plate (right) as analysed by SEM.

In Figs. 12 to 16 the results obtained on the second uncoated and NANOmel version 2 coated HE plates are presented. Note that this scaling test was performed with different water chemistry, and therefore the need of another control uncoated HE. The pump power is shown in Fig. 12. It had a constant value of 36 watts until 3060 min, after which it increased as the system tried to attain the required flow rate. The corresponding cold flow rate through the uncoated PHE during the test run was relatively constant until ca 3100 minutes at which point it suddenly decreases (Fig. 13), after a moderate recovery (3300 min) it completely stops at 3400 minutes.

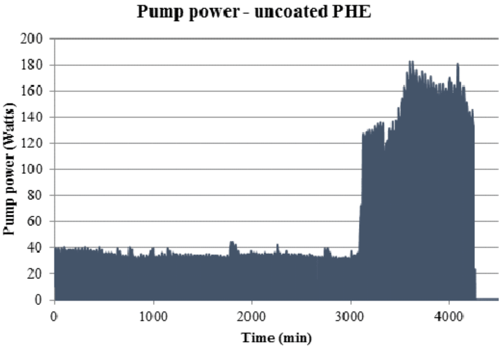

Fig. 12 Pump power (Watts) recorded for the uncoated PHE during the 2nd scaling test.

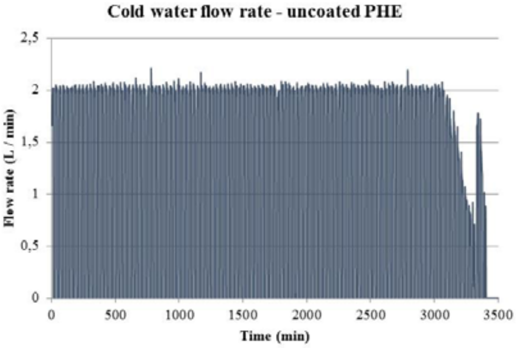

Fig. 13 Flow rate (L/min) recorded for the uncoated PHE during the 2nd scaling test.

The performance of the NANOmel version 2 PHE during the 2nd scaling test is represented in Figs. 14 and 15. The pump power started at ca 36 watt, and stayed at this level until near the end of the test, when it rose steadily to ca 60 watt (ie from 9233 min to 10 364 min) (Fig. 14). The flow rate on the cold side remained at the required 2 L/min for the entire test run, ca 10 364 min. There were no blockages, only a small restriction in the flow, ca 10 074 min, which was flushed from the system (Fig. 15). This might indicate that scaling was slowly developing on the plates. This is in strong contrast to the uncoated unit, where the system was completely blocked by day 3.

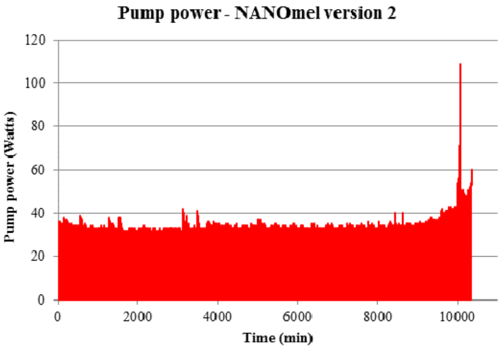

Fig. 14 Pump power (Watts) recorded for the NANOmel version 2 PHE during the 2nd scaling test.

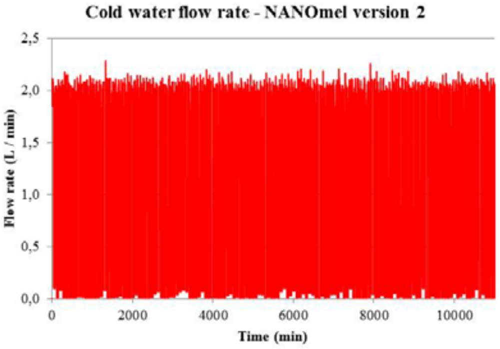

Fig. 15 Flow rate (L/min) recorded for the NANOmel version 2 PHE during the 2nd scaling test.

