Reducing Corrosion and Potential Boiler Failure with Superior Iron Transport Technology

Joan Estil·les / Manuel Soria

PA Manager Boiler / PA Manager and EMEA Coordinator

GE Water & Process Technologies

2nd Technical Meeting of NACE Jubail Section –KSA

27th January 2009

imagination at work

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

imagination at work

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

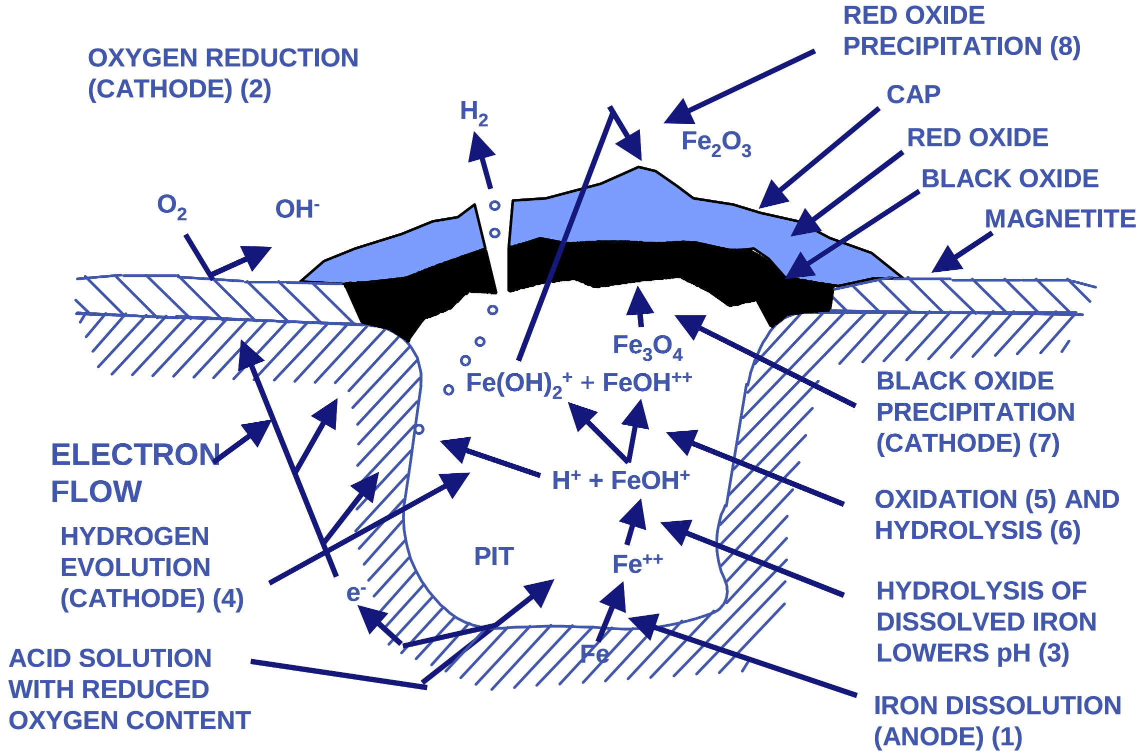
All corrosion mechanisms in steam, condensate and boiler feed water section that will impact in higher metal load to boiler

- 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_3O_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.**

imagination at work

NACE JUBAIL

Pre-boiler corrosion
pH related metal protective layer stability

The stability of passivating Fe_3O_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.

imagination at work

Pre-boiler corrosion

Ammonia Cu corrosion / Galvanic corrosion

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

$$\tfrac{1}{2}\,O_2 + 2\,Cu + 4\,NH_3 + H_2O \rightarrow 2\,Cu(NH_3)_2^{\ +} + 2OH^-$$

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

$$2\,Cu(NH_3)_2^{\ +} + \tfrac{1}{2}\,O_2 + H_2O + 4\,NH_3 \rightarrow 2\,Cu(NH_3)_4^{\ +2} + 2\,OH^-$$

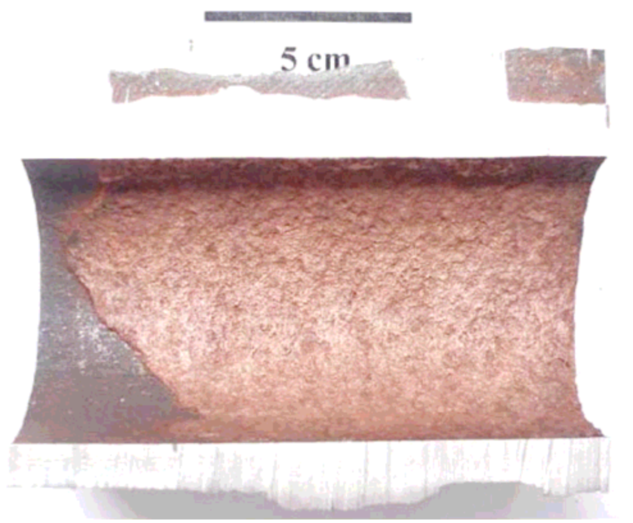
When copper corrosion occurs, and soluble copper is in water, **galvanic corrosion appears**, and steel surface plating can be observed

$$Cu(NH_3)_4^{\ +2} + Fe^0 \rightarrow Cu^0 + 4\,NH_3 + Fe^{+2}$$

Pre-boiler corrosion
Ammonia Cu corrosion / Galvanic corrosion

Steam condensate copper alloy tube corrosion due to ammonia

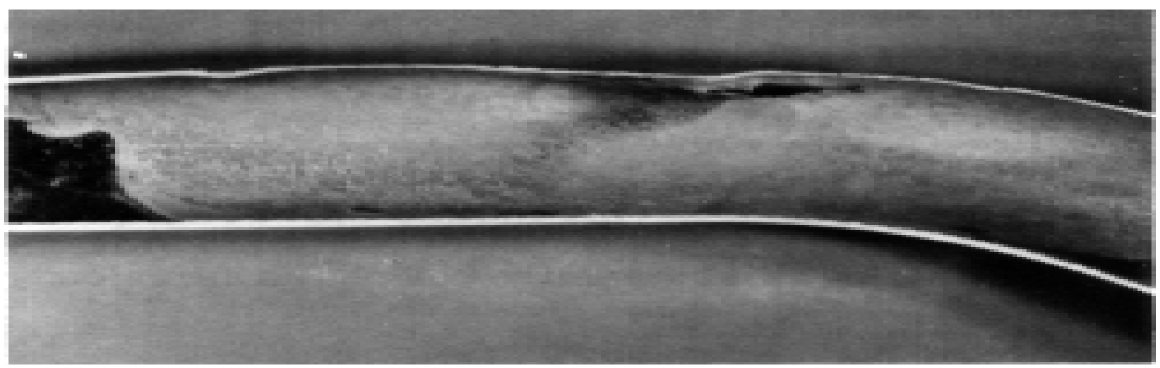
Boiler tube plating due to copper in boiler feed water



