Biofilm: A hidden threat

A new approach to the costly problem of biofilm formation in refinery and petrochemical operations

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Refineries and petrochemical operations rely on water-cooled heat exchangers in many areas of their facilities. These heat exchangers provide the heat removal from refining processes required for the production of various products and intermediates. The efficient transfer of heat in these exchangers often determines production rates. Fouling of the heat exchanger surfaces or flow restriction resulting from biofilm, scale, or debris may limit production and result in downtime for cleaning. Additionally, corrosion of the heat exchangers because of microbiological deposits may result in failures that require downtime, maintenance, and capital expenses.

Expenses can run into millions of dollars, particularly if they include unscheduled downtime and heat exchanger replacement. Proper management of heat exchanger performance includes analysis of heat transfer data and understanding failure mechanisms. Data management tools can assist in the development of preventative maintenance guidelines and in the optimisation of chemical treatment programmes that minimise these expenses. Many refineries and petrochemical plants struggle with heat exchanger bundle failures and efficiency losses between turnarounds. Inspections of failed bundles often reveal under deposit corrosion (UDC) with biofilm as the culprit.

Traditional monitoring and control techniques

Warm cooling tower water containing microorganisms and nutrients fosters ideal conditions for microbial growth and biofilm formation. Microorganisms and nutrients enter the cooling system through multiple paths. They enter the system in the make-up water – even though it may have been treated for microorganisms, the treatment only renders the water sanitary, not sterile. As the water flows over the tower during the evaporation process, microorganisms and nutrients enter the system through the scrubbing process. Nutrients enter the cooling system from hydrocarbon leaks on the process side of heat exchangers, and they enter in the form of phosphate corrosion inhibitors applied to protect the carbon steel piping and heat exchangers from corrosion.

Figure 1 depicts various stages of biofilm formation on a surface as microorganisms and nutrients continually inoculate the cooling water system. In the first stage, the cooling water transports these microorganisms to the surface. In the second stage, the microorganisms begin to attach themselves to the surface and within 20-30 minutes of system inoculation begin colonisation. In the third stage, because microorganisms reproduce through cell division at a geometric rate, within one to two days significant growth can occur.

Part of this growth involves the production of extracellular polymeric substances (EPS). The composition of the EPS includes polysaccharides, proteins, extracellular DNA (eDNA), and lipids. The EPS from various microorganisms interact with each other and form a slime matrix that encompasses and protects the microorganisms. In the fourth stage, within three days to three weeks, the thickness of the biofilm matures. In the fifth and final stage, at maturation, detachment occurs because of turbulence or ecological conditions. This detached biofilm can then populate other regions of the cooling water system.

Most microbiological control programmes using strong oxidising biocides, such as bleach or chlorine gas, even when used in combination with non-oxidising biocides, can only control biofilm up to a point. The matrix formed by the EPS encapsulates the microorganisms and provides a level of protection from these biocides. The EPS creates a demand for strong oxidisers, which generally cannot be

