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Field experiences with a high resolution corrosion monitoring system

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Abstract

The continuous improvement process for corrosion inhibitor development and applications requires an active program for testing new chemistries and the performance of it. The original process for field testing or evaluation corrosion inhibitors required 36 days for different products or changes in the process. The high corrosion monitoring technology is allowing the same testing but in a few days. In order to show the benefits of using high resolution corrosion monitoring it is going to describe three specific applications, field applications, where the users were be able to discover several issues in their process which allowed them to improve their process, choosing the better chemical and applications, taking preventive action for assets preservation and extend the life, among others.

Key words: Corrosion Inhibitor, field applications, corrosion monitoring, high resolution electrical resistance.

Introduction

Control of corrosion is frequently achieved through the use of corrosion resistance alloys. These, however, add significantly to capital cost (CAPEX), therefore, alternative corrosion prevention strategies are often considered. In many cases the most cost-effective option is the use of low carbon steel with a corrosion inhibitor program. (1)

However, because of concerns regarding the potential for significant corrosion of carbon steel piping if there were a problem with corrosion inhibitor treatment, the decision of installing a state of the art on – line corrosion monitoring system can reduce the risk without so much CAPEX. (3) Even that combination, the CAPEX will be lower than use a higher resistance alloy.

The alternative of use low alloys plus chemicals is taking importance with High Resolution Corrosion Monitoring System, because allow us to work in a proactive way, allowing to take decisions at the moment of any process upsets, either changing some process variable like chemicals treatment or optimizing your process, and finally the coupons and inspection results will be better than working only with coupons and inspection activities. In other words, including a High Resolution Monitoring Corrosion System into your corrosion program you will be working in equilibrium with: persons, assets, environment, and safety, with quick

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return on investment (ROI), savings, and you will be working into the circle of the regulations and standards.

When a new technology is launched, we are always listening a lot of wonder words about the technology. Therefore, how can we translate to the field all above mentioned? Or, how will you see these facts in the field? The purpose of this document is to show very specific experience got from the first hand during the commissioning stage, in different customer in the region, basically South America. We will see that these data was very helpful for the users just at the beginning of use the technology.

Part 1. Electrical Resistance (ER) vs. High Resolution ER

Corrosion, an expensive and potentially disastrous phenomenon, is the leading cause of process equipment and piping failures, requiring companies to pay billions of dollars annually in replacement costs and down time. In response to the need to rapidly, safely, and accurately determine corrosion changes, a High Resolution Electrical Resistance was developed in 1999. Its primary benefit is its increased speed of response over conventional monitoring techniques (coupons, electrical resistance measurements).

High Resolution Technology combines the rapid response of linear polarization resistance (LPR) and the universal applicability of ER. With High Resolution Corrosion Systems, you are able to make rapid, accurate corrosion rate measurements in any process environment, conductive or non-conductive liquids, brines, or gases, single or multiphase flows, underground or in concrete. Short term changes in corrosion rate, which would be undetectable with conventional techniques, are clearly visible using a High Resolution Electrical Resistance. This makes the technique ideal for process and pipeline monitoring, process control, inhibitor evaluation, and cathodic protection studies. In fact, currently corrosion rate data can be easily plotted in real time and correlated with other process variables such as temperature, pressure, pH, dissolved oxygen and inhibitor concentration.

1.1. Electrical Resistance and High Resolution Electrical Resistance

The electrical resistance monitoring technique is the preferred, on-line, method of monitoring corrosion in mixed phase, and predominantly non-aqueous environments. A sensing element of known, and regular, geometry manufactured in the alloy of construction of the pipe, or vessel, of interest, is inserted into the process. The increase of the electrical resistance of the sensor is measured, as its cross-section is reduced by corrosion. This translates into a metal thickness loss and, by reference to time, into a corrosion rate. The basis of the technique can be in figure 1 below (6)

High Resolution Electrical Resistance technology is, essentially, a refinement of the basic electrical resistance technique. Like electrical resistance, High Resolution Electrical Resistance measures the increase in the resistance of a sensing element, as its cross-section is reduced by corrosion. The improved capabilities result from a systematic design audit of conventional electrical resistance measurement technology to identify, and minimize, significant sources of measurement noise, Temperature in our case. The outcome of this design audit improvement exercise is that measurement noise, in the high resolution resistance system, is suppressed by two orders of magnitude, when compared with basic electrical resistance measurement (see figure 2 below). This permits the user to take advantage of the increased measurement resolution of modern instrumentation. High Resolution Electrical Resistance measurements will reliably detect thickness changes in the range of 0.2 -2 micro-inches (18 bits or 4 ppm), as opposed to the conventional limit of about 40 micro-inches (10 bits or 1000 ppm). (5)

The key aspects of design that have been considered in system noise suppression are three:

Isothermal Probe Design:

As discussed above, the most significant noise source results from readings that are taken when the corroding, and reference, elements are at different temperatures. This will, typically contribute 1:250 parts of noise, in thermally unstable systems. (6)

In order to minimize these effects, only probe designs where the reference element is located in extremely close proximity to the corroding element, offer the opportunity for low noise levels. Further, the residual space between the reference, and the corroding, element needs to be filled with material that has very high electrical insulating properties, combined with a high degree of thermal conductivity. Such designs minimize both the duration, and size, of any thermal gradients, that may develop during system temperature changes. (1)

Based on this criteria, only cylindrical, and flush, elements designs can be considered, since wire, and thin walled tube, designs cannot be constructed with the necessary proximity of reference, and corroding elements, as illustrated in figure 3, below: (1)

By restricting element designs to cylindrical, or flush, greatly reducing the separation of the reference, and corroding electrodes, carefully selecting the insulation material between the reference, and corroding elements, so as to maximize heat conduction, while providing electrical insulation, enhanced performance electrical resistance probe designs are now available that can take advantage instrument resolutions as high as 1:262,144 (18 bits or 4 ppm). (1)

Minimizing Measurement Circuit Resistive Components

Conventional electrical resistance instruments use a constant current excitation signal, and measure the resultant voltage drops across the reference, and corroding, elements to produce the resistance ratio. For constant current measurements, the resistance path between the excitation current source, and the sensing elements, needs to be as short as possible. This is because any instrument-to-probe cables, and intervening connectors, form a resistive component of the constant current circuit and, as this resistive component changes, with changes in ambient temperature, the “constant” current changes in magnitude, producing signal noise. (5)

Temperature drift

The circuit components of a conventional electrical resistance measuring instrument all have response characteristics that change with temperature, and the whole measurement circuit has a temperature response characteristic, that is the combine effect of temperature responses of the individual circuit components. This “drift” will normally produce a systematic, and regularly varying noise pattern. (5)

Therefore, in realizing the full resolution of the High Resolution Electrical Resistance approach, it is necessary to make such adjustments as are possible, to suppress instrument temperature drift. This is accomplished in three ways. Firstly the whole instrument is designed to counteract temperature changes within the instrument, using carefully designed heat sinks, and component spacing, to dissipate heat, and resist rapid, or extreme temperature change in components. Secondly, premium circuit components are used with optimum temperature drift characteristics, over the operating temperature range of the instrument. (5)

Finally, circuit design is such that components are selected, wherever possible, that exhibit drift of comparable magnitude, in opposing direction, thus minimizing net drift with temperature. (5)

In a comparison of response time of various corrosion monitoring techniques, at 10 mpy, the common 5 mil span probe requires nearly 3 days to respond, compared to only 50 minutes for a 5 mil span HR-ER probe (See figure below 4). HR-ER saves you money by saving you time. The amount of time needed to evaluate inhibitors and implement any corrective action to damaging corrosion upsets can be greatly reduced.

The very high resolution of the metal loss measurements enable the corrosion rate to be determined in minutes or hours and provide rapid feedback on changes of corrosion rates, 50 to 100 times faster than other metal loss methods. That response turns corrosion monitoring into a process parameter. So with these response times why would you not treat corrosion like any other process parameter? After all, corrosion is probably more critical to economic plant operations than most temperature pressures and flows, since it has a more important effect of the management of costly inhibitors and allows better asset management and a balance to be struck between plant performance and its cost on plant life.

Finally, the goal of corrosion mitigation programs is to control corrosion rates to acceptable levels. Corrosion rates are not static, however, they can dramatically increase or decrease depending on fluid properties or changes in conditions that affect the efficacy of corrosion inhibitors. For that reason, locations that are prone to corrosion damage, or where damage has been identified, need a continuous corrosion monitoring system rather than inspections as often as every three to six months.(2)

While the initial cost of installing the system may be more than the existing manual monitoring, it has a rapid pay back since on-line monitoring will allow better management of the existing chemical inhibitor program which runs around $250,000 per year. Savings on inhibitor costs up to 50% are not uncommon, but more importantly it allows better matching of the inhibitor requirement to the demands, that can vary significantly with changing crudes under present day operations. That better control directly improves asset management. (4)

Part 2. Study Cases

In order to translate all above mentioned to the real life, this part is going to review three specific application with High Resolution Corrosion Monitor Systems, which in, the user was be able to discovery opportunities to improve their process and therefore confirmed everything that we were talking until. Additionally, it will allow reviewing what kind of improvements the user found out.