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_3O_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**:

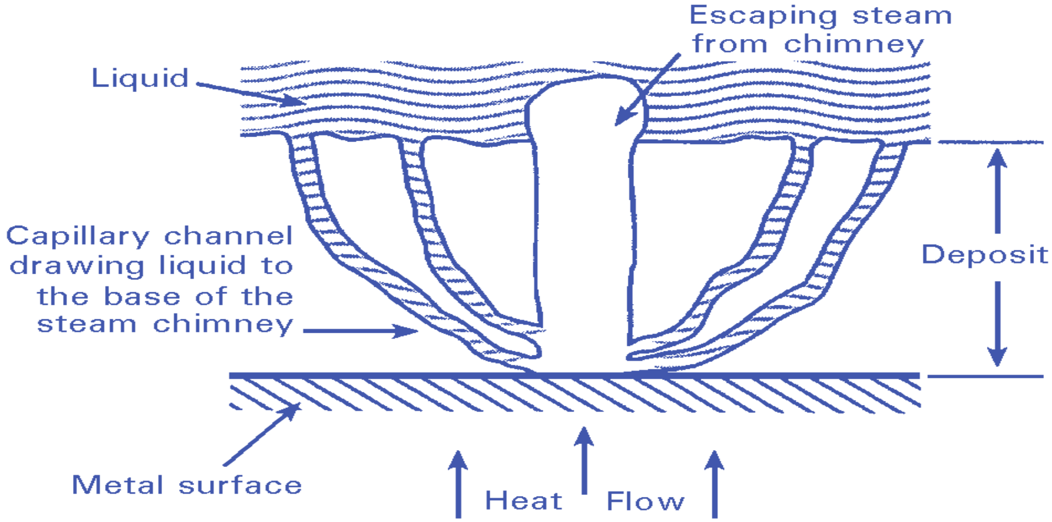
- Caustic gauge corrosion
- Acid corrosion
- Hydrogen Embrittlement

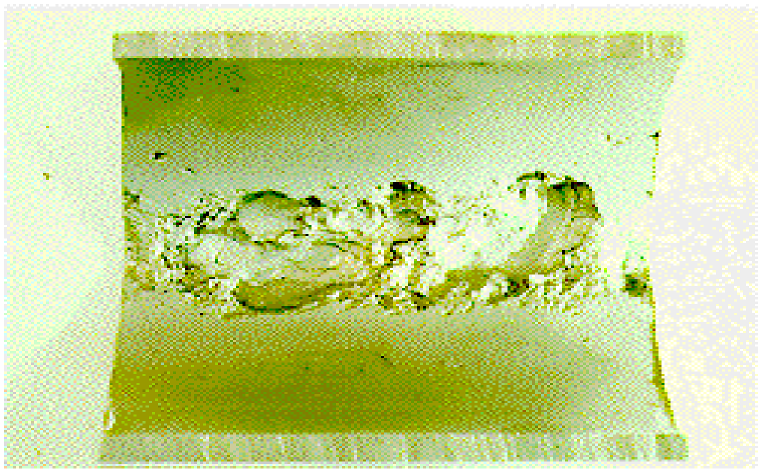
Are usually influenced by boiler tube deposit formation.

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

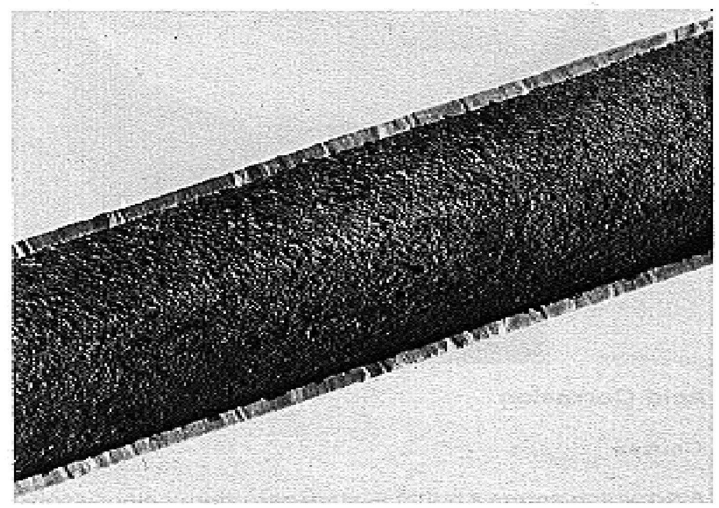
In some cases **deposit impacts on acid corrosion** as concentration of contaminants in non-homogeneous porous deposit may produce pH depression.

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

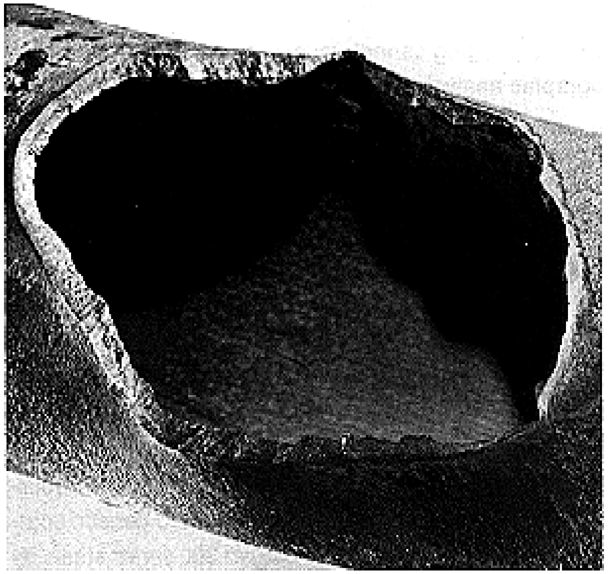
$$MgCl_2 + H_2O \rightarrow 2HCl + Mg(OH)_2$$

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$$

$$2\,Fe + 2H^- \rightarrow 2Fe^{+2} + H_2$$



Internal-boiler corrosion
Hydrogen Embrittlement



Usually high pressure (>105 kg/cm²)
Usually associated with low pH excursions
Formation of nascent hydrogen (H^O)
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

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

.

