



Reducing Corrosion and potential Boiler Failure with Superior Iron Transport Technology

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Abstract

Boilers in Refineries and Petrochemical industries are critical systems to assure a profitable business, in most of the cases the boilers are directly related to the operating units by the Waste Heat boilers always critical as they are directly linked to the production.

These systems have evolved over recent years to operate with higher drum pressures, more complex feedwater pretreatment systems, higher purity feedwater, and tighter restrictions on steam purity. The reliability of these units is the primary reason for water treatment, and since the water make up is of high quality, scale deposits are of less concern and corrosion has become the major subject to control. Special attention is needed to reduce iron pick up along the systems and avoiding that iron arriving the boiler system, as it could create iron-deposits in critical boiler areas.

Commodities as Hydrazine, ammonia and phosphates are used in some places, but increasing stressing conditions demand superior technologies to better achieve results both from the energy saving point of view and on long time operation.

This article is intended to provide the reader with a basic understanding of the iron transport process, the way the iron-oxides could affect the heat transfer areas and will explain the advantages of superior technologies solutions with the most appropriate treatment regime for a long run plant operation without risk.

1. Introduction

In recent years in Refinery and Petrochemical industry high purity make up water for boiler systems has become a standard, therefore former calcium, magnesium or silica scaling is not anymore the main concern.

Nowadays condensate process contamination and / or metal corrosion products from condensate network and boiler feed water section corrosion have become the main source of boiler contaminants.



This paper will cover two main topics.

- 1) Reducing corrosion on condensate network and boiler feed water section to minimize iron and copper concentration arriving to boiler.
- 2) Reducing the impact of boiler feed water metal oxides concentration in boiler water.

It is improving the efficiency, reducing the corrosion and increasing reliability.

First we will discuss the optimal chemical water treatment approach in order to reduce corrosion on condensate and preboiler sections and second technologies to increase iron transport in boiler to avoid metal deposition on critical high flux areas.

Condensate process contaminants (like Hydrocarbon, cooling water, etc...) and their impact on boiler fouling and corrosion will not be covered on this paper, as this is more an upset situation that requires adequate and dedicated actions. Iron and / or copper is a general potential problem while process contaminants typically only appear few times along boiler life. In cases process contaminants are more likely to be presents on recovered condensates, a condensate-polishing unit is usually implemented.

Data and examples shown on this paper are related to typical refinery and chemical / petrochemical industry using demineralized water as boiler water make up. Even though they are still some plants still using Softening processes, this is the minor case in Middle East refineries and Petrochemical plants.

According to water source the water preparation plant may include as primary treatment: Ion exchange, one or two pass Reverse Osmosis, Electro Dialysis Reversal (EDR) or Thermal Desalination may be used in front of Mixbed Ion Exchange or Electro Deionization units (EDI) to produce the high purity water required.

Other systems with pourer make up water quality may experience more severe corrosion problems in similar boiler working conditions, as higher chlorine or sulphate depolarization ions would be present.

The described corrosion mechanism and best chemical treatment approach presented on this document can be applied to auxiliary boilers and also Waste Heat Boilers (WHB). WHB are usually more sensitive to failure than auxiliary boilers and the economical impact is much higher as they are directly linked to plant production. WHB are used in Ethylene, Ethylene Glycol, Polyethylene, Hydrogen plants, in convection sections of Refinery furnaces and in many other processes in Refinery and Chemical / Petrochemical industry.



For example iron deposits in WHB may impact system efficiency and system production in some cases, ending on boiler tube failure due to under deposit corrosion or long term overheating will have an enormous economical impact because it will force plant shut down.

On section 2 different corrosion mechanisms will be described. We will focus the corrosion types on condensate and boiler feed water section that will increase the metal that is picked up and transported to the boiler and also the corrosion mechanism in boiler itself due to iron and copper deposit fouling on boiler transfer areas.

On section 3 boiler fouling build up due to metal load will be described and analyzed. Also the impact of this deposits on corrosion, efficiency and finally on tube failure will be also covered.

How to reduce iron and / or copper corrosion on condensate and boiler feed water section in order to reduce the metal load to boiler will be discussed on section 4.

Metal transport in boiler or how to minimize boiler tube fouling due to metal load will be the main fact on section 5 of this paper. And finally on section 6 we will summarize article conclusions.

2. Corrosion mechanisms

Reduced reliability due to corrosion attack is one of the main problems in boiler systems costing billions of dollars per year.

2.1. Pre-boiler corrosion – Metal transport to boiler from external equipments

Pre-boiler corrosion will include corrosion in all steam – condensate network and also in boiler feed water section. Therefore corrosion in all areas that at the end will impact in higher iron or copper concentrations arriving to boiler will be included in this definition. Pre-boiler corrosion defines the area where the phenomenon takes place, but it may includes different corrosion mechanism like:

- Oxygen corrosion
- pH related metal protective layer stability
- Ammonia – Copper alloys associated corrosion
- Galvanic corrosion
- Erosion-Corrosion and Flow Accelerated Corrosion

Even in the absence of oxygen iron corrodes in water. Iron surface acts as a car battery, the metal surface is divided into microscopic anodes (+) and cathodes (-). Iron acts as an anode so that it is oxidized giving its electrons to the cathode.



The cathode in pure water is a proton or hydrogen ion (H^+). When iron metal is oxidized, electrons pass from the iron surface to hydrogen ions, resulting in the formation of ferrous ion (Fe^{2+}). The fate of the ferrous ion (Fe^{2+}) depends on water temperature, pH, and flow conditions. At low temperatures, Fe^{2+} reacts with water to form insoluble ferrous hydroxide, $Fe(OH)_2$. If the stream velocity is high enough, colloidal $Fe(OH)_2$ is swept into the water and carried downstream to deposit elsewhere.

In low flow areas, $Fe(OH)_2$ deposits near the oxidation site, forming a porous oxide layer. At temperatures above $50\text{ }^{\circ}\text{C}$ the deposited ferrous hydroxide reacts further to form surface bound magnetite (Fe_3O_4) crystals. At even higher temperatures (above $150\text{ }^{\circ}\text{C}$), Fe^{2+} spontaneously forms magnetite without first forming $Fe(OH)_2$.

This magnetite forms a nonporous, tightly adherent layer on the metal surface. In most condensate systems, two or three forms of iron oxide are present. In pure water, a tightly adherent magnetite layer is formed, which is indicative of a well-passivated iron surface. In the absence of contaminants, this oxide layer greatly retards any further oxidation reactions.

2.1.1. Pre-boiler Oxygen Corrosion

In the presence of oxygen, the corrosion process described above is modified. Dissolved oxygen replaces hydrogen ions in the reduction reaction. This reaction occurs more readily than the direct reaction between iron and protons. Oxygen usually enters the system through water make up or direct absorption of air in condensate tanks, or in vacuum zones in complex condensate networks, like it is the case in Refineries and Petrochemical plants

With effective mechanical deaeration and chemical oxygen scavenging, all but a trace of oxygen is eliminated from boiler feedwater, in complex condensate networks and in vacuum condensate areas, some air intrusion may occur and oxygen corrosion could be a problem in those areas. High distribution ratio oxygen scavengers will reduce corrosion, in those zones, as it will be distributed all along complex steam and condensate network.

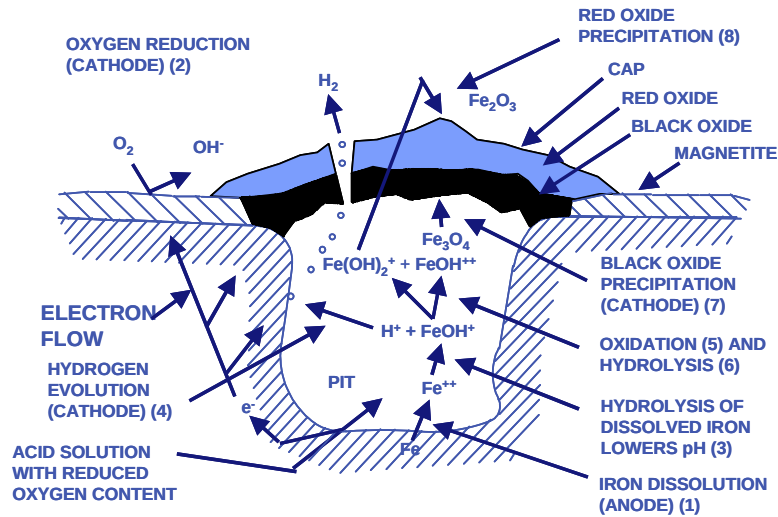
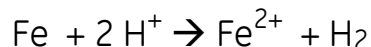
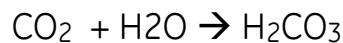


Figure 1. Detailed oxygen corrosion of iron

2.1.2. pH related metal protective layer stability

The stability of the passivating iron oxide layer is critically dependent on pH and temperature. Any contaminants in the system that cause the pH to decrease cause dissolution of the oxide layer and increased corrosion. Carbon dioxide (CO₂) is the primary cause of decreased condensate pH. Carbon dioxide enters the system with air leaking in condensate vacuum areas, in atmospheric condensate tanks or from decomposition of feedwater alkalinity. The latter should not be a problem in refinery and petrochemical industry using demineralized makeup water.

Low pH causes a generalized loss of metal rather than the localized pitting caused by oxygen corrosion.



Another important effect of pH modification is the impact on magnetite stability. In high-pressure condensates or boiler feed water section, even at alkaline pH, working out of optimal pH range will affect the magnetite stability, resulting in higher iron concentration in boiler feed water.

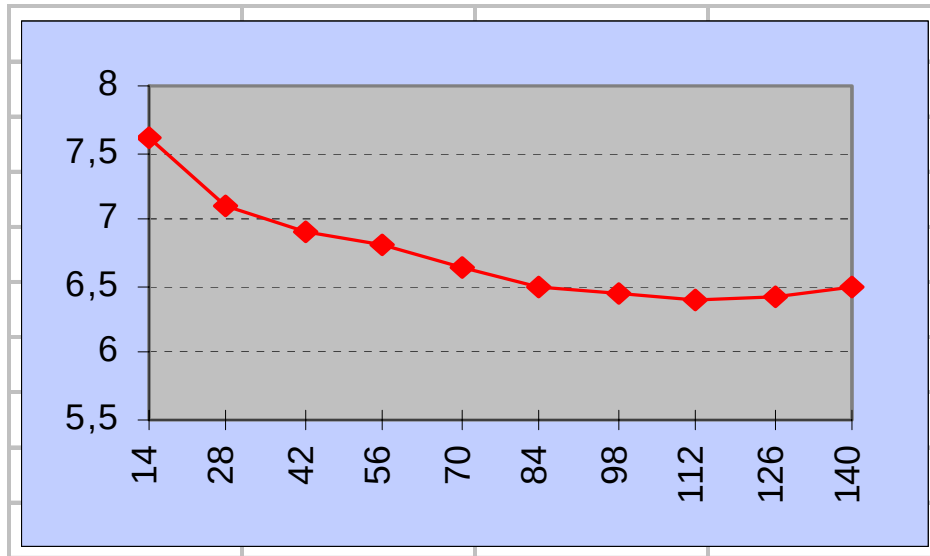


Figure 2. Magnetite stability as a function of pH @ t at different pressures

In section 4 we will discuss chemical treatment considerations we should take into account in order to avoid general acid corrosion on condensate and boiler feed water pipelines, and also localized corrosion on flash tanks and in Phase Transition Zone on turbines.

