IWC 23-35

Film Forming Products: Application, Corrosion Reduction, Layup Benefits, and Heat Transfer Improvement

GEORGE PATRICK

Veolia Water Technology & Solutions
Trevose, PA

KEYWORDS: Case Studies, Film Forming Amines, FFA, Film Forming Products, FFP, Film Forming Substances, FFS, Volatile Filmer, Distribution Ratio, Drop Wise Condensation, Heat Transfer, Boiler Storage Protection, Layup Improvement, Steam System Corrosion Reduction, Turbine Backpressure, Condenser Cleanliness Factor

ABSTRACT

Film Forming Products (FFP) have been used for many years, but the benefits were limited by the filmer properties. In the last two decades, the application of new FFP with higher distribution ratios provided complete system protection from a single feed point. Lower corrosion rates in the boiler/steam system reduced boiler chemicals, mechanical cleanings, and operational costs. FFP can change the condensation mechanism from Film Wise Condensation to Drop Wise Condensation in the steam condenser providing significant savings.

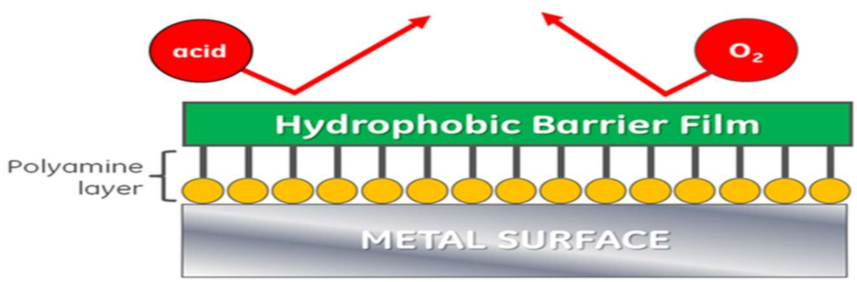
INTRODUCTION

Film Forming Products (FFP) were used to protect condensate systems from areas of high carbon dioxide (CO_2) and air infiltration by forming a protective barrier film on the metal surface. Figure 1 compares a normal untreated surface that is wetted by a water drop and a surface that is hydrophobic and causes the water droplet to bead on the surface. The filmer has a hydrophilic end that attaches to the metal surface and an opposing hydrophobic end which prevents water and its contaminants from contacting the metal surface. The first generation filmer had several issues. Low volatility required feeding the filmer directly into the area of the boiler/steam cycle that required the added protection. High viscosity of the product required a high-pressure pump with a low flow rate to feed directly into the steam header. High viscosity filmer often formed thick layers of the filmer on low flow surfaces and created agglomerations of filmer combined with corrosion products and suspended solids found in the system. The problems with the filming products made it so that many users turned back to treatment programs based on neutralizing amines and other chemistries. Several decades later, a new generation of filming products with improved characteristics were developed to meet the needs of the power industry. The power industry has moved from a base loaded operation mode to peaking operation, experiencing numerous load swings, rapid shutdowns, rapid restarts, and extended layups, based on the energy market demand.

Figure 1: Left coupon is wetted and untreated while the right coupon shows water drop beading from hydrophobicity

The second generation of filmer had several improvements to the earlier filmer products. Filmer product formulations had a lower viscosity with a lower active filmer concentration for better feed control. Higher volatility enabled direct feed to any part of the boiler/steam system including the lower pressure condensate. A higher distribution ratio with the higher volatility created a single point of filmer feed to protect the entire boiler/steam cycle. Figure 2 provides a simplified schematic of the filming mechanism for the newer polyamine filmer.

Figure 2: The single layer of FFP molecules attach to the metal surface and the hydrophobic tails create the barrier film to protect the metal surface from CO_2 and dissolved oxygen (O_2).



FILM FORMING AMINE FEED AND CONTROL

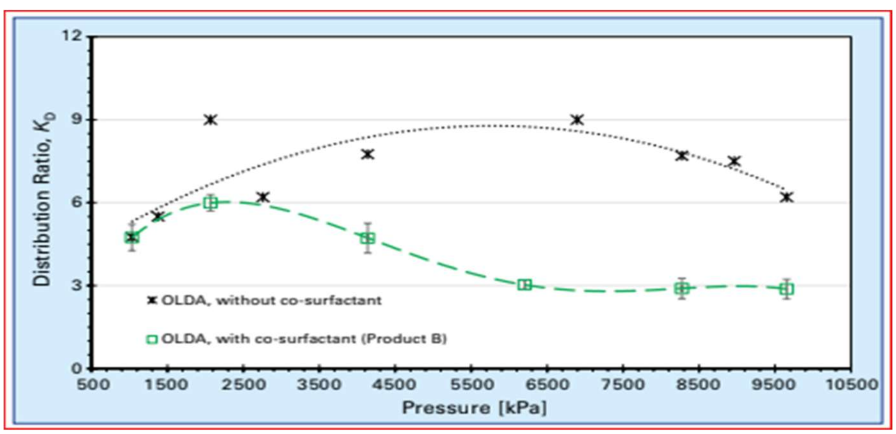
The current filmer market has a choice of different filmer products to provide the best protection for their system. The paper will continue with discussion on filmer applications using Film Forming Amine (FFA) products. The selection of a FFA is based on experience from the author with this type of film forming product. The information provided on the FFA product is to explain the characteristics of an FFA, and not meant to directly compare FFA performance to the performance of other types of Film Forming Products.