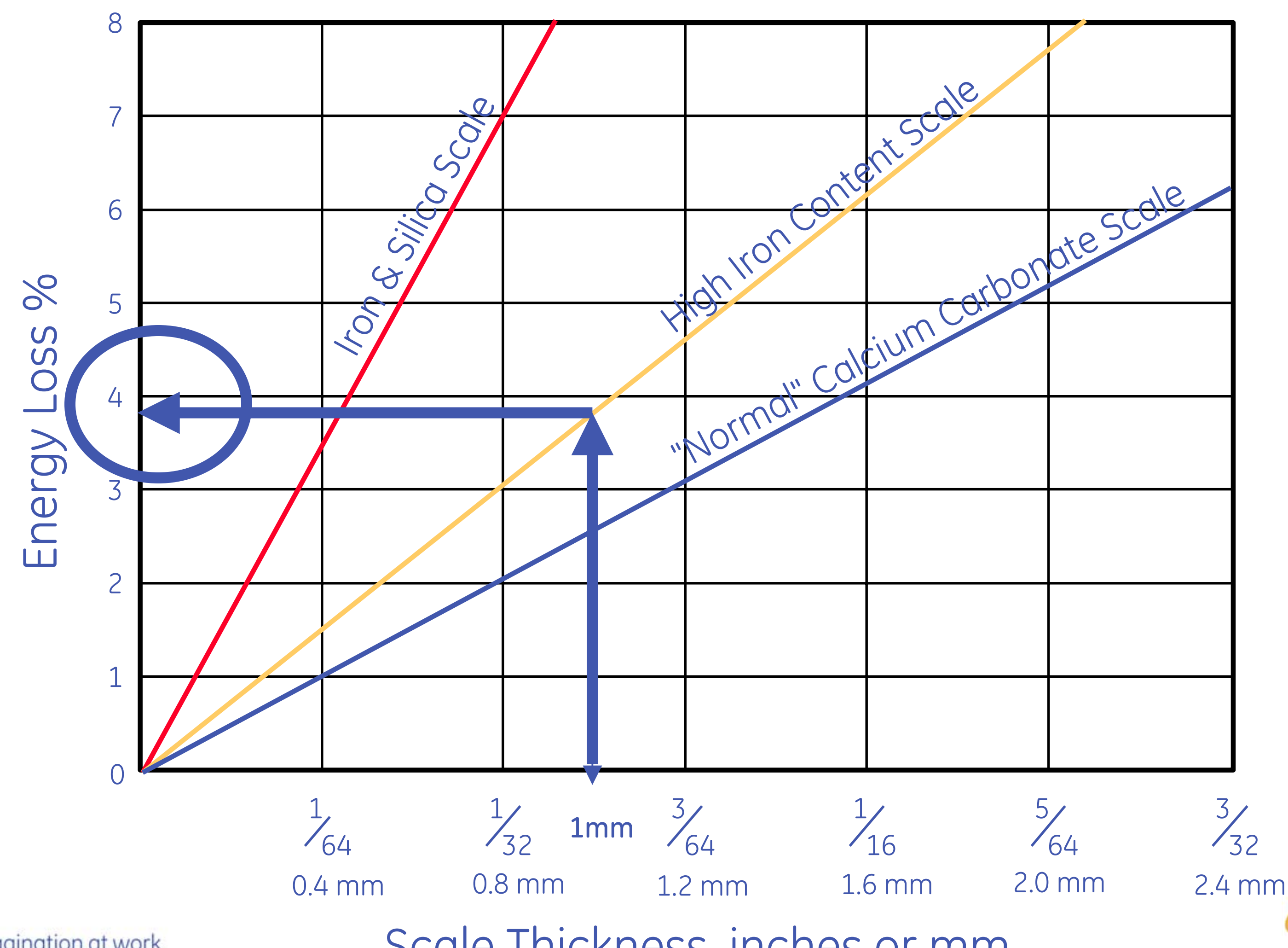
- Energy Loses versus deposit thickness and composition
- Metal temperature changes due to deposition
- Thermal tube degradation or tube failure due to overheating