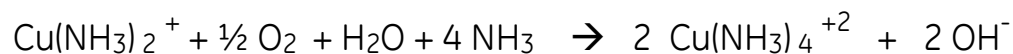
In refinery and petrochemical industry using demineralized water, a little amount of air intrusion or small organic contamination in the acid form will result in a condensate pH depression, getting pH lower than optimal for magnetite stability. The addition of volatile alkalis (amines) is mandatory for avoiding high iron pick up ratios.

2.1.3. Ammonia – Copper alloys associated corrosion

Corrosion on copper or copper alloys is influenced by pH and also oxygen and ammonia concentrations. The anode semi reaction is as follows:



The oxygen will then oxidize the bi-ammonia group to tetra-ammonia, still with ammonia present:



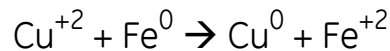
This reaction will take place in cold area of condensers or heat exchangers because of ammonia and oxygen high distribution ratios.



2.1.4. Pre-boiler Galvanic Corrosion

Galvanic corrosion occurs when a metal or alloy is electrically coupled to a different metal or alloy. The most common galvanic corrosion in refinery and petrochemical industry is by contact of dissimilar metals, as iron and copper.

When copper corrosion occurs, and soluble copper is present in water, galvanic corrosion appears, and steel surface plating can be observed.



To minimize galvanic corrosion, copper corrosion should be minimized, working at right pH and minimizing ammonia and oxygen compound in condensate. High distribution ratio oxygen scavengers will help to minimize oxygen content in condensate areas where some air intrusion may occur.

2.1.5. Erosion-Corrosion and Flow accelerated corrosion

Erosion is a type of corrosion phenomena affected by several factors:

- Velocity
- Geometry
- Metallurgy
- Water Chemistry

Velocity is frequently the major factor in erosion – corrosion. We may have liquid impingement corrosion due to high velocity in certain steam or condensate areas.

Geometry is also very important, typically erosion will occur in changes in direction of fluid flow, in places where pressure changes or in case we have an abrupt piping discontinuity.

It is known that higher alloy material will increase erosion resistance. In some cases when erosion is localized in a small area, changing that section to a more resistant alloy may be the best option.

Chemistry has a minor impact on erosion, but a good control on pH and creating conditions for the most stable magnetite layer may slightly reduce problem severity.

Flow Accelerated Corrosion (FAC) is a particular type of erosion that results in a localized attack of carbon steel components in steam production systems. The attack is from the waterside and can result in piping and tube failures. This type of failure as



all erosion corrosion is quite site specific, as main factors are metallurgy, geometry and velocity. FAC can occur where there is single-phase liquid or two-phase flow.

Flow-accelerated corrosion is essentially a process whereby the normally protective magnetite (Fe_3O_4) layer on carbon steel is dissolved in a stream of flowing water (single-phase) or wet steam (two-phase). This phenomenon reduces the protective oxide layer (magnetite) that may cause the removal of the base steel material, to the point of metallurgical failure. The FAC attack may be rapid – wear rates in excess of 3 mm/yr (0.12 in./yr) have been reported.

Single-phase FAC occurs where all of the water is in the liquid phase – there is no vapor or steam generation in that pipe or tube section. The general appearance of the attack can be described as an orange peel, bubble-like texture.

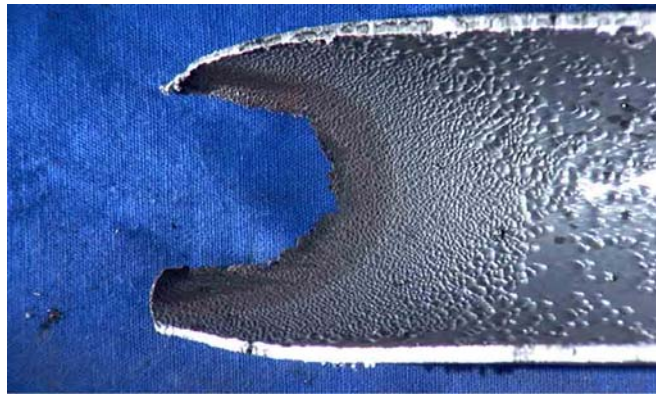


Figure 3. Flow Accelerated Corrosion

Carbon steel components with water velocities greater than 2.4 – 3 m/s. are particularly susceptible to FAC attack. Also the rate of FAC attack is at a maximum around 130 – 150 °C for single-phase flow and 150 – 200 °C for two-phase flow.

Two-phase FAC can occur whenever a turbulent water-steam mixture comes into contact with a carbon steel surface. Steam quality also has an impact since FAC can only occur if the steel surface is continuously wet. It is the liquid phase that causes the FAC wear. Generally, two-phase flow conditions are more turbulent than in single-phase, and therefore FAC rate of attack is greater. Under severe two-phase FAC, the prevailing turbulent conditions can lead to a rapid deterioration of the base steel, through exfoliation and spalling of the particulate iron into the water stream. The particulate iron concentration in severe cases can be very high, exceeding 10 mg/L in the evaporator water. The corresponding sample can appear dark in color, and is often called “black water”.

Operating at lower than design pressure can sometimes cause FAC problems. This is because the specific volume of steam / water mixtures increases as pressure is



reduced. As the specific volume increases, the velocity also increases and can exceed the threshold necessary for an FAC problem to develop.

Increasing feedwater pH is known to reduce FAC rates. A strongly reducing environment (negative oxidation reduction potential or ORP) is known to increase FAC rates, and reduced concentration of the chemical oxygen scavenger / passivator, it is avoiding overdosing can be beneficial. Both measures should be evaluated by iron (Fe^{+2}) testing.

In this section we have described main corrosion mechanism producing an increase on boiler feed water iron or copper concentration. This metal concentration in boiler feed water at the end may cause a potential fouling in boiler heat transfer areas, unless proper chemical treatment is applied.

Next section will focus on this potential boiler fouling due to metal load. Also we will describe the corrosion phenomena related to this type of deposits.

2.2.Internal Boiler Corrosion. Deposition of external metal oxides supply and internal metal production

Internal boiler corrosion is a general concept to define all possible corrosion mechanisms we may find in boiler tubes, including also fouling that may result in tube failure. We are not considering economizers or pre-heaters as we included them in the pre-boiler corrosion section.

Internal corrosion mechanism has been widely described in many articles. We will focus on the corrosion phenomena linked to the deposition on boiler transfer surfaces of metals arriving via boiler feed water. Also we will include the internal iron production that at the end will have a contribution on tube boiler deposition.

Due to boiler deposition on tube heat transfer areas, we may get three main types of corrosion or tube failure.

- Caustic gauge corrosion
- Acid corrosion
- Hydrogen Embrittlement

2.2.1. Caustic Gouging Corrosion

Caustic corrosion is related to the concentration of free caustic. The concentration of NaOH in the boiler water is normally not high enough to create corrosion but caustic concentration can occur either as a result of steam blanketing (which allows salts to concentrate on boiler metal surfaces) or by localized boiling beneath porous deposits



on tube surface. Therefore localized caustic concentration is related to non-uniform oxides deposition on boiler.

Nonuniform deposition may be related to operating condition, high flux areas, or internal iron deposit formation.

When caustic concentrates dissolves the protective magnetite layer.



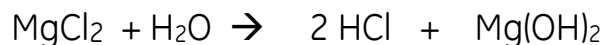
Reducing the amount of porous magnetite or iron deposit the potential caustic gouging is reduced. Also pH-phosphate treatment approaches can be used to avoid or reduce the amount of free caustic in boiler (Coordinated Phosphate Treatment, Congruent Phosphate Treatment, Phosphate Treatment, Equilibrium Phosphate Treatment or Phosphate Continuum) in order to minimize potential caustic corrosion.

In this article we are not covering the description of different phosphate treatment and advantages and disadvantages comparison between them, as this have been already covered in many other articles in the past. We will focus on the minimization of porous deposit layer as a benefit for lower caustic corrosion potential.

2.2.2. Acid Corrosion

In same cases, the deposit formation may impact on acid corrosion. The mechanism is similar, concentration of contaminants in non-homogeneous porous deposit. In case some contaminants enter in boiler systems, the acid corrosion may occur.

Condensate failures may produce some cooling water intrusion. Acid hydrolysis of chloride compounds in porous deposits may create a localized acid corrosion.



2.2.3. Hydrogen Embrittlement

Another particular type of corrosion related typically to low pH excursions in high-pressure boilers (>105 kg/cm²) is the formation of nascent hydrogen at the boiler tube surface. Hydrogen penetrates the tube where it can react with iron carbides Fe₃C (cementite) to form the methane gas and other hydrogen atoms to form hydrogen gas, weakening the metal structure Gases collected at grain boundaries



increase pressure and microfissures occur within the material and weaken the tube. This type of corrosion is called hydrogen embrittlement corrosion and often blows out a “window”.

The existing deposits can act as concentration areas for acidic compounds making the problem more critical. Again a concentration mechanism due to the deposition.

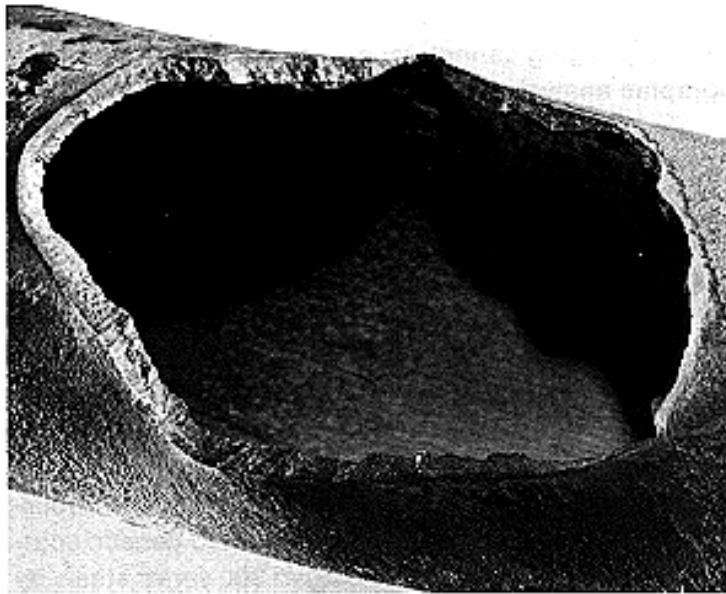


Figure 4. Typical window failure caused by hydrogen embrittlement

3. Deposition

The deposition problems we find in high-pressure boilers can't generally be explained on the basis of the water bulk conditions like; bulk water quality parameters, boiler pressure and temperature. The problems are normally located in higher flux areas while in most of the other parts of the boiler the impact is much lower.

