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Calcium sulfate scale deposition on coated carbon steel and titanium

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ABSTRACT

Scaling/fouling is a thermal barrier in heat transfer equipment which badly impedes heat-exchanger efficiency and renders production losses. The application of thermally conductive polymer coatings on low-cost materials is common to cope with the problem of fouling and corrosion, and is also a cost-effective alternative for the replacement of expensive materials in petroleum industry. Calcium sulfate ($CaSO_4$) is one of the commonly found scales in Arabian Gulf region. An experimental study was undertaken using rotating cylinder electrode equipment to assess the performance of a polymer (SAKAPHEN Si57E) coating applied on carbon steel with regard to $CaSO_4$ scaling on coated steel and titanium metal. The scale was obtained at 60°C, atmospheric pressure and at various rotational speeds ranging from 100 to 2,000 rpm on both the materials. The results of the study showed that the growth of calcium sulfate scale on bare titanium metal increased significantly while it remained almost invariant on the coated carbon steel surface, with increasing rotational speeds. The anomalous behavior of coated steel samples was attributed to the competing effect between scale deposition and scale removal process due to the fluid flow and to the coating's antifouling characteristics, which resulted in less scale adhesion on coated steel compared to bare titanium metal surface. In addition, the field performance and economic appraisal of the selected coating are presented, as well.

Keywords: Calcium sulfate scale; $CaSO_4$; Scale deposition; Coated carbon steel; Titanium; Polymer coating; Rotating cylinder electrode

1. Introduction

Synergistic effect of scaling/fouling and corrosion is a major culprit for the heat transfer equipment in the process industry. Heat-exchanger fouling is a major economic problem accounting to about 0.25% of the total gross domestic product in highly industrialized countries [1]. The scale build-ups are thermal barriers to heat conduction in boilers, process heaters, and heat exchangers in petroleum refineries, chemical, and power plants. To mitigate corrosion, expensive corrosion-resistant alloys are used for shell and tube heat exchangers. The use of titanium tubes in heat exchangers is a well-established common practice since 1970s which has significantly increased the service life

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of many refinery heat exchangers [2]. Titanium, being a corrosion resistant material, has been used successfully either as original equipment or as replacement retubing in heat exchangers. In addition, the copper-based alloys such as Cupro–Nickel (Cu–Ni:90–10) are the most suitable tube materials used in desalination plants. However despite all these efforts, the corrosion (crevice, galvanic, hydrogen embrittlement, stress corrosion cracking, microbial, etc.) still remains a serious problem to be dealt with through out the plant's life [3]. Polymers coatings applied on low-cost material (e.g. carbon steel) offer a suitable alternative in process industry, as they can cope with the problem of corrosion and scaling, and they are also cost effective [4,5]. Thus, capital and maintenance costs of heat exchangers can be greatly reduced, if less expensive carbon steel tubes are coated with low-cost coatings that also provide corrosion protection comparable to that of costly high-grade alloy materials. In aggressive environments, heat exchangers capital and maintenance costs are high due to the use of expensive corrosion resistance materials [5].

To a limited extent in the laboratory, the rotating cylinder electrode (RCE) system has been successfully used to obtain scale deposition on different metals [6–10]. The RCE technique has advantages over conventional flow loops test methods due to the ease of creating turbulent flow conditions. Silverman [11,12] successfully modeled the velocity induced corrosion in RCE and compared it with conventional pipe flow geometry under similar turbulent hydrodynamic conditions, which showed identical mass transfer coefficients in both the geometries.

Hopkinson et al. [2] investigated the use of titanium tubes in petroleum refining heat exchangers. The investigation was conducted on forty in-service heat exchangers. The results revealed that the use of titanium tubes for heat exchangers exceptionally increased the service life in many refinery heat exchangers. They concluded that service life of the exchangers and plant production was improved by the use of titanium tubes.

Keith et al. [4] tested different types of polymer coatings. They coated carbon steel tubes in four heat exchangers to mitigate scale formation and corrosion. The laboratory and field tests of coated tubes showed that deposit on the coated tubes was weak compared to bare stainless steel and titanium. They found that cleaning of coated tubes using conventional hydro-blasting was relatively easier without coating damage but for noncoated titanium tubes it was difficult as scale strongly adhered to the bare metal surface.