2nd 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

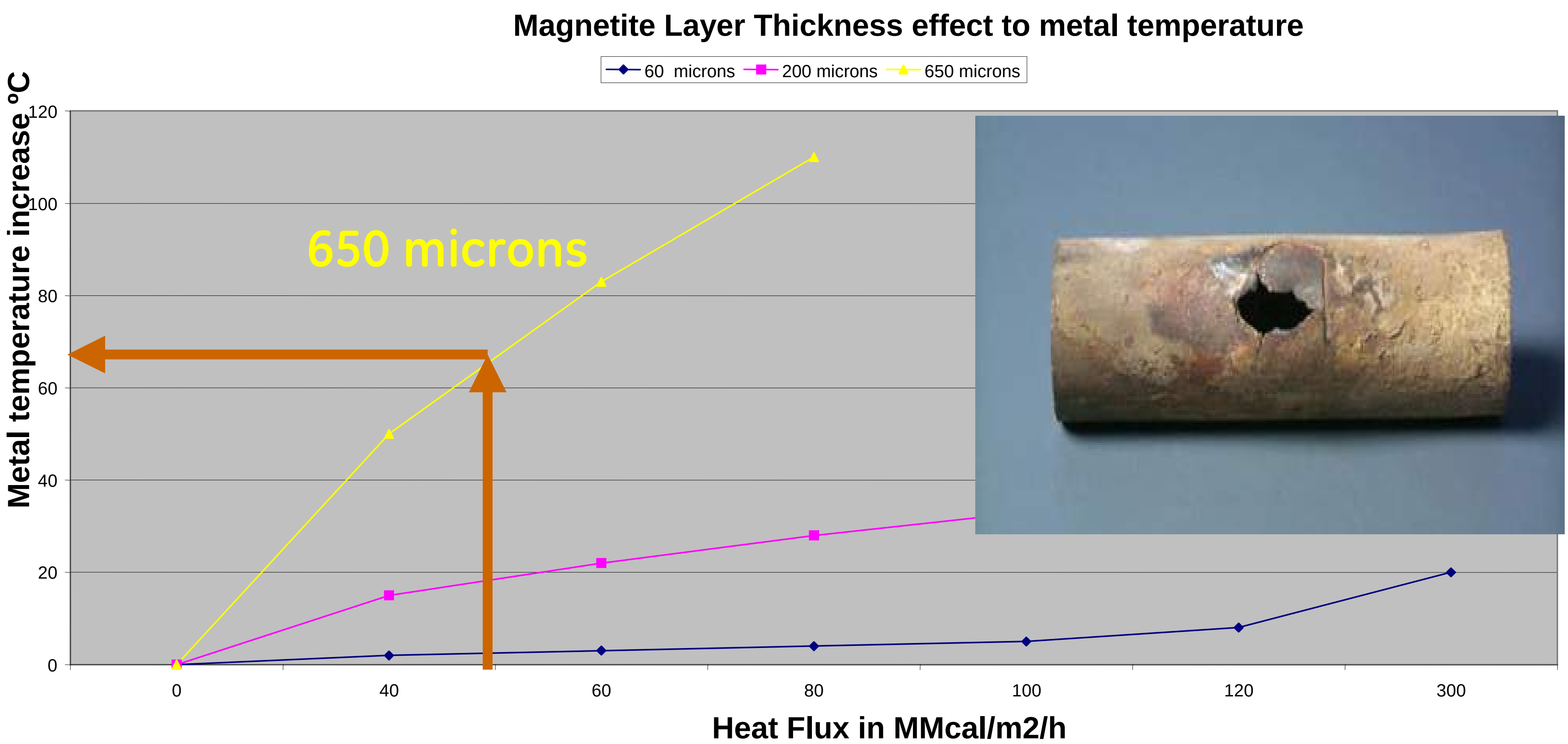
(from Energy Conservation Programme Guide for Industry & Commerce)



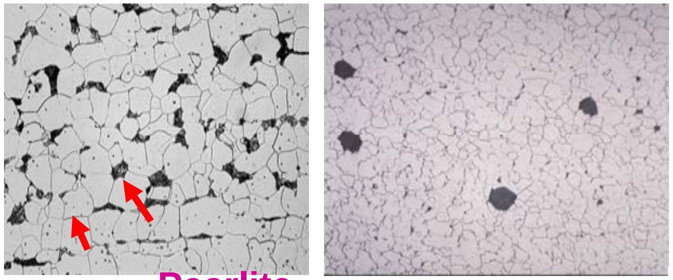
imagination at work

NACE JUBAIL

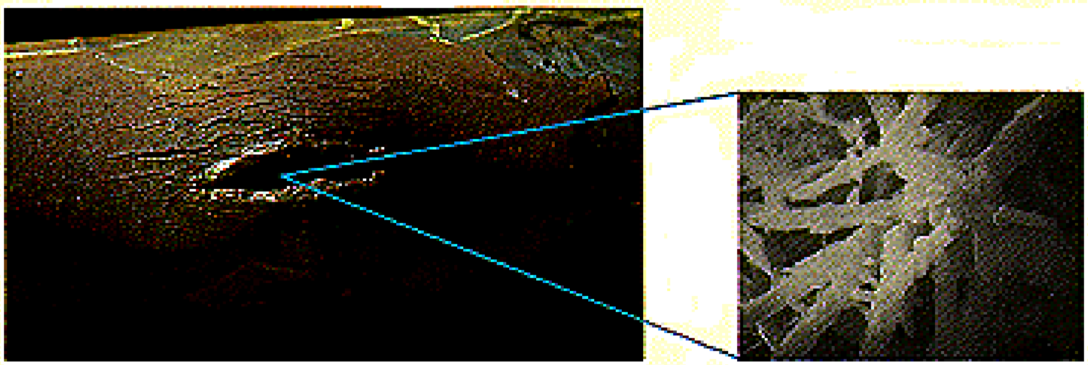
Metal temperature rise versus layer thickness and Heat Flux



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 450-540ºC. carbide spheriodization 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 Loses versus deposit thickness and composition
- Metal temperature changes due to deposition
- Thermal tube degradation or tube failure due to overheating

2nd 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

Deposit Weight Density –Cleaning Criteria

Pressure range Bars	DWD g/m2	mg/cm2	g/dm2
<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

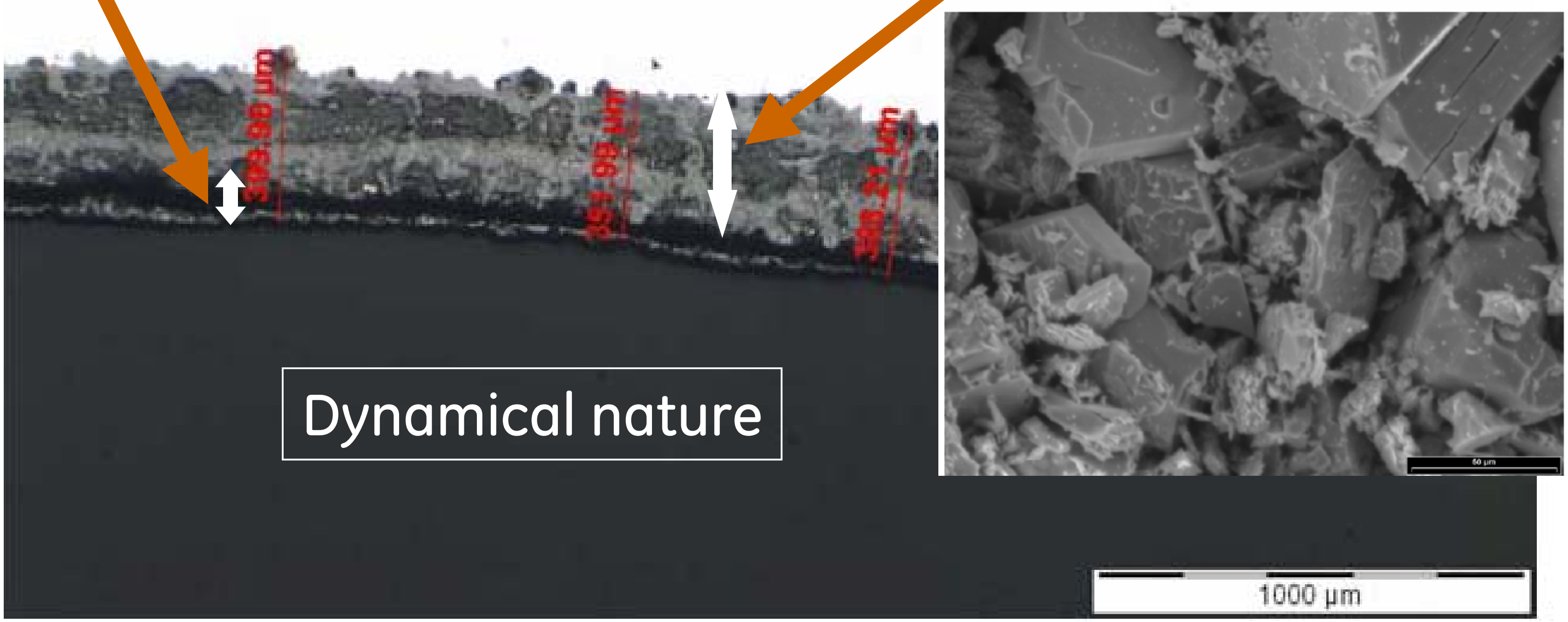
The measure of the total deposit weight amount per unit of surface is called Deposit Weight Density.