These cases are:

1) Petrozuata, Upgrader Facility, located in Venezuela
2) Sincor, Upgrader Facility, located in Venezuela
3) Andes Petroleum, Oil Field, located in Ecuador

2.1. Case: Petrozuata, Udgrader Facility. Topping (DCU) Plant Fin Fan Coolers.

Background:

Petrozuata is an upgrader located in Venezuela producing 120.000 BPD of heavy crude (between 19 and 25 API) from extra heavy crude (with 9.3 API). PDVSA own the 100% of stock of Petrozuata. The final product (heavy crude) is called Synthetic Crude, and this product is easier to treat or to process by refinery around the world.

The process can be separate in three basic steps:

- ✓ Heavy oil / Bitumen (8-9 API) is mixed with naphtha to be transported via pipeline from the oil fields to the upgrading facility. The mix is called Diluted Crude Oil (DCO).

- ✓ Upgraders plant uses a distillation process and specialized delayed coking technology to break thermally the heavy molecule into a lighter.

- ✓ The Synthetic crude is obtained after mix different process stream (straight and treated) previously separated from the DCO. The gravity range could be between 16-32 API.

Situation before use High Resolution Corrosion Monitoring:

The process was facing high corrosion problems in the inlets G and H of Fin Fan Coolers of the Topping Plant. Before use High Resolution Corrosion monitoring, coupons were used determine the corrosion rate. After several months, it couldn't find certainly what was happening, and all the time, the corrosion rate was over the target which is 5 mpy. (See figure 5)

Application and results:

It was necessary to find a way to troubleshoot the corrosion problem. Decision was to install a High Resolution Corrosion instrument in the inlet H of the Fin Fan Coolers, providing online, real-time monitoring that gives plant operators access to time-trended general data, which it could be correlated with plant process information.

After installing the probe, the user was able to identify four clear situations, each one with only some days of duration, which were contributing with the high corrosion rate in this side of the Fin Fan Coolers:

- Corrosion increased when production was increased
- Film Inhibitor test from 12 ppm to 8 ppm
- Problem with sour water with 1500 ppm NH_3
- Problem with carryover from Desalter.

Data collected from the transmitter for the period under analysis are shown in figure 6.

The first process upset was between August 17, 2006 and August 19, 2006 the corrosion increased when production was increased because of velocity effect and higher H_2S level amongst. The situation was handled increasing the corrosion inhibitor until reach 5 mpy which is the target to operate this unit to ensure five years life of the asset. Figure 7 shows the frame of this period.

Between August 30, 2006 and September 6, 2006 in order to look for optimizing of chemical injection, a chemical trial was carried out with the corrosion inhibitor changing the dosing from 12 ppm (nominal dosing) to 8 ppm. Before the trial the corrosion rate was 2 mpy. The target was look for the optimum concentration to operate at 5 mpy to avoid chemical waste. After the trial period, on September 6, 2006, the chemical dosing was re established to the nominal rate at 12 ppm, which force to corrosion rate decrease to 3 mpy. Thanks to the High resolution Corrosion Monitoring this trial was observed, see Figure 8.

Between September 18, 2006 and September 19, 2006 the corrosion rate started to increase again until reach 9 mpy. Several activities were activated to look for what was happening. After reviewed some process variables such as H_2S level, Flow, Temperature, chlorides, chemical actives, etc. the problem was found out in the sour water. It had a very high level of NH_3, about 1500 ppm, causing high corrosion rate problem. Some adjusts in the process were taken to put under control the corrosion rate again below target of 5 mpy. (Figure 9)

Finally, during NH_3 carry over problem, other overlap problem was indentified with the Desalting Unit, which brought to the distillation process higher level of chlorides. Only after fit these two facts, the corrosion rate fell under 5 mpy, and this happened 6 days after, on September 25, 2006. See Figure 9 for this situation.

<u>Benefits of this case:</u>

The main benefits was be able to view corrosion in real time, just like any other process reading, and it allows make decisions which preserve our equipment while producing. On other hand, with each upset fitted, it allowed to safe money reducing chemical dosing when the process didn’t need it, especially in variable charge period.

Despite the iron data was not possible to put in this inform, iron always was out of phase two or three days from corrosion rate, which confirm that high resolution corrosion monitoring is a very good complement within Reliability and Corrosion Program.

2.2. Case: Sincor, Udgrader Facility, Condensate Accumulator Steam System in the Vacuum Distillation Unit.

Background:

Sincor is a similar company like Petrozuata and also it is located in Venezuela. The only different in this case, Sincor produce 200.000 BPD of heavy crude (between 30 and 32 API) from extra heavy crude (with 8 - 9 API). The final product (heavy crude) is called Synthetic Crude, and this product is easier to treat or to process by refinery around the world.

Situation Before use High Resolution Corrosion Monitoring:

The corrosion problem in the steam system of the Vacuum Distillation Unit (VDU) is treated with Neutralizing Amine. The chemical is injecting before ejectors inlet, and the point of monitoring is in the Vacuum Condensate Accumulator, which receives all the condensate from the system. (See figure 10). The function of Neutralizing Amine is stabilizing pH and it is controlled by monitoring the condensate pH from samples taken at the end of the condensate system.

Despite the neutralizing amine dosing, corrosion rate reached and remain over 50 mpy in some cases, and the pH stay in the normal range of control rising a suspicious about chemical treatment. The corrosion monitoring system consist of standard ER corrosion probe and handheld. On the other hand, there was several high level of iron (over 2 ppm, which is the target), and it seems the behavior is independent of corrosion rate behavior.

Some questions comes up such as what should be the chemical rate to achieve a good corrosion control?, Does the system need a combination of chemicals?, How to follow the corrosion rate in real time to optimize chemicals and asset life?.

Application and results:

In order to confirm corrosion problem and follow the problem exactly when it is happening, and therefore correlate process variable with corrosion rate, a high resolution on line corrosion monitoring was installed in the outlet line of condensate accumulator to approach to this problem. Data from the real time system are in figure 11 (print screen of the software). It shows a very important period (5 days) where corrosion rate passed over 40 mpy (the target is 5 mpy).

The behavior of process variable like Fe, pH, and H2S was correlated with corrosion rate. (See figure 12). It is important to mention that MS Excel was used to analyze data imported from the OEM software, just to look in the same graph some parameters involve in the corrosion process. One of the most important outcome was discovery the formation of NH4HS (Ammonium Bisulfide) in cases where H2S and NH3 have a ratio of 2:1. The Ammonium Bisulfide works mainly like pH buffer not allowing see the corrosion problem with laboratory analysis, and therefore not allowing good control of the chemical without corrosion probe.

The figure 12 shows three periods, two of them, with high level H2S, and the last one (in the middle) with low level H2S, although is still high for the system design. It is obvious that the corrosion problem is not only a merely matter of pH. The corrosion problem was confirmed by iron measurements, which however, has one or two days out of phase with corrosion rate.

Therefore, high resolution probe helped to adjust the chemical rate to find out what is the best rate for the corrosion control, however, after 50 ppm of H2S there is not effect of the chemical, at any dosing. The problem was needing and additional solution.

Benefits of this case:

The great benefit was to evaluate the performance of the chemical treatment in a very short time (real time), and discovery the potential of the high resolution corrosion monitoring in the fight against corrosion. After this experience, high resolution corrosion monitoring was implemented as part of the Corrosion Program.

Other benefits, was identify a risk situation by correlating corrosion rate with the process variables. This was possible using a high resolution corrosion monitoring.

After test results using high resolution corrosion monitoring some activities were taken:

- Additional treatment with lighter inhibitor corrosion was evaluated and implemented, to preserve the asset against others kind of corrosion attack.

- With low level of H2S (< 20ppm) it not necessary the chemical, this represent saving about $ 600M/year of chemical treatment.

- Continue with on line corrosion monitoring and correlate this with H2S and others important process parameter

- With high level of H2S, optimize the chemical injection based on real time corrosion monitoring

Using High Resolution corrosion monitoring allowed to work without interruption and we know when any upset is happening, allowing make change to improve the process and fighting to keep corrosion rate in acceptable values.

2.3. Case: Andes Petroleum, Oil Field Production, Topping Plant (DCU)

Background:

Andes Petroleum Ecuador Ltd. operates the Tarapoa Block and the Lago Agrio Storage and Transfer Station (Sucumbios) located in Ecuador. The average daily production is calculated at 60,000 barrels per day. Within the oil production process there is a Topping Plant to produce gasoline for internal demand which is having corrosion problem.