The boiler/steam cycle in power generation facility typically requires a proper water treatment program primarily meant to protect the system from corrosion. Conventional treatment may be and is often based on an oxygen scavenger, neutralizing amine (or ammonia) and internal treatment chemistry using phosphate and/or caustic. The FFA treatment does not replace the conventional treatment of the boiler, but instead adds to the level of protect in the system and may provide some reduction in the conventional boiler treatment levels.

The current FFA product offered by Veolia WTS has two actives: a film forming amine and a co-surfactant, together blended in a single product. The co-surfactant has a dual function of providing filming protection in the system while also changing the mixture to a water-based product.

The simplicity of the FFA is the ability to feed the product to any point in the boiler/steam cycle and have it form a barrier film on all surfaces. The remaining FFA will continue to recycle throughout the boiler/steam system without forming excessive accumulation. The distribution ratio of the blended product was researched in the lab and is shown in Figure 3. (Budhathoki, 2021) The benefit of the lower distribution ratio is the balance of the filmer to the steam and boiler systems.

Figure 3: Distribution ratio for blended product with and without the co-surfactant



The distribution ratio of the FFA was confirmed in a case study at a large coal fired facility in the United States. The facility agreed to treat their boiler/steam cycle with FFA and to remove tube samples after the trial to identify the level of filmer protection in each area of the system. The system was treated for 6 weeks with FFA and then the samples were collected during the shutdown. The XPS (surface composition analysis) values in Figure 4 were the average of six samples from each of the sample points. The XPS scan identified levels of nitrogen on each sample from the system. The nitrogen levels show the distribution of the FFA throughout the system. A sample of an untreated economizer tube was also tested, and no nitrogen was found in that sample.

FIGURE 4: Percent nitrogen levels from the FFA tested on the surface of metal samples.

Economizer	Waterwall	Superheater	Reheater	Condenser	Economizer NOT TREATED
3.8	3.0	5.8	3.0	1.3	0.0

The body of knowledge surrounding the feed rate of the FFA that can enable the formation of a barrier film sufficient for corrosion protection throughout the system has changed significantly over the last five years. The first steam generators treated were at a high filmer level which showed very quick corrosion reduction, within a few days or weeks. As the data from applications was monitored and the equipment was inspected, some small deposits of FFA were found in low flow areas of the boiler system. Continued monitoring of corrosion rates and deposition were used to adjust the FFA feed rate.

The application of a FFA product should be based on four factors:

1. Control the feedrate of the FFA with the flow of the system (condensate, boiler feedwater, or steam flow). Automation of the chemical feed pump is highly recommended.
2. Inspection of systems using FFA whenever the equipment is available. Inspection should look for hydrophobicity, overfeed of FFA, fouling or buildup of material, active corrosion, and corrosion products in the system.
3. Monitoring of the iron (and copper) corrosion rate in the system during continuous operation and immediately after a system startup.
4. Neat addition of all products fed to the system. These products are formulated to maintain solubility of the actives until they disperse in the main circulation loops. Some new filmer products are water based and can be mixed with demineralized water.

Figure 5: Sample on left is the product before feeding to the system. Sample on the right shows how mixing other products with water can cause gunking in the feed line.

There is a test method to monitor active FFA in the various streams of the system. The Rose Bengal Test can be performed with most spectrophotometers by determining the adsorption at 560 nm wavelength. The data collected during the first few years of application of the FFA did accurately identify feedrate and distribution of the FFA in the system. However, as the feedrates were reduced based on plant data and inspections, the current feed rate is now below the Rose Bengal Test detection levels. The current test method can identify an overfeed, but not the actual active levels in the system. Hence, measurement of feed through automated modules is strongly recommended.

