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MINIMIZING CALCIUM CARBONATE SCALING BY MODIFIYING THE SURFACE OF HEAT EXCHANGERS WITH FLEXIBLE CERAMIC COATINGS

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ABSTRACT

Calcium carbonate scaling on stainless steel and coated heat exchanger plates was investigated in a scaling lab with flowing hard water. The two coatings tested, namely CORE Coat 010 and CORE Coat 030, are organic inorganic hybrid sol gel with low surface energy and thickness. The first scaling trial consisted in a small coated plate heat exchanger (PHE). Three copper brazed heat exchangers (CB) out of which two were coated were included in the second trial. At the end of both trials the coated plates were visually inspected. The following parameters were assessed: Scaling amount and strength of adhesion to the plate, coating condition and repellency. The coating was found to be successful in minimizing the amount of scaling and reducing its adhesion to the plate. However, one of the coatings, CORE Coat 010, showed extensive delamination making it unsuitable for water applications. The coating CORE Coat 030 showed a good resistance to warm hard water where no coating failure was observed. Different calcium carbonate polymorphs were detected on the plates depending on the solid surface energy.

The use of CORE Coat 030 on both PHE and CB led to a reduction of both the amount and adhesion of calcium carbonate scaling, making it an attractive solution for the scaling problem. The lower amount of scale together with the easy of removal of the formed scales will result in a significant benefit for the end user not only in terms of increased process efficiency but also lower cleaning related costs (time, energy and chemicals).

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. Other factors like pH, water hardness, flow rate, pressure, etc. will also influence the crystallization process.

Scaling occurs in diverse applications like pulp and paper, oil production, power plants and cooling water processes (Yang et al., 1999; Keysar et al., 1994; Alahmad, 2008; Cho et al., 2003; Muller-Steinhagen, 2000; The US 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⁻¹ k⁻¹ (Muller-Steinhagen, 2000)). In extreme cases the scale layer will be so thick that the result is a clogged heat exchanger impossible to flush 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 US department of energy, 1998; Tijing et al., 2011). Another approach is to modify the steel surface making it unattractive for the crystals to strongly adhere to. Alfa Laval focused on the last strategy, i.e, coating the surface of the heat exchanger with a flexible ceramic coating. The coatings investigated are smooth, have a low thickness $(5 - 10 \,\mu\text{m})$ and are hydrophobic. Scaling is a well-studied phenomenon (Hasson et al., 1968) but due to its complexity its mechanism is still not fully understood. The effect of the substrate (roughness and wettability) on the adhesion and crystallization of calcium carbonate was investigated by Cheong et al. (2013) using polymer surfaces with different topographies and coated stainless steel surfaces. The influence of the solid surface energy on scaling has also been studied by other groups (Zettler at al., 2005). In the majority of the studies scaling is achieved by mixing aqueous solutions of two soluble salts, CaCO₃ and CaCl₂ [Tijing et al., 2011; Cheong et al., 2013; Keysar et al., 1994; Alahmad et al., 2008). This leads to a fast crystallization resulting in large amounts of CaCO₃ crystals. In contrast scaling in industrial applications occurs much slower. For ex., in pulp mills the CaCO₃ 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 tap hard water in order to better simulate industrial conditions.

Two coatings formulated by the Danish Technologist Institute (DTI), namely CORE Coat 10 (CC010) and CORE Coat 30 (CC030) were tested in a scaling lab located in Denmark. The aim was to compare the performance of the two coatings to stainless steel alloy 316 (SS316) regarding the resistance to scaling. The coatings were applied both on small plate heat exchangers (PHE) (38×12 cm) and internally on one channel of copper brazed heat exchangers (CB14). Two scaling tests were performed at different times: The first one with only one coated PHE and the second with the same PHE and the addition of three CB14 units out of which two were coated.

EXPERIMENTAL

Coated Surfaces

The coatings tested in this paper have a thickness of 5-10 µm (information provided by the coatings supplier). The properties of both coatings relative to the reference stainless steel surface are presented in Table 1. The static contact angle was measured using a MobileDrop goniometer from Kruss and the values analysed with the DSA2 software. The samples were cleaned with water and detergent and then rinsed with water, ethanol, water before the measurements. The values presented are the average of five measurements and the volume of the water drop placed on the surface was 10 µl. The surface energy was mesured based on the two liquid method "Owens-Wendt-Rabel & Kaelbe" with the liquids being water and diiodomethane. The arithmetic mean surface roughness (Ra) was measured by a Mahr MarSurf M400/SD26 profilometer on 10 different locations with a measuring length 8 mm. The measurements were made on flat samples.