Situation before use High Resolution Corrosion Monitoring:

The Topping Plant has a severe corrosion problem due to high level H2S and chlorides. Coupons are used in order to monitoring the corrosion rate and optimizing chemical injection without success. Corrosion rate is over the target (5 mpy) the most of the time, therefore corrosion problem is still present. Figure 13 shows data from coupon, corresponding period of seven month.

As important note, both inlets have the same behavior and similar corrosion rate, case different already reviewed in Petrozuata case, which corrosion rate has the same behavior however only two inlets of eight has a very high corrosion rate comparing between them. See figure 5.

Sometimes, as shows Figure 13, corrosion rate in the V-126 were higher, possibly due to higher concentration of chlorides, due to long time between wash water operations.

The chemical treatment consists in two chemicals: Corrosion Inhibitor and Neutralizing Amine (points 4 and 5 on figure 14), both are injecting at the output of the DCU and the corrosion is being monitored downstream in the same line, before Topping Coolers in each inlet. Figure 14 shows the diagram flow process.

Besides high level of H2S and Chlorides, there are some others possible facts for example, proximity to the dew point (or Salt Point in this case), wash water operation, and chemical as it. The question here is How to know? Because, depending of the temperature and pressure, dew point can move along the pipe between DCU and Coolers, on other hand, wash water remove from system chlorides efficiently, and perhaps, the chemical treatment needs timely adjust during production.

Application and results:

How to know? The answer to this question was to install a high resolution corrosion monitoring in one of the inlets. The outcome immediately came up. After wash line with sweet water, which is batch process (perhaps every month) the corrosion rate fell under 0.5 mpy. Figure 15 shows when it is happening in real time on October 2, 2007.

Using the calculation tools of the OEM software, corrosion rate before wash water is 26.39 mpy and after wash water is 0.47 mpy, as shows Figure 16 and 17. Another important fact is that corrosion rate for the whole period (from September 25, 2007 to October 4, 2007) is 19.26 mpy, showed in the right bottom box of the figure 15. Corrosion coupon between September 20, 2007 and October 2, 2007 is 16 mpy (See figure 13), confirming the results from the high resolution monitoring probe, error allowed, considering a little out of phase in the time.

Benefits of this case:

It is obviously that implementing a continue wash water could help chemical treatment reducing consumption of it. Of course, it is more water for the V-126 that is necessary to consider. Additionally, working with corrosion in real time allowed better control of the chemicals adding value to the process, and finally, less time operating the plant with upset (over 5 mpy) allowing detects upset timely, which, it means asset preservation, working with more reliability and safety, an finally, surely saving money.

Conclusions

The main benefits is able to view corrosion in real time, just like any other process parameter such as pressure, temperature, etc and correlate the corrosion rate with other important parameter such as Fe, CO2, H2S, pH, Chlorides, etc.

This feature (high resolution and fast response) allows make decisions in order to preserve equipments while producing. Therefore, with each upset fitted, it allowed the follows:

- Save money reducing chemical dosing when the process didn’t need it. $ 600M / year in one of the cases or simply optimizing the chemical dosing for continue process.

- Make process change such as water wash to help chemical treatments

- Indentify, when it is happening, high risk situation when corrosion rate is correlated with other parameter involve in the corrosion process

- A reliability and continue data base of corrosion rate, very important variable to calculate a long term corrosion rate for the RBI program or Risk Assessment Program