Therefore for an accurate analysis of the problem it is necessary to dig into the local conditions that water may reach under a certain operating conditions in a specific area. The deposits that accumulate in a restricted area may be caused either because the water chemistry related and/or operating conditions related, and based on where they accumulate the situation is more or less critical. It seems logical that the areas with higher Heat Flux are likely the most affected.



The figure 5 shows the loss of efficiency-energy due to the deposition of different species in the heat transfer surfaces.



Figure 5.
Energy Loss versus Scale Thickness and composition

The way to analyze how important is the deposit and how it may affect the heat flux exchange across the tube includes:

- Measuring the amount of total deposit respect the surface and deposit thickness.
- Analysis of the deposit bulk composition and analysis of deposits located in different positions respect the tube.

3.1 Measuring the amount of total deposit respect the surface and deposit thickness.

The measure of the total deposit weight amount per unit of surface is called Deposit Weight Density (DWD), and it gives an indication on whether the surface has too much deposit and risk to have problems due to overheating. For determination of deposit-weight-density (DWD), a tube section is weighed before and after removal of the internal/external deposit. Dimensional measurements before and after the deposit removal are performed to determine the deposit thickness. The deposits are carefully removed from the surfaces for further deposit analysis. The surfaces are subsequently cleaned using a sandblasting unit.

The value for DWD that can be acceptable for a safe operation depend on three main aspects:

- 1) The heat flux in the area where the deposit is located
- 2) The composition of the deposit and
- 3) Porosity of the deposit

The table 1 gives the recommended DWD to initiate a boiler cleaning.



Pressure range Bars	DWD g/m ²	mg/cm ²	g/dm ²
<40	535	53,5	5,35
40 - 60	480	48	4,8
60 - 70	215 - 430	21,5-43	2,15 - 4,3
70 - 135	130 - 215	13-21,5	1,3 - 2,15
>135	107 - 130	10,7-13	1,07 - 1,3

Table 1. Recommended DWD to initiate a boiler cleaning program

The DWD when complemented with the deposit thickness can further estimate whether the deposit is congruent with the results and the composition.

For example the boiler analysis of a tube with measured DWD values of 13,88 g/dm² and 13,06 g/dm² and with an oxide thickness of average about 31 micron and for which the main deposit was identified as Magnetite can be compared with actual the theoretical calculated DWD value. As the density for magnetite is 5.045 g/cm³, the calculated DWD value would be 15 g/dm² which is close to the measured value of 13,47 g/dm².

When using the DWD as control parameter it is critical that the tube selected is taken from the area of higher heat transfer. In some cases a tube may have sides with different heat flux. This is normally the case in boilers with water circulation inside the tubes, in this case it is important to clearly identify the side where the heat is higher.

3.2 Analysis of the deposit bulk composition and analysis of deposits located in different positions respect the tube.

The technique used Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM-EDXA) is used to identify the elemental composition of the internal corrosion products/deposit and of the base alloy material of the tube sections. Elemental determination with the SEM-EDXA system is based on analysis of X-rays produced via electron beam excitation of a sample area. This technique allows analysis of a sample in selective areas. The limited depth of analysis (typically a few microns), and the possibility to select the area of interest under the electron beam, allows for local analysis to reveal differences in composition.

Representative (bulk) analysis of a deposit sample is performed by grinding a representative sample to a fine, homogeneous powder.

The identification and measurement of individual peak intensities in the X-ray spectrum is done with a computerized multichannel analyzer. With this system, the range of detectable elements is from carbon to uranium. With the current light element detector using an ultra thin window, the light elements down to Carbon can



be detected (atomic number = 6). However, the light elements cannot be accurately quantified by SEM-EDXA.

Based on the X-ray intensities, the concentration of the elements with atomic number >10 can be calculated. Sensitivity approaches 0.5 weight percent. The semi-quantitative analysis is reported as weight percents, and only elemental constituents are reported. For the elements with atomic number >10, elements not reported are not present, or are below detection limit.

The analysis can be additionally completed with the WDXRF (Wavelength Dispersive X-ray Analysis by X-ray Fluorescence) to have the composition of crystalline structure of the deposit. It is a technique similar to SEM-EDXA, is used for determination of elements based on analysis of X-rays produced. However, instead of electron beam excitation, an X-ray Cathode tube is used for excitation of the sample area. Besides, the Wavelength Dispersive method identifies the elements on basis of the wavelength of their X-radiation instead of the Energy Dispersive method that discriminates on basis of the energy of the detected photons.

The XRF technique allows the use of standards of known concentrations, and hence full quantitative analysis with the elements reported in absolute concentrations. With this technique, the range of detectable elements is from oxygen to uranium.

The table 2 shown an example of compositions range typically found in deposits for WHB deposits.

	XRF and LOI	Weight%	
	Fe as Fe ₃ O ₄	80 –98	
	Ca as CaO	0 – 2	
	Phosphate as P ₂ O ₅	0-10	
	Cr as Cr ₂ O ₃	0 – 1	
	LOI at 550°C	< 1 – 5	
	at 840°C as %CO ₂	< 1 – 5	
	Ash residue	> 99 –95	
	SEM EDAX Element	Weight%	
	Mg	0.0 –1	
	Al	0.0 – 5	
	Si	0.5 – 10	
	P	0.2 – 5	
	Ca	0.2 – 3	
	Cr	0.2 – 4	
	Mn	0.5 – 2	
	Fe	80 – 95	



	Cu	0.5 - 15	
	Element	Underside deposit /corrosion products	
	Si	0.1 - 5	
	Cr	0.2 - 2	
	Mn	0.2 - 2	
	Fe	80 -99	
	Cl	0 - 1	
	Na	0 - 4	

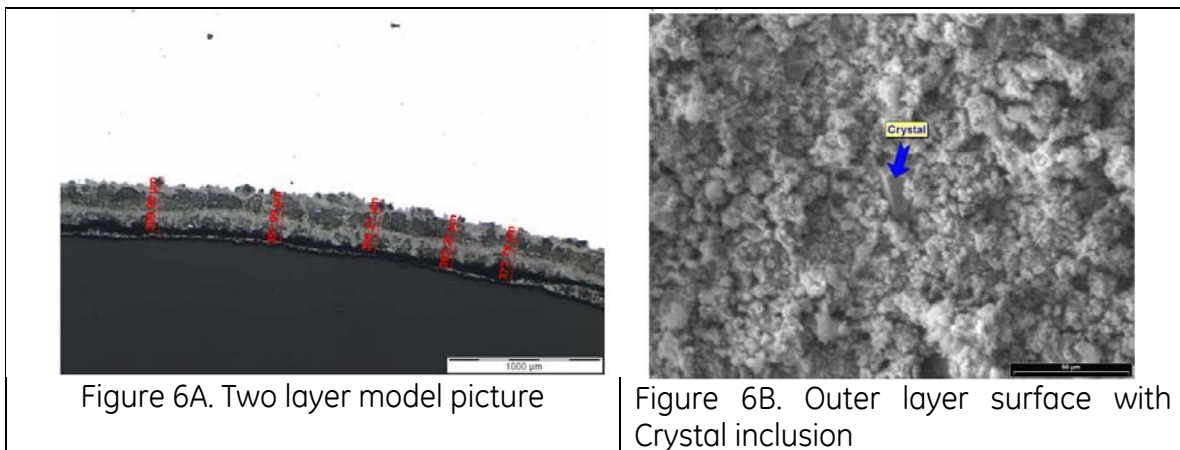
Table 2. Deposit composition in WHB

3.3 Protective and Deposit Layers

When trying to analyze the heat transfer problem we can simplify considering the deposit structure as made of two layers. In this way we can differentiate two main layers in the deposits.

- 1) One internal that is dense and adherent to metal surface and
- 2) Another external layer that is more porous.

The figure 6A and B shown this two-layer model in a heat exchange surface

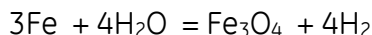


While the dense and adherent layer is consider protective and it should be mainly formed by magnetite Fe_3O_4 , the external layer is acting as a resistance to the heat flux transfer and hence it is creating a rise in the tube temperature.

The magnetite is basically associated to the fact that at the normal operating pressure in boilers, usually higher than 40 Bar, the iron of carbon steel that is the



base of the surface material reacts directly with water to produce magnetite as per the reaction:



The external porous layer is normally consequence of:

- a) Growing up of the internal layer due to transport of iron ions through the magnetite and its hydrolysis on the surface. It is related with the passivation and stability conditions of the existing internal magnetite surface. In fact the presence of depolarizing anions like Chloride or low localized pH at the operating temperature increases significantly this internal transport and growth. The table 3 gives information about the solubility of the magnetite in water at normal boiler operating water temperatures for different pH measured at 25 °C. The values clearly shown that a low pH increases the magnetite solubility by a factor of 100.

pH at 25°C	Water Temperature, °C	Magnetite Solubility as Fe(+2) concentration, mol/l
9	300	$2,5 \times 10(-8)$
8	300	$5 \times 10(-8)$
4,5	300	$2 \times 10(-6)$
9	250	$3 \times 10(-8)$
8	250	$1 \times 10(-7)$
4,5	250	$7 \times 10(-6)$

Table 3. Magnetite solubility at temperature and pH.

- b) As mentioned before the accumulation of material that arrives from other sections of the system, either the same boiler or carried by the boiler feed water from outside the boiler, due to pre-boiler corrosion. The ferrous ions transported from other parts of the system, at temperatures above 50 °C, the deposited ferrous hydroxide reacts further to form surface bound magnetite (Fe_3O_4) crystals. At even higher temperatures (above 150 °C), Fe^{2+} spontaneously forms magnetite without first forming $\text{Fe}(\text{OH})_2$.
- c) The mechanism of mechanical erosion of this layer as consequence of the water velocity.
- d) And the mechanical of compression and expansion on this layer due to the plant load changes, and eventually the oxidation of the layer during the lay-up of the boiler system.

In boilers where the deposits are mainly iron oxides we find normally the two layers model, moreover with DWD that is higher in the areas with high Heat Flux (HF).



To avoid high differences in the HF in the boiler, the design would require conceptual changes that in most of the cases are not possible or easy to do, either because cost investments or because the chemical reaction itself.