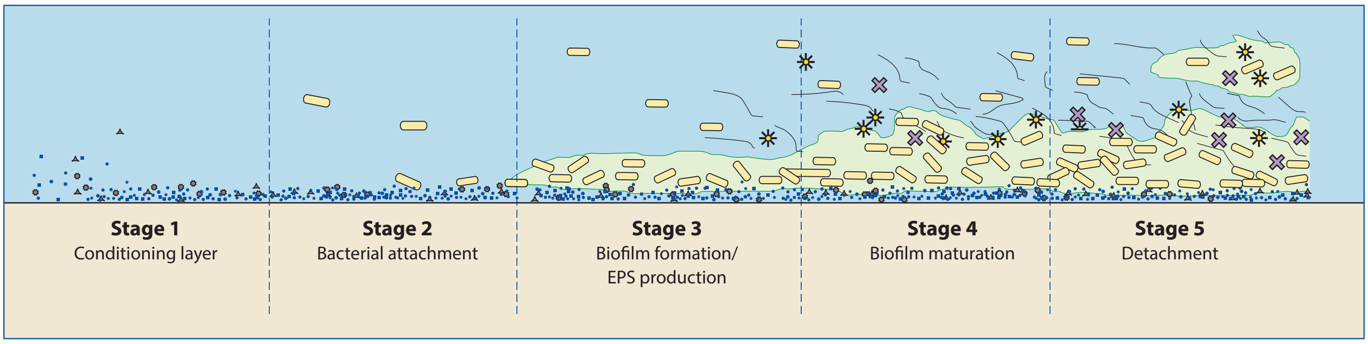

Figure 1 Five stages of biofilm formation

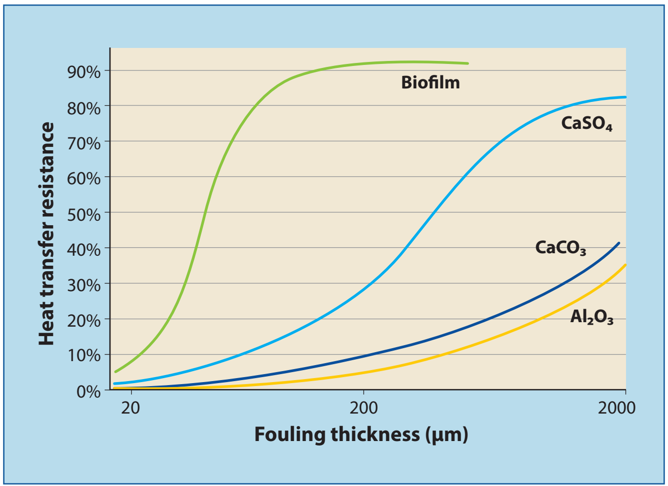

Figure 2 Thermal effect of biofilm and typical mineral scales

exceeded at typical dosages. Dosages that can exceed the demand have a negative impact on the corrosion rates of metal surfaces themselves and degrade dispersants that are used to provide protection from inorganic deposition. Non-oxidising biocides similarly have difficulty penetrating the EPS's protective slime matrix without reacting with the EPS. Economics do not favour traditional approaches to biofilm control.

Underappreciated and underestimated aspects of industrial cooling water treatment include the effect of biofilm on heat transfer and the resultant heat exchanger failure from microbiologically induced corrosion (MIC). As shown in **Figure 2**, thinner biofilms, as compared with mineral scale, exhibit a more severe resistance to heat transfer. Microbiological fouling inhibits heat transfer up to four times that of calcium carbonate fouling. Additionally, once the biofilm exceeds 50 microns, approximately the thickness of adhesive tape, the resulting anaerobic conditions support the growth of acid-producing bacteria. The acidic waste products from anaerobic bacteria often aggressively pit heat exchanger tubes and eventually cause leaks, requiring repair or replacement.

Traditional techniques for monitoring microbial growth and biofilm formation cannot measure biofilm. Biofilm forms when planktonic (free-floating) microorganisms begin to adhere on surfaces, such as pipe walls, heat exchangers, and cooling tower fill. Traditional approaches to monitoring microbial activity include measuring halogen residuals, heterotrophic plate counts, and adenosine triphosphate (ATP) levels in the bulk water. Unfortunately, no correlation exists between any of the results of these monitoring techniques and the attached, sessile microorganism levels that cause biofilm.

Since traditional approaches to monitoring neither predict nor indicate biofilm, mechanical approaches have been employed to monitor the efficiency of heat exchangers to determine if biofilm fouling is present. However, detecting biofilm by measuring heat exchanger approach temperatures, unfortunately, only indicates the presence of biofilm after the fact. Similarly, flow studies only show restrictions and loss of velocity after biofilm has formed.

New approach

Solenis' proprietary ClearPoint biofilm detection and control programme provides a new approach to the costly problem of biofilm fouling. This programme comprises three components: a novel biofilm analyser, proprietary chlorine stabiliser chemistry, and expert service. Employing the biofilm analyser, the programme provides early detection and accurate measurement of biofilm growth in real-time. The chlorine stabiliser chemistry is used to produce a patented, in situ stabilised active chlorine solution. The solution significantly reduces microbiological activity without the adverse side effects associated with strong oxidising biocides. Field service personnel provide the expertise required to maintain clean and efficient heat exchangers.