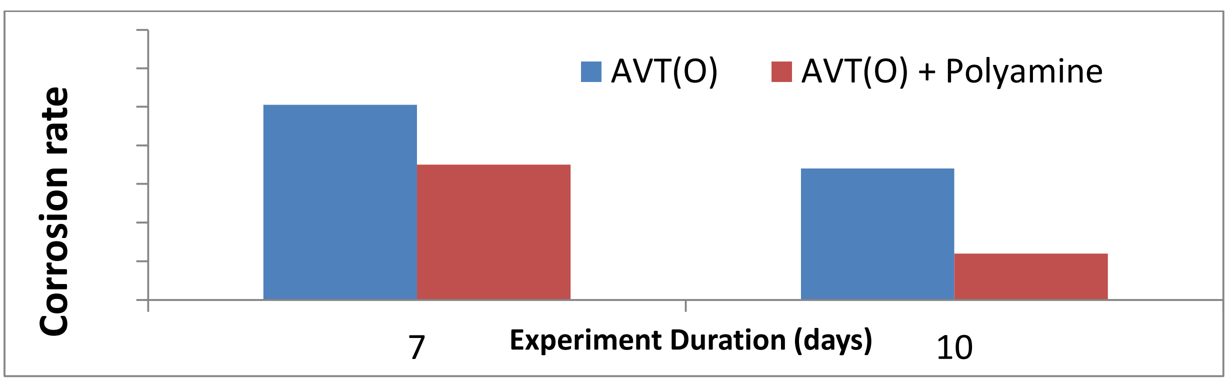
An online analyzer for FFA products is available on the market, but it also has a low detection limit above the current feedrates used. While these test methods should not be used for control, they can be useful to detect a potential overfeed in the system.

SYSTEM LAYUP CASE STUDY

Many power facilities have reduced carbon steel corrosion in their boiler/steam system by adding a FFA to the conventional boiler treatment. The FFA applies a barrier film protecting the metal surface during operation and wet or dry layup. No supplemental addition of FFA is required before a layup/shutdown. Just maintaining the continuous feed, at the normal rate will protect the system. The facility should still apply a proper wet or dry layup procedure to protect the equipment. The protection from the FFA is to improve the typical layup protection, especially when the shutdown is immediate.

The mechanism that provides the fast barrier film and the long-lasting barrier film is the adsorption and desorption properties of the FFA. The FFA is rapidly adsorbed to form the barrier film. The pH of the boiler water and steam is above 8.8 so the solubility of the filmer begins to decrease and the fast adsorption facilitates adherence to the metal surfaces. Several case studies have shown quick reduction of iron corrosion in a few days or weeks. Figure 6 presents data for a situation where adsorption is tested in the laboratory.

Figure 6: Laboratory experiment showing iron reduction in a short period of time from the rapid adsorption of the FFA when compared to a non-FFA treated (AVT-O only) system.



The slow desorption was also verified in several case studies. One combined cycle plant was using the FFA for several years on four HRSGs in their facility. The site had continuous feed of FFA with iron corrosion levels below 2-ppb as Fe (test equipment low limit was 2-ppb) The site went into a shutdown without any changes to the treatment program. The equipment was left dry for 30 days and then restarted the facility. The facility was instructed to keep the FFA feed off until signs of iron corrosion were observed. After operating for 45 days without FFA addition, the daily condensate iron test was above the 2-ppb benchmark. The FFA feed was re-started at normal feed rate.

The speed of the desorption is affected by temperature and mechanical movement in the plant. During layup, temperatures are low, and velocities of the water and steam are very low or zero.

CORROSION REDUCTION CASE STUDY

A facility in the Northern United States operates two large coal fired boilers with a low annual capacity factor for the facility, so both units spend significant periods offline. The trends (Figures 7 and 8) of the iron levels in the condensate to boilers 1 and 2 show the daily iron levels over a nine-month period. The blank areas are indications that the unit is offline. The feed of the FFA product started at the beginning of the chart with a feed rate of 0.5 ppm as product. The feed was increased to 1 ppm after the first month of the application.

Figure 7 & 8 show the steady decline of iron in the two condensate systems. Many of the shown data points are below the 1 ppb as Fe detection limit so they were assigned 0.5 ppb. Samples were taken daily when operating. More specific data needs to be collected on startup.