Due to a restriction in the hot water feed to the NANOmel version 2 PHE, the hot water valve had to be kept 100% open for the entire test run to keep the set temperature of 87°C at the cold water outlet. Therefore, the position of the hot water valve cannot be used to compare the performance of the uncoated and coated unit. Instead, the cold water outlet temperature for both uncoated and NANOmel version 2 coated PHEs is plotted in Fig. 16. On the uncoated PHE the cold water outlet temperature was kept constant until ca 2940 min where it slowly decreased to 84°C. After a further ca 400 min into the test the temperature decreased steeply to 25°C, indicating a blockage in the system. In contrast, the NANOmel version 2 PHE was able to keep the temperature of the cold side outlet at the set 87°C for ca 4800 min, where the outlet temperature gradually decreased over the test duration to a final temperature of 83°C.

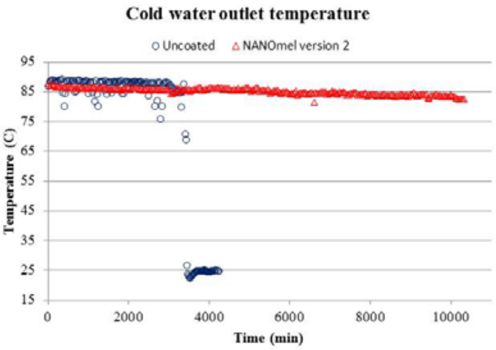

Fig. 16 - Comparison of the cold water temperature during the whole scaling test, for the uncoated and NANOmel version 2 coated plates.

The visual aspect and quantity of scaling on both tested PHEs after the 2nd scaling test is shown in Figs. 17 and 18.

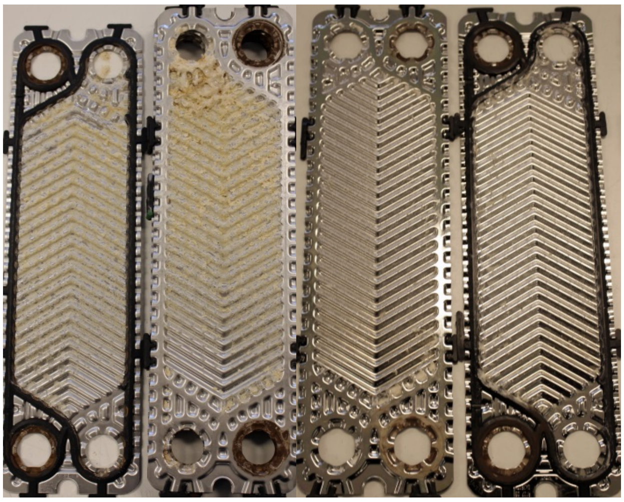

Fig. 17 Amount of scaling on the uncoated (left) and version 2 coated (right) HE plates after the scaling test.

Fig. 18 shows clearly the effect of the coating on scale reduction. The uncoated plate was covered with a compact layer of calcium carbonate scaling whereas on NANOmel version 2 coated plates the scaling was in the form of a loose powder.

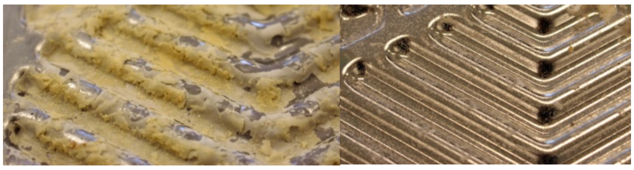

Fig. 18 Closer view of the scaling formed on the HE plates: Uncoated (left) and NANOmel version 2 coated (right).

Fig. 19 shows how the scaling was formed on the uncoated and NANOmel version 2 coated HE plates during the second test. The observations in the two tests were similar. On both version 1 coating and version 2 coating the crystal structure of the formed scale particles was calcite (Fig. 20).

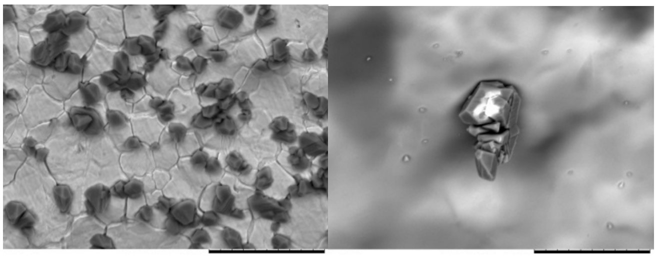

Fig. 19 Scale formation on a 2B steel surface (left); Scale formation on a NANOmel version 2 coated surface (right). Scale bar is 30 µm.

