PERFORMANCE SUMMARY // INDUSTRY DEVELOPMENT

Case Study:

Scientific data summary of Anodamine performance to provide guidance in the field of power generation and water treatment

ANODAMINE

The Control of Two-Phase Flow-Accelerated Corrosion (FAC)

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Abstract

Flow-accelerated or flow-assisted corrosion (FAC) describes a form of unwanted and uncontrolled dissolution and transportation of iron oxides in a steam-water cycle system that poses a serious threat to the safety and reliability of a system[1]. This paper focuses on the attempted plant optimizations and eventual introduction of Anodamine HPFG in a 870 MW CCGT plant located in Europe. After application of the Anodamine HPFG product, two-phase FAC was drastically mitigated, along with reduced maintenance costs, shorter start-ups, and removal of costly shutdown methods of nitrogen blanketing and dehumidified air. Results were validated using total iron digestion analysis, millipore filter tests, online laser nephelometer, and physical equipment inspections.

Two-Phase FAC Control

In the power generation industry, a substantial amount of research has been performed on a corrosion mechanism known as flow-accelerated corrosion (FAC) and understanding the mechanism behind it in both it's single and two-phase form (single-phase FAC and two-phase FAC).

Generally speaking, both forms of FAC are an unwanted and uncontrolled dissolution and transport of iron oxides in a steam-water cycle system that pose serious threats to the safety and reliability of a system. This dissolution and transport of iron oxides can happen in single-phase areas where only liquid (water) is present (known as single-phase FAC) and can also occur in two-phase areas where a mixture of water and steam is present (two-phase FAC). While single-phase FAC has been, to some degree, successfully mitigated by chemical controls, two-phase FAC is a largely unaddressed corrosion mechanism due to the challenging nature of both liquid and steam presence in the same area. There are specific

circumstances and conditions that contribute to FAC. Some of these circumstances can be controlled, while others cannot.

Factors influencing FAC are:

- **Design**
    - Velocity in the system
    - Metallurgy used
- **Chemistry**
    - pH
    - Oxygen level (or ORP)
- **Temperature**

From these factors influencing FAC, there are only a few which can be changed after the construction of a plant. Usually, design and temperature are difficult, if not impossible, to change. The plant design and metallurgy used in a plant can technically be changed after construction, but this is a very expensive endeavor and is thus not a commercially viable option. Changing or altering the running temperature of a plant is not possible.

However, oxygen and pH can be influenced and changed by the chemical treatment program used.

Typically, the common mitigation technique to control single-phase FAC is the addition of oxygen to the feedwater. As soon as an oxygenated environment is present, single-phase FAC will be greatly reduced if not stopped, because single-phase FAC relies on the formation of an unstable oxide called magnetite, which is formed in oxygen-depleted environments.

Two-phase FAC on the other hand, is more difficult to mitigate. The factor with the most influence on two-phase FAC is pH. In a power plant, there exists a limited number of chemicals that can be used to affect/control pH, due to the temperatures present in the system. Some plants use solid alkalizing agents, such as

caustic soda or trisodium phosphate (TSP), to increase pH in the liquid phase, which will reduce the chances of FAC occurring. But this type of alkalization has its disadvantages. One significant disadvantage is the risk this alkalization poses of carry-over of pollutants to the superheater section, and even worse, to the steam turbine. Further, deposits can be formed when solid alkalization is transferred to the steam.

With volatile alkalization, commonly performed with the addition of ammonia, it is difficult to control a good liquid phase pH, because of the volatility of ammonia. Also, depending on local regulations, a discharge permit limiting the amount of ammonia that can be used is sometimes required.

The use of organic alkalization agents is usually not recommended due to steam purity standards. At temperatures above 450°C, alkalizing amines (organic molecules) tend to break down into small organic acids and CO_2 which cause unwanted, increased cation conductivities throughout the system.
Small organic acids are also a potential danger to the phase transition zone (PTZ) in the last stage of the LP turbine. There is also a possibility that low pH condensate can be formed in these locations, which poses significant consequences to the integrity of the turbine.