DWD gives an indication whether the surface has to 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



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.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Some interesting data....

imagination at work

NACE JUBAIL

EN-12952-12 and ASME guidelines for BFW

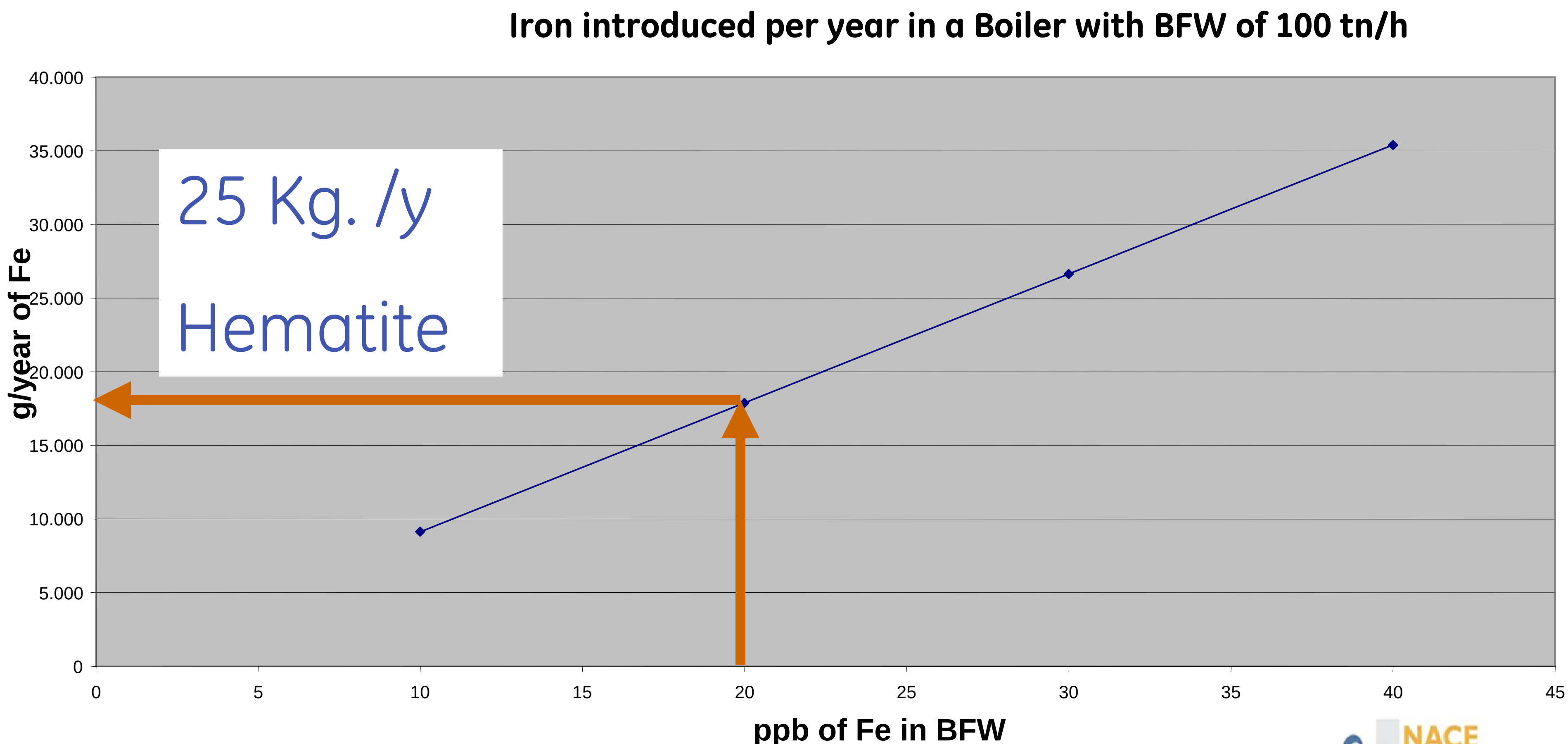
Boiler Feed Water ASME /*(EN12952-12)*	LP 10 bars	MP 25 bars	HP 45 bars	UHP 100 bars	UHP * 100 bars CC<0.2 us/cm
Oxygen, ppb O2	< 7 / *< 20*	< 7 / *< 20*	< 7 / *< 20*	< 7 / *< 20*	*< 100*
Iron, ppb Fe	< 100 / *< 50*	< 50 / *< 30*	< 25 / *< 20*	< 10 / *< 20*	*< 20*
Copper, ppb Cu	< 50 / *< 20*	< 25 / *< 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