Scholl [5] reported that capital cost of a typical heat exchanger can be reduced to 67% if polymer-coated carbon steel tubes, tube sheets, and headers are used in place of titanium tubes and titanium-clad plates. Scale deposit on coated surfaces is reduced tremendously compared with noncoated parts and its mitigation on heat transfer equipment improves equipment performance and reduces plants production losses.

Scaling/fouling is a severe problem which results from the accumulation of suspended particles in liquid or gas streams onto heat transfer surfaces [13]. Settlement of particulate matters due to gravity in the form of sludge and slime is referred to as sedimentation. The suspended particles could include ambient pollutants such as sand, iron, and microbial organisms in cooling water systems.

Precipitation fouling occurs chemically on hot surfaces, which happens when the process conditions are favorable for the creation of supersaturation of the dissolved inorganic salts in the fluid stream or commingling of incompatible waters such as seawater or groundwater. The driving force for crystallization is the chemical potential difference between the substances in the fluid (solution) and deposit formed on the metal surface [13]. The industrial systems that experience precipitation fouling are: saline desalination plants, geothermal brine systems, cooling water systems, steam generation systems, and potable water supply systems.

The effect of supersaturation, pH, Reynolds number, and concentration of ions in the brine solution on the formation of silica scale in heat-exchanger tubes were discussed and a silica deposition model was proposed by Neusen et al. [14].

Chemical reaction fouling includes deposits that are formed as a result of chemical reactions within the process fluid. Although heat-exchanger surface does not act as reactant, it sometime behaves as a catalyst [15]. This type of fouling is commonly occurring in chemical process industries, refineries, and dairy process.

The crystallization and scale formation due to calcium sulfate (gypsum) is common in the industrial situations and was investigated experimentally earlier on flat plate [16], metal surfaces [17] and heat-exchange surface [18,19].

Calcium sulfate ($CaSO_4$) is considered one of the most commonly found scale in Arabian Gulf and Red Sea regions, this was confirmed by the laboratory analysis and characterization carried out on the actual scale samples obtained from the Gulf region by Singh and Abbas [20].

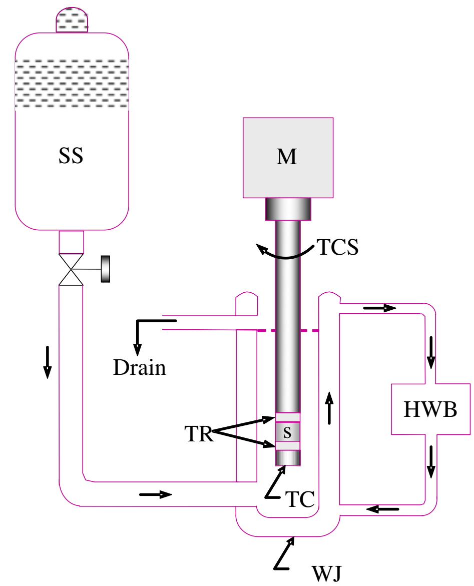
Scale formation impedes heat transfer and badly affects equipment performance efficiency [21] and to cope with the problem of scaling and as well as to minimize the effect of corrosion thermally conductive coatings are beneficial.

The objective of the present experimental work was to assess the performance of a thermally conductive polymeric coating from scaling/fouling standpoint. The selected polymer coating with trade name – "SAKAPHEN Si57E" [22], is a phenolic epoxy resin which can withstand temperatures from −20˚C to 180/200˚C, pH range of 3–14 (i.e. resistant to strong alkalis and weak acids) and is heat cured duroplast coating with oxide red/brilliant color [22].

Currently, "SAKAPHEN Si57E" coating is practically utilized on the heat-exchanger tubes, condensers, evaporators, water treatment equipment, salt units, and the piping systems at different oil refineries of Gulf region since 2004.

The subject coating was applied on low-cost carbon steel and compared with bare titanium metal, with regard to the deposition of calcium sulfate scale on these materials and hence, no electrochemical aspects were explored in the present investigation.

The effect of solution hydrodynamics was studied at different rotational speeds, ranging from 100 to 2,000 rpm at 60˚C and at atmospheric pressure, to assess the calcium sulfate ($CaSO_4$) scale deposition on coated carbon steel and bare titanium metal surface. Moreover, field performance experience gained over the past nine years and appropriate inherent economic appraisal that could possibly be realized by the use of selected candidate coating are also highlighted.