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Figures Section

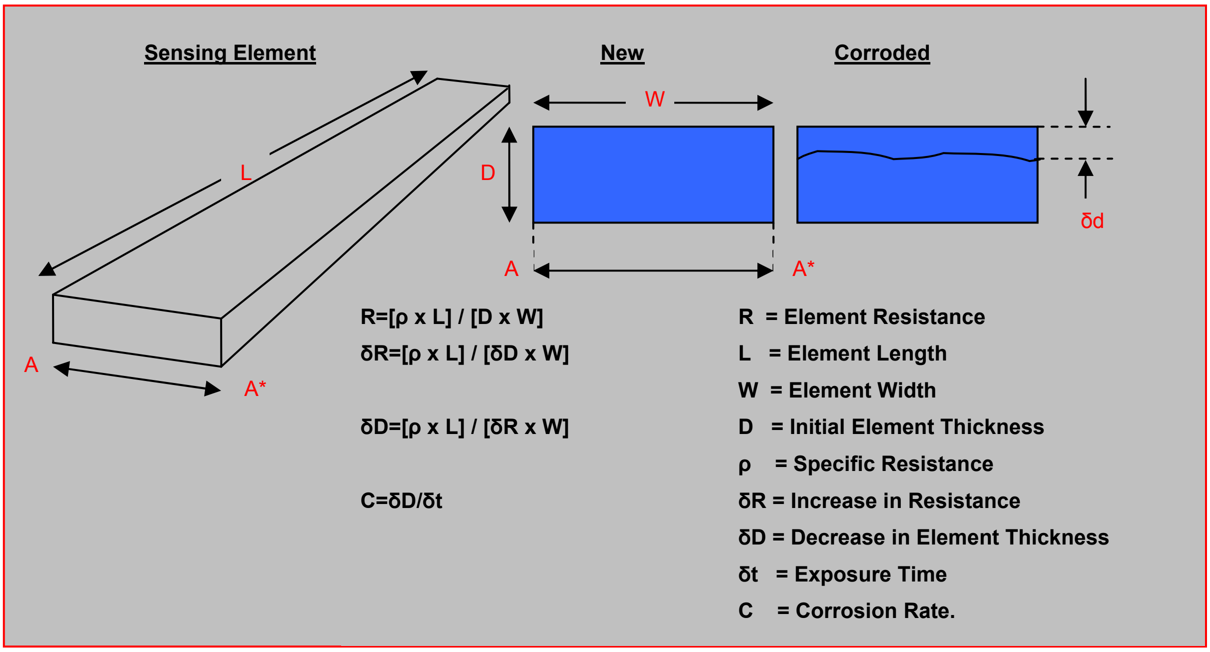

Figure 1. Basic Principle of Electrical Resistance

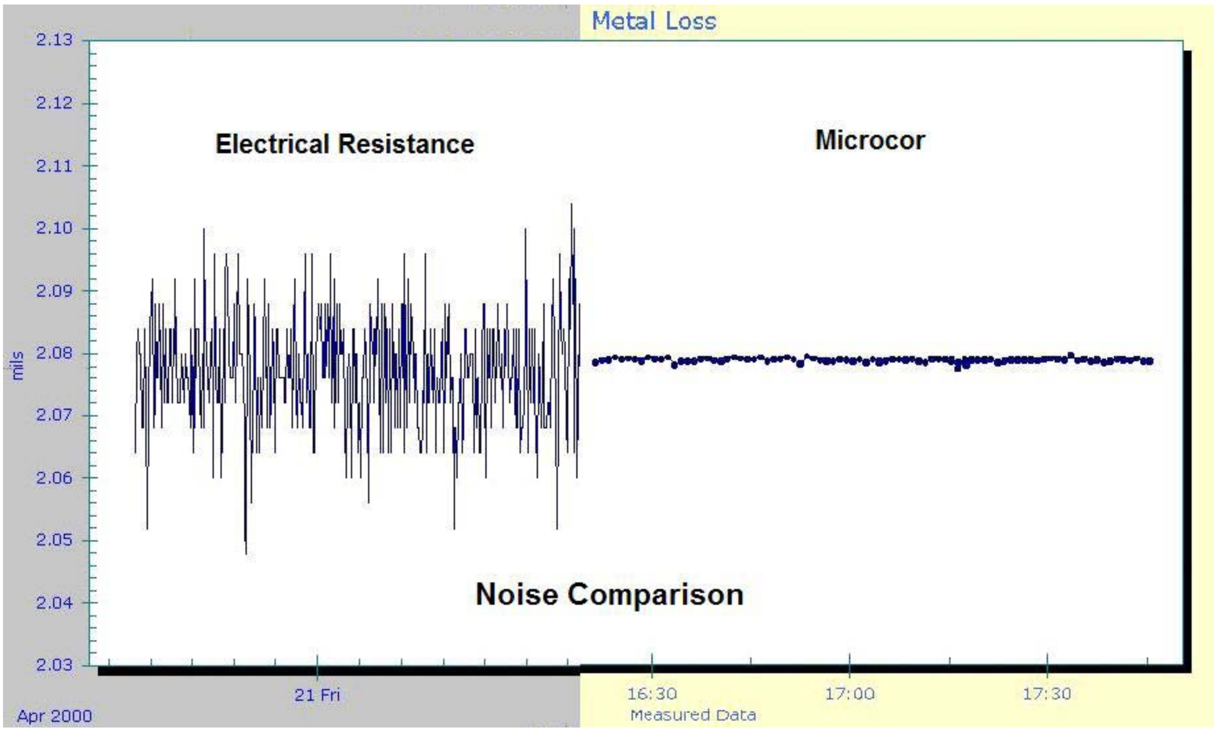

Figure 2. Noise Comparison between HRER and ER

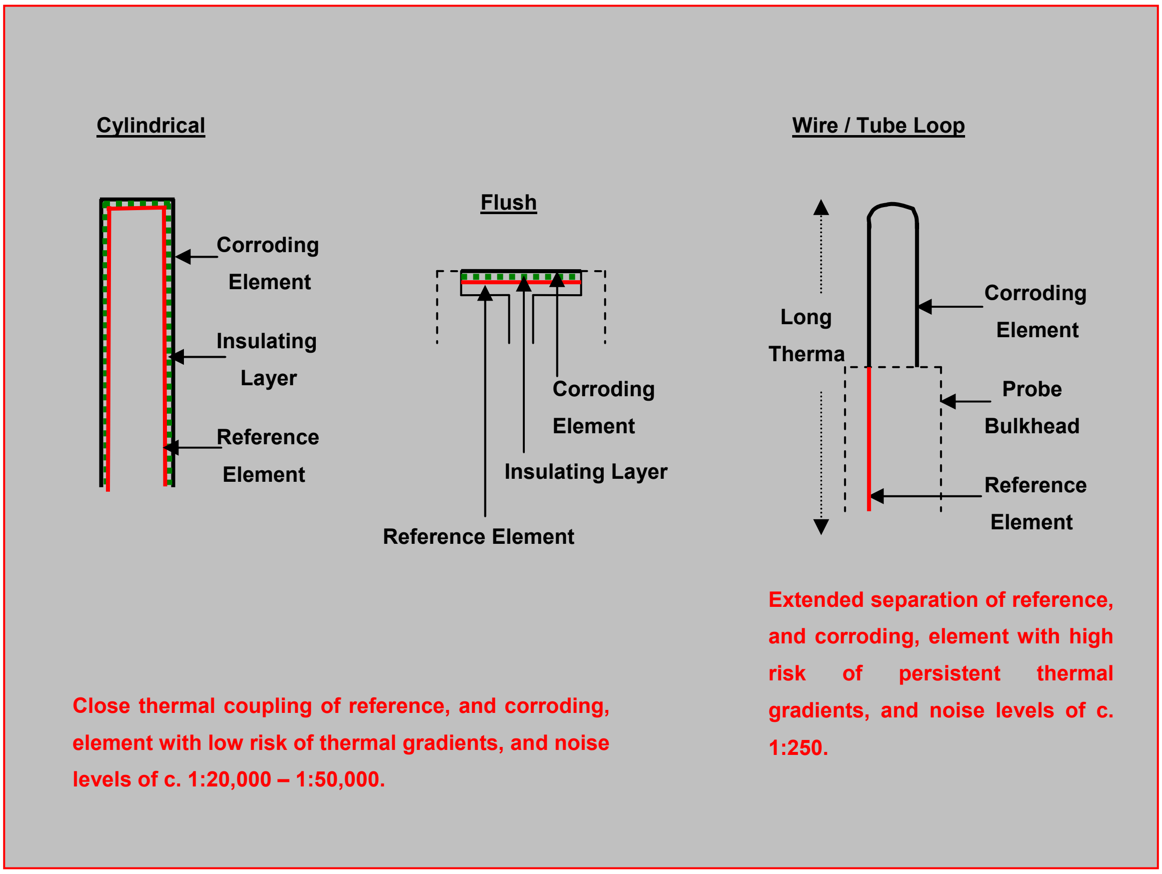

Figure 3. Sensing Element Design

