

Thin ceramic coatings and their suitability 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 that can meet these requirements. Initial tests with this coating in hard water were performed and the ability of the coating to minimize calcium carbonate nucleation / deposition and the easiness 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

1 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 form of scale is 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 [1, 2, 3, 4, 5, 6]. 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 $2,9 \text{ W m}^{-1} \text{ K}^{-1}$ [5]. 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 [6, 7]. Another approach is to modify the steel surface by making it unattractive for the strong crystal adhesion. For the last years, Alfa Laval has been focusing on the latter strategy, i.e. coating the surface of the heat exchanger with a ceramic coating [8, 9]. In the majority of the studies, scaling is achieved by mixing aqueous solutions of two soluble salts, NaCO_3 and CaCl_2 [2, 3, 7, 10]. 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 [11]. In this study scaling was achieved by heating hard tap water in order to simulate industrial conditions better.

2 EXPERIMENTAL

2.1 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 coating had an average thickness of 400 nm. 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.

2.2 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.

Plate	$\Theta_{\text{water}} (^{\circ})$	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

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

2.3 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.

2.4 Experimental set-up

The scaling test was run with 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 7days. The tap water entered the heat exchanger at a flow rate of around 2 L / min and was heated up to 88°C by circulating water at 95°C in the adjacent channel. The PHEs were running intermittently for 15 min and then 15 min without flow. Additionally, the coating was also applied and tested on copper brazed (CB) HE in a simmlar manner, since they are the standard in district heating applications.

3 RESULTS

The amounts of scaling after testing on an uncoated and NANOMel version 1 coated plates, are shown in Fig. 1 for stainless steel plates and in Fig. 2 for the copper brazed plates. 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. 3). 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.

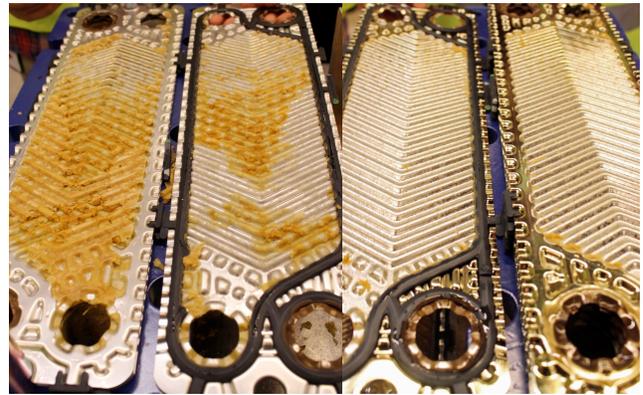


Figure 1: Amount of scaling on the uncoated (left) and NANOMel version 1 coated (right) HE plate after the scaling test.

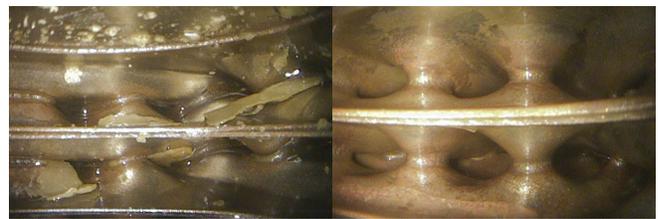


Figure 2: Amount of scaling on the uncoated (left) and NANOMel version 1 coated (right) copper brazed HE after the scaling test.

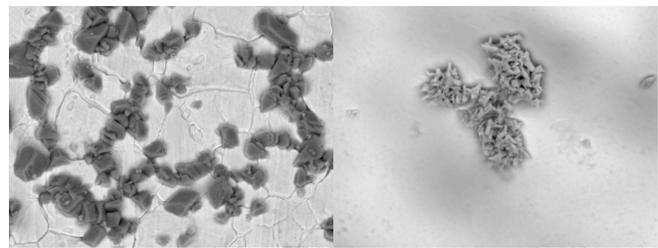


Figure 3: Scale formation on a 2B steel surface (left); Scale formation on a NANOMel version 1 coated surface (right). Scale bar is 30 μm .

The crystal structure of the calcium carbonate particles formed on both the uncoated and coated plates was investigated by SEM (Fig. 4). It can be seen that on both the uncoated and coated plate calcite crystals were formed. The only difference was that the size of the calcite crystals were larger on the uncoated plates.