Figure 7: Trend of iron levels in the condensate of Unit 1

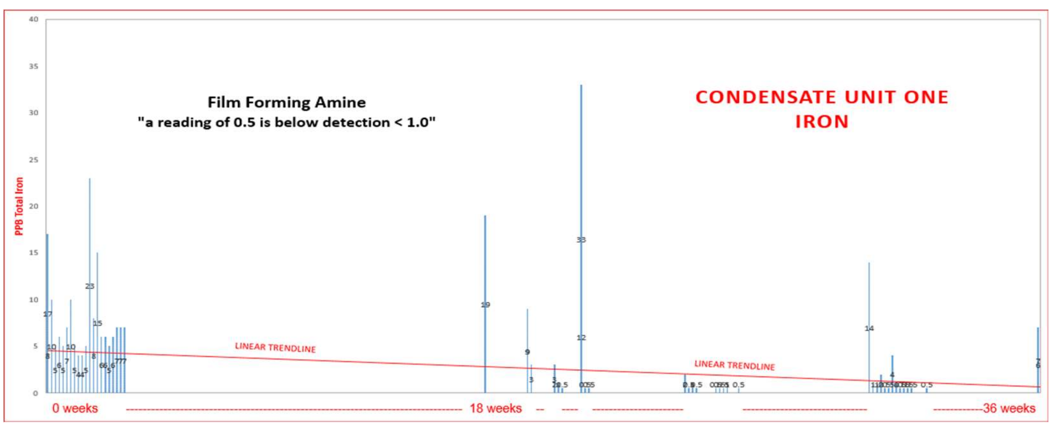
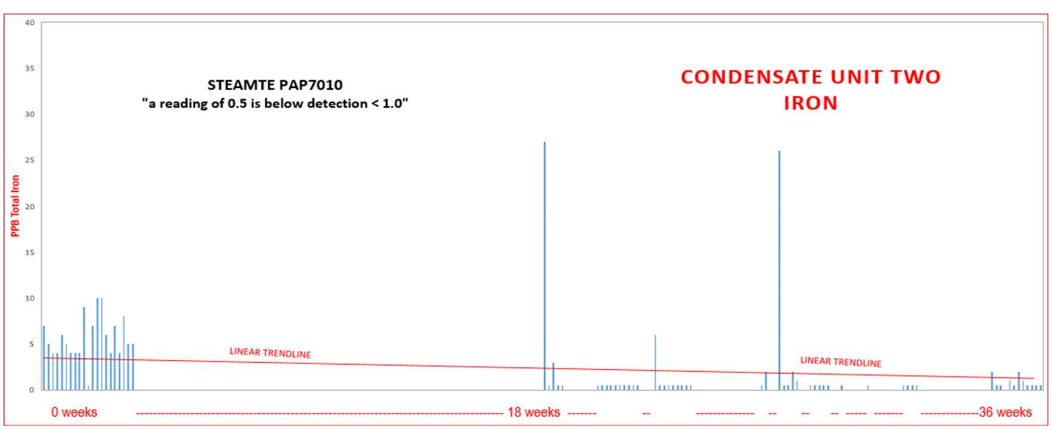


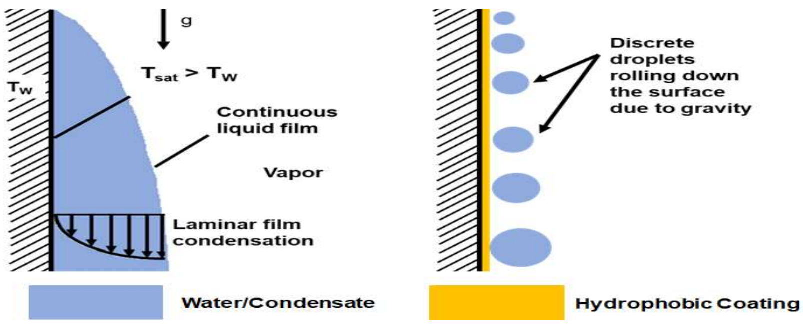
Figure 8: Trend of iron levels in the condensate of Unit 2



HEAT TRANSFER RESEARCH

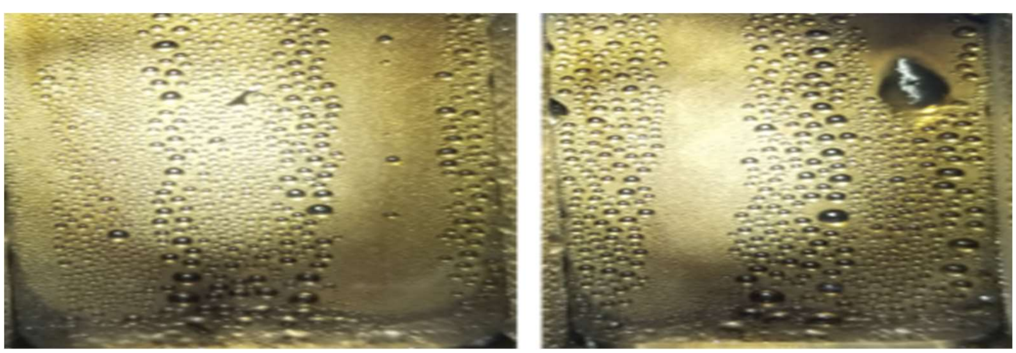
The company worked with Advanced Cooling Technologies (ACT) in collaboration with the Department of Energy to investigate FFA's effect on Drop Wise Condensation (DWC). DWC has been studied for nearly one hundred years, but the reliability of DWC was difficult to control with the older filmer. The formation of DWC in heat exchangers and condensers improves their efficiency by promoting better cooling of the condensate. Film forming amines are now applied at many power facilities for corrosion protection of metal surfaces in the boiler and condenser. Application of the FFA to the metal surfaces in the condenser is the first step in reaching DWC. The second step is controlling the FFA level in the steam to form small droplets in the condenser. The FFA adjusts the surface tension of the steam to form droplets of different sizes. Figure 9 (Budhathoki, 2023) presents a schematic comparing heat transfer for Film Wise Condensation (FWC) consisting of a continuous liquid film and for DWC consisting of discrete droplets flowing down a metal surface.