M = MOTOR TO ROTATE SPECIMEN AT FIXED RPM
TCS = TEFLON COATED SHAFT.
TR = TEFLON RING
S = CYLINDRICAL SPECIMEN
TC = TEFLON CAP
HWB = HOT WATER CIRCULATION BATH
SS = SUPERSATURATED SOLUTION
WJ = WATER JACKET

Fig. 1. Schematic of the experimental setup of RCE apparatus.

2. Experimental

The experimental set-up of a RCE equipment is shown in Fig. 1. Cylindrical samples (1/2 in. diameter and 1/2 in. long) of coated carbon steel and titanium were fitted on the shaft of the equipment so that their peripheral surfaces were exposed to supersaturated scale forming solution in double wall glass test cell. The heating of the scaling solution was carried out by a hot water circulating bath connected to the glass cell. Further details can be found in [7].

To keep the solution composition constant, fresh solution was continuously supplied to the glass cell from the reservoir tank at a rate of 1.0–1.5 l/h and overflow fluid was drained. Equal volumes of $CaCl_2$ and Na_2SO_4 solutions prepared form the regent grade chemicals in distilled water were added in the supersaturated solution tank whenever necessary. The concentration used for both the solutes was 0.03 mole/l. The rotation speeds used in the experiments were from 100 to 2,000 rpm. All experiments were conducted at 60˚C temperature and atmospheric pressure for 6 h duration.

At the beginning of the experiment, each specimen was thoroughly cleaned with distilled water and acetone, weighed and mounted on the shaft of the rotating equipment. At the end of experiment, the specimen was rinsed with water and carefully removed from the shaft and dried in an oven and reweighed to determine the mass of scale deposited on the specimen.

The deposition rate of scale was calculated as the weight gained of the scaled specimen divided by the surface area of the specimen and the experimental time. A minimum of three experiments were conducted at each test parameter, and the average deposition rate was determined. The experiment was repeated if found necessary. The uncertainty in the deposition rate was found to be ±8% for coated carbon steel while it was ±12% for titanium.

The surface roughness profile of the as-received coated carbon steel sample was measured by Bendix Model-5054 profiling system and almost similar roughness profile was reproduced on the bare titanium samples by polishing with silicon carbide (SiC) emery paper for comparison purpose.

For present work, the selected coating was applied to 200 microns (μm) thickness on cylindrical carbon steel samples at a local company's facility and Titanium SB-338 Grade 2 was used for bare titanium samples. Flat round (1/2 in. diameter) discs of titanium and as-received coated specimen were used for the morphological study of the scale crystals.

3. Results and discussion

3.1. Surface roughness

The average surface roughness "Ra" values measured by the Bendix Profilometer Model 5054 are presented in Table 1. It can be seen from the table that the surface profile generated by polishing titanium samples with 600 grit SiC emery paper replicated almost a similar surface profile to that of as-received polymer coated carbon steel specimen. Therefore, both the coated carbon steel and titanium specimens used in the present investigation have almost identical surface profiles having Ra value of 17.5 μ in. (Table 1).

3.2. Scale deposition

The continuous flow of fresh solution to the glass cell assured that the test specimens were exposed to a solution of constant composition. The analysis of the data obtained in the study was carried out by converting the respective rotational speeds (rpm) used in the experiments to the equivalent Reynolds numbers (Re) as suggested by Gabe [23] and is shown in the following equation:

$$\mathrm{Re} = R_1\omega[(R_2 - R_1)/v]$$

where Re, equivalent Reynolds number (dimensionless); R_1, radius of the rotating specimen (cm); R_2, radius of the glass cell (cm); ω angular velocity of the rotating specimen (rad/s); and v fluid kinematics viscosity (cm^2/s).

It is worth mentioning that during our experiments no signs of corrosion on coated carbon steel samples or turbidity of solution was observed, and at the initial stages of the work, the immersion test of coating in distilled water demonstrated its imperviousness to water absorption and also its nonreactive nature to acetone.

The data analysis showed that mixing of the solution due to an increase in rotational speed had a strong influence on the precipitation and rate of deposition of calcium sulfate scale. The higher the speed of rotation the more scale crystals formed and adhered on the titanium metal surface; however, the deposition behavior on the coated carbon steel was on the contrary (different) with respect to an increase in rotational speed.

The following paragraphs present a comparison of calcium sulfate scale deposition obtained on titanium and coated carbon steel samples, under almost identical surface roughness conditions (Table 1) at various Reynolds numbers used in the study.