The proprietary OnGuard 3B analyser uses a patented ultrasonic sensor, shown in **Figure 3**, to accurately measure the thickness of biofilm that accumulates on a heated target assembly, shown in **Figure 4**. The sensor detects biofilm with a measurement accuracy of approximately 10 µm and at a resolution of ±5 µm. The analyser mimics critical heat exchanger conditions in real-time by duplicating the shear stress on a surface while also simulating the local surface temperature to provide continuous fouling factor measurements that inform the adjustment of chemical feed when

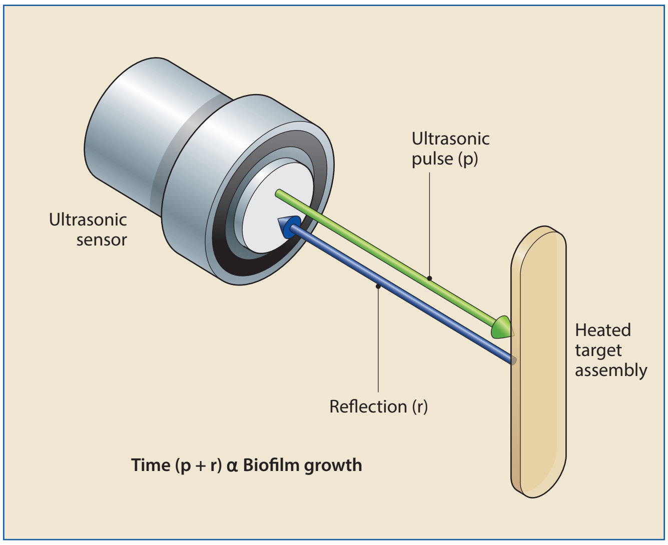

Figure 3 Working principle of the ultrasonic sensor

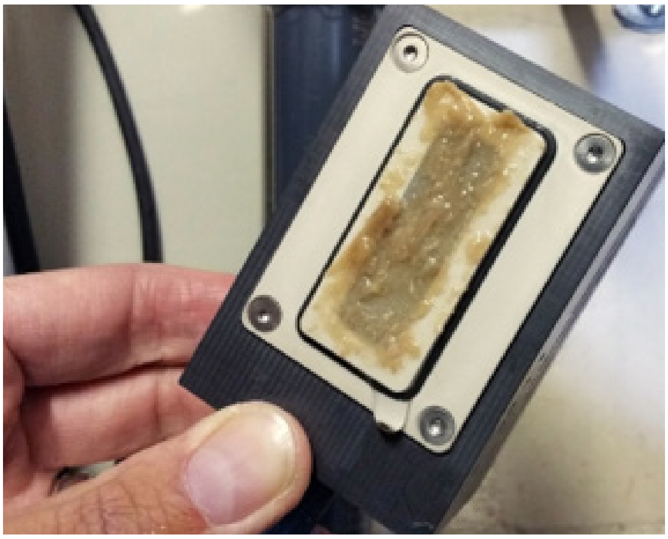

Figure 4 Heated target assembly showing presence of biofilm

required. The analyser can also differentiate between soft deposits (organic and microbiological fouling) and hard deposits (scaling). The early detection capability of the analyser allows corrective actions to be taken before biofilm can cause heat transfer loss or equipment damage.

The advanced chlorine stabiliser chemistry employed as part of the biofilm detection and control programme is used in combination with sodium hypochlorite to produce a patented, in situ stabilised active chlorine solution. The resulting solution is not consumed when reacting with the EPS's protective slime matrix, thereby allowing the solution to penetrate the biofilm, where it reacts only with the hydro-sulphur and sulphur-sulphur bonds of the biological proteins on the cell membrane and within the microorganisms. The in situ stabilised active chlorine solution not only controls both planktonic and sessile microorganisms but also removes existing biofilm and inhibits biofilm regrowth. The solution also effectively controls biofilms that harbour legionella.

The in situ stabilised active chlorine solution does not increase the corrosion of metal substrate because of its lower oxidation reduction potential (ORP). For the same reasons, the solution does not degrade cooling water inorganic deposit inhibitors or react with other organics potentially present in the water. Thus, adsorbable organic halogen (AOX) and trihalomethane (THM) production does not occur. The lack of these reactions provides desirable environmental and health advantages over strong oxidising biocides.

Unlike strong oxidising biocides, ammonia and amine contamination in cooling water does not increase the demand for the in situ stabilised active chlorine solution. Additionally, the patented solution results in lower chloride levels and reduced overall corrosivity of the cooling water. Stainless steel, in particular, has a reduced risk of chloride-induced stress cracking.