Plant Chemistry Optimization

This paper is covering the specific results of the chemistry optimization of a combined cycle gas turbine (CCGT) plant. This plant has the following configuration:

- Single shaft unit
- 435 MW electrical output
- Triple pressure HRSG
- Metallurgy
  - HRSG: all ferrous
  - Condenser: titanium tubes

- High-pressure (HP) section: once-through Benson
- Up to 100% condensate polishing with mixed bed resin
- Once-through cooling
- Operational regime: 2-shifting - regular start and stop

History

Since commissioning, the CCGT has been operating on an AVT(O) treatment program, including:

- Ammonia dosing for pH control
- Oxygen dosing for an oxidizing environment

Ammonia dosing was performed in three locations: the condensate, the LP feedwater, and the IP feedwater. This plant's configuration provided flexibility in controlling pH in the different systems at different levels. Dosing control was based on specific conductivity.

Oxygen was dosed in the condensate and controlled with an oxygen analyzer connected to a controller.

First Inspection

During the first inspection of the unit, a significant amount of two-phase FAC was found in the LP drum. In the picture below (Figure 1), an impression of the surface of the LP drum is shown. The picture clearly shows shiny black metal, a validated indication of two-phase FAC.

Figure 1: First inspection LP Drum

With the results of the first inspection, the OEM chemistry being applied was investigated and optimized (i.e. the pH of the feedwater was increased).

Results of the Optimized OEM Chemistry

The OEM pH control was increased to a higher level in order to get a higher pH in the liquid phase of the LP drum.

This resulted in an increased control of two-phase FAC in the LP drum, however, there were still some locations indicating two-phase FAC was still taking place. Shiny black surfaces were still present, a lot less than with the lower pH, but still present.

The color of the drum changed from black (magnetite) to a red (hematite) color (see figure 2). This showed that the pH and oxygen level in the system increased to a level where hematite was the preferred oxide formed in the system. As hematite is much less soluble in water compared to the black magnetite, this was an improvement in the conditions.

Figure 2: LP drum after OEM chemistry optimization

However, in the drum, there were still some locations where two-phase FAC was taking place. These locations were high-velocity locations where the expansion of drum water would take place. In these locations, the pH of the liquid phase was clearly too low, causing local shiny black spots. An example is shown in figure 3.

Figure 3: Localized two-phase FAC

Further Optimization

Investigations into further optimization showed that additional chemistry could bring a solution

or further improvement to the situation. There are a number of solutions available: increased ammonia dosage, solid alkalization, alkalizing amines, film-forming products (amines and others).

The level of ammonia would need to increase significantly to mitigate the two-phase FAC present. Theoretically, you can calculate the required amount (with the distribution ratio of ammonia). As a consequence of this increased ammonia dosage, the condensate polisher run lengths would be reduced significantly. And the bottleneck for this option is the environmental discharge permit required, which limits nitrogen discharge. There would exist a clear risk in exceeding the permit.

Solid alkalization (caustic or phosphate) could provide improvement, but the plant did not want to introduce impurities into the system. With the risk of carry-over of sodium to the steam turbine and the feedwater containing sodium, the choice was made not to apply solid alkalization.

Alkalizing amines were not an option due to the decomposition products and increased steam cation conductivity they create. Also, the environmental impact of alkalizing amines was not acceptable. For these reasons, the choice was made to not apply alkalizing amines.

Film-forming amines were an option, but in addition to the negative aspects they share with alkalizing amines, there are additional negative aspects to take into account. For example, dosing these products can be very tricky. Overdosing can cause significant issues, including the risk of the formation of unwanted deposits in the system (with corrosion products). Moreover, the toxicity and associated environmental concerns of these products is a known issue.

After eliminating solid alkalization, alkalizing amines, and film-forming amines, the continued search for optimization led to the application of a product called Anodamine HPFG. When looking at the properties and performance characteristics of this product, the downsides mentioned of other options do not exist.

Anodamine HPFG is a non-toxic, thermally stable chemistry. It will not pollute the steam-water cycle and protects the entirety of the cycle from one dosing location. Further, the product poses no risks with overdosage.

Implementation and Follow-Up

When the plant implemented dosage of Anodamine HPFG into the cycle, it was the only variable of the cycle treatment that was changed (pH and oxygen control remained the same). This selective variable control was done in order to reasonably be able to draw the correct/accurate conclusions.

The following methods were used for follow-up of the application:

- Total iron analysis
- Millipore filter tests
- Online turbidity - laser nephelometer
- Physical equipment inspections

Total Iron Analysis

The total Iron analysis was performed using a digestion with thioglycolic acid at 150°C. After digestion, the sample was analyzed with an ICP analyzer. The method detection limit was 1 ug/l.