Fig. 2 shows an average deposition rate of calcium sulfate ($CaSO_4$) scale on both titanium and coated carbon steel samples as a function of Reynolds number. It can be clearly seen that an increasing deposition rate of calcium sulfate scale is obtained on titanium samples at each Reynolds number as shown by the best line fit in the data. The accumulation of scale on the titanium metal is significantly higher compared to coated carbon steel at all Reynolds numbers studied. The enhanced rate of deposition of calcium sulfate scale observed on the bare titanium metal can be related to its higher surface activation energy which consequently promotes strong adhesion of scale on titanium surface.

In addition, Fig. 2 also presents an average deposition rate of calcium sulfate scale on the coated carbon steel samples which is relatively very less compared to bare titanium metal. It can be noticed that the rate of scale deposition does not vary much, and is almost constant on the coated carbon steel samples and remains insensitive to increase in rotational speed as indicated by the best fitted line in the data. The invariant behavior of scale deposition on coated carbon steel shows that there exists a balance between the rate of deposition and rate of removal of scale, and the overall scaling process on the coated steel is not influenced by any increase in Reynolds number (fluid flow). This seems to be an added benefit of using the selected polymer coating on carbon steel which reduces the accumulation of scale on the

Table 1
Average surface roughness (Ra) values of polymer coated carbon steel and titanium specimens

Specimen type	Measured average roughness Ra (μ in.)		Maximum average Ra (μ in.)
	Forward travel	Backward travel	
Coated carbon steel (as-received)	17.5	17.5	17.5
Titanium (600 grit polish)	17.5	17	17.5

Uncertainty: ±4 μ in., conversion factor: 1 μ in. = 0.0254 μm.

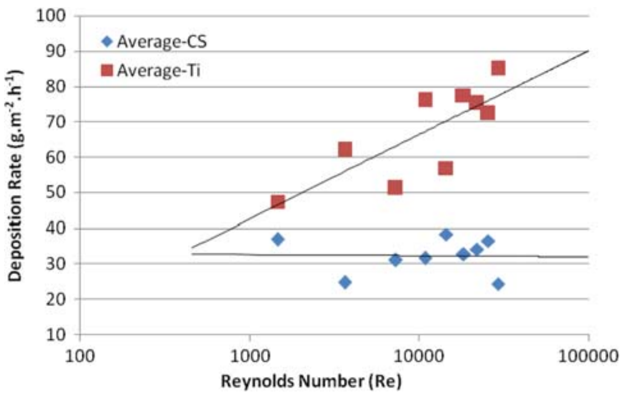


Fig. 2. Average deposition rate of calcium sulfate scale deposited on coated carbon steel and titanium samples as a function of Reynolds number (CS – carbon steel coated with "SAKAPHEN Si57E" coating, Ti – titanium).

coated surface because of its antifouling characteristics and hydrophobic nature.

It is conspicuous from the results of Fig. 2 that the "SAKAPHEN Si57E" polymer coating on carbon steel samples reduced excessive scale build-up. However, in the case of titanium samples the scale growth was quite significant. The coated carbon steel samples showed better resistance to fouling compared to titanium metal. The accumulation of calcium sulfate scale on the titanium metal increased but it remained almost invariant on the coated carbon steel surface with the increasing Reynolds numbers. It is noteworthy that the results of the present investigation are in agreement with the earlier researchers [4,5].

Based on the performance evaluation from the scaling perspective of the selected coating in the present study and because of the its antifouling properties, hydrophobicity, corrosion protection as well as cost-saving benefits (see economic appraisal section) associated with the use of coatings, we can assert that the application of polymeric thermally conductive coatings on low-cost steel can offer a promising and viable alternative choice for the replacement of the expensive titanium metal and its alloys in the heat exchangers manufacturing industry.

3.3. Morphology

The morphology of calcium sulfate scale crystals deposited on the titanium and as-received coated carbon steel samples obtained by scanning electron microscope (SEM), is shown in the micrographs of Figs. 3 and 4. It is evident that the scale crystals originate at preferential nucleation sites present on the samples. In general, a needle-like growth mechanism prevails on both specimens. The dense population of randomly distributed calcium sulfate ($CaSO_4$) crystals on entire surface of titanium substrate can be seen in Fig. 3(a). While, a patchy growth of crystals at nucleation sites can be observed on coated sample which is not covering the entire surface of the specimen as shown in Fig. 4(a).