As a complement to the biofilm detection and control programme, the Solenis HexEval performance monitoring programme is available. Using advanced monitoring and predictive modelling capabilities, this programme enables decision-makers to identify which heat exchangers pose the greatest threat to reliable operation because of biofouling, scale or both. As a result, plant personnel can develop appropriate action plans.

Solenis experts work directly with plant engineers to assign a critical rating score to each exchanger based on its impact on production if taken offline for cleaning or repair. The algorithm, developed from more than five million hours of study time on thousands of heat exchangers, then analyses the flow study data of each exchanger, within the context of its design, to calculate a hydrothermal stress coefficient (HSC) – a discrete value used to assess the reliability of the heat exchanger and identify factors threatening its performance.

Case history: Marathon refinery

Marathon Petroleum Corporation operates the Garyville oil refinery on the banks of the Mississippi River in southeastern Louisiana between Baton Rouge and New Orleans. The facility has a crude oil refining capacity of 596,000 barrels per calendar day. Crude refining takes place in 19 processing units using 10 cooling towers and more than 400 individual heat exchangers. Heat exchanger reliability and efficiency have a dramatic impact on the profitability of the operation. The facility and its water treatment supplier, Solenis, monitor the conditions of the water chemistry and the individual heat exchangers to ensure smooth operation.

Hidden biofilm cost

Despite maintaining corrosion coupon rates of less than two mils per year (mpy) and controlling water treatment parameters within key operating indicators (KOIs) for mineral saturation and corrosion inhibitor residuals, the refinery struggled with heat exchanger bundle failures and efficiency losses between turnarounds.

Even with corrosion coupon results well within industry standards, heat exchanger bundle lifespans averaged seven years, lower than predicted. Corrosion coupon data suggested that the exchanger longevity should have been 50-80% longer. Agar dip slides, used to measure aerobic planktonic bacteria growth, routinely yielded results well within the Cooling Technology Institute (CTI) guidelines of 10^1–10^2 cfu/ml. Halogen residuals, used to control planktonic microorganisms, conformed to recommended values. The programme used a non-oxidising biocide, selected by laboratory kill studies, fed to the system two to three times per week. Still, summer conditions resulted in constrained refinery capacity, with exchangers being taken offline for cleaning because of water side fouling and requiring unscheduled shutdowns for cleaning, repair, and replacement. The negative impact on plant production and profitability ran into the millions of dollars annually.

> **Underappreciated and underestimated aspects of industrial cooling water treatment include the effect of biofilm on heat transfer**

Because the heat exchangers were typically removed from service for decontamination, deposit analysis did not show the true cause of the corrosion, which was ultimately determined to be biofilm. The steaming required to decontaminate the process side dehydrated the biofilm. Despite deposit analysis that predicted a different corrosion mechanism, closer inspections of failed bundles revealed UDC and pitting resulting from biofilm. In addition, corrosion coupon visual examination and laboratory testing confirmed that biofilm was the root cause of the problem.

A million-dollar problem

Marathon and Solenis set about defining the problem and developing a plan to address the root cause. Before changes to the existing treatment programme could be recommended, the hypothesis that biofilm was the root cause of the exchanger problems required additional validation. To do this, Solenis, working with the local Marathon team,

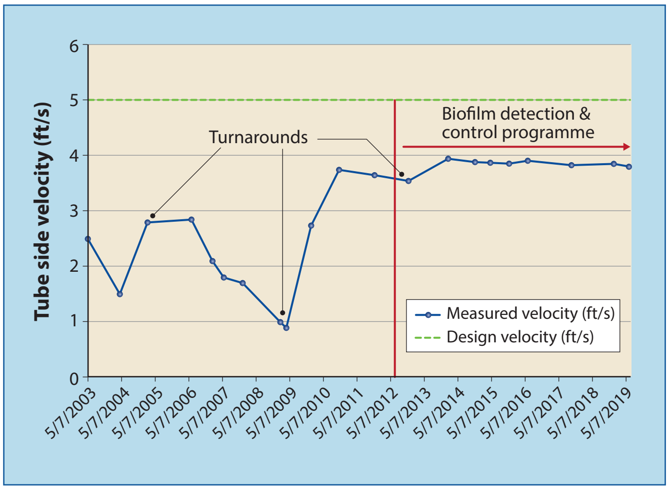

Figure 5 Heat exchanger water velocity before and after implementation of the biofilm detection and control programme

used the modelling capabilities of the HexEval performance monitoring programme to categorise the heat exchangers at risk of developing biofouling, scale or both.