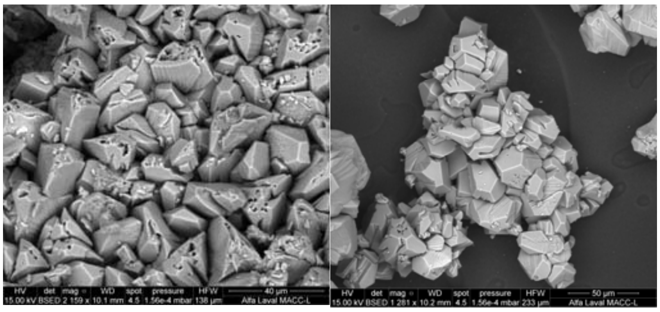

Fig. 20 Crystal structure of the scaling particles collected from the uncoated (left) and NANOmel version 2 coated HE plate (right) as analyzed by SEM.

DISCUSSION

On both PHE and CB coated units a dramatic decrease in the amount and adhesion of the scaling was seen. This can be explained by the different surface properties the coating provides. The uncoated plate has a rougher surface (Table 1) which together with the grain boundaries will lead to a higher amount of scaling compared to the smooth surface of the coated plates (Figs. 8, 9 and 17-18). The coating fills in the gaps between the grains which masks the grain boundaries. It is generally accepted that scaling amount and strength is influenced by surface roughness (Keysar et. al., 1994; Alahmad, 2008). A higher surface roughness leads to a larger amount and a higher strength of the scaling layer. This is explained by the increased surface area of the rougher surface and the change for the peaks to act as nucleation sites and for the valleys to act as a shield for the crystals against removal by the shear stress (Epstein, 1983). In addition, the induction time is also influenced by the surface roughness, where a higher roughness leads to a shorter induction time (Förster and Bohnet, 2003).

The NANOmel version 1 and 2 coatings differed in their surface free energy: version 1 was hydrophilic (high surface energy) and version 2 hydrophobic (low surface energy). Both versions led to a decrease in the amount and adhesion of scaling. The surface free energy is a direct measure of intermolecular forces that affect the attraction of the bulk liquid to the surface layer (Yang, 1994). Several studies have shown a lower crystal adhesion on the surfaces with the lower surface energy (Cheong et. al., 2013; Yang, 1999). Cheong et. al. (2013) observed higher amount of scaling for stainless steel surfaces as compared to coated stainless steels having a higher water contact angle. Other studies have also reported that a higher surface energy leads to lower amount of scaling on surfaces (Förster and Augustin, 1999). Obviously the reduction of scaling on a certain solid surface cannot be attributed to only one surface property but is the combined effect of different surface properties. The lower amount of scaling on the NANOmel version 1 coating can therefore be attributed to both its smoother surface as compared to the uncoated but also to its higher surface energy. The latter will result in a thin water film adjacent to the surface which will prevent bulk crystal deposition.

The different scaling behavior observed on the two uncoated PHE units is a result of the different Ryznar indexes (Table 2) of the flowing tap water. On the first scaling test with a Ryznar index of 5.3, the loss of thermal performance occurred gradually until final blockage of the PHE. On the second test where the water had a lower Ryznar index (4.6) and therefore more prone to scale, the blockage of the PHE occurred suddenly and required only half the time (3 days as compared to 6 days).

The same crystal polymorph was observed on the coated and uncoated plates which are contrary to a previous study on another type of coating (Santos, 2015b). The difference between these two studies was the temperature. On the previous test the scaling test was run at 60°C while the present tests were run at 87°C. Taking into account the Ostwald-Lussac law of phases (Nancollas, 1982), according to which, the pathway to the final crystalline state will pass through all less stable states in order to increase stability, the nucleation of $CaCO_3$ will start with an amorphous phase which then transforms into vaterite, aragonite and calcite. The higher temperature of the present study will lead to a faster scaling process where only the most stable crystal structure (calcite) is observed at the end of the test.

CONCLUSIONS

The NANOmel coatings, version 1 and 2, were efficient in reducing the amount of calcium carbonate scaling and had improved ease to cleansing compared to the uncoated SS316. This can lead to significant cost reductions for the operators who will experience longer uptime for their PHEs between cleanings. The lower scaling adhesion to the plates will further translate into shorter and milder cleaning programs. No coating failures were observed in versions 1 and 2 coating systems.

It was also demonstrated that it is possible to coat internal surfaces like those of copper brazed heat exchangers with these new types of coatings.

ACKNOWLEDGEMENTS

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