This method was used a couple of months before the application of Anodamine to form a record of baseline data. The baseline data can be seen in Figure 4. This data shows a statistical analysis of the LP feedwater total iron results.
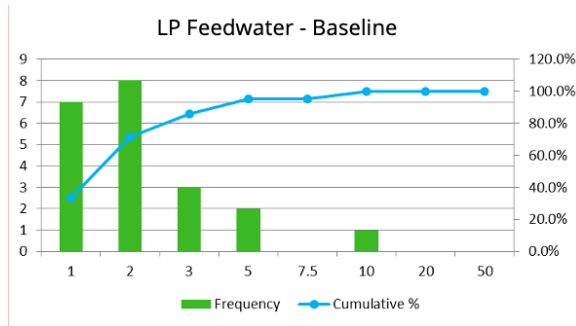
Figure 4: LP feedwater iron baseline

After the application of Anodamine, the same analysis was performed. The results are shown in figure 5.
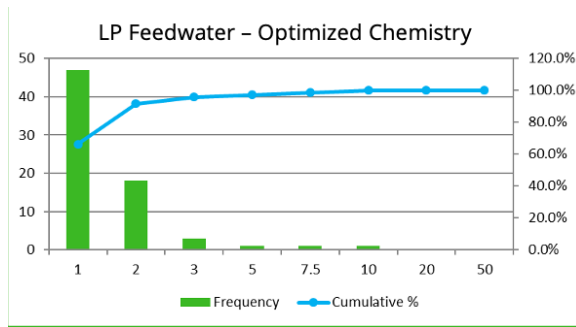
Figure 5: LP feedwater iron optimized chemistry

In the histogram of figure 5, it is clear that the majority of the total iron levels improved. More values are in the low range compared to the original situation. It must be noted that the amount of data is larger after the application, but it is still a very significant change.

The other samples showed similar results but, in an effort to keep this paper concise, are not included in this paper.

Millipore Filter Tests

Visual follow-up of these samples was performed by filtering 1 liter of the sample over a 0.45 µm filter pad. This was performed a number of times before and after the application of the Anodamine HPFG. On these filter papers, a clear visual improvement was observed.

Figure 6 shows an example of the LP feedwater before application of the Anodamine HPFG treatment.

Figure 6: Filter pad LP feedwater pre-Anodamine HPFG treatment

The total iron level of this sample was analyzed to be 129 ug/l.

Figure 7 shows an example of the LP feedwater sample after 2.5 months of applying Anodamine HPFG.

Figure 7: Filter pad LP feedwater 2.5 months after beginning Anodamine HPFG treatment

The total iron level of these samples was analyzed as 3.7 ug/l.

Both samples were taken 1.5 hours after flame-on of the gas turbine.

Although the light/color of both pictures is slightly different, it is practically and visibly clear

that the system situation has improved significantly.

Online Turbidity

In a typical steam-water cycle, the water is usually very clean and any turbidity found in the water is caused by corrosion products. This has been investigated and confirmed by a number of turbidity analyser suppliers[2,3]. Laser nephelometers are a type of analyzer that have the best response and are capable of detecting the smallest hematite oxide particles, down to sub-micron particle sizes.

To measure turbidity in the steam-water cycle is to measure the amount of corrosion products. It is difficult to put an exact formula on these measurements, because the response/sensitivity of the equipment used to different types of oxides is not the same. The response for hematite oxides is higher than the response for magnetite oxides. However, when the chosen analyzer is used on one sample location consistently, the trends can be compared very accurately.

Cold Start Comparison (>60 hours)

In Figure 8, the trend of turbidity in the condensate is shown for three different cold starts. A cold start is a start after more than 60 hours offline. In between stop and start there were no differences in the operational status; the unit was treated the same way across all variables during the offline period (with regard to vacuum, sealing steam etc.). The only difference between the cold starts was the application of the Anodamine HPFG program.