Prior to the implementation of the performance monitoring programme, American Petroleum Institute (API) guidelines were in use. The guidelines identified at-risk exchangers as having a water velocity less than 0.91 m/sec (3 ft/sec), a cooling water outlet temperature greater than 48.9°C (120°F), and a process inlet temperature greater than 60.0°C (140°F). According to these guidelines, 233 of the 400 exchangers in the refinery were at risk of developing deposition.

Managing the risk to 233 heat exchangers would have been a daunting task. However, the Marathon engineers used the heat exchanger performance monitoring programme to calculate each exchanger's HSC value. The HSC assesses the reliability of each heat exchanger and identifies factors threatening their performance. The higher the HSC value, the greater the risk of deposition. An HSC value less than 2.0 identifies a low risk, and a value greater than 2.0 identifies an increasing risk of biofouling or scale. The calculated HSC values reduced the number of at-risk bundles from 233 to 94.

After identifying the 94 at-risk exchangers in the plant, the engineers concentrated on improving the mechanical aspects of the cooling system to reduce the overall risk of biofouling and scale formation. Better transient debris mitigation using improved tower screens combined with other mechanical modifications helped to reduce the risk of fouling in the at-risk exchangers and improved the overall performance of the cooling system. These modifications included flow balancing across the exchanger network, using a hot process bypass instead of throttling the cooling water flow, adding supply side jumpers for back wash assistance, introducing metallurgical changes, and making exchanger design changes. The number of at-risk exchangers was reduced to 37.

Reducing the number of 'bad actors' from 233 exchangers to 37 exchangers brought focus to the problem. Recalculating the HSC values revealed biofouling risk factors for 32 of the 37 problem exchangers. Clearly, these results warranted a change in the microbiological control programme.

To address the biofouling issue, Solenis recommended implementation of its biofilm detection and control programme on one of the refinery's cooling towers on a trial basis. The recommended chemistry for the trial was the patented, in situ stabilised active chlorine solution. After the six-month trial, the general corrosion rate was cut by a factor of three and the pitting rates were cut by a factor of two. The refinery's leadership decided to adopt the biofilm detection and control programme for all of its cooling towers.

General corrosion rate and corrosion pitting, measured by metal coupon testing, and average weighted wall loss, measured during heat exchanger inspections by non-destructive testing, all showed dramatic improvement. After converting to the in situ stabilised active chlorine solution, corrosion rates of 0.2-0.3 mpy were achieved without pitting. Eddy current testing data collected before and after the implementation of the in situ stabilised active chlorine solution showed a decrease in heat exchanger wall loss of 45%. This loss corresponded to a 50-80% increase in bundle life. Solenis continued to monitor heat exchanger flows and cooling tower efficiency. Monitoring of the heat exchangers revealed that exchangers that historically had lost flow rapidly shortly after a turnaround now maintained their start-up flows. This improvement was validated during annual flow studies, as shown in **Figure 5**.

Furthermore, the biofilm detection and control programme effectively eliminated algae on the cooling water return hot decks. Prior to implementing the programme, even with aggressive doses of conventional biocide, algae covered the hot decks, short-circuited the cooling tower fill, and drove up supply water temperatures, resulting in production rate reductions, until the hot decks were cleaned. After the algae build-up was removed by the new in situ stabilised active chlorine solution, the hot decks remained clean and the supply side approach to wet bulb temperatures immediately improved by -17.2°C to -16.7°C (1-2°F).

Towers with high-performance fill experienced the greatest gains. The approach to wet bulb readings were monitored closely for three years. In the first year, the approach to wet bulb temperatures decreased by -16.1°C (3°F) and in the third year by almost -13.9°C (7°F). The colder water flow to the process improved vacuum on overhead exchangers, resulting in production gains with only a negligible increase in operational expense. Additional data analysis would corroborate the evidence of improved performance and profitability.

Next, Solenis analysed the data and determined how many heat exchangers required cleaning outside of turnarounds and how many experienced failures before and after the implementation of the biofilm detection and control programme. If biofilm caused the fouling, then the implementation of the programme should result in fewer heat exchanger cleanings during production runs. As shown in **Figure 6**, the number of heat exchanger cleanings outside of turnaround decreased by 89% with the programme.