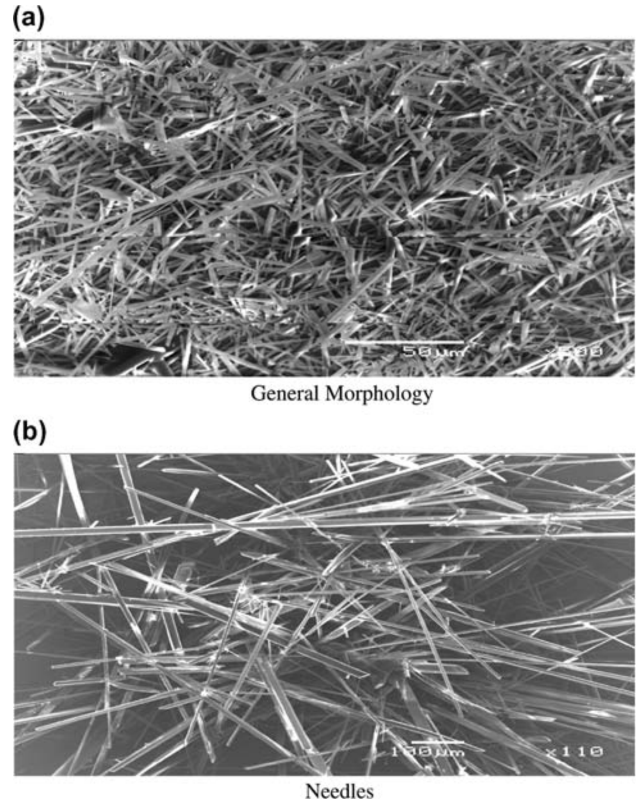


Fig. 3. Micrographs showing the morphology of $CaSO_4$ deposited on titanium metal specimens.

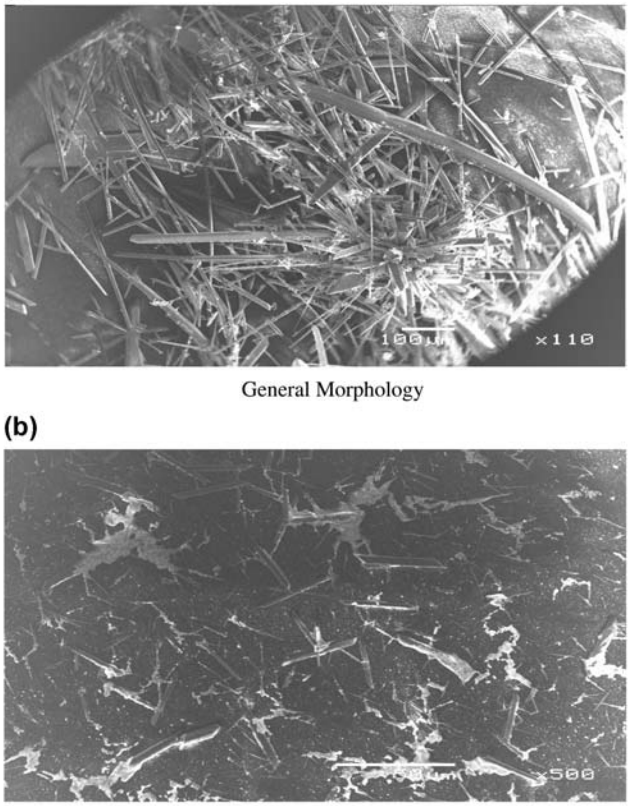
The SEM examination revealed crystal structures comprising prismatic needles- and rods-like growth (Figs. 3 and 4). It has been noticed that the calcium sulfate ($CaSO_4$) crystals initially tend to grow perpendicular to the substrate surface and then branch out randomly in all directions, this typical feature was also observed earlier during calcium sulfate ($CaSO_4$) scale deposition on stainless steel, aluminum and copper substrates [7–10].

3.4. Economic appraisal

The ensuing cost benefits of using thermally conductive polymeric coating on carbon steel as compared to the use of costly titanium metal and its alloys in heat exchangers are significant. A simple comparative economic analysis highlighting the cost savings is presented below.

Consider a shell-and-tube heat exchanger comprising 1,000-tube bundle, wherein each tube is of

(a)



General Morphology

(b)

Needles

Fig. 4. Micrographs showing the morphology of $CaSO_4$ deposited on "SAKAPHEN Si57E" coated carbon steel specimens.