Figure 9: Film Wise Condensation versus Drop Wise Condensation



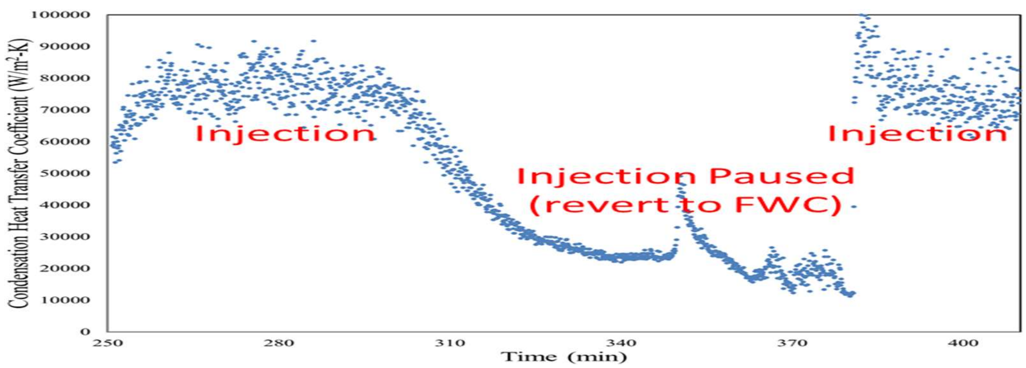
The first part of the research used a flat plate to create the drop wise condensation on copper, stainless steel and carbon steel. The three types of metals were tested and all showed an increase in efficiency. Figure 10 (Budhathoki, 2023) shows a photograph of the drops on the flat plates used in the tests.

Figure 10: Continuous DWC on flat plates.



The heat transfer was monitored to determine the level of efficiency gained during the experiment. DWC changed to FWC when the FFA feed to the boiler stopped, dropping the efficiency of the heat transfer process. Figure 11 (Budhathoki, 2023) shows that the measured heat transfer coefficient decreased when the filming agent feed to the boiler ceased. The change in heat transfer was attributed to a transition from DWC to FWC heat transfer. The heat transfer coefficient increased when the filming agent feed was resumed. The filming agent was fed at a dose of 6 ppm product to the boiler.

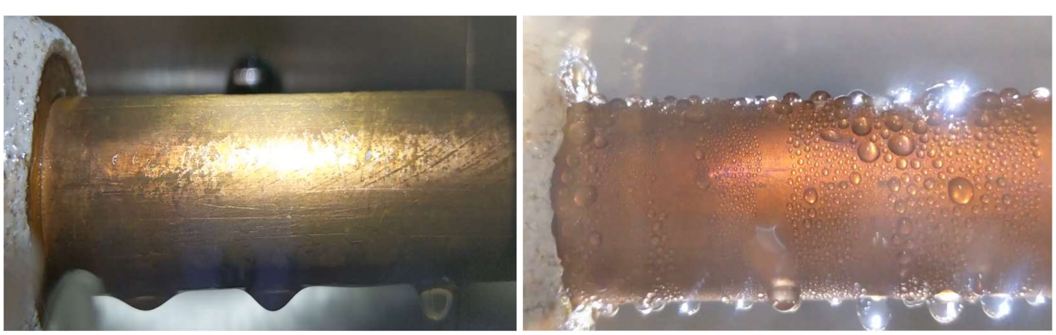
Figure 11 : DWC reverted to FWC when the FFA feed to the water was stopped.



The next phase of experimentation changed from flat plates to condenser tubes that had a similar diameter as typical condenser tube. Figure 12 (Budhathoki, 2023) shows a carbon steel tube in place for the trial. The surface of the tube has already been treated with FFA to form a hydrophobic surface. Droplets of demineralized water were applied to the tube to see the size of the drops with untreated water or condensation.

Figure 12: Carbon steel tube with FFA treatment and demineralized water drops showing hydrophobicity.