3.4 How iron introduction may affect the DWD in a boiler system?

Normally in the daily operation the analyzed iron values for boiler water treated with trisodium phosphate or low transport activity polymers, are lower than the theoretical due value based in the Boiler feed water concentration and boiler cycles:

$$\text{Theoretical Fe in Boiler water} = \text{Fe in BFW} \times \text{Boiler Cycles} + \text{Internally generated Fe}$$

Internally generated iron usually remains as a deposit in nearby areas unless high efficiency polymer for iron deposits it is used. Therefore in many cases the former formula is simplified to the following one:

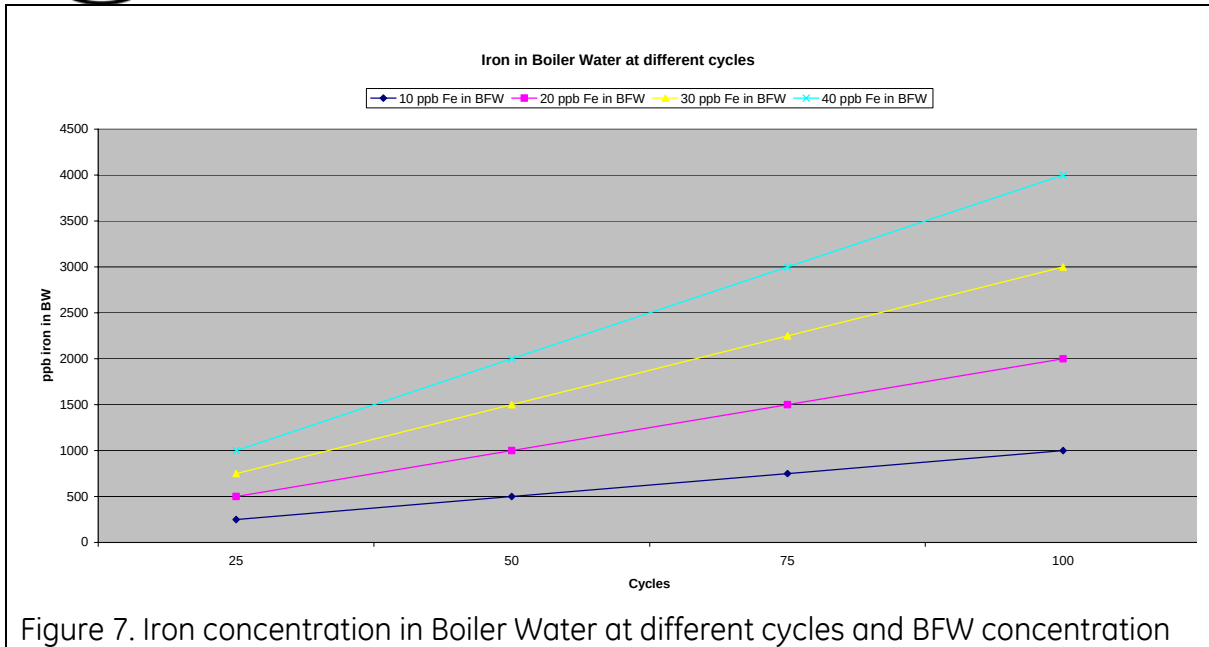
$$\text{Theoretical Fe in Boiler water} = \text{Fe in BFW} \times \text{Boiler Cycles}$$

This would confirm that 100% of the iron introduced via BFW is removed and then not deposited on the metal surfaces. Normally the values are lower than this and in most of the cases below 30% of this theoretical target. One can therefore consider that the difference is retained in the boiler surfaces, producing an increase in the DWD by depositing on the outer layer.

Earlier it was explained that the DWD increases because grow up of the magnetite layer on the tube surfaces either by external supply of material, mainly iron oxides, or by internal protective magnetite transformation into porous magnetite.

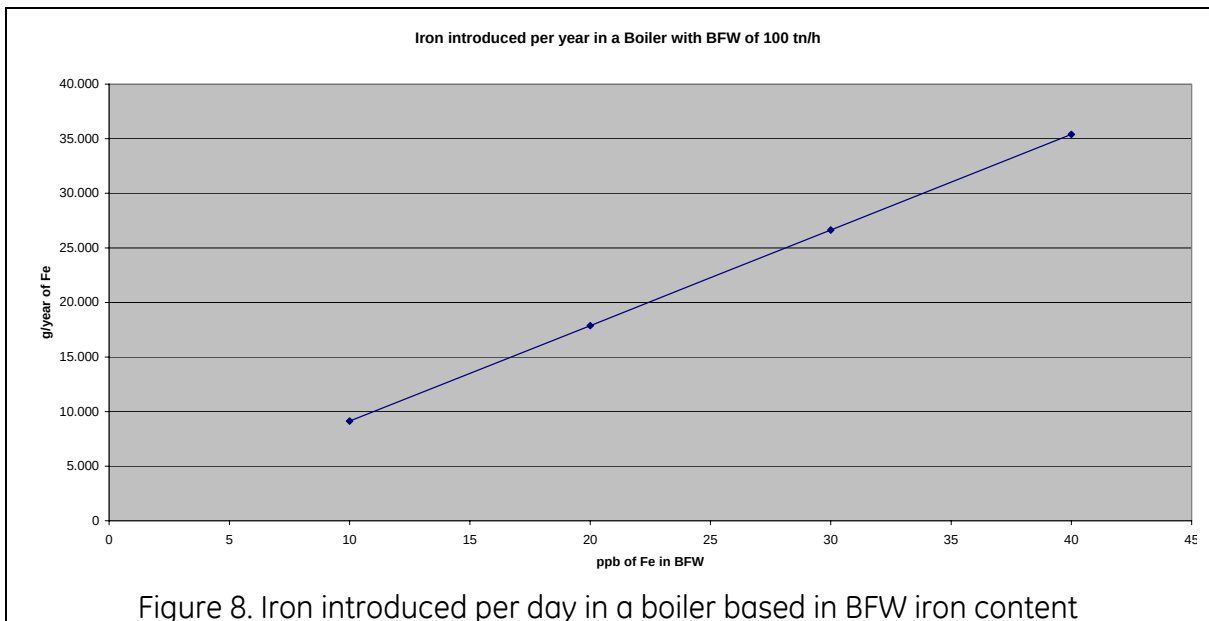
The external metal oxides supply to the boiler is produced mainly because the pre-boiler corrosion of the surfaces of the boiler feed water systems, including the deaerators, transfer and pipes lines, low and high temperature heaters and all the associated steam and condensate return lines, as described in section 2.

The metal ions picked up from different surfaces may finally end in the boiler system. Just to illustrate how is this pick up important lets consider a Boiler that has a steam rate of 100 tn/h. The figure 7 gives the amount of iron we should find in boiler water at various cycles of concentration and with different iron concentration in the Boiler Feed water (BFW).



Lets consider values in BFW as low as 20 ppb of iron. This value is the maximum recommended concentration for iron given by different regulatory bodies. See tables 7 and 8.

With this concentration and with a production of 100 Tn/h we would introduce in the boiler 17.878 g/y of Iron or approximately 25 Kg of hematite Fe_2O_3 . Figure 4 gives the iron introduced per day as a function of the BFW iron content.





For this boiler producing 100.000 Kg/h of steam, if we consider a specific steam rate as 100 Kg/m²/h (values for high Heat flux systems use to range from 60 Kg/h/m² to 120 Kg/m²/h), the total exchange surface would be 1.000 m². Further we can calculate the amount of deposit that at maximum can be created in the surface of the tube due to the total deposition of the iron in the BFW would be: 25 g/m²/y. Or 17,5 g/m²/y if we consider a 30% of iron transport.

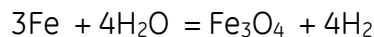
At this point we must consider, as well, the fact that the deposition will take place in the areas of higher heat flux. Values of DWD for high heat flux rate are in the range of 3 – 5 times the values for DWD in low heat flux rate for the same boiler. Consequently if we consider this we may forecast that in some tubes the DWD due to the external supply may reach values as high as 30 - 40 g/m²/y.

Therefore when comparing this value with the values given in the table 1, the conclusion is that for one year operation it could account for approximately the 30% of the maximum value recommended for a 135 bars boiler. This is really high. And we shall keep in mind that this calculation was made based in a very low Iron level in BFW like 20 ppb.

The reasons why we have external supply of metal oxides are corrosion rate in all the preboiler systems. And even if the corrosion rates are very low the accumulation of the iron will generate iron concentrations that after in the boiler may generate problems.

3.5 How iron produced internally is affecting the DWD?

The second way the DWD will increase is due to the direct magnetite production based in the reaction;



Normal values for Hydrogen production in high-pressure boilers could be in the range of 1 – 3 ppb (mg Hydrogen/Tn Steam). And they dramatically rise in case of pH drop. We can calculate the theoretical amount of magnetite produced in this boiler producing 100.000 Kg/h of steam to be around 29 – 87 mg of Fe₃O₄/Tn of steam. This is even higher than what is introduced in the boiler through the BFW having 20 ppb of iron.

We could make with these figures a similar calculation than we have done in the previous point. The results will lead to values around 60 – 120 g/m²/y. They are even higher and as they grow up from inside the layer, most of it will remain and directly increase the DWD.



Of course in practical operation not all the metals that are introduced in the boiler will deposit and increase the DWD. Providing the solids are kept under suspension in the boiler water, the boiler blow-down will remove an important part of them. But this removal is not only related to the % of the blow down but as well is about how long the solids are retained in the boiler and kept dispersed in the boiler water.

Here we can think in terms of chemicals reactions. The solids trend "thermodynamically" to settle and deposit on the boiler tube, but this process has "kinetics", and will take some time to settle.

3.6. Long Term Overheating

As we have been explaining in refinery and petrochemical industry using high purity make up water for boiler applications, iron oxides are the main boiler tube deposit.

An increase of the iron deposit layer impacts on the metal surface temperature, as the iron porous layer has different heat transfer coefficient compared to metal iron Fe^0 . Higher temperatures in metal surfaces reduces tube life.

The figure 9 gives information on how the metal external temperature rises as consequence of magnetite thickness.

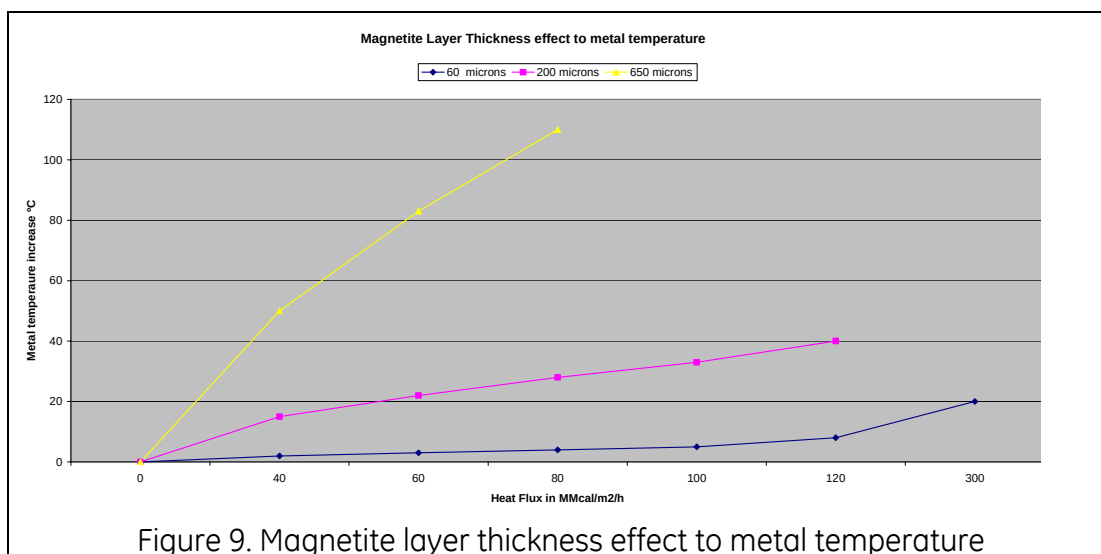


Figure 9. Magnetite layer thickness effect to metal temperature

Metal grain structure undergoes thermal degradation (oxidation) at elevated temperature and as a result the tensile strength of the metal is dramatically reduced. The tube ultimately ruptures - generally known as overheating failure.