19.05 mm outside diameter and 6.1 m long, and all the pressure components are made from normal carbon steel.

The capital cost of an exchanger made of titanium tubes having carbon steel pressure components is assumed as $400,000. A similar exchanger entirely made of carbon steel (tubes and pressure components) is assumed to cost $150,000 as a capital cost and an additional $30,000 is assumed for the cost of internal coating's application, which brings the cost to $180,000 for the carbon steel heat exchanger. The net saving in the capital cost for an exchanger unit made of coated carbon steel tubes compared to titanium tubes thus is $220,000. This is an appreciable saving of 40% on the capital cost of one heat-exchanger unit only employing coated carbon steel tubing. A typical cooling system plant contains at least four heat-exchanger units and if coated carbon steel is used for the tube material in these four heat exchangers, an overall cost saving of $880,000 would be achieved. It is to be noted that this cost saving does not include operational and maintenance costs, and also the production losses due to unscheduled shutdowns. The coated carbon steel mitigate fouling, corrosion and is expected to extend the service life of the exchanger, therefore the operational life span of the plant might be increased from two to four years.

A titanium tubular heat exchanger is designed to have 20 years of lifecycle. Titanium tubing material is usually replaced every 10 years. Thus, the replacement of heat-exchanger tubing material is two times during its operational lifecycle. In contrast, coated carbon steel tubes are expected to last for a maximum of 10 years before coating lose its integrity which means that the replacement of coated carbon steel tubes is also two times during the total lifecycle. Therefore, for both the coated carbon steel and titanium tubing, the replacement will be two times during the heat-exchanger operational lifecycle.

The simple comparative economic appraisal presented ascertains that the coated carbon steel can deliver more cost benefits compared to the use of expensive titanium metal or its alloys during the whole operational lifecycle span of a heat exchanger. A minimum of 40% capital saving are anticipated in the present study for the replacement of titanium tubes bundle only with the coated carbon steel tubes bundle. However, if the replacement of a complete titanium made exchanger is considered then 60% or more cost saving would be achieved in the capital. The literature repots a saving of 67% in the capital cost [5]. Additionally, owing to the use of coatings, there are considerable reductions in maintenance schedules and fortuitous outages which translates into scores of extra savings (i.e. increase in production and minimal cost of operational disruptions) depending upon the process involved in the plant. We foresee that the use of selected proprietary coating(s) can turn investments (expenditures) into huge savings as these coatings can be refurbished repeatedly on the same substrate a number of times, keeping the original substrate material intact (material-cost saving).

3.5. Field exposure

The "SAKAPHEN Si57E" polymer-based thermal conductive coating is presently in use at oil production facilities of Gulf region. The coating was applied on the heat-exchanger tubes, condensers, evaporators, water treatment equipment, salt units, and the piping systems in March 2004. Fig. 5 shows typical photographs of a field heat exchanger of the condenser/cooler unit before and after three years of field service with the application of the selected coating. The enlarged view of a portion of the exchanger tubes (shown in the inset of Fig. 5(b)), clearly depicts that