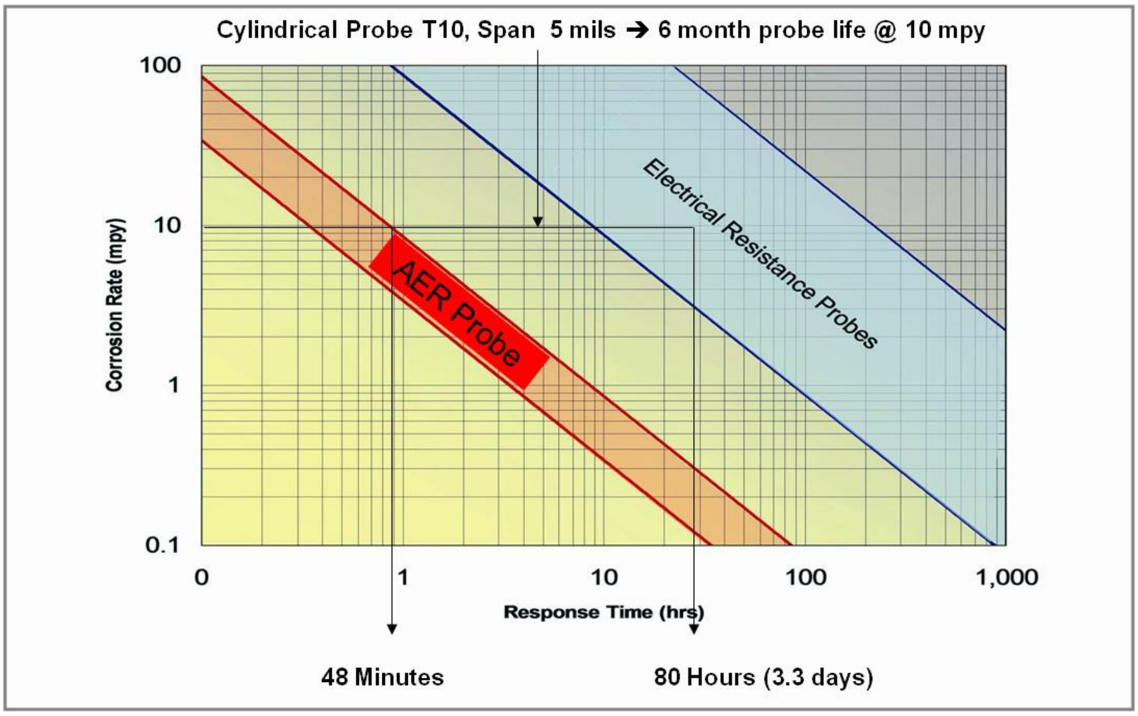

Figure 4. Probe Response Time

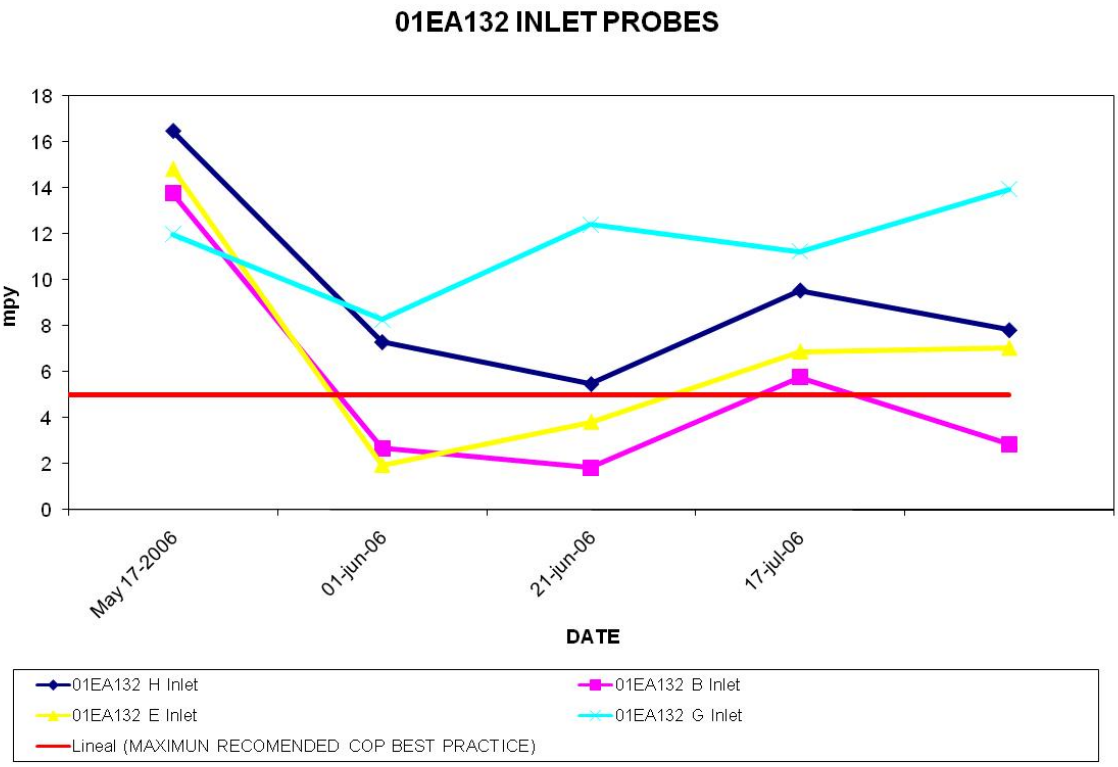

Figure 5. Inlet Probes Fin Fan Coolers Unit 132

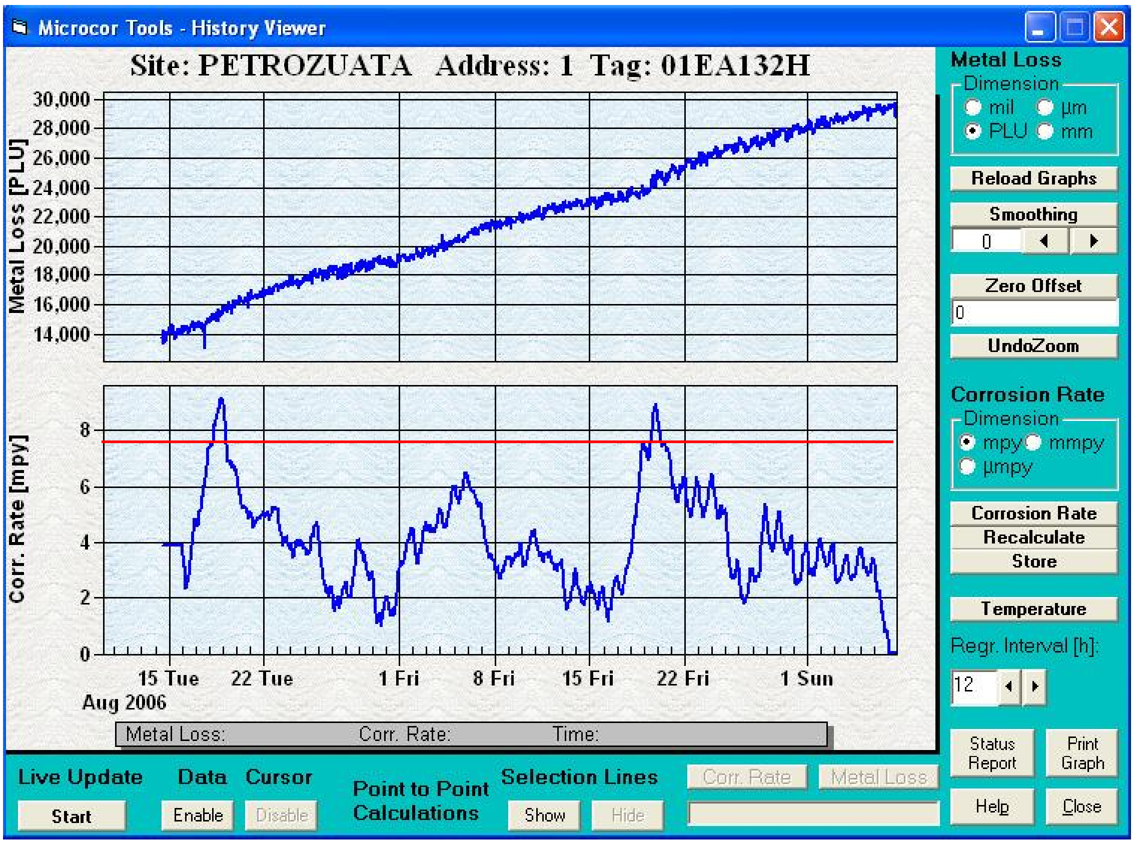

Figure 6. Period under analysis

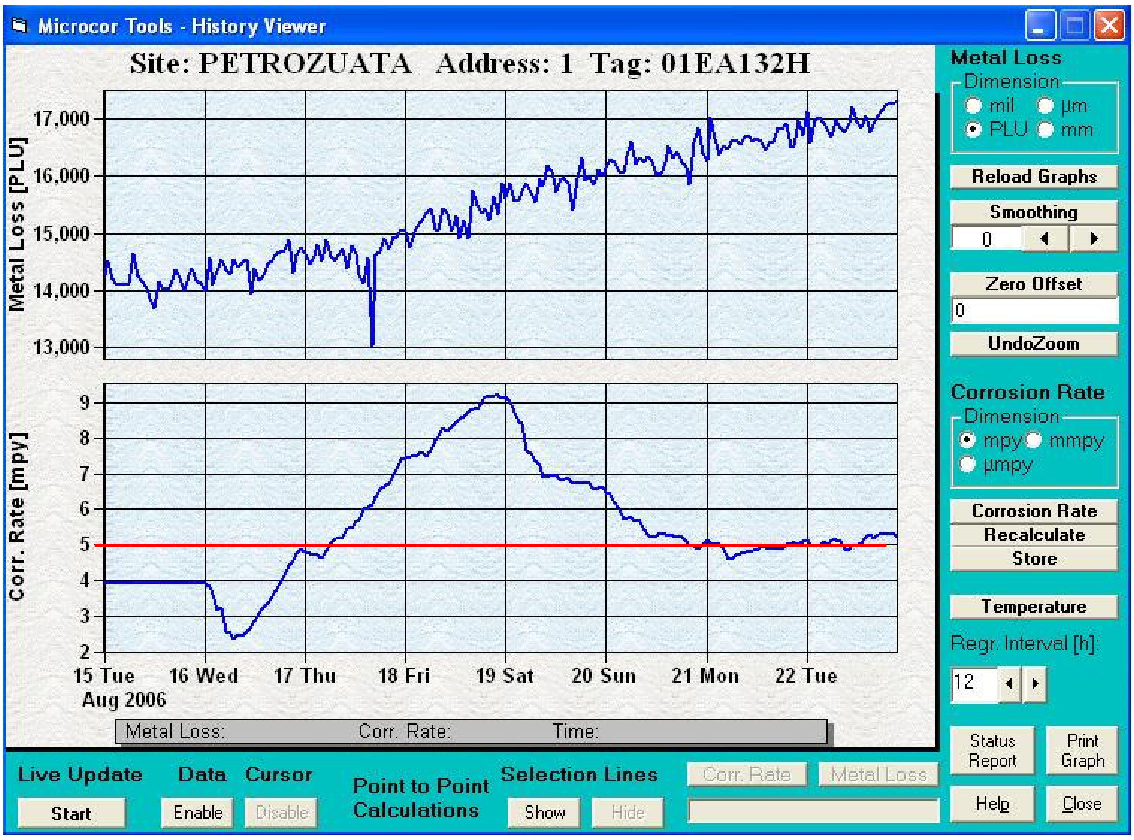