At 450-540°C, carbide spheroidization or graphitization (formation of graphite globules) occurs and overheating may take place over a period of months or years producing the Long Term Overheating

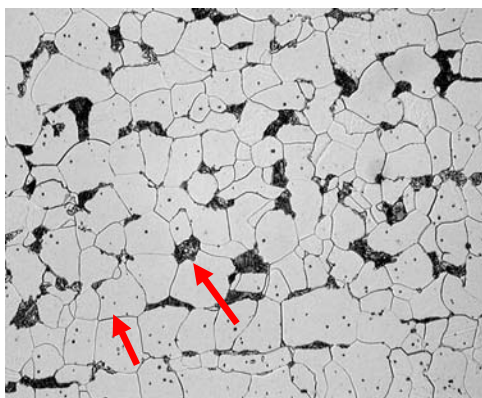


Figure 10A

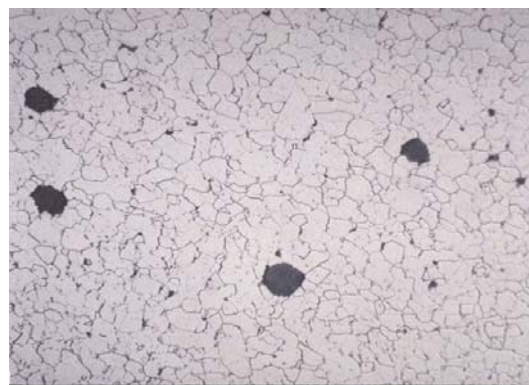


Figure 10B

Application	Specification	Nominal Composition	Max Use Temp C
Ecomomizer	SA-178A/178D SA-192 SA-210A1/210C	Carbon Steel	510
Furnace Wall Tubes	SA-178A/178D SA-192 SA-210A1/210C	Carbon Steel	510
Furnace Wall & Superheater	SA-209/250 T1 SA-213/250 T2	0.5 Mo 0.5 Cr-0.5 Mo	523 552
Superheater	SA-213T11	1.25Cr-0.5Mo-Si	566
Reheater	SA-250T11	1.25Cr-0.5Mo-Si	566
	SA-213T22	2.25Cr-1.0Mo	602
	SA-250T22	2.25Cr-1.0Mo	602
	SA-213TP304H	18Cr-8Ni	760
	SA-213TP347H	18Cr-10Ni-Cb	760
	SA-213TP310H	25Cr-20Ni	816

Table 4

4. Reducing boiler metal load

As mentioned in section 2, pre-boiler corrosion might be related to different corrosion mechanisms. The feedwater and condensate systems can be chemically treated to reduce metal corrosion, this include neutralizing amines and oxygen scavengers.

4.1. Amine Selection Criterion

Ammonia and neutralizing amines are used to neutralize the acid (H⁺) generated by the dissolution of carbon dioxide or other acidic process contaminants in the



condensate. These amines hydrolyze when added to water and generate the hydroxide ions required for neutralization. By regulating the neutralizing amine feed rate, the condensate pH can be elevated to within a desired range (e.g., 8.8 - 9.2 for a mixed copper/carbon steel condensate system, or > 9.5 for mixed carbon steel /inox systems).

Many amines are used for condensate acid neutralization and pH elevation. The ability of any amine to protect a system effectively depends on:

- a) The neutralizing capacity,
- b) Recycle ratio and recovery ratio,
- c) Basicity,
- d) Distribution ratio, and
- e) Thermal stability of the particular amine.

Table 5 gives information of these relevant properties of amines.

Amine	Neutralizing Capacity (Note 1)	Base Strength (Note 2)	Distribution Ratio at Pressure			
			15 psig (1.1 kg/cm ²)	50 psig (3.5 kg/cm ²)	100 psig (7 kg/cm ²)	200 psig (14 kg/cm ²)
Aminomethylpropanol	2.0	66	--	--	0.5	1.0
Morpholine	2.0	3.4	0.6	0.8	1.0	1.2
GE Betz Diamine	1.2	200	0.7	1.3	1.7	2.0
Methoxypropylamine	2.0	102	---	1.6	2.5	2.4
Diethylaminoethanol	2.7	68	6.8	5.9	5.3	4.5
Cyclohexylamine	2.3	489	23.7	19.2	15.9	12.3

Notes:
 1. Neutralizing capacity: ppm (mg/L) amine required to neutralize 1 ppm (mg/L) of carbonic acid (expressed as CO₂).
 2. Base Strength at Room Temperature: Expressed as the Basicity Constant (Pkb) X 1,000,000.

Table 5. Neutralizing amines properties

Neutralizing capacity is the concentration of acidic contaminants that is neutralized by a given concentration of amine. The neutralizing capacity of an amine is inversely proportional to molecular weight (i.e., lower molecular weight yields higher neutralizing capacity) and directly proportional to the number of amine groups. Neutralizing capacity is not the only measure of a required product feed rate.

In determining product feed rates, *recycle and recovery* ratio are important factors. Because some amine is returned with the condensate, the total amine in the system is greater than the amount being fed. Recovery ratio is a measure of the amount of amine being returned with the condensate.

Basicity is the amine's ability to boost pH after neutralizing all of the acid species. In chemical terms, it is a measure of an amine to hydrolyse in pure water. As the value



of K_b increases, more OH^- is formed (after all of the acid has been neutralized) and pH increases.

Figure 11 gives the effect on pure water pH at different concentrations of amines.

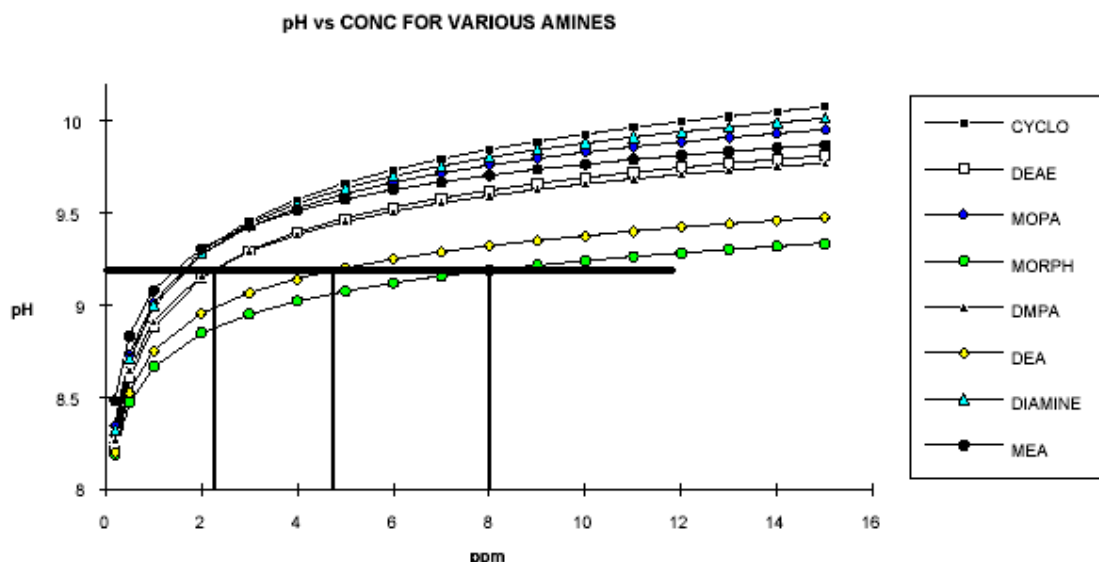


Figure 11. pH of pure water with amines dosage

In condensate systems, the *distribution ratio* of amines between steam and liquid phases is as significant as basicity or neutralizing capacity. As the steam condenses, acidic contaminants can either remain in the steam or dissolve in the liquid phase. Some contaminants, such as carbon dioxide, stay mainly in the steam phase while others, such as hydrochloric acid, go largely into the liquid phase. Neutralizing amines must be chosen according to their distribution characteristics to "chase" acidic contaminants. This choice must be tailored to the condensate system and the process contaminants.

In practice, blended products containing a variety of amines with differing steam/liquid distributions provide the best protection. To compare the relative steam/liquid distribution of amines, the distribution ratio (DR) is traditionally used. The distribution ratio of an amine is:

$$DR = \frac{AS}{AW}$$

Where, AS is defined as the quantity of amine in the steam phase and AW is the quantity of amine in the water phase at any given pressure.



Amines with a DR greater than 1.0 produce a higher concentration of amine in the vapor phase than in the liquid phase. Conversely, amines with a distribution ratio less than 1.0 produce a higher concentration of amine in the liquid phase than in the vapor phase.

Distribution ratios are not true physical constants but are a function of pressure and pH. The effect of temperature and pH of the condensation site must also be considered. In a complex condensate system, the distribution of chemicals between different condensation sites is difficult to estimate without the use of computer modeling packages specifically designed for this purpose.

GEW&PT technologies has developed the Condensate Modeling System CMS, a modeling packages that provide detailed information of the achievable pH values in different points of the system and moreover consider the effect of contaminants in the pH at temperature. This allows the selection of the best amines blend to control the right pH and protect the complete system, including BFW, boiler and steam and condensate network.

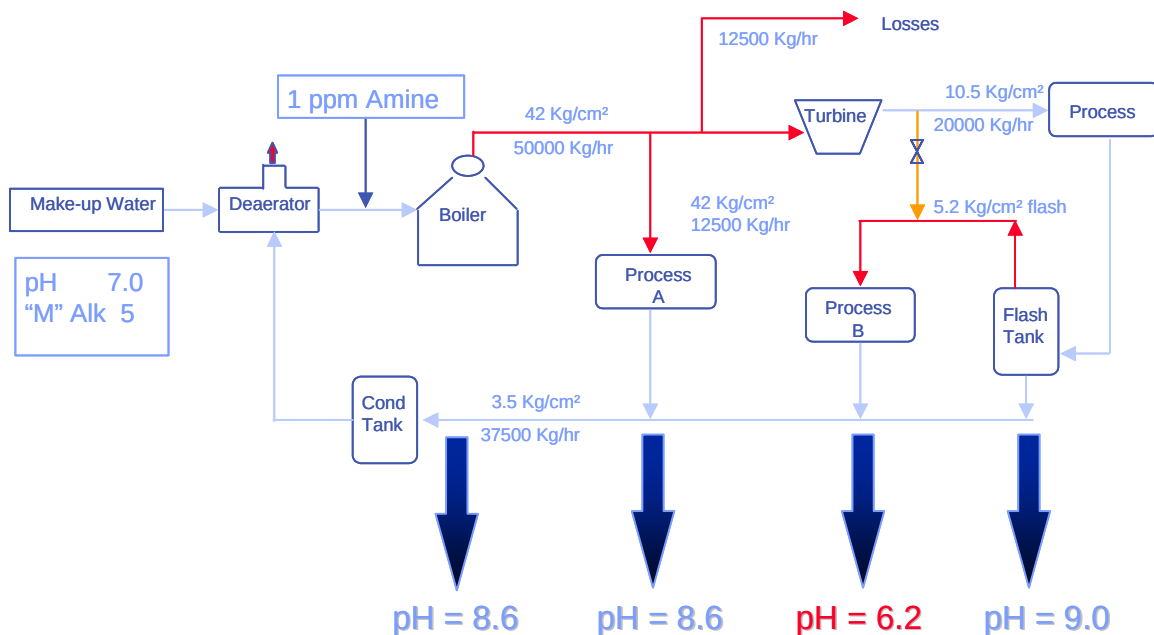


Figure 12. Condensate ph evaluation

In this example of a process plant, localized condensate corrosion on process B stream was observed. After simulating the system and taking samples for confirmation, the localized pH on B stream resulted in low pH range. In order to solve the problem two approaches could be considered: a) increasing amine dosage to all



system or b) installing a localized supplementary amine dosage. CMS Simulation program allowed evaluation of the most efficient solution.