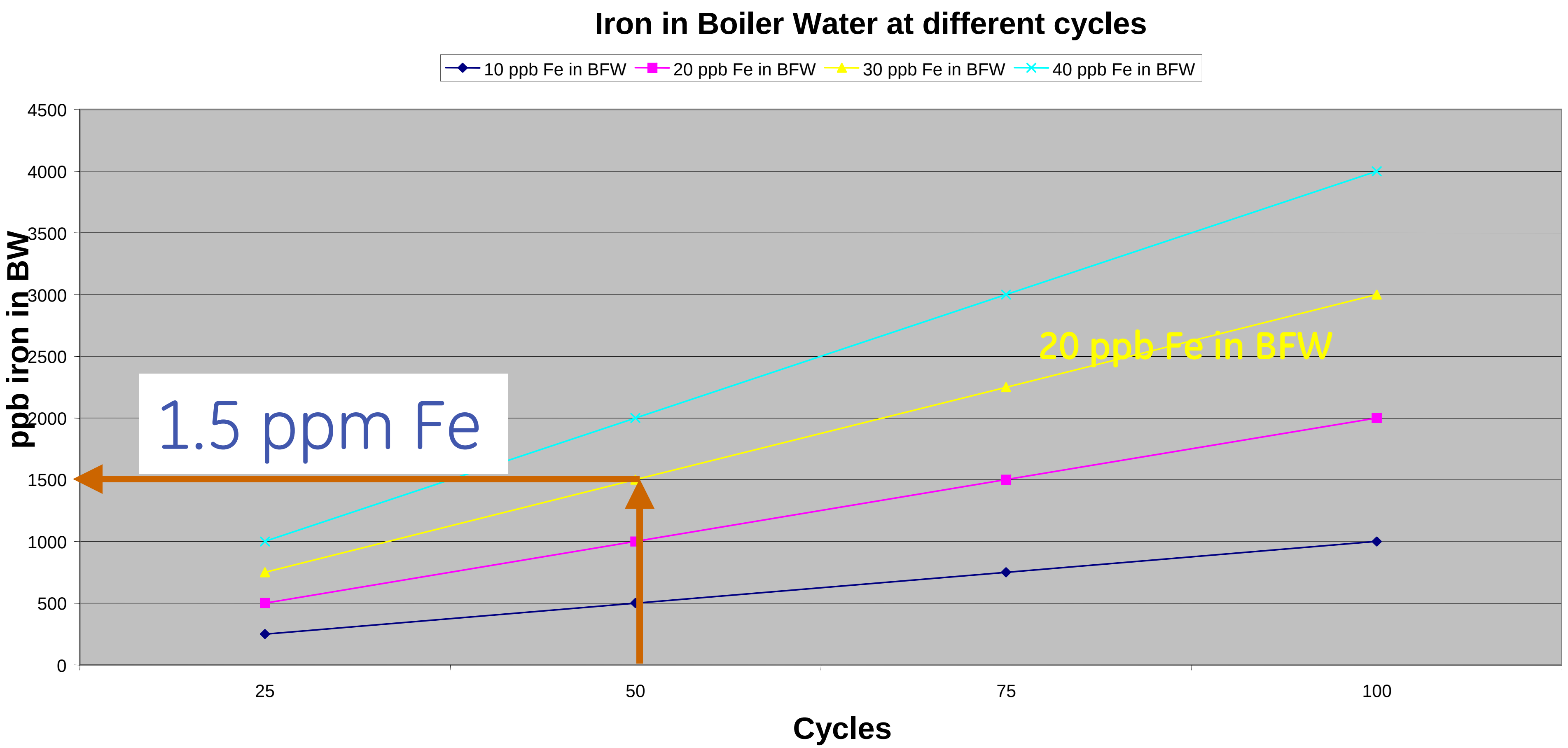
**Excluding added chemicals for boiler treatment

Typical iron limits are in ppb values, 20 ppb Fe according EN12952-12 for HP boilers

Iron Introduced into boiler following guidelines EN12952-12 for Fe in BFW



Iron that should be found in Boiler water



What really happen with a Na3PO4 treatment or NH3 control?, only 30% of feed iron is transported out of the boiler !!!!!

imagination at work

NACE JUBAIL

Consequences in DWD of 20 ppb Fe

Pressure range Bars	DWD g/m2	mg/cm2	g/dm2
<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

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

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

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

Pressure range Bars	DWD g/m2	mg/cm2	g/dm2
<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

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

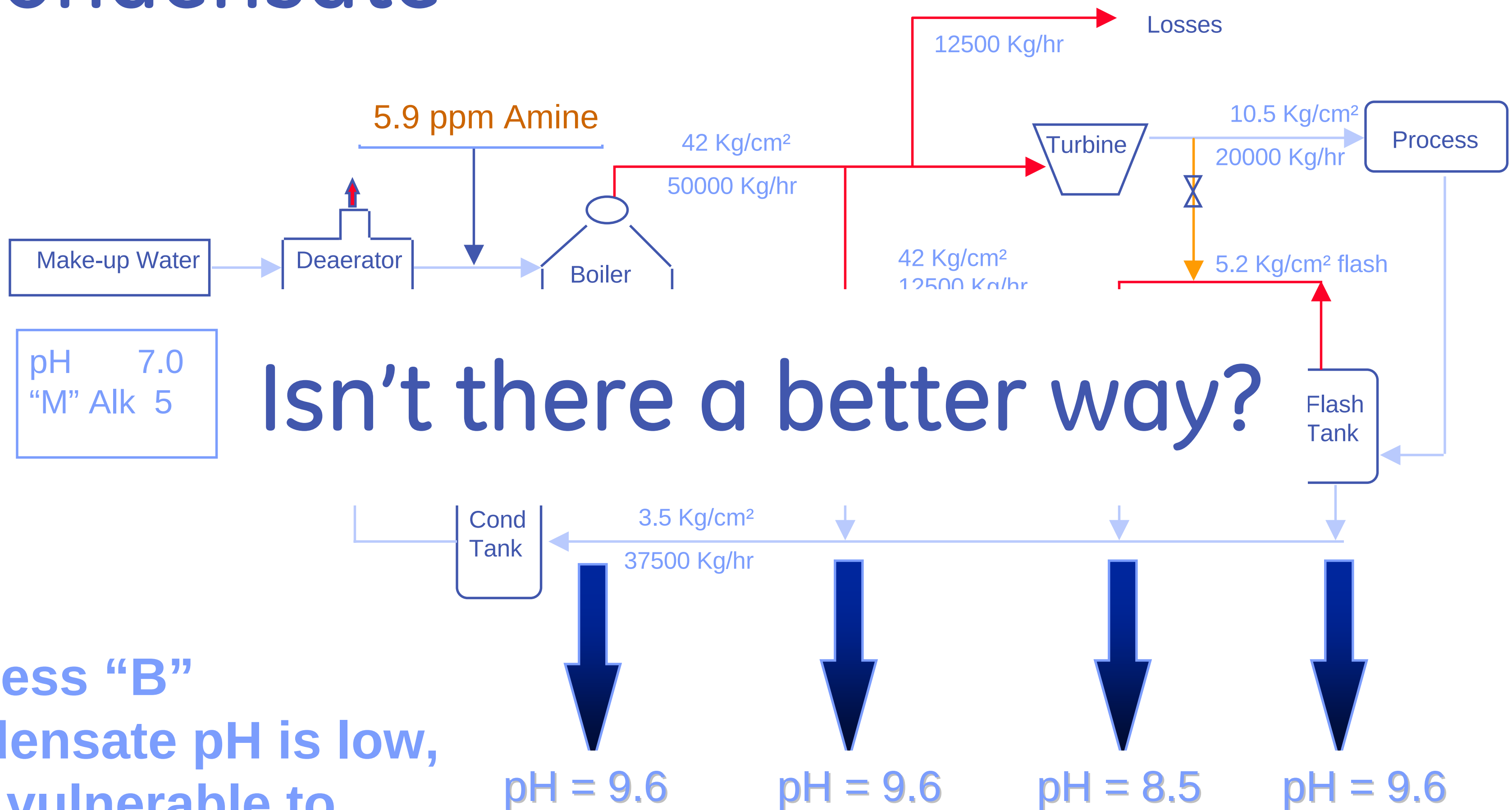
Recovery ratio is the amount of amine recovered via condensate return

