Reducing Corrosion and Potential Boiler Failure with Superior Iron Transport Technology

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2nd Technical Meeting of NACE Jubail Section –KSA
27th January 2009

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Reducing Corrosion and Potential Boiler Failure

- Introduction
- Pre – Boiler corrosion mechanisms
- Internal boiler corrosion
- Deposition and tube failure
- Reducing boiler metal load
- Increasing internal boiler metal transport
INTRODUCTION

Demineralized water as boiler make up is an standard in Middle East for Refinery and Chemical / Petrochemical Industry.

Therefore traditional calcium, magnesium or silica scaling is not anymore the main issue in boiler reliability

Condensate contamination with process streams or iron and copper from pre-boiler corrosion have become the main contaminants arriving to boilers.

In this presentation we will focus on iron and copper contaminants.

Reducing iron and copper corrosion and avoiding metal deposition on high flux transfer areas will be reviewed.
Refinery and Chem/Petrochemical Boilers

All topics described will be of applicability to **auxiliary boilers and Waste Heat Boilers**.

Waste Heat Boilers units are widely used in Chemical and Petrochemical industry (Ethylene, EG, PE, H2 plants,...) and in Refinery in convection section of furnaces.

• These units are directly **linked to plant production**.

• Units working at **critical conditions**:
  • High pressures and localized high Heat Flux rates
  • Design of heat exchange area

• Huge Shutdown cost
Pre-boiler corrosion

*Metal transport to boiler from external equipments*

All corrosion mechanisms in steam, condensate and boiler feed water section that will impact in higher metal load to boiler

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

In absence of oxygen iron corrodes to produce Fe$_3$O$_4$ magnetite.
This magnetite forms a nonporous, tightly adherent layer on the metal surface that greatly retards any further oxidation reactions.

In presence of oxygen the reaction is modified and pitting corrosion is developed.
Pre-boiler corrosion
pH related metal protective layer stability

The stability of passivating $\text{Fe}_3\text{O}_4$ magnetite layer is critically dependent on pH and temperature.

Some air intrusion may reduce condensate pH as Carbonic Acid is formed.

Proper amine – ammonia treatment will be discussed latter.
Pre-boiler corrosion
Ammonia Cu corrosion / Galvanic corrosion

Corrosion on copper and copper alloys is influenced by pH and also oxygen and ammonia concentrations.

\[
\frac{1}{2}O_2 + 2Cu + 4NH_3 + H_2O \rightarrow 2Cu(NH_3)_2^+ + 2OH^- 
\]

The oxygen will then oxidize the bi-ammonia group to tetra-ammonia

\[
2Cu(NH_3)_2^+ + \frac{1}{2}O_2 + H_2O + 4NH_3 \rightarrow 2Cu(NH_3)_4^{+2} + 2OH^- 
\]

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

\[
Cu(NH_3)_4^{+2} + Fe^0 \rightarrow Cu^0 + 4NH_3 + Fe^{+2} 
\]
Pre-boiler corrosion
Ammonia Cu corrosion / Galvanic corrosion

Steam condensate copper alloy tube corrosion due to ammonia

Boiler tube plating due to copper in boiler feed water
Pre-boiler corrosion
Erosion – Corrosion

Erosion is a corrosion phenomena affected by:

- **Velocity** (frequently is the major factor. Liquid impingement due to high velocity in some steam or condensate areas)

- **Geometry** (in changes of direction of fluid flow, in pressure changes, in abrupt piping discontinuity)

- **Metallurgy** (higher alloy material will increase resistant)

- **Water Chemistry** (Fe$_3$O$_4$ stability conditions will help)
Pre-boiler corrosion
Flow Accelerated Corrosion

FAC is a particular type of erosion.

Is quite site specific.

**Single-phase** (all water is in the liquid phase) or **two-phase** (mixture of liquid and steam) FAC may occur.

Maximum attack at 130-150°C for single-phase and 150-200°C for two-phase flow.

Increasing feed water **pH** is known to reduce FAC.

A strongly reducing environment (ORP) is known to increase FAC, avoiding overdosing of oxygen scavenger can be beneficial.
Internal-boiler corrosion
Deposition of external metal oxides supply and internal metal production

Iron or copper supply to boiler due to pre-boiler corrosion will increase boiler tube fouling unless proper chemical treatment is applied.