Finally an amine feed point to the process "B" steam was added. By adding the amine here, we could significantly reduce the amount of amine required to protect the entire condensate system. CMS calculated that 8.2 ppm of amine was required to obtain a pH of at least 8.5 in process "B". Since this system has 75% condensate returns, amine recycle does have a significant impact. The amine feed rate to the feedwater was reduced by 50% because the amines added to process "B" steam are recycled back to the deaerator and find their way back to the steam and condensate. Overall, a 50% increase in amine feed was required using a satellite feed system instead of 490% with a single feed-point.

All organic chemicals exposed to a high-temperature, alkaline, aqueous environment eventually degrade to some degree. Most amines eventually degrade to carbon dioxide and/or acetic acid and ammonia. The time required varies greatly with different amines. The most stable amines commonly used are Morpholine and Cyclohexylamine. These remain substantially intact at pressures up to 170 Barg.

Ammonia as mentioned in before has an impact on copper corrosion, so unless no copper or copper alloy is present ammonia is not recommended.

When copper or copper alloys are not present and ammonia is used, the combination with another amine with lower distribution ratio will help to reduce corrosion on Phase Transition Zone (PTZ), as ammonia distribution ratio is too high to protect it.

Copper corrosion will impact in iron corrosion due to galvanic corrosion when soluble copper is present in water.

Reducing copper corrosion by:

- Adjusting proper pH range
- Minimizing oxygen concentration (in next section we will discuss this topic)
- Avoiding ammonia dosage, or using amines with high thermal stability and using oxygen scavengers with little impact on ammonia concentration

All the above will benefit not only copper corrosion also iron corrosion due to potential galvanic corrosion

4.2. Oxygen scavenging and passivation

The feed of oxygen "scavengers" is believed to serve two functions in boiler systems.



- a) First, scavengers remove residual molecular oxygen in feedwater and condensate systems to prevent oxygen-pitting attack.
- b) Second, the scavengers are believed to prevent metal release to the water and subsequent deposition in the boiler.

Most of the oxygen present in feedwater is removed in the deaerator by so-called "mechanical means". The scrubbing sections of deaerators heat incoming water by mixing it with steam. The solubility of oxygen and other dissolved gases is greatly reduced at elevated temperatures and most of the gases are vented to the atmosphere. In industrial boiler feedwater systems, such treatment usually reduces the oxygen concentration to below 20 ppb

Because oxygen can be harmful to feedwater systems even at this concentration, chemicals are generally feed to the storage section of the deaerator to react with the remaining molecular oxygen. Oxygen scavengers do not actually remove oxygen in the sense that mechanical deaeration does. Instead, the scavengers react with oxygen to render it harmless by reducing it to a lower oxidation state. Reduced oxygen is incapable of initiating pitting attack.

The success of this endeavour is dependent on two factors:

- 1) The speed (reaction rate) at which the chemical and oxygen react and
- 2) The time available for the reaction (i.e., residence time in the storage section).

For example, a scavenger removing 99% of the oxygen in a deaerator with a 30-min residence time is considered successful. In a second deaerator with a 6-min residence time, that same scavenger may only remove 10% of the residual oxygen. In this case, the scavenger is not judged as an effective scavenger.

Residence time is fixed by the deaerator storage section design and the feedwater flow rate. The speed of reaction can be directly or indirectly influenced by many factors, both chemical and mechanical, including venting efficiency, pH, oxygen concentration, absence or presence of catalysts, scavenger concentration, temperature, and the presence of contaminants.

Some of these factors are only significant in laboratory evaluations, while some affect both laboratory appraisals and actual field performance.

Scavengers are also used in boiler systems to prevent metal transport to the boiler and subsequent deposition. There are three schools of thought concerning the ability of scavengers to influence metal corrosion rates.

The most radical school suggests that scavengers directly react with metal oxides to promote the formation of passive oxide layers, even in the presence of oxygen. This is



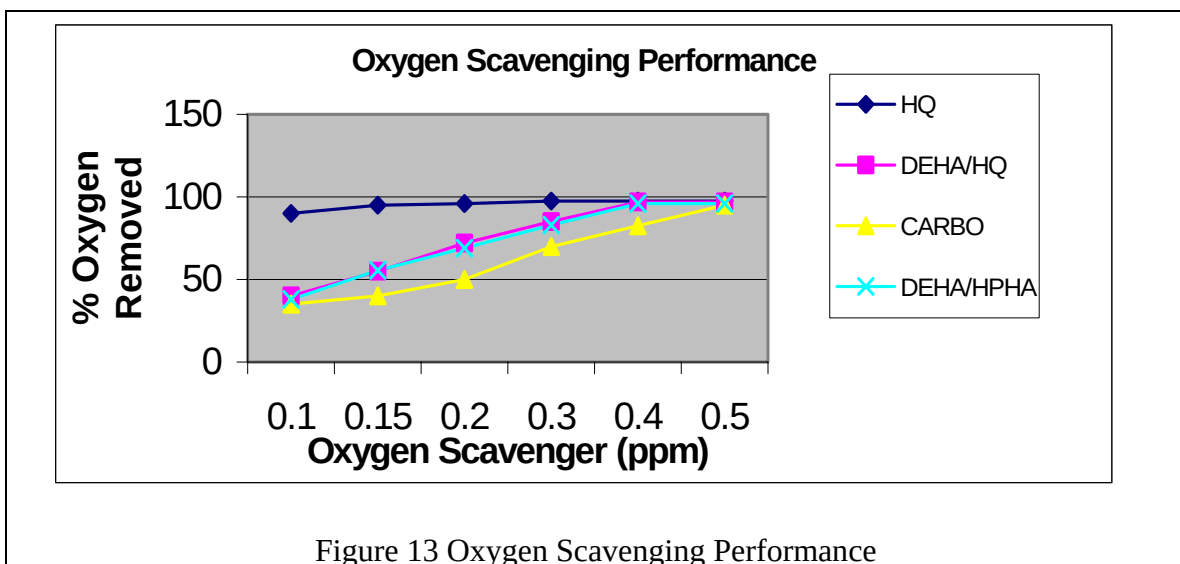
usually called "direct metal passivation". At the other extreme, the most conservative school advocates that oxygen scavengers indirectly influence metal corrosion rates by creating conditions (i.e., low oxygen concentrations) that promote the formation of a passive oxide layer. This is sometimes called "metal conditioning". The last school, which falls somewhere between the two extremes, claims that oxygen and some scavengers interact synergistically with the metal form a passive surface.

The range of oxygen scavengers available includes different active ingredients as; Hydrazine, Carbohydrazine, Diethylhydroxylamine, Hydroquinone, sulphite, ascorbic acid...is wide and with different pros and contras.

Many other articles have explained in detail differences between different oxygen scavengers. In this paper we will focus on medium to high-pressure boilers with demineralized water and deaerators. And we will compare the three ones more commonly used, Hydroxylamines, Carbohydrazine and Hydroquinone.

The three products are good to reduce oxygen concentration in boiler feed water storage tank. There fore desired concentration of oxygen in boiler feed water section is achieved.

The comparison between Alkanol Hydroxilamines as Diethylhydroxylamine or Hydroxypropylhydroxylamine, Carbohydrazine and Hydroquinone can start based in the fate and effect. In general, the alkanol Hydroxilamines, have measurable faster reaction rates with oxygen under boiler feedwater conditions. See figure 13.



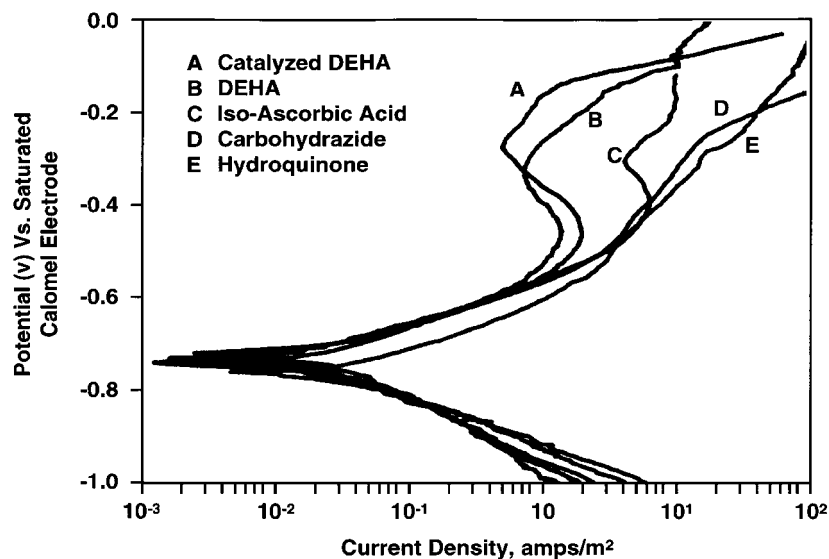
The working mechanism in his reaction with Oxygen for Diethylhydroxylamine or Hydroxypropylhydroxylamine is basically scavenging of oxygen. Eliminates the



oxygen from the water avoiding electrochemical reduction of oxygen at cathodic areas on the metal surface. This effectively inhibits one of two key electrochemical processes driving the corrosion reaction. The initial reaction between DEHA/HPHA and oxygen occurs rapidly.