Figure 7. Upset between August 17, 2006 and August 19, 20

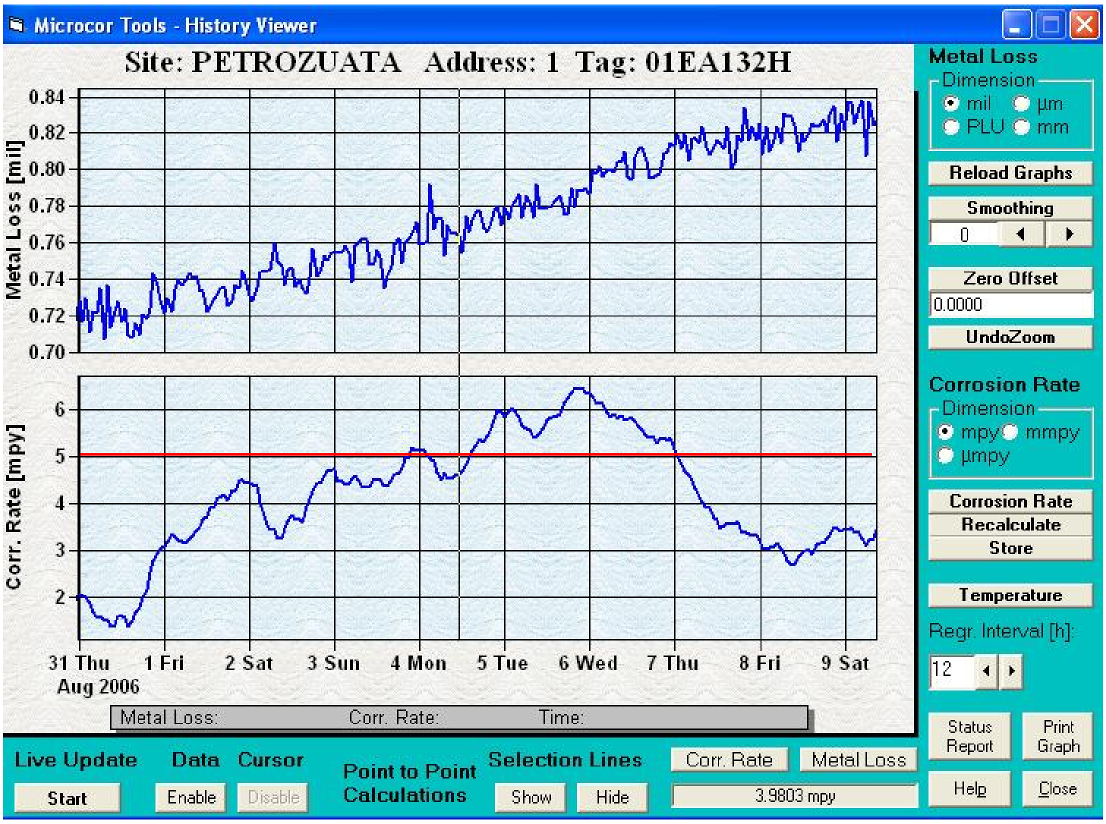

Figure 8. Film Inhibitor Trial from 12 ppm to 8 ppm

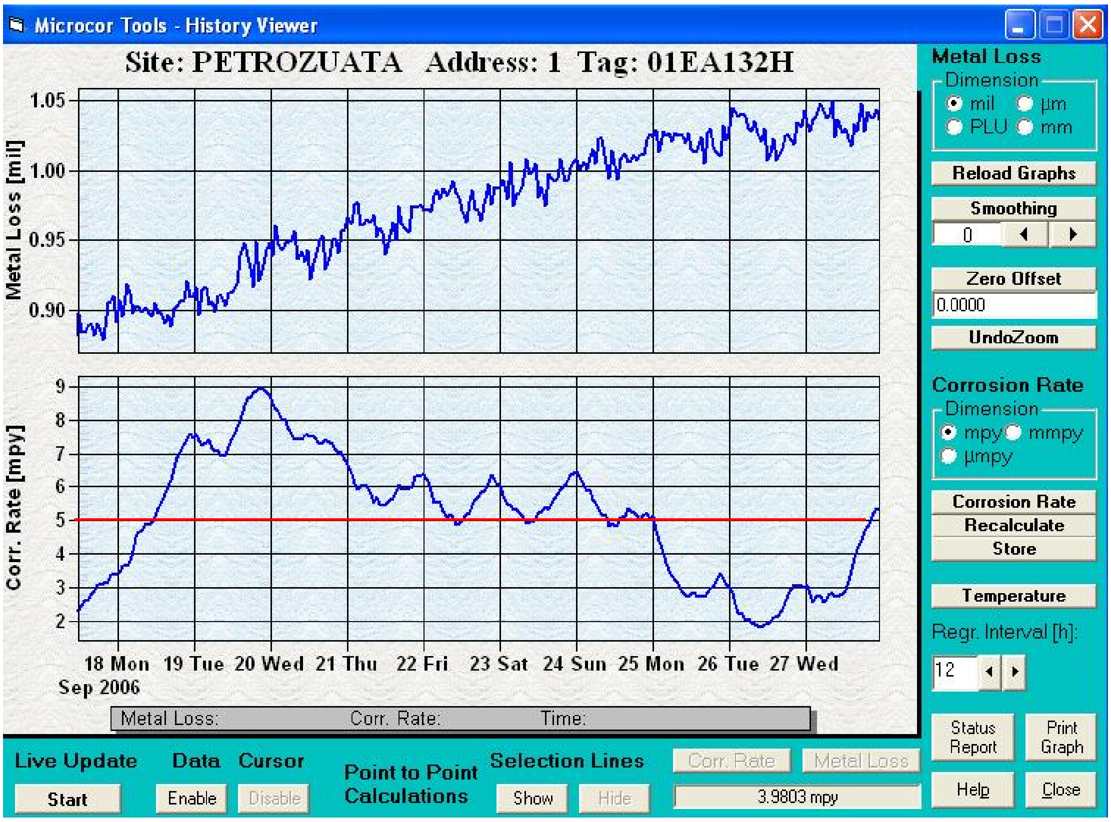

Figure 9. Carry over from Desalting Unit and NH3

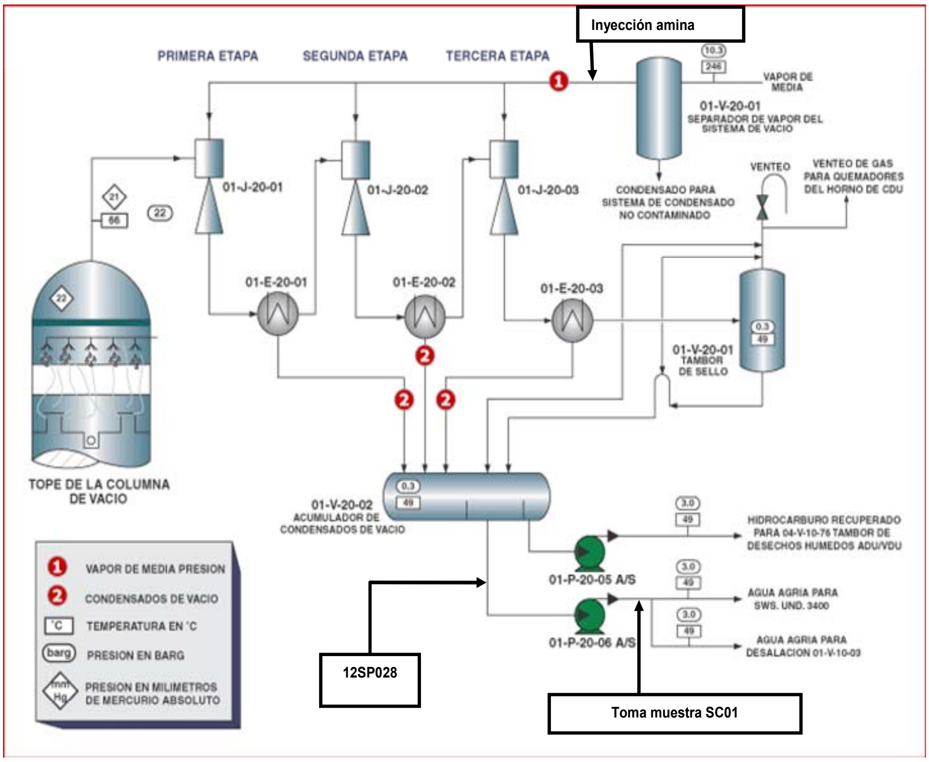

Figure 10. VDU Steam System

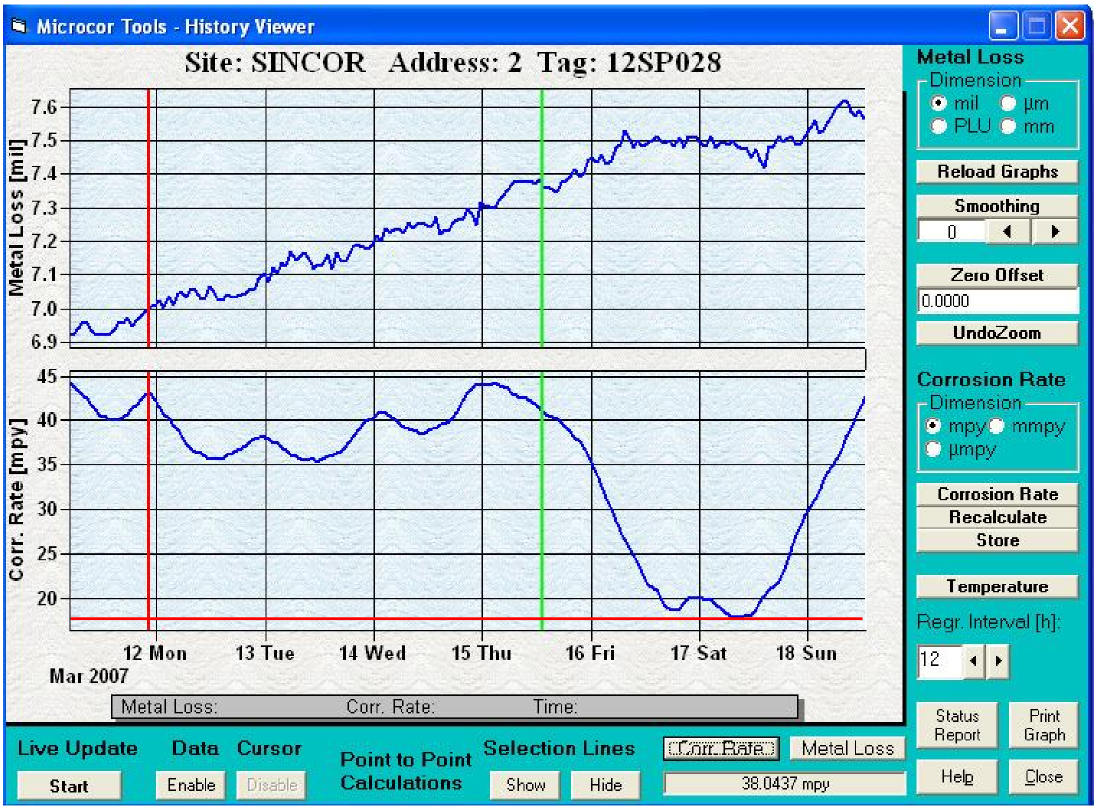