Iron fouling on high heat transfer areas may result in corrosion:

• Caustic gauge corrosion
• Acid corrosion
• Hydrogen Embrittlement

Are usually influenced by boiler tube deposit formation.
Internal-boiler corrosion
Caustic Gauge

Concentration of caustic in boiler is normally not high enough to create corrosion, but caustic concentration can occur by localized boiling beneath porous deposits.

Several phosphate treatment to limit the free caustic concentration, and minimization of deposit layer will reduce it.
Internal-boiler corrosion
Acid Corrosion

In some cases deposit impacts on acid corrosion as concentration of contaminants in non-homogeneous porous deposit may produce pH depression.

Acid hydrolysis of chloride compounds from cooling water intrusion due to condensate failure may produce acid corrosion

\[
\begin{align*}
\text{MgCl}_2 + H_2O & \rightarrow 2HCl + \text{Mg(OH)}_2 \\
\text{Fe}_3\text{O}_4 + 8\text{HCl} & \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O} \\
2 \text{Fe} + 2\text{H}^- & \rightarrow 2\text{Fe}^{+2} + \text{H}_2
\end{align*}
\]
Internal-boiler corrosion
Hydrogen Embrittlement

Usually high pressure (>105 kg/cm²)
Usually associated with low pH excursions
Formation of nascent hydrogen (H₀)
at the boiler tube surface
Hydrogen permeates the tube
where it can react with:
  a) Iron carbides to form methane gas
  b) Other hydrogen atoms to form hydrogen gas
Gases collect at grain boundaries to increase pressure
Micro fissures occur within the material and weaken the tube
Brittle failure - often blows out a “window”
Deposit can act as concentration areas for acidic compounds
Deposition
High Heat Flux Areas Analysis

1\textsuperscript{st} Need to be conscious of consequences of deposits in a tube

- Energy Loses versus deposit thickness and composition
- Metal temperature changes due to deposition
- Thermal tube degradation or tube failure due to overheating

2\textsuperscript{nd} How to analyze the problems

- What is Deposit Weight Density, how is it measured, criteria
- Deposit composition and relation with the DWD
- pH @ temperature calculation
Energy Loss from Scale Deposits
(from Energy Conservation Programme Guide for Industry & Commerce)
Metal temperature rise versus layer thickness and Heat Flux

Magnetite Layer Thickness effect to metal temperature

- 60 microns
- 200 microns
- 650 microns

Heat Flux in MMcal/m²/h

Metal temperature increase °C

650 microns
Deposition
Thermal tube degradation or tube failure due to overheating

Metal grain structure undergoes thermal degradation (oxidation) at elevated temperatures and as a result the tensile strength of the metal is dramatically reduced.

At 450-540°C, carbide spheroidization or graphitization occurs and overheating may take place over a period of months or years, producing a Long Term Overheating.
Deposition
High Heat Flux Areas Analysis

1st Need to be conscious of consequences of deposits in a tube

- Energy Losses versus deposit thickness and composition
- Metal temperature changes due to deposition
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2nd How to analyze the problems

- What is Deposit Weight Density, how is it measured, criteria
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Deposit Weight Density – Cleaning Criteria

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The measure of the total deposit weight amount per unit of surface is called Deposit Weight Density.

DWD gives an indication whether the surface has too much deposit and risk for long term overheating.
Surface deposit 2 layers model

Internal magnetite dense and adherent protective layer

External porous. It is a resistance to heat flux transfer, creating a rise in tube temperature

Dynamical nature
Surface deposit growth model?