The red trend line is before the application of Anodamine HPFG, the blue and green trend lines are after the application of Anodamine HPFG. The curve starts at flame-on of the gas turbine and on all occasions the same start-curve was used.
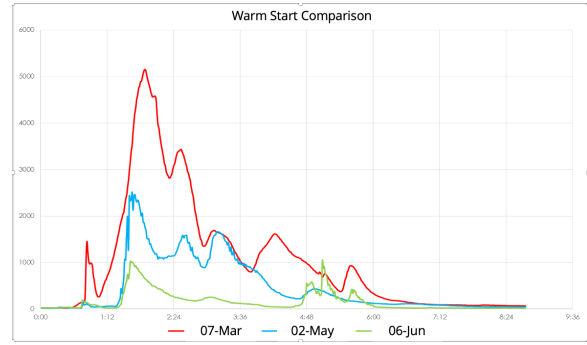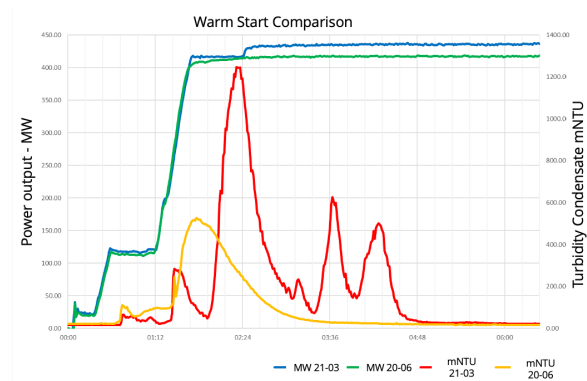

Figure 8: Comparison of turbidity during cold starts

It is clear from the figure that the longer the application of Anodamine HPFG was in place, the less corrosion products were circulating throughout the system. The peaks of the curves post Anodamine HPFG treatment and the total area below the trend lines have reduced significantly. This means that protection during stand-still had clearly improved with the application of Anodamine HPFG.

Warm Start (after the weekend)

In Figure 9, a comparison is shown of two warm starts. In both cases, the unit was shut down on a friday night and started early monday morning. As you can see from the power output, the same start curve was used.

Figure 9: Comparison of turbidity during warm starts

The red turbidity trend line shows the turbidity before application of Anodamine HPFG and the

yellow trend line is after application of Anodamine HPFG. Even for a warm start, the improved corrosion protection during stand-still is noticeable. The peak and area below the yellow curve/trend line are much lower.

The online turbidity trending confirmed the improved protection of the unit during stand-still, during cold AND during warm starts.

Inspections

It is very important that visual inspection results match the data and results found (as described in prior sections). When the total iron, filter pads, and turbidity show an improvement in system conditions, it is a reasonable expectation that the visual inspections also must show improvement. If the data/scientific results show improvement, but the visual inspection results do not show improvement (or vice versa), one must question both forms of validation.

In Figure 10, 11, and 12, a comparison is shown of the same locations in the cycle. Inspection before the application of Anodamine HPFG treatment clearly shows black and shiny surfaces, indicating the presence and occurrence of two-phase FAC. The comparative pictures on the right hand side show the improved condition and resulting protection on these locations as well as the positive regrowth of hematite oxides. The time between the pictures is approximately 1 year and 4 months.

Figure 10: LP drum comparison (top of riser box)
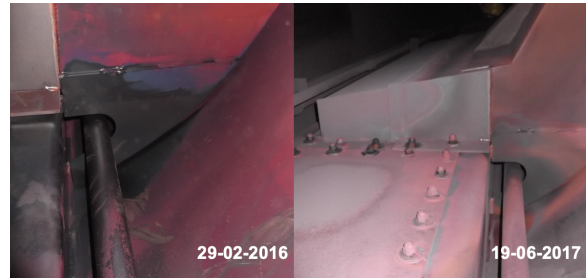
Figure 11: LP drum comparison (outside of riser box)

Figure 12: LP drum comparison (outside of riser box detail)

Conclusions

In the pursuit of comprehensive chemistry improvement for this specific plant, the first crucial step was to first optimize the conventional chemistry controls. This increased control in conventional chemistry improved the plant's operational situation to a certain extent, but the plant was unable to successfully mitigate two-phase FAC in multiple locations. A further optimization was necessary in order to successfully mitigate the two-phase FAC mechanism and get the plant's chemistry on a world-class level.

This optimization was found to be the addition of Anodamine HPFG to the steam-water cycle. Different methods and instruments were used to monitor conditions and results, all of which all showed significant improvement after the application of Anodamine HPFG into the system.

Because of the improved protection achieved with the Anodamine HPFG, the following goals were successfully achieved:

- Reduced corrosion product transport
- Reduced maintenance costs
- No additional measures needed for lay-up (short or long term)
- Shorter start-up curves
- Reduced cost during start

References

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