Figure 11. Corrosion Rate of Accumulator Vessel Tag 12SP028

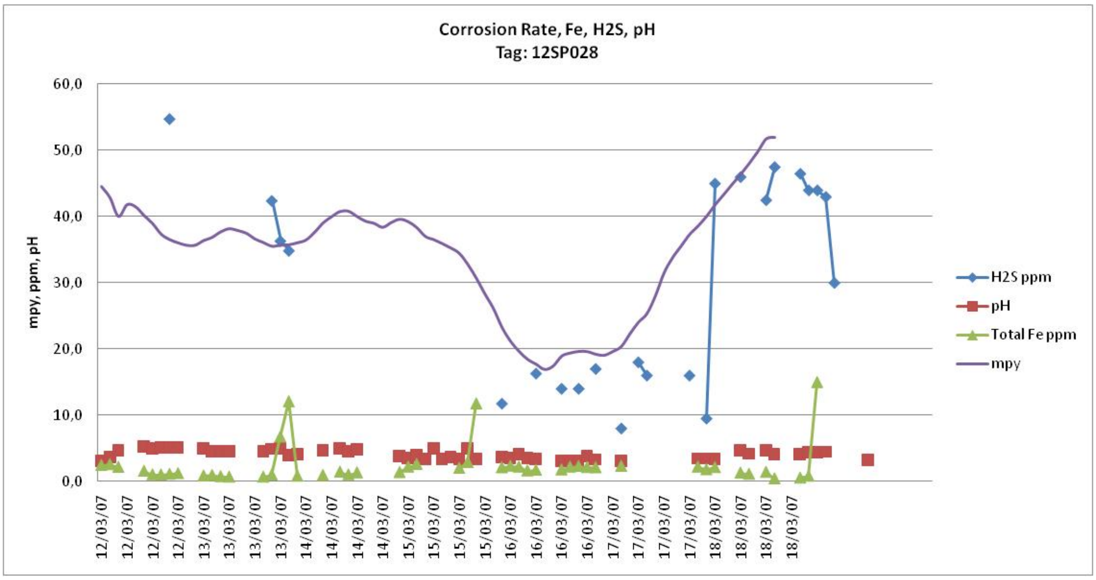

Figure 12. Corrosion rate correlated with process parameters such as H2S, Fe and pH

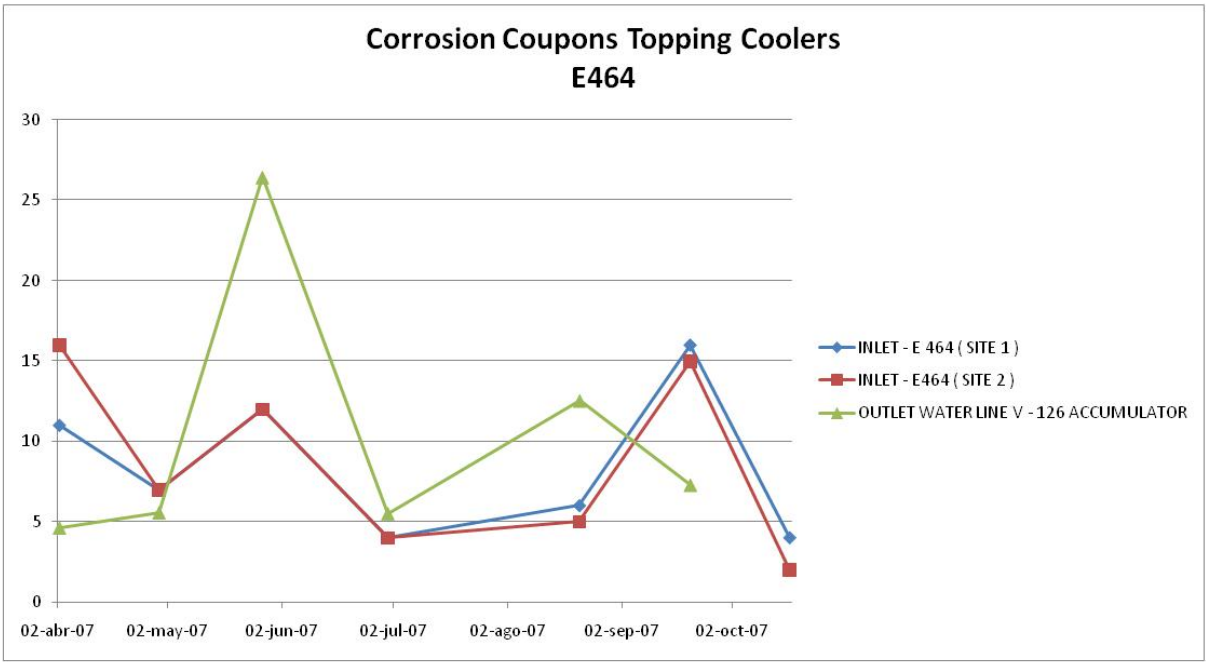

Figure 13. Corrosion Coupons Topping Coolers E464, inlet 1 and 2.