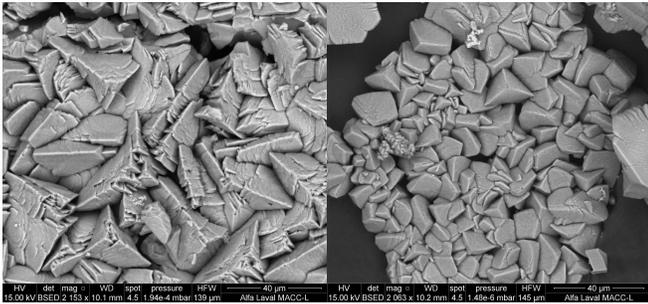


Figure 4: Crystal structure of the scaling particles collected from the uncoated (left) and version 1 coated HE plate (right) as analysed by SEM.

In the figures below the results obtained on NANOMel version 2 coated HE plates are presented. Similar observations regarding the amount of scaling were made (Figs. 5 and 6). It should be noted that this scaling test was performed with a different water chemistry, and therefore the need of another control uncoated HE.

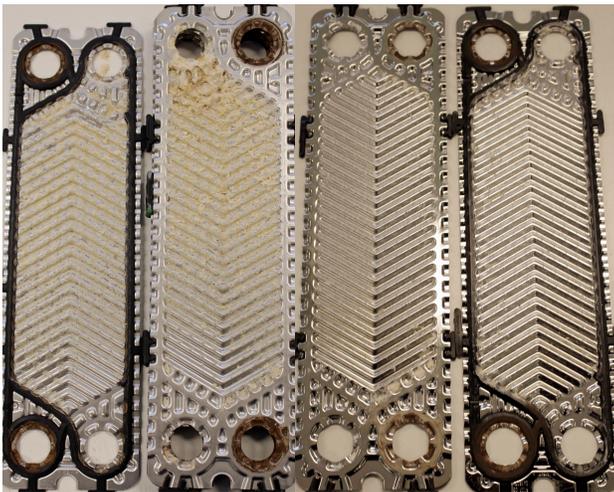


Figure 5: Amount of scaling on the uncoated (left) and version 2 coated (right) HE plates after the scaling test.

Fig. 6 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 plate the scaling was in the form of a loose powder.



Figure 6: Closer view of the scaling formed on the HE plates: Uncoated (left) and NANOMel version 2 coated (right).

Fig. 7 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. 8).

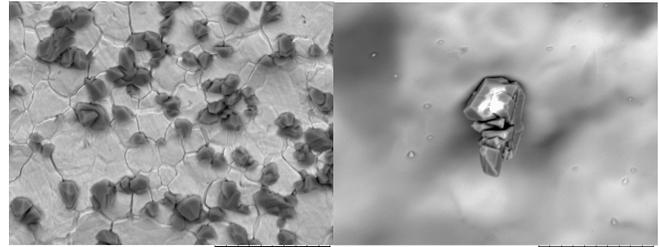


Figure 7: Scale formation on a 2B steel surface (left); Scale formation on a NANOMel version 2 coated surface (right). Scale bar is 30 µm.

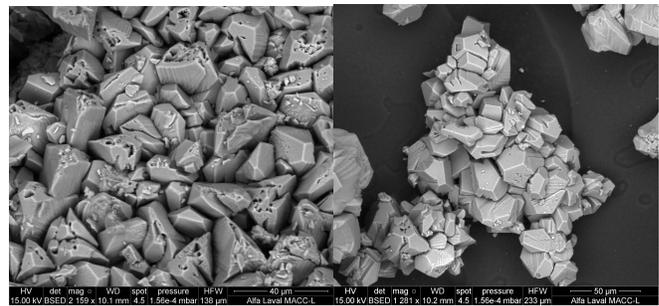


Figure 8: Crystal structure of the scaling particles collected from the uncoated (left) and NANOMel version 2 coated HE plate (right) as analysed by SEM.

4 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. 1, 2 and 5-7). The coating fills in the gaps between the grains which masks the grain boundaries. It is general accepted that scaling amount and strength is influenced by surface roughness [2, 3]. 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 [12]. In addition, the induction time is also

influenced by the surface roughness, where a higher roughness leads to a shorter induction time [13].

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 [14]. Several studies have shown a lower crystal adhesion on the surfaces with the lower surface energy [10, 14]. Cheong et al. [10] 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 [15]. 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 be therefore 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 same crystal polymorph was observed on the coated and uncoated plates which is contrary to a previous study on another type of coatings [16]. The difference between these two studies is the operating times. On the previous test the scaling test had the same duration for both the coated and uncoated units. On the present test the uncoated unit was blocked after 3 days while the coated units were only stopped after a period of 6 days. Taking into account the Ostwald-Lussac law of phases [17], 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 longer operation time for the coated units might have resulted in aragonite crystals (less dense deposits that are easier to remove) which have detached from the surface.

5 CONCLUSIONS

The NANOMel coatings, version 1 and 2, were efficient in reducing the amount of calcium carbonate scaling and had improved easy to clean properties 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.

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.

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