Iron Oxides are main component, they comes from:
- External Fe-ions dissolved into the BFW due to corrosion in pre-boiler and condensate systems.
- By direct production of magnetite under operation conditions.

\[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]

Some interesting data....
EN-12952-12 and ASME guidelines for BFW

<table>
<thead>
<tr>
<th>Boiler Feed Water ASME / (EN12952-12)</th>
<th>LP 10 bars</th>
<th>MP 25 bars</th>
<th>HP 45 bars</th>
<th>UHP 100 bars</th>
<th>UHP * 100 bars CC&lt;0.2 us/cm</th>
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</thead>
<tbody>
<tr>
<td>Oxygen, ppb O2</td>
<td>&lt; 7 / &lt; 20</td>
<td>&lt; 7 / &lt; 20</td>
<td>&lt; 7 / &lt; 20</td>
<td>&lt; 7 / &lt; 20</td>
<td>&lt; 100</td>
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<tr>
<td>Iron, ppb Fe</td>
<td>&lt; 100 / &lt; 50</td>
<td>&lt; 50 / &lt; 30</td>
<td>&lt; 25 / &lt; 20</td>
<td>&lt; 10 / &lt; 20</td>
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<tr>
<td>Copper, ppb Cu</td>
<td>&lt; 50 / &lt; 20</td>
<td>&lt; 25 / &lt; 10</td>
<td>&lt; 20 / &lt; 3</td>
<td>&lt; 10 / &lt; 3</td>
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<tr>
<td>pH</td>
<td>8.3-10 / &gt; 9.2</td>
<td>8.3-10 / &gt; 9.2</td>
<td>8.3-10 / &gt; 9.2</td>
<td>8.8-9.6 / &gt; 9.2</td>
<td>&gt; 9.2</td>
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<tr>
<td>TOC, ppm C **</td>
<td>&lt; 1 / -</td>
<td>&lt; 1 / -</td>
<td>&lt; 0.5 / &lt; 0.5</td>
<td>&lt; 0.2 / &lt; 0.2</td>
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*For BFW with Cation conductivity < 0.2 us/cm

**Excluding added chemicals for boiler treatment

Typical iron limits are in ppb values, 20 ppb Fe according EN12952-12 for HP boilers
Iron introduced per year in a Boiler with BFW of 100 tn/h

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Iron i
Iron that should be found in Boiler water

Iron in Boiler Water at different cycles

What really happen with a Na3PO4 treatment or NH3 control?, only 30% of feed iron is transported out of the boiler !!!!!!
## Consequences in DWD of 20 ppb Fe

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- **Boiler Pressure**: 135 Barg
- **Iron Transport**: 30%
- **Fe in BFW**: 20 ppb
- **Steam Rate**: 100 tn/h
- **Specific Steam Rate**: 100 kg/m²/h
- **Total Surface**: 1000 m²
- **Ratio DWD in HF sections**: 3 - 5 times
- **DWD Calculated average**: 17,5 g/m²/y
- **DWD in HF section calculated**: 30- 40 g/m²/h

*30% in one year*
Internal Layer Growth Effect in DWD

\[ 3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]

Increase in DWD associated may be 60 – 120 g/m²/y

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Boiler deposits conclusion

Even though the BFW iron level is low and the magnetite growth is limited and controlled, the DWD may increase very fast creating high risk for HP boilers and WHB in Refinery and Petrochemical Industry.

Major concerns are:

- Iron contamination from condensate and feedwater line corrosion and erosion
- Magnetite growth linked to pH control in BW. (*pH*@*temperature*, concept)
- Iron transport in boiler
Reducing boiler metal load
Amine Selection

Ammonia and amines are used to neutralize the acid generated by the dissolution of carbon dioxide or other acidic process contaminants in the condensate and boiler feed water section.

The ability of any amine to protect the system effectively depends on:

- Neutralizing capacity
- Recycle ratio and recovery ratio
- Basicity
- Distribution ratio
- Thermal stability
Reducing boiler metal load
Amine Selection

**Neutralizing capacity** is the concentration of acidic contaminant neutralized by a given amine concentration.

**Recovery ratio** is the amount of amine recovered via condensate return.

**Basicity** is the amine’s ability to boost pH after neutralizing all acid species.

**Distribution ratio** is the amount of amine in the vapor phase compared to the liquid phase at a given pressure.

**Thermal stability** defines the maximum working temperature to avoid amine degradation to ammonia, carbon dioxide or acetic acid.
Extra amine required to protect flash condensate

Isn’t there a better way?