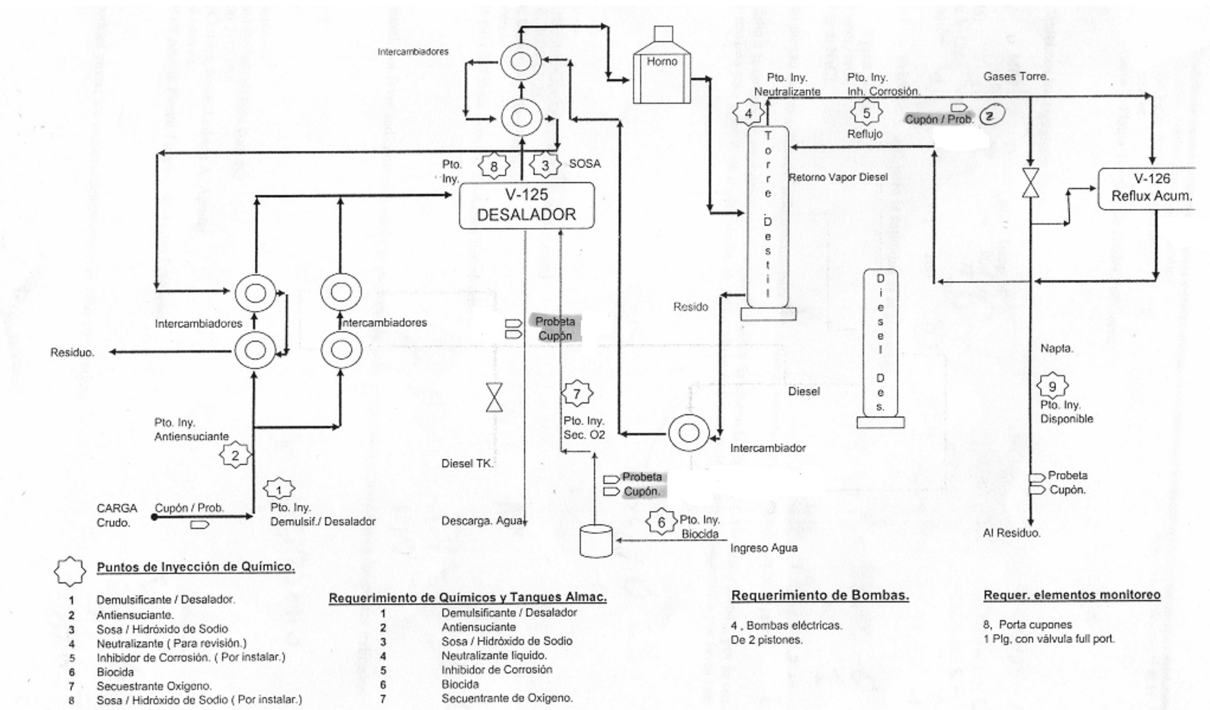

Figure 14. Topping Plant Diagram Flow Process

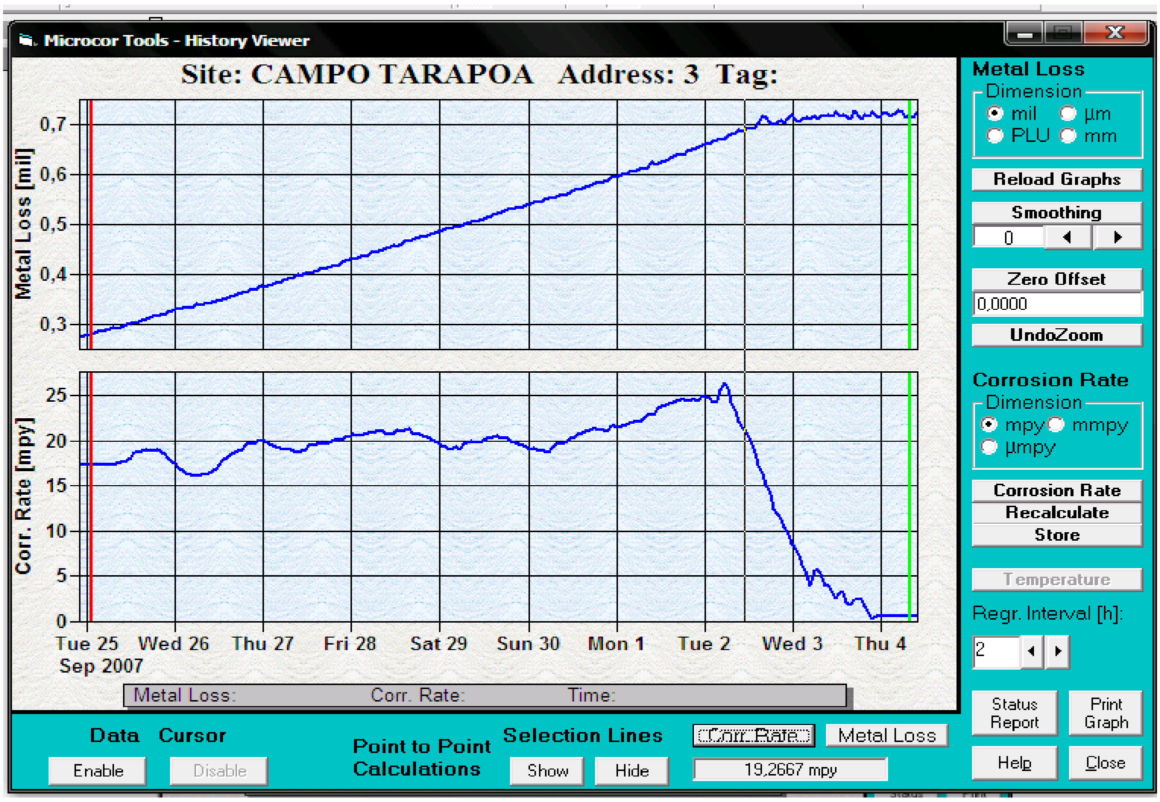

Figure 15. Cooler Inlet Corrosion

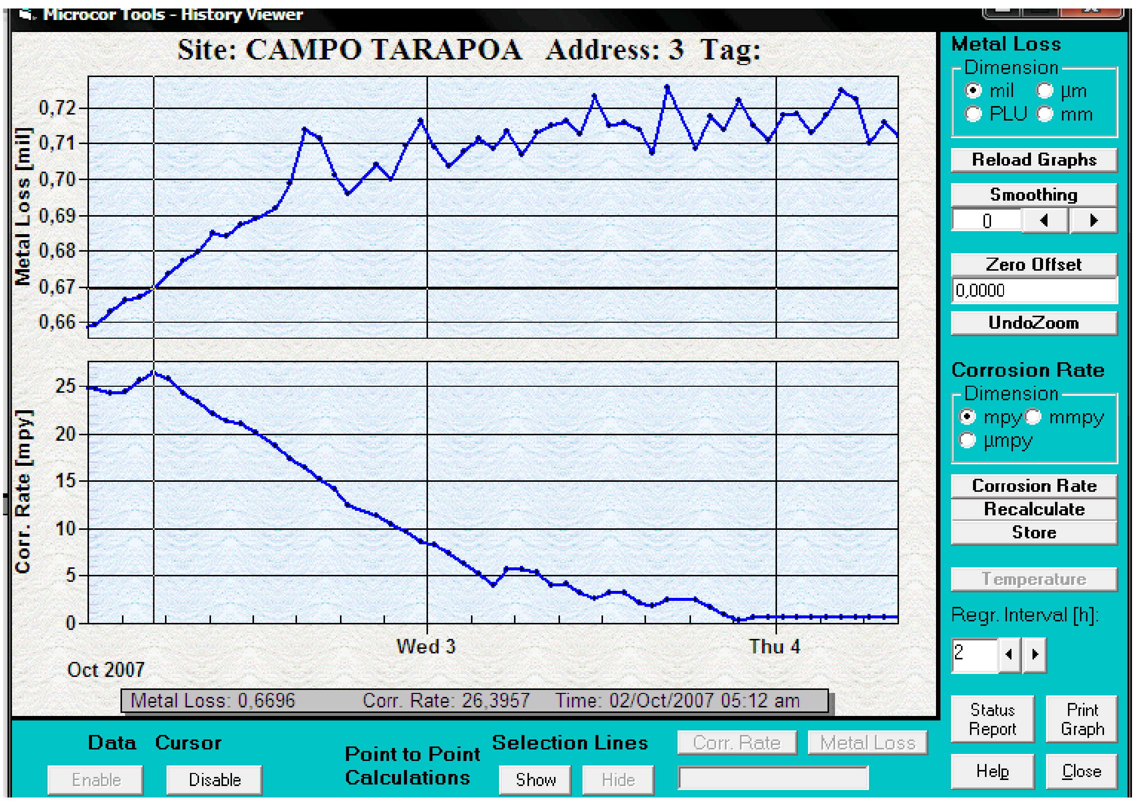

Figure 16. Corrosion rate 26.3957 mpy before wash water process

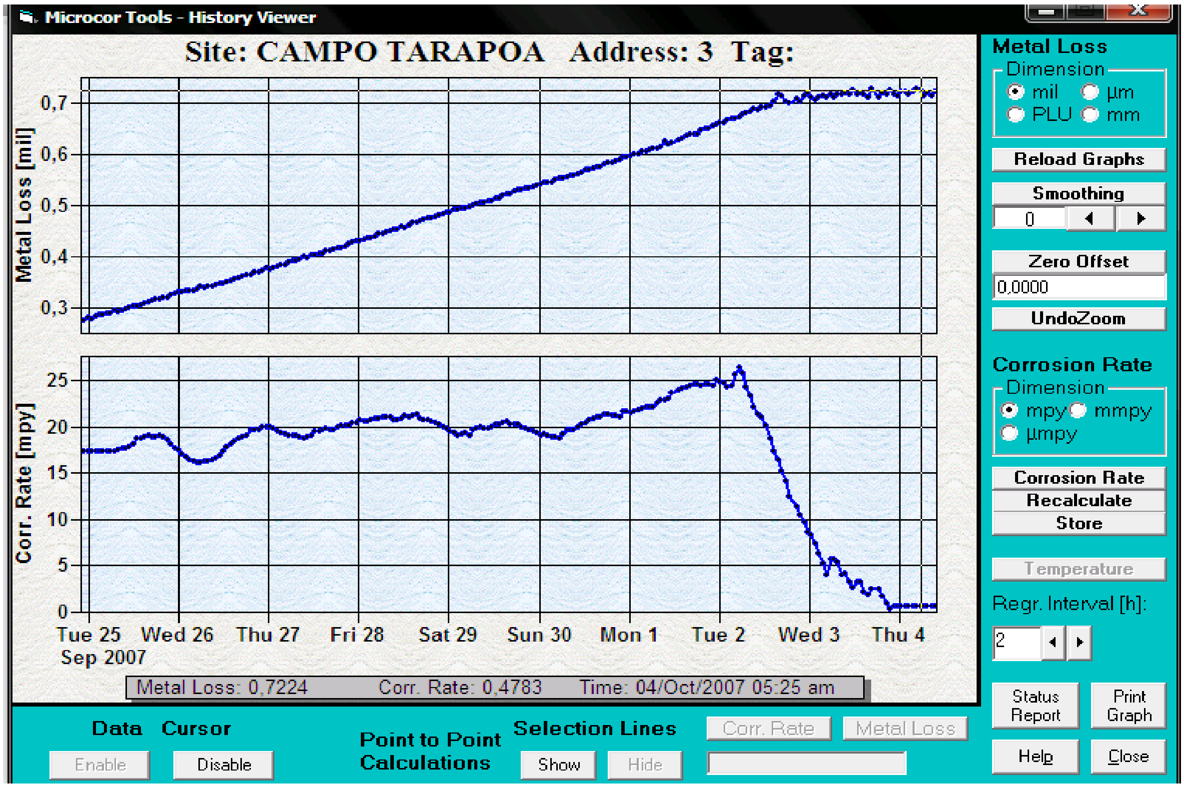

Figure 17. Corrosion rate 0.4783 mpy after wash water process