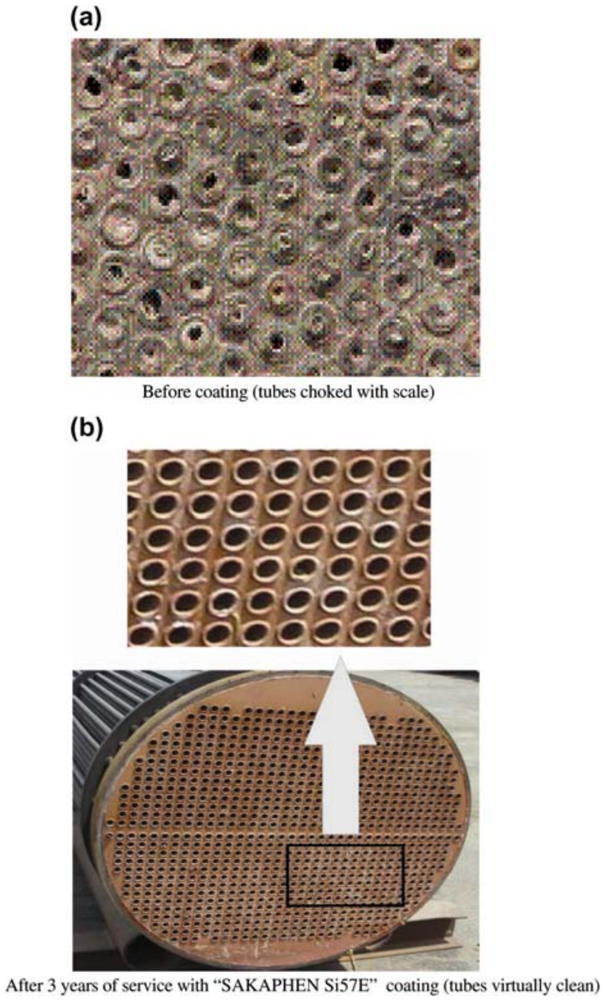


Fig. 5. Photographs of a field heat-exchanger unit: (a) before coating and (b) after three years of exposure with "SAKAPHEN Si57E" coating.

heat exchanger's tubes are virtually clean and devoid of scale after three years of successful operation. The routine test and inspection (T&I) has shown that this particular unit is providing excellent trouble free and smooth service over the past 9 years after the application of subject coating up to reporting (December 2012) without any further dire need for maintenance (dismantling) or emergent shutdown.

Albeit, it seems too early to judge the long-term performance ($\geq$20 years) of the subject coating, however, the short-term field exposure of nine years so far has been satisfactory as no case of coating failure has been reported after its industrial adoption in 2004. The field engineers and operators of the plants contacted are experiencing a nearly maintenance free substitution of the subject coating as it has reduced the scaling/fouling frequency and unexpected shut downs to considerably lower levels than experienced with bare titanium components and the regular and scheduled preventive maintenance, test and inspection durations have been reduced. The introduction of the selected coating has resulted in the reliable and smooth operations of the refineries/plants with minimal outages and down time, increased production, and a host of additional intrinsic revenues.

Polymer coatings are innovative environmental friendly products as well, as they significantly reduce the heavy metal pollutants discharge such as arsenic, copper, and zinc which otherwise leach out from the bare metals during operation, into the environment. This advantage further eliminates totally or partially the need of chemical water treatment (saving).

With the modern technological advancement in the development of new materials and the flexibility in coating's application techniques (in-situ internal, external, on the job/site, and factory), the thermally conductive polymer coatings are potentially suitable and can offer low-cost solution with minimal capital investment for the replacement of highly expensive materials such as, titanium and its alloys in the petrochemical, oil, and gas production industries. We expect based on our reported study that the "SAKAPHEN Si57E" coating will accrue all the underlying intended benefits satisfactorily during its service life.

4. Concluding remarks

To cope with the problem of scaling and as well as to minimize the effect of corrosion, thermally conductive coatings are beneficial.

The growth of calcium sulfate scale on the titanium metal increased with increasing rotational speed but it remained almost invariant on the coated carbon steel surface. The reduced scaling tendency is observed on coated carbon steel. The anomalous behavior of coated steel samples can be attributed to the competing effect between scale deposition and scale removal process due to the fluid flow and the coating's antifouling characteristics and its hydrophobicity, which resulted in less scale adhesion/deposition on coated steel compared to bare titanium surface.

Simple economic appraisal demonstrated a minimum of 40% saving in the capital cost with the use of coated carbon steel as compared to the use of expensive titanium metal. Additional benefits can be realized due to smooth operation of the heat transfer equipment (i.e. enhanced efficiency and reduced maintenance and downtime) resulting in increased annual production and revenues. The use of coatings can turn investments (expenditures) into huge savings.

Owing to the antifouling properties, corrosion protection as well as cost saving benefits associated with the use of thermally conductive polymeric coatings in oil refineries, coated carbon steel is now considered a viable alternative choice to replace the expensive titanium metal in the heat exchangers manufacturing industry. The polymer coating materials are appropriate and offer low-cost solution with minimal capital investment for the replacement of highly expensive materials in the petrochemical, oil, and gas production industries.

The "SAKAPHEN Si57E" polymer coating is currently utilized in the oil industry of the Gulf region since 2004. The nine years of field performance experience of selected coating has been satisfactory thus far as no case of coating failure has been reported after its incorporation in oil industry of Gulf region in 2004. It is anticipated that the subject coating investigated will accrue all the underlying intended benefits satisfactorily during its service life.

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