Process “B” condensate pH is low, area vulnerable to corrosion
Amine savings: satellite feed

Satellite feed protects system with a 50% increase in amine feed instead of 490%

0.5 ppm Amine

Make-up Water

Deaerator

pH 7.0

“M” Alk 5

Boiler

42 Kg/cm²

50000 Kg/hr

0.5 ppm Amine

12500 Kg/hr

42 Kg/cm²

50000 Kg/hr

12500 Kg/hr

10.5 Kg/cm²

20000 Kg/hr

Turbine

Process A

8.2 ppm Amine

Process B

Cond Tank

Flash Tank

3.5 Kg/cm²

12500 Kg/hr

37500 Kg/hr

pH = 9.2

pH = 8.9

pH = 8.6

pH = 9.4

Losses
Reducing boiler metal load

Oxygen Scavenger Selection

Most of the oxygen present in feed water is removed in deaerator. Remaining oxygen still harmful to feed water systems is chemically removed with oxygen scavenger.

![Graph showing oxygen scavenging performance](image-url)
Reducing boiler metal load
Oxygen Scavenger Selection

Oxygen gas will go to steam phase mainly, so high distribution ratio oxygen scavengers will be where needed. In case of air intrusion on complex condensate networks high DR oxygen scavenger will provide protection all along the steam condensate system.

<table>
<thead>
<tr>
<th>Substance</th>
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<th>Pressure 1,000psig (69 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEHA</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>0.15</td>
<td>0.8</td>
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<tr>
<td>Hydroquinone</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Carbohydrazide</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Erythorbate</td>
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</tr>
</tbody>
</table>
Reducing boiler metal load
Oxygen Scavenger Selection

Pasivation promotion capacity is an important parameter for oxygen scavenger selection. Condensate and boiler feed water pasivation is essential to reduce boiler feed water iron content.

DEHA is confirmed as better pasivation agent from polarization curves.
Hydroxylamine reduce iron picked up in condensate

DEHA / HQ or DEHA/HPHA has resulted in the best choice in order to reduce metal load to boiler due to:
  a) oxygen removal performance, b) High distribution ratio and c) excellent metal pasivation promotion
Increasing boiler metal transport
Polymer Selection

In Refinery and Petrochemical industry using demineralized water for boiler make up, three typical treatment approaches could be considered.

• All Organic Polymer treatment
  Phosphate free treatment with some mineral alkalinity and polymer

• All Volatile Treatment
  Amine treatment, some mineral alkalinity from demi water

• Phosphate based treatment
  Several options, the best choice in terms of magnetite stability is APT (Alkaline Phosphate Treatment)
Alkaline Phosphate Programs

- Alkaline Phosphate Treatment:
  - 4 – 10 ppm PO4
  - Maximum 1 ppm NaOH free

- Pressures <120 bars, all will benefit from polymer dispersants
  - ✓ High Temperature Polymers to prevent iron oxide deposition - HTP
  - ✓ Long boiler water retention times. High Boiler cycles 100
  - ✓ Allowing APT-pH-PO4 programs

Fe$_3$O$_4$ stability = f (pH@t)

pH

pressure (bars)
Traditional Polymer Structures

POLYACRYLATE

POLYMETHACRYLATE

ACYRILATE-ACRYLAMIDE COPOLYMER

SULFONATED STYRENE-MALEIC ANHYDRIDE COPOLYMER
High Temperature Polymers HTP-2

Poly (isopropenyl phosphonic acid) . . . PIPPA

**HTP2** polymer has shown the higher iron transport performance in boilers, allowing reduce DWD, increase unit efficiency, and reduce potential long term overheating and caustic gauging.
Measured hydrogen levels on steam slightly declined when HTP2 was introduced.
1,500 psig boiler
Boiler Iron Transport

![Graph showing iron transport percentage over time with a significant increase at Start HTP-2 and a general declining trend.](image)
High iron transport and on line cleaning performance when used at higher dosages
Conclusions

- **Iron oxides** either internally produced or externally introduced are a major concern in HP and WHB at Chemical and Petrochemical industry using demineralized make up water.
- Iron deposit accumulation on HF areas reduces efficiency and tube life.
- **Hydroxylamine** oxygen scavengers and right amine selection for pH control is key to reduce metal transport to boiler.
- But it is essential to keep iron dispersed in boiler.
- High temperature Polymer HTP-2 (PIPPA) works two ways:
  - Providing effective dispersion
  - Supplying the Alkaline Phosphate Treatment pH-PO4 control required for magnetite stability
Thank you very much for your attention