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

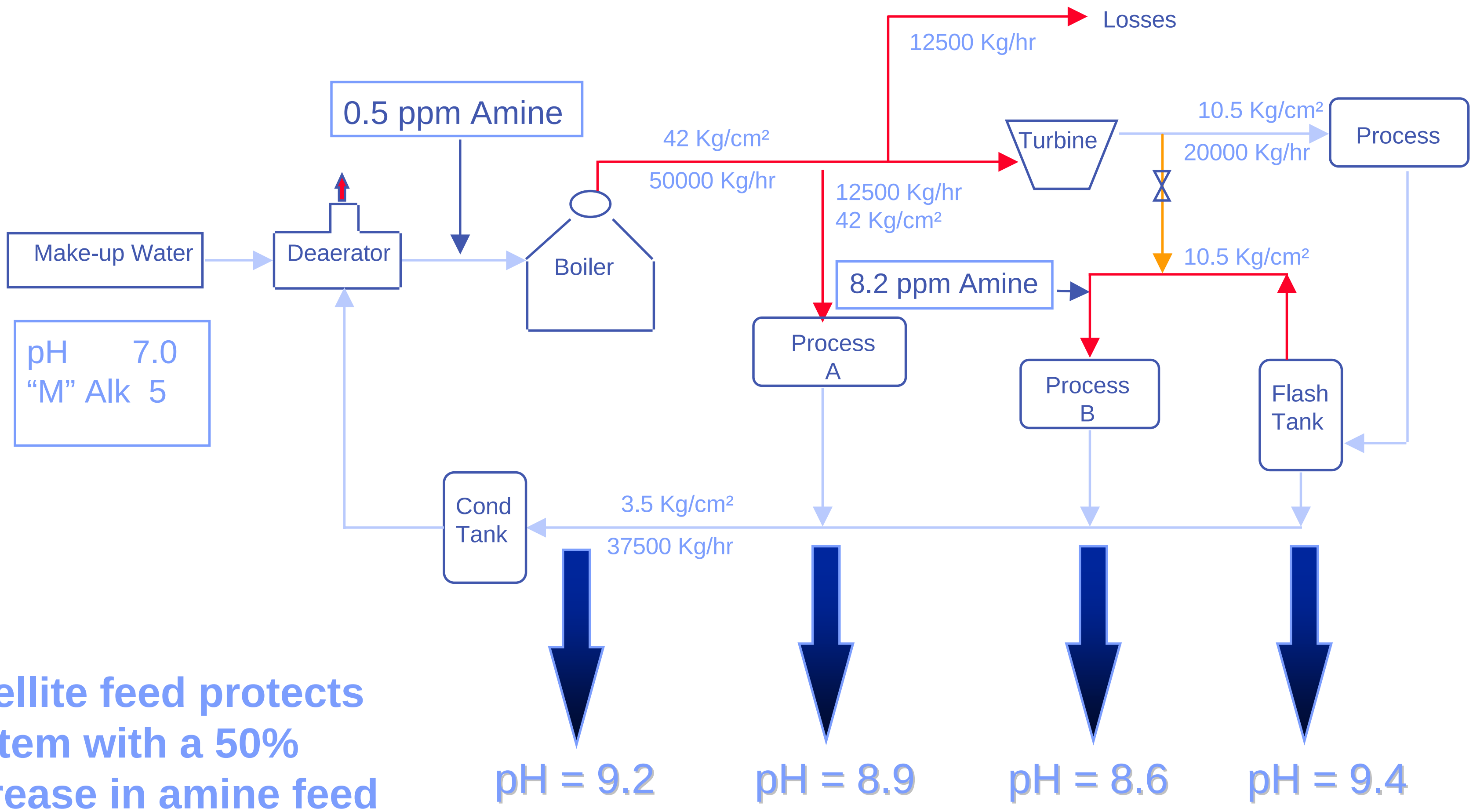
Extra amine required to protect flash condensate



Isn't there a better way?