If biofilm causes corrosion, fewer heat exchanger failures should result from improved biofilm control. The data

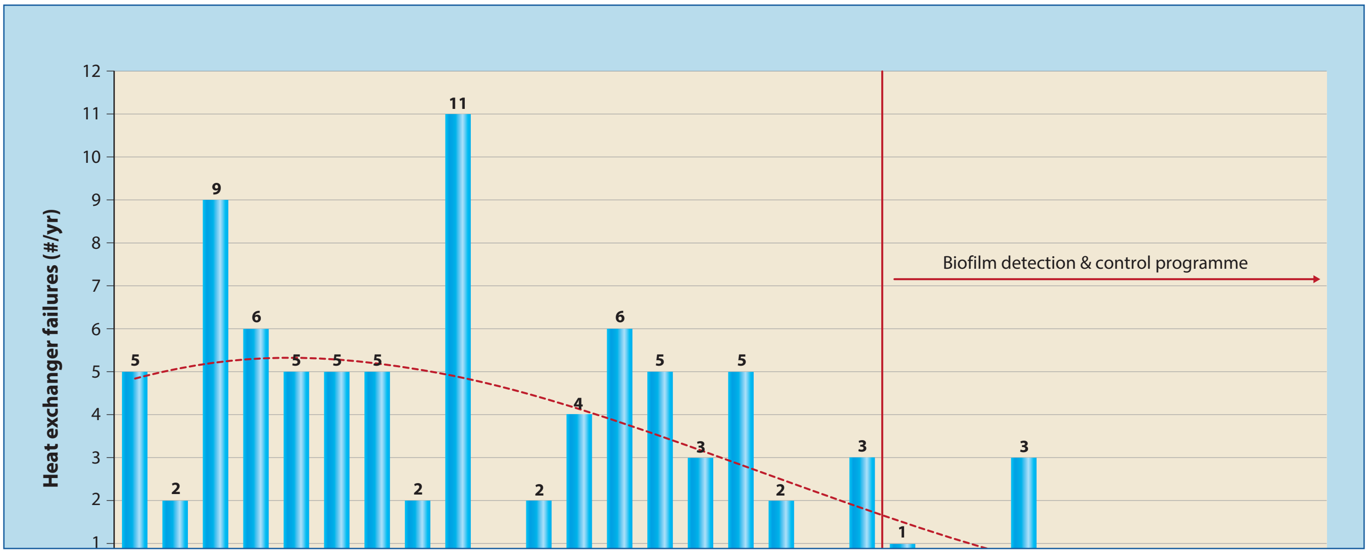

Figure 6 Heat exchanger cleanings before and after implementation of the biofilm detection and control programme

presented in **Figure 7** shows fewer heat exchanger failures with the implementation of the biofilm detection and control programme. The number of heat exchanger failures decreased by 85%, and no new failures have been recorded since February of 2016.

Implementation of the performance monitoring and biofilm detection and control programmes provided a documented annual net return on investment (ROI) of seven figures. This ROI was based on increased crude charges, increased production through the FCC, overall increased production, reduced propane in the fuel gas, reduced frequency of exchanger cleanings, reduced frequency of cooling tower deck cleanings, and increased heat exchanger life. Overall, the programmes significantly improved the refinery's profitability.

Continued success

A sister refinery experienced issues with biofilm and MIC on a large cooling water system, so much so that the expense for sodium hypochlorite and non-oxidising biocide had soared to almost $85,000 per month with its existing treatment programme. The refinery leadership implemented the heat exchanger performance monitoring programme and new biofilm detection and control programme. After the implementation of the programmes, the monthly chemical expenditure decreased to roughly $10,000 per month.