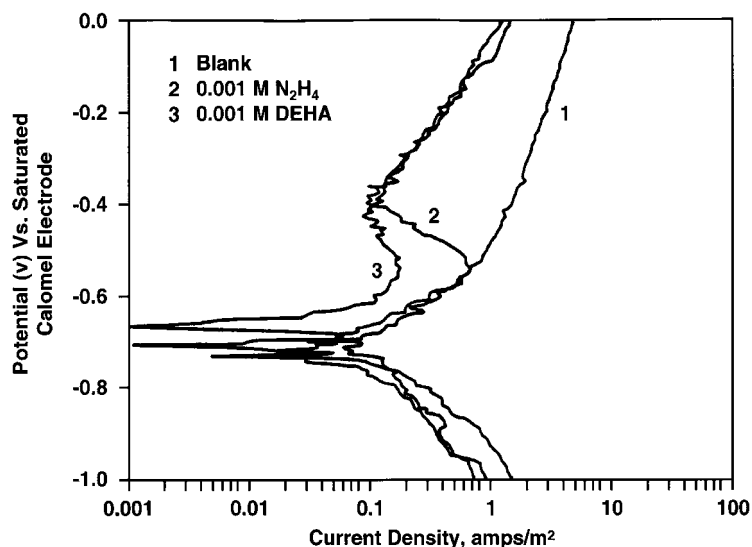
The second mechanism is related to the activity as passivator of the Alkanol Hydroxilamines. By providing a reducing environment the electrochemical corrosion process that drive the metal loss at anodic surfaces on the metal is controlled and hence allowing to maintain iron in a lower oxidation state.

Different studies have been done to determine the real passivation capacity. As mentioned before different schools may explain these phenomena in different ways, but in pilot studies and on field Hydroxylamines have demonstrated a higher passivation capacity compared to Carbohydrazine and Hydroquinone.



Polarization curve for 1010 mild steel at 25°C in the presence of oxygen scavengers at 150 mg/L at pH 8.0

Figure 14. Polarization curve – Passivation Effect.



Polarization curve for 1010 mild steel at 25°C in the presence of hydrazine and diethylhydroxylamine under laminar flow conditions at pH 8.0 relative to a blank.

Figure 15. Polarization curve Hydrazine vs. Hydroxylamines.

Polarization curves show at the end the ability of oxygen scavengers to promote passivation of metal surface. In the Figure 9 and 10 we can identify Hydroxylamines as the more powerful passivation capacity compared to other oxygen scavengers.

Very low dissolved oxygen levels combined with reducing conditions and elevated temperatures result in formation of a passive magnetite layer on the iron surface temperatures as low as 55°C

Another important fact is the distribution ratio. As mentioned in the amine section, the distribution ratio is the relative distribution of the compound between the vapour phase and the liquid phase at certain pressure.

Substance	Pressure	
	200psig (14 bar)	1,000psig (69 bar)
DEHA	3.5	4.0
Hydrazine	0.15	0.8
Hydroquinone	<0.1	<0.1
Carbohydrazide	nil	nil
Erythorbate	nil	nil

Table 6 . Oxygen Scavengers distribution ratios



As shown in Table 6 DEHA hydroxylamine has the highest distribution ratio between them. As oxygen gas would mainly leave the boiler to the steam phase in case it is present in boiler feed water, higher concentration of oxygen scavenger in the steam phase will better protect the steam drum itself and also all steam and condensate network.

In some cases we may have some air intrusion, oxygen intrusion, in some condensate vacuum sections or atmospheric tanks, in those cases the presence of some oxygen scavenger reduces iron and copper corrosion, allowing less metal transport to boiler. In addition to the oxygen scavenger reaction to oxygen, the ability of Hydroxylamines to passivate the metal also influences in this phenomena.

In different plans an effective iron reduction has been observed when replacing another oxygen scavenger by hydroxylamines.

Regarding the oxygen passivation activity, a clear example is the iron licked up during start up after a plant shutdown. Normally shutdown conditions strongly affect the protective metal oxide layer. In order to evaluate the performance behaviour of the Hydroxylamines, iron picked up from the condensate system can be measured.

The figure 16 shows the reduction in iron pick up in condensate system working with weekly shutdowns with Carbohydrazide control based versus the DEHA/HPHA (Hydroxylamines) control, while for the same plant the amount of iron after the magnetic filter. Considering that the total condensate recovered per hour is of 50 tn/h the reduction achieved in the iron pick up is very relevant.

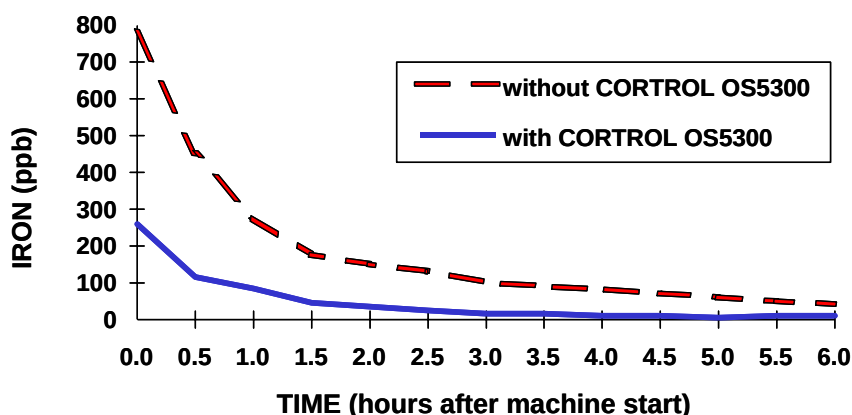


Figure 16. Iron reduction after boiler layout



5. Increasing boiler metal transport and minimizing internal iron production

Iron oxides depositions and build up control is a major goal for a reliable boiler operation in refinery and petrochemical industry. In fact the different recommended water guidelines for Boiler Feed water and Boiler water have it as an essential objective. The table 7 and 8 shows the target values for ASME and EU guidelines.

Boiler Feed Water ASME / (EN12952-12)	LP 10 bars	MP 25 bars	HP 45 bars	UHP 100 bars	UHP * 100 bars CC<0.2 us/cm
Oxygen, ppb O ₂	< 7 / < 20	< 7 / < 20	< 7 / < 20	< 7 / < 20	< 100
Iron, ppb Fe	< 100 / < 50	< 50 / < 30	< 25 / < 20	< 10 / < 20	< 20
Copper, ppb Cu	< 50 / < 20	< 25 / < 10	< 20 / < 3	< 10 / < 3	< 3
pH	8.3-10 / > 9.2	8.3-10 / > 9.2	8.3-10 / > 9.2	8.8-9.6 / > 9.2	> 9.2
TOC, ppm C **	< 1 / -	< 1 / -	< 0.5 / < 0.5	< 0.2 / < 0.2	< 0.2

*For BFW with Cation conductivity < 0,2 us/cm

**Excluding added chemicals for boiler treatment

Table 7. Boiler Feed Water recommended limits

Boiler ASME / (EN12952-12)	LP 10 bars	MP 25 bars	HP 45 bars	UHP 100 bars	UHP * 100 bars CC<0.2 us/cm
Silica, ppm SiO ₂	< 150 / < 80- 160*	< 90 / < 70- 120*	< 30 / < 25- 30*	< 2 / < 2	< 2
Conductivity, us/cm 25°C	< 5400 / < 1500	< 4600 / < 1500	< 1500 / < 1300	< 150 / < 150	< 100

*Related to boiler water alkalinity. Higher boiler water alkalinity higher silica limit

Table 8. Boiler Feed Water recommended limits

European EN 12952-12:2003 guidelines consider different boiler feed water possible qualities. For refinery and petrochemical sector we consider demineralized water. Demineralized water may be slightly different from site to site and also final boiler feed water may have a small amount of contaminants from condensate return, so we consider in tables two different types of boiler feed water, the first one will fit with many industrial application (considering boiler feed water direct conductivity < 30 us/cm) and the second one may be available in some high pressure plants (with boiler feed water cation conductivity < 0.2 us/cm).

In both guidelines iron and copper concentrations in boiler feed water are restricted to ppb levels, as metal load impacts on boiler fouling and potential failure.

Here below we are going to summarize how to approach different aspects in boiler internal water treatment in order to succeed and minimize boiler fouling and final tube failure.



Several internal treatment programs may be used when using demineralized water in chemical and petrochemical industry.

- All Organic Treatment
 - Polymer treatment
 - Amine Volatile Treatment
- Phosphate based Treatment

All organic polymer treatment is a phosphate free boiler internal treatment. Polymer and some free mineral alkalinity are used to stabilize magnetite layer and neutralize potential contaminants. As free mineral alkalinity is used in some cases caustic gauging has been observed.

Amine Volatile Treatment is the treatment of choice for high pressure and high purity water. Amine Volatile Treatment will allow producing high purity steam to turbines. In cases steam blanketing or tube dry out phenomena are described, this treatment also is the first choice. In systems with some boiler carryover this approach has improved the steam purity. The main disadvantage of this treatment is the lower buffering capacity and no dispersion capacity on iron or other contaminants in boiler feed water, so condensate polishing or special monitoring is recommended.

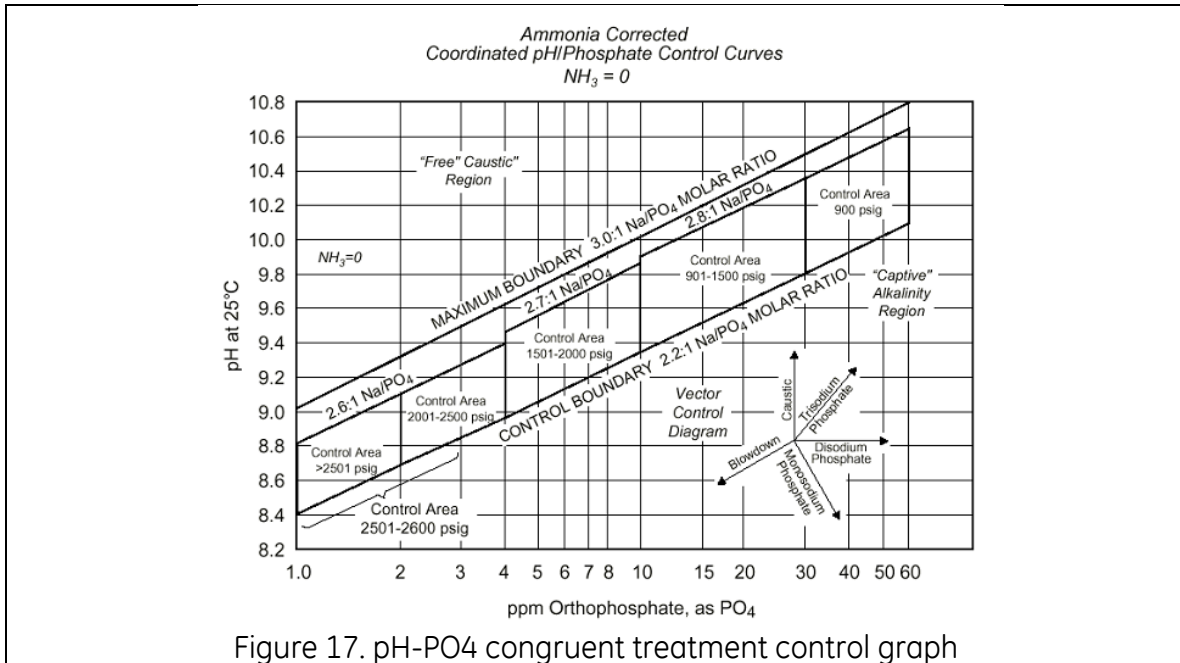
From the universe of pH-PO₄ treatment approaches, the treatment of choice is the Alkaline Phosphate Treatment APT. The APT is basically a slight modification of the pH-PO₄ congruent approach.