Figure 13: Film Wise Condensation left and Drop Wise Condensation right (Budhathoki, 2023)



Research showed that the FFA must be present in the entire boiler/steam cycle for the DWC to occur. The presence of the DWC was achieved by maintaining a proper level of FFA on the condenser tubes and a proper amount of FFA in the steam. FFA concentration control was the key to ensuring DWC occurs instead of FWC.

Figure 14 (Budhathoki, 2023) shows a tube with FWC. This tube was exposed to 5 times the normal FFA feed rate (6 ppm) to see the effects. The condensation on the tube went from DWC to FWC as the FFA feed to the steam was increased. The amount of FFA in the steam is the controlling factor for achieving Drop Wise Condensation.

Figure 14: The tube shows the loss of hydrophobicity when the FFA level is too high

RESULTS OF ACT RESEARCH PROJECT: (Hoenig, 2021)

The ACT research project found that FFA provides a self-healing film on the condenser surface. Control of FFA in the steam controls the drop size of the condensation. The FFA application resulted in the following performance improvements:

38.% reduction in the condenser thermal resistance (size)
59.% improvement in the overall heat exchanger performance
0.54 inches of Hg reduction in back pressure
0.84% increase in power plant efficiency
24.% reduction in net levelized condenser cost

CASE STUDY OF CONDENSER PERFORMANCE

The research project where a FFA was used on a water-cooled condenser showed a significant improvement on the turbine back pressure from the improved efficiency in condensation. After completing the research on the Drop Wise Condensation, a search for a trial site was conducted. A high percentage of sites using a film forming amine with a water-cooled condenser are sites with carbon steel corrosion issues. Fewer sites with continuous operation and minimum load swings or layup have added a filming product to their treatment program. The typical facilities using film forming amines experience many load swings, sudden layups, and quick restarts. Finding a site with enough condenser performance data (without numerous load swings) was difficult.

The Case Study was performed at a Combined Cycle Power Plant in the United States. The site produces over 400 MW of electricity and used 300 MW as a lower limit for collecting data during the study. The site operated with a typical AVT boiler chemistry program and had never fed a film forming product to their system. The product used for the test was a FFA with two actives (a long chain filming amine and a co-surfactant).

Two proprietary software programs were used for the trial calculations. The data collection program organizes data, makes calculations, and compares with limits. The program can also be used for reviewing data, identifying trends, and alerting when operating parameters are out of specification. The second program is specific for condenser performance (or heat exchanger). The data is forwarded to the condenser performance program. As shown in Figure 15, the results are displayed on a dashboard designed for the user with outputs including: Cleanliness Factor, Excess fuel penalty, Excess greenhouse gas emissions, and other data for evaluating operations. Note that the graphs in Figure 15 are not from the actual trial period, but examples of the display the software can provide.

Some of the data required for the calculations includes: steam flow to the condenser, cooling water inlet temperature, cooling water outlet temperature, condenser back pressure, power generation, number of tubes, number of tube passes, tube internal diameter, tube thickness, cooling water flow, tube inlet pressure, tube outlet pressure, low pressure stage design efficiency, condenser steam chest temperature, low pressure stage inlet temperature, low pressure stage inlet pressure, dissolved oxygen in condensate, air removal rate, conductivity of condensate, fuel type, unit cost of fuel, calorific value of fuel, tube material type, etc.

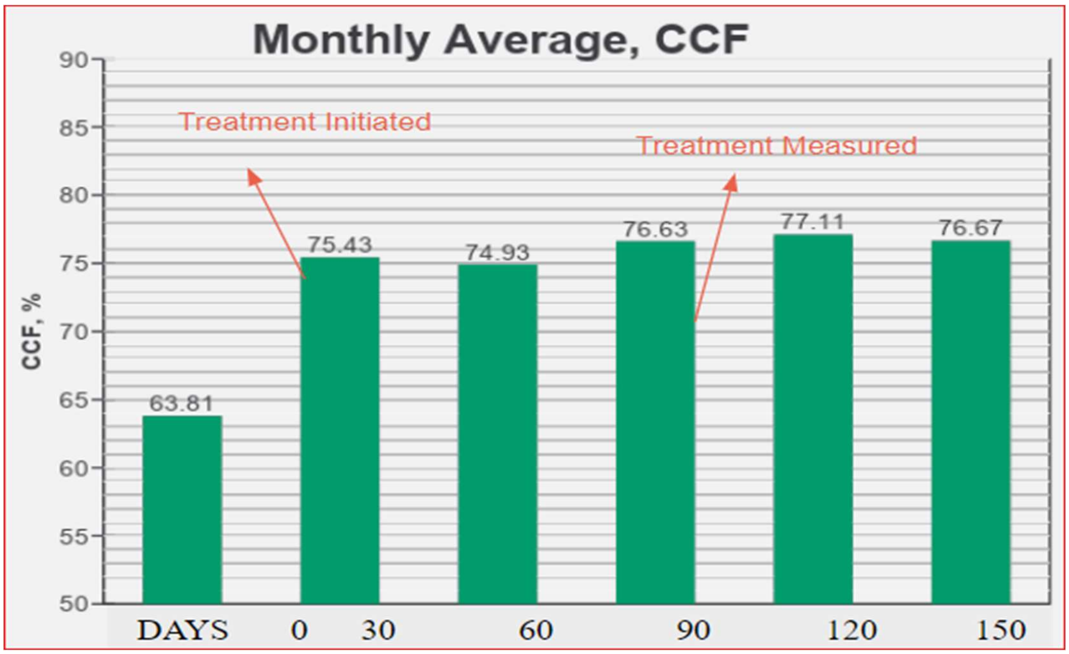
Figure 15: Typical Dashboard for monitoring condenser performance