The system that once had experienced leaks at least annually, now saw only one leak in the three years after the implementation of the new programmes. Shortly after implementation, that 'annual' leak, unrelated to water chemistry, occurred again. Under normal circumstances, that amine-related leak would have resulted in an immediate need to shut down to repair the heat exchanger. Instead, the biofilm detection and control programme maintained microbiological control and corrosion rates in the system for

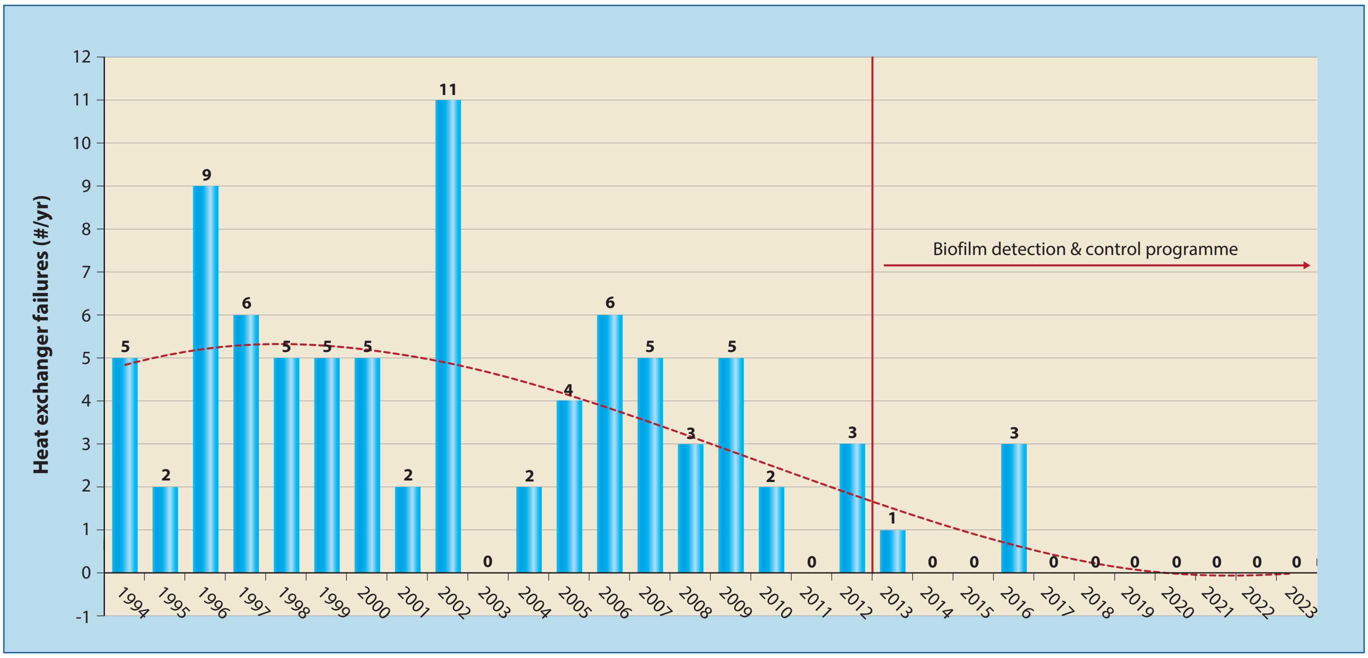

Figure 7 Heat exchanger failures before and after implementation of the biofilm detection and control programme

six months, enabling the exchanger to be repaired during a scheduled unit turnaround.

This system has operated without a leak for more than two years and without the need for an unscheduled cleaning. The refinery intends to implement the biofilm detection and control programme in the coming year on an additional cooling tower and the influent water system. Another Marathon refinery has plans to install the biofilm detection and control programme on its two cooling towers.

Marathon's success has motivated other refineries and petrochemical operations. A petrochemical plant using impound water ran a successful trial using the performance monitoring and biofilm detection and control programmes on part of its pond system, resulting in the expansion of the programmes to two large circulating cooling water systems.

Another refinery that implemented the programmes increased the flow through its cooling system by 25% within a month of implementation because of the removal of biofilm. Refinery leadership plans to expand the programmes to several cooling towers. Successful implementation at an ammonia plant allowed continued operation of the plant at a reduced cost, compared with the previous programme, despite a 50 ppm ammonia leak into the cooling water system. Thus far, a shutdown for repair has been avoided for nine months. Actual turnarounds at this facility may be yet another year away.

The number of success stories continues to grow at an accelerating rate. These examples show that careful analysis of heat exchanger data to determine the causation of failure and loss of efficiency due to biofouling resulted in the implementation of a biofilm detection and control programme that delivered a large ROI for a wide variety of industrial operations. Thanks to these innovative programmes, biofilm – the hidden threat – can no longer hide.

ClearPoint, OnGuard, and HexEval are marks of Solenis LLC.

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