The APT employs 4 to 10 ppm of trisodium phosphate (TSP expressed as PO₄) and less than 1 ppm of sodium hydroxide (NaOH) to buffer the boiler water against small amounts of acidic feedwater contamination. It is most applicable where phosphate hideout is of concern and high solids cooling water may contaminate the boiler feedwater.

With an APT program, minimum sodium to phosphate mole ratio of 2.8 to 1.0 is maintained so small amounts of acidic condenser leakage are readily neutralized and acid phosphate corrosion is averted even under high temperature hideout conditions.

The controls allow up to 1 ppm of sodium hydroxide in the boiler water. Therefore, under-deposit caustic corrosion in the boiler and caustic cracking of steam system components due to boiler water entrainment in the steam are possible.

In systems using APT control with relatively low phosphate concentrations (less than about 5 ppm PO₄), some corrections must be made to the control ranges shown on Figure 17. If necessary, corrections to Figure 12 can be developed for ammonia and/or neutralizing amines using the GE W&PT Condensate Modelling System (CMS) computer software package.



To better control the iron deposition this programs are better complemented with polymer dispersant. The application of a boiler water dispersant will help maintain clean heat transfer surfaces protecting the steam generator from both overheating and corrosion failures. The selection of the suitable dispersant should consider the primary contaminant: Iron oxide.

The High Temperature Polymers HTP-2 is basically Poly (isopropenyl phosphonic acid), PIPPA polymer has proven highly effective Figure 18, significantly outperforming all other treatments.

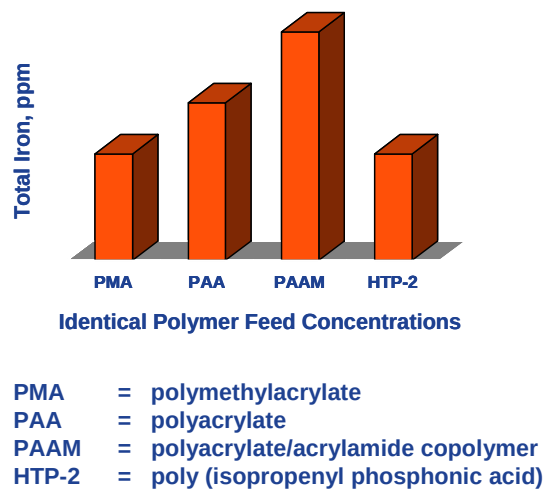


Figure 18, Performance data for iron oxide production and polymer type in use



The comparison of the PMA and PIPPA polymers are shown in Figure 14, below:

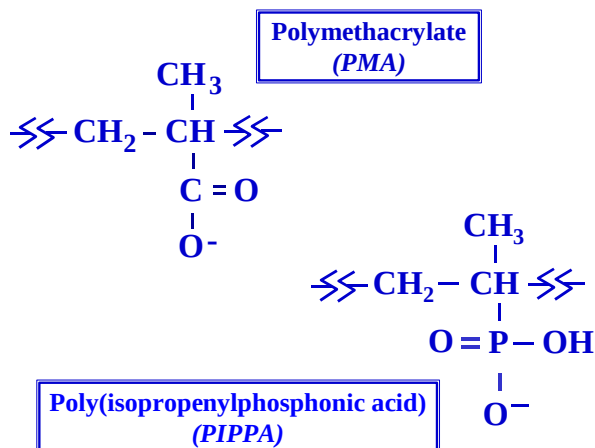


Figure 19

HTP2 was designed with the methyl group on the polymer backbone, reducing any significant corrosion potential from overfeed, and a phosphonate group replacing the carboxylate group in the molecule, to enhance the iron oxide dispersion. The phosphonate functionality is a known and effective metal oxide dispersant. With HTP2, there is a strong interaction between the phosphonate group and the iron oxide.

Internal treatment programs, containing the HTP2 molecule, maintain optimum metal oxide deposit control performance under the higher pressures and longer residence times than traditional polymers with carboxylate functional groups. This has been consistently demonstrated both in research-scale test boilers, and in numerous commercial applications of HTP2, following the application of carboxylated polymers. HTP2 provided superior results in terms of both boiler tube iron oxide deposit control and blowdown rejection of iron oxide from the boiler.

The major decomposition product of HTP2 is ortho-phosphate. The de-phosphorylation of HTP2 is dependent on temperature/pressure, and boiler residence time. The de-phosphorylation rate is slightly variable, dependent on the individual system dynamics. The PO_4 is used then to control the system in a Alkaline Phosphate treatment approach, balancing the advantages of the pH- PO_4 program with the effectively performance of the PIPPA polymer in iron oxides dispersion.

The dephosphorylation of the PIPPA molecule does not reduce the ability of the polymer to disperse metallic oxides. Our research data and field application data, has clearly shown that the partially dephosphorylated polymer retains excellent



efficacy as an oxide dispersant, over the full range of boiler pressures and retention times for which it is recommended and applied.

As dispersants are basically organics compounds, they increase the cation conductivity at high-pressure systems. In those facilities where it is necessary to meet strict steam cation conductivity limits the application of a boiler water polymer will usually cause those limits to be exceeded. Then based in relevance of the problem to treat and the final effect on Cation Conductivity a decision should be taken to protect the system.

Figures 20, 21 and 22 give the values for an application in a 42 Bars petrochemical plant boiler after start up of the HTP-2 treatment program, replacing and trisodium phosphate approach.

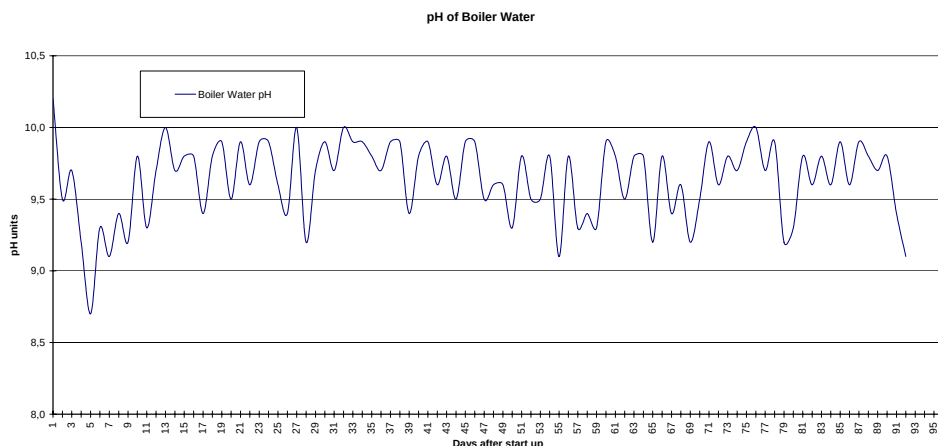


Figure 20

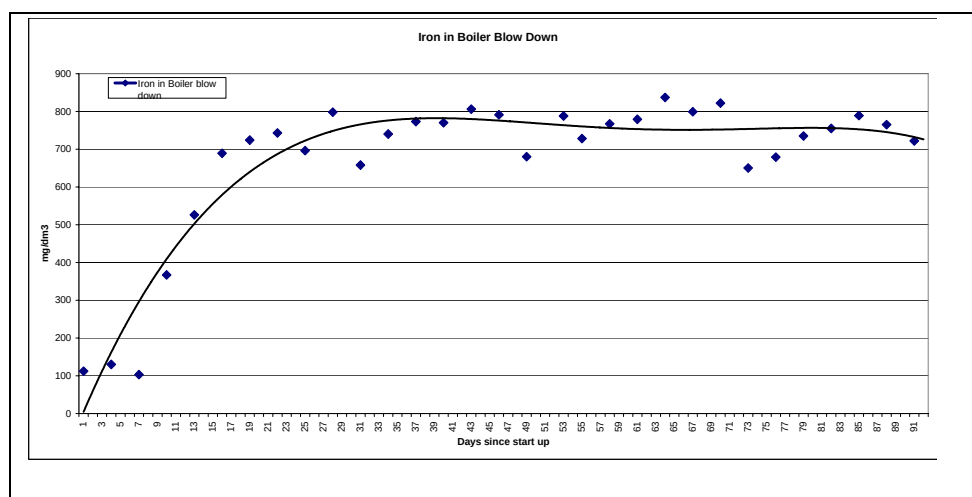


Figure 21

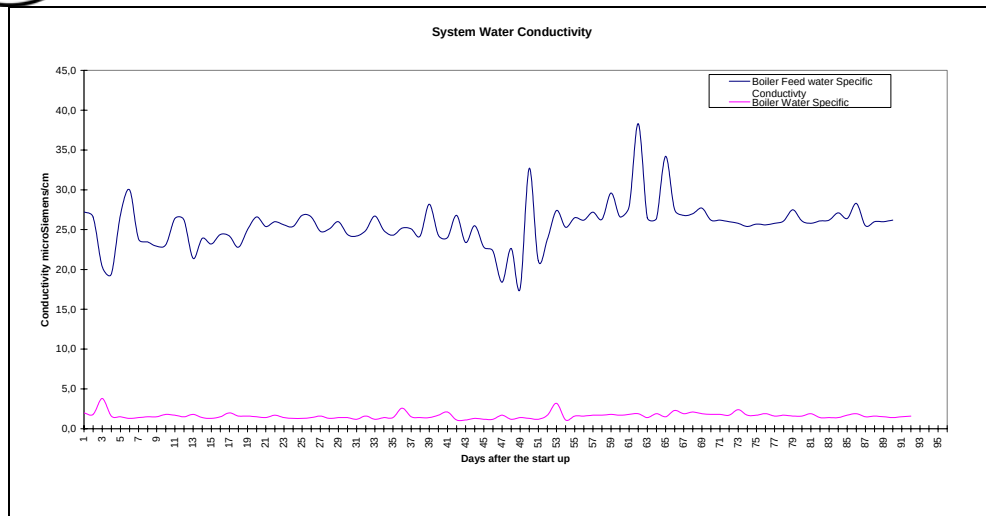


Figure 22

Conclusion

Boilers treatment in refinery and petrochemical industry is a difficult task due to the elevated heat fluxes the boilers are submitted in localized areas. In order to reduce the potential risk of deposition of iron oxides the boiler users trend to apply the consensus guidelines for Boiler feedwater and boiler water.

Even in this situation small amounts of iron may create, when localized, an important increase of the deposits, DWD. The deposits are mainly composed by iron oxides, and the iron oxides have two main sources. One is internal and related to the direct reaction of the iron with the water, and the other is external and is linked to the introduction of iron oxides from others parts of the system.

Effective amine and oxygen scavenger selection reduces boiler feed water iron load to boiler minimizing further potential fouling. Superior effectiveness of Hydroxylamines oxygen scavengers has been observed in complex condensate network systems.

The most effective way to manage this iron introduction is with polymers, and the PIPPA molecule has demonstrate that works much better than any other polymer for controlling the iron deposition, by increasing the metal transport in boiler.



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