The field study was performed for 150 days as the data was collected and evaluated. The FFA feed commenced on day 0 at 0.5 ppm as product for 14 days to verify there were no issues with the FFA feed. After 14 days the feed was increased to 1 ppm as product.

CALCULATIONS FOR THE CONDENSER PERFORMANCE CHANGE

The Condenser Cleanliness Factor (CCF) was the first calculation reviewed in this trial. Figure 16 (Budhathoki, 2023) shows the FFA was started at day zero and verified the amount of FFA used by day 90. The CCF increased after the first 60 days of the trial by just over 1.5% for the last three months of the trial (day 60 to 150). The increase in CCF% represents a potential energy cost savings for the facility. The data shows the increase after the FFA was feeding for 60 days, but there may be other factors that caused the increase at that point of the trial.

Figure 16: Monthly Averages in column format show increase in CCF% after day 60



In Figure 17 (Budhathoki, 2023) the turbine backpressure was plotted with the cooling water supply temperature. The trial was started in the spring and continued through the summer into early fall. The seasonal changes may influence the cooling water supply for this trial. The cooling water temperature increased from day 0 to day 100 and then dropped after day 130 in the trial.

Like the CCF% data shows there is a noticeable improvement in turbine back pressure after 80 days of FFA feed. The cooling water continues to remain above 85 deg F until day 130, while the back pressure showed the same readings as before the trial, but with significantly higher water temperature. Other factors may be affecting these readings, but the general trend is positive for the data in figure 16 and figure 17. The calculations of the turbine back pressure after the 80 days of FFA feed dropped by 0.55 inches of mercury.