Table 1. Surface properties of the reference and coated substrates.

Surface	Water	γ_d / γ_p	γ^{TOT}	Surface
	contact	(mN/m)	(mN/m)	roughness
	angle			(µm)
	(°)			
CC010	101 ± 1	34 / 11	23	$0,05 \pm 0,01$
CC030	96 ± 1	22 / 1	25	$0,03 \pm 0,01$
SS316	66 ± 6	23 / 2	45	$0,\!10\pm0,\!05$

First Scaling Test

The PHE tested was a model T2 unit $(38 \times 12 \text{ cm})$ with 15 SS316 plates, of which 5 were uncoated, 5 were coated with CC010 and the remaining 5 coated with CC030. All plates have a chevron profile. The T2 unit was operated for 27 days with hard water at a flow rate of 10 L/min (flow velocity at the heat exchanger port holes of 0.53 m/s). The temperature profile was: Cold side 10-60°C, hot side 85-60°C as shown in Fig. 1. During the 27 days the PHE was operated in the following way: once through flow with hard water for 15 min and then the hard water flow was stopped for 45 min . The hot side was continuously operated and therefore the hard water inside the PHE was still heated to 85°C. The flow diagram is represented in Fig. 1.

Second Scaling Test

For the second test in addition of the PHE from the first test three copper brazed units were added: an uncoated CB14, a CB14 coated with CC010; and a CB14 coated with CC030. The operating time was of 6 weeks with a flow rate of 5 L/min (half as compared to the first test, flow velocity

at the port holes of 0.26 m/s) and the same temperature profile as the previous test. The experimental set-up is shown in Fig. 2.



Fig. 1. Flow diagram showing the T2 unit during the first trial.



Fig. 2. PHE and CB units installed at the scaling lab.

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 60°C with the values from the water analysis supplied by the scaling lab.

Total alkalinity HCO ₃ ⁻ (mg/L)	Calcium (mg/L)	Conductivity (µS/cm)	рН	Ryznar Index ^a
319	212	856	7,5	5,8

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

^aCalculated at a temperature of 60°C

First Scaling Test

After disassembling the T2 unit it was observed that the uncoated plates had more scaling than the two different coated plates (Figs. 3 to 5). It was also seen that the scaling particles had a different shape depending on the plate they adhered to (coated vs uncoated). This observation was made by comparing the scale particles formed on all the uncoated plates to the ones formed on all the coated plates. The scaling particles were both flake and spherical shaped on the uncoated plates (Fig. 3) whereas on the coated plates the scaling particles were mainly spherical shaped (Figs. 4 and5). Samples of the scaling were collected from the three different plates and analyzed by scanning electron microscopy (SEM) by DTI to understand the reason for the different shapes. The pictures are shown in Figs. 6, 7 and 8.

Regarding the easy to clean properties it was found that the scaling had a higher adhesion to the uncoated plates compared to the coated plates from which it was easily removed with a dry cloth.

The stability of the two coatings was quite different, the coating CC030 appeared unaltered while CC010 delaminated in some areas in all 5 coated plates (Fig. 9). After analysis the PHE was reassembled and re-installed at the scaling lab for a further 6 weeks.



Fig. 3 Scaling particles on the uncoated plate.



Fig. 4 Scaling particles on the CORE Coat 030 coated plate.



Fig. 5 Scaling particles on the CORE Coat 010 coated plate.

Second Scaling Test

Inspection of the T2 unit. Figure 10 to 12 shows the scaling on the uncoated T2 plates, on the plates coated with CORE Coat 010 and on the plates coated with CORE Coat 030, respectively. On the uncoated and coated plates both a thin scaling layer and particles were present. One can also see that part of the scaling was detached from the coated plates when separating them (Figs. 11 and 12). This confirms the weak scaling adhesion strength to the coated plates. Even after wiping the uncoated plates with a dry cloth the thin scaling layer remained at the surface.



Fig. 6 SEM picture of a scaling particle collected from the uncoated plate.



Fig. 7 SEM picture of a scaling particle collected from the CORE Coat 030 coated plate.



Fig. 8 SEM picture of a scaling particle collected from the CORE Coat 010 coated plate.