Process "B" condensate pH is low, area vulnerable to corrosion

Amine savings: satellite feed

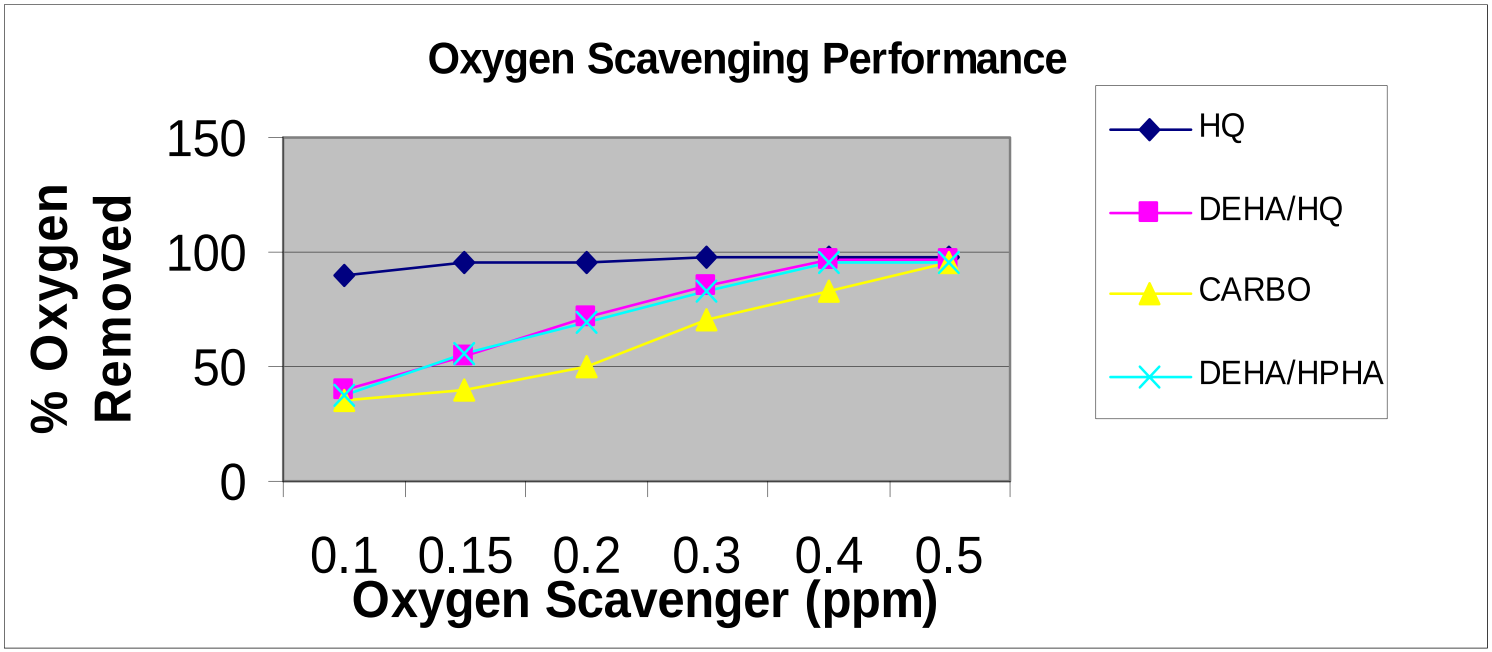


Satellite feed protects system with a 50% increase in amine feed instead of 490%

imagination at work

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.



imagination at work

NACE JUBAIL

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.**

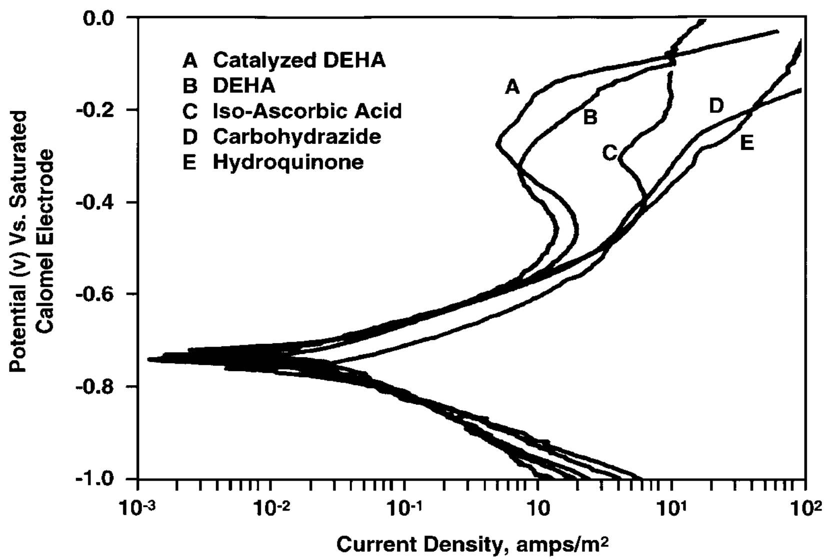
	Pressure	
Substance	200psig (14 bar)	1,000psig (69 bar)
DEHA	**3.5**	**4.0**
Hydrazine	0.15	0.8
Hydroquinone	<0.1	<0.1
Carbohydrazide	nil	nil
Erythorbate	nil	nil

imagination at work

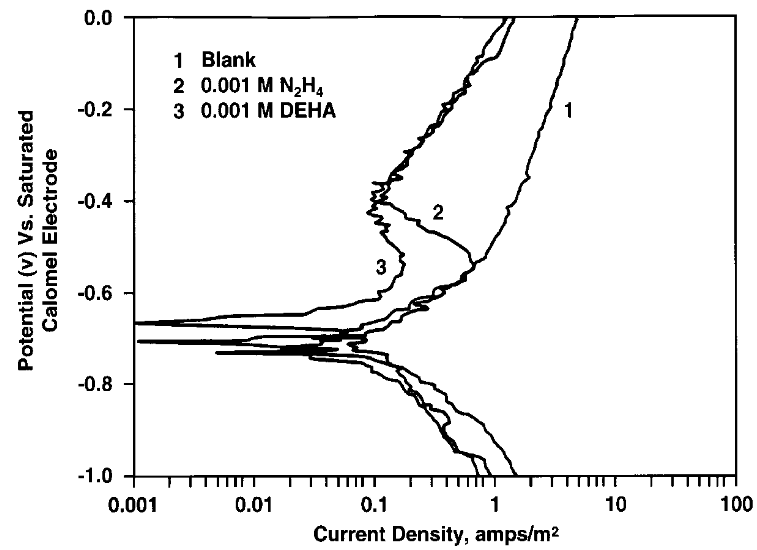
NACE JUBAIL

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.



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