Figure 17: Back pressure reduced by nearly 0.55inch Hg despite CW temp increase

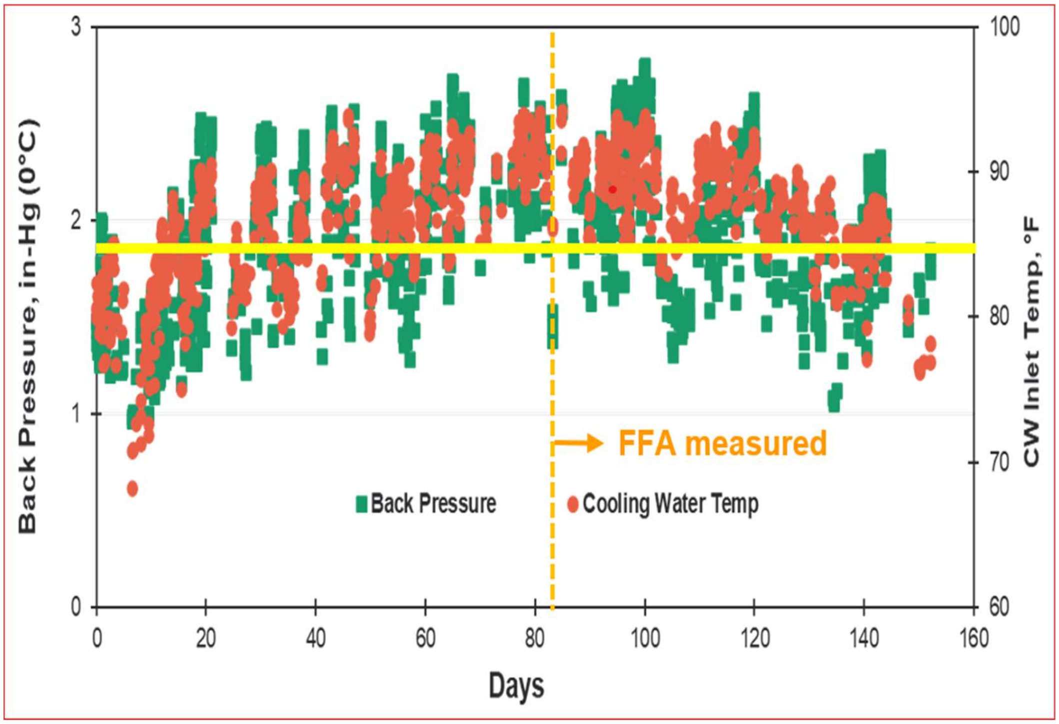


Figure 18 (Budhathoki, 2023) shows a continuing trend of slightly reduced fuel costs and reduced carbon emissions. It is cautioned that other factors, may have contributed to this improvement. Nevertheless, with all other factors being equal, improved condenser performance leads to lower fuel consumption & less carbon emissions.

Figure 18: Reduction of Fuel Costs Savings and Carbon Emissions

In retrospect, while the research work was able to control the results and minimize interference on the data and calculations, it found Drop Wise Condensation (DWC) to have great potential to improve heat transfer in the condenser. Calculations enabled by the research conditions indicated that improvements through DWC could lead to smaller condensing units being used. The results from the research work and the field trial were very similar, as they both indicated improvements in heat transfer followings introduction of FFA treatment. The field trial showed 1.5% improvement in Condenser Cleanliness Factor (%) after feeding the FFA for 80 days and the Turbine back pressure reduction was almost identical to the performance observed in the lab at just above 0.55 inches Hg. The backpressure also improved after 80 days of feeding FFA. Looking at the figures for the field trial, there is an improvement on all the figures presented. The field trial data was influenced by multiple external factors that could not be controlled nor accounted for in the calculations. The field trial was conducted during a period that underwent many load swings and temperature changes through several seasons. Hence the results of the field trial are positive but not proven because of the limited data and the large variability in the operation during that period. Both the research and the field trial have shown a potential energy saving from the benefits of Drop Wise Condensation. The amount of change to the heat transfer efficiency is small because we are looking at the cleaner side of the condenser tubes. If the power facility is using FFA for other reasons, such as corrosion control, it is possible they may get an additional value from energy efficiency thanks to Drop Wise Condensation.

CONCLUSIONS

1 Boiler/Steam cycles using a Film Forming Amine will require conventional boiler treatment with a volatile and nonvolatile alkalizing product. The filmer creates a barrier between the water/steam and the metal surface, but the water quality still requires certain parameters to maintain the barrier film.

2 Film Forming Amines create a barrier film on the metal surface and will protect the metal surface during operating conditions and during wet/dry layups. FFA has a quick adsorption to the metal surface and slow desorption from the metal surface providing excellent protection in layups and startups.

3 FFA added to a standard alkaline boiler chemistry program may reduce costs of the boiler treatment. With a functioning thermal deaerator, the oxygen scavenger may be eliminated if the dissolved oxygen level is low enough. The volatile alkalizing treatment feed rate may be reduced once the complete system protection is achieved.

4 Drop Wise Condensation on the condenser tubes is created by the film on the tube surface and the film in the droplet. The amount of filmer in the droplet controls the size of the droplet by affecting the surface tension of the droplet.

5 DWC can improve the heat transfer coefficient and may improve the CCF, reduce turbine backpressure, reduce fuel consumption, and reduce carbon emissions. This trial required a lot of data and the variability in operating conditions makes the data difficult to interpret, although a positive trend is observed and matches the laboratory study in controlled conditions. The application of a FFA for corrosion protection, layup protection and upset protection, may also provide energy savings, and performance improvements to the steam turbine condenser.

REFERENCES

(Budhathoki, 2021) Budhathoki, Mahesh Amine-based Filmer Chemistry for Boilers with Improved Water Solubility and Performance, International Water Conference IWC 21-25, Engineers' Society of Western Pennsylvania, pp. 395-411.

(Hoenig, 2021) Sean H. Hoenig, Mahesh Budhathoki, Gregory Robinson, Claudia Pierce, Don Meskers, Michael C. Ellis, and Richard W. Bonner III, Technoeconomic Benefits of Film-Forming Amine Products Applied to Steam Surface Condensers, PPCHEM JOURNAL 23, 2021/01, pp. 04-16.

(Hoenig, 2019) Sean H. Hoenig, Michael C. Ellis, and Richard W. Bonner III, Vertical Surface Dropwise Condensation Heat Transfer Using Self-Healing Coatings, 19th IAHR International Conference on Cooling Towers and Heat Exchangers, October 2019

(Budhathoki, 2023) Mahesh Budhathoki, Film Forming Substance Presentation, 6th International Film Forming Substances Conference, Prato Italy, March 21, 2023