Inspection of the CB14 units. After the scaling test the CB14 units were inspected with a borescope. It was seen that more scaling was deposited on the uncoated unit compared to the coated ones (Figs. 13 to 15). Between the two tested coatings, the CORE Coat 030 showed the



Fig. 9 Delamination observed on the CORE Coat 010 after the scaling test.

best results, i.e. the minimum amount of scaling with no observed coating failure. The coated CB14 units were sectioned and in general not much scaling was observed inside the channels.



Fig. 10 Scaling on the uncoated T2 plates (the plates form a channel). The scaling consists of small particles on top of a thin layer.



Fig. 11 Scaling on the CORE Coat 010 coated plates (the plates form a channel). The scaling consists of big lumps on top of a thin layer. Note that the lumps have detached from the adjacent plate.



Fig. 12 Scaling on the CORE Coat 030 coated plates (the plates form a channel). The scaling consists of big lumps on top of a thin layer. Note that the lumps have detached form the adjacent plate.



Fig. 13 Scaling on the uncoated CB14 unit viewed from the outlet a) and inlet b).



Fig. 14 Scaling on the CORE Coat 010 coated CB14 unit viewed from the outlet a) and inlet b).



Fig. 15 Scaling on the CORE Coat 030 coated CB14 unit viewed from the outlet a) and inlet b).

DISCUSSION

Calcium carbonate scaling was observed on the plates after both tests confirming the scaling tendency of the water. Differences were seen on the scaling amount, adhesion strength and particle shape depending on the surface properties. The uncoated plate being the rougher and having the highest surface energy (Table 1) gave the highest amounts of scaling together with the highest adhesion strength (Figs. 3-5 and 10-15). It is general accepted that scaling amount and strength is influenced by surface roughness (Keysar et al., 1994; Alahmad et al., 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 possibility 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 surface free energy is a direct measure of intermolecular forces that affect the attraction of the bulk liquid to the surface layer (Yang et al., 1994). Several studies have also observed a lower crystal adhesion on the surfaces with the lower surface energy (Cheong et al., 2013; Yang et al., 1994; Förster and Augustin, 1999). Cheong et al. (2013) observed higher scaling for stainless steel surfaces as compared to coated stainless steels having a higher water contact angle. However, there are also reports on lower scaling amounts on surfaces with low surface energies and even others where no correlation between scaling and surface energy was seen (Zhao and Muller-Steinhagen, 2001). Therefore, prediction of scaling taking only the surface energy into account is not a straightforward task.

The different crystal polymorphs observed on the coated and uncoated plates was attributed to the surface energy. Yang et al. (1999) reported that the nucleation rate on low energy surfaces is slower than that on a higher energy surface. This leads to a longer induction period on surfaces having lower surface energy. Taking into account the Ostwald-Lussac law of phases (Nancollas, 1982), which states that the pathway to the final crystalline state will pass through all less stable states in order of increasing stability, then the nucleation of CaCO₃ will start with an amorphous phase which then transforms into vaterite, aragonite and calcite. One tentative explanation for the different polymorphs observed can then be attributed to the different phases in calcium carbonate crystallization. On the surfaces with the lowest surface energy (CORE Coat 010) the nucleation rate is slower leading to a longer induction period and the crystals observed are still in the aragonite phase while for surfaces with higher surface energy (SS316 and CORE Coat 030), nucleation occurs faster leading to ashorter induction period and the crystals observed have transformed to the more stable calcite phase. On both SS316 and CORE Coat 030 surfaces, even though the same crystal polymorph seems to have formed, the scale particles were more spread at the SS316 surface increasing the number of bonds between the surface and crystal and therefore its adhesion strength.

Albeit both coatings have similar properties (Table 1) the CORE Coat 010 was observed to be sensitive to water leading to coating delamination (Fig. 9). This can be explained by the different composition of the coatings

making the CORE Coat 030 softer, denser and more flexible.

CONCLUSIONS

The conclusions of this study are as follows:

- 1. The two coatings, CORE Coat 010 and 030, were efficient in reducing the amount of scaling and had better easy to clean properties compared to the SS316. However, the coating CORE Coat 010 suffered delamination in several areas in all of the coated plates.
- 2. Coating of internal surfaces like the copper brazed heat exchanger proved to be feasible with the sol gel type of coatings.
- 3. CORE Coat 030 showed promising results in reducing both the amount and adhesion of calcium carbonate scaling on plate and brazed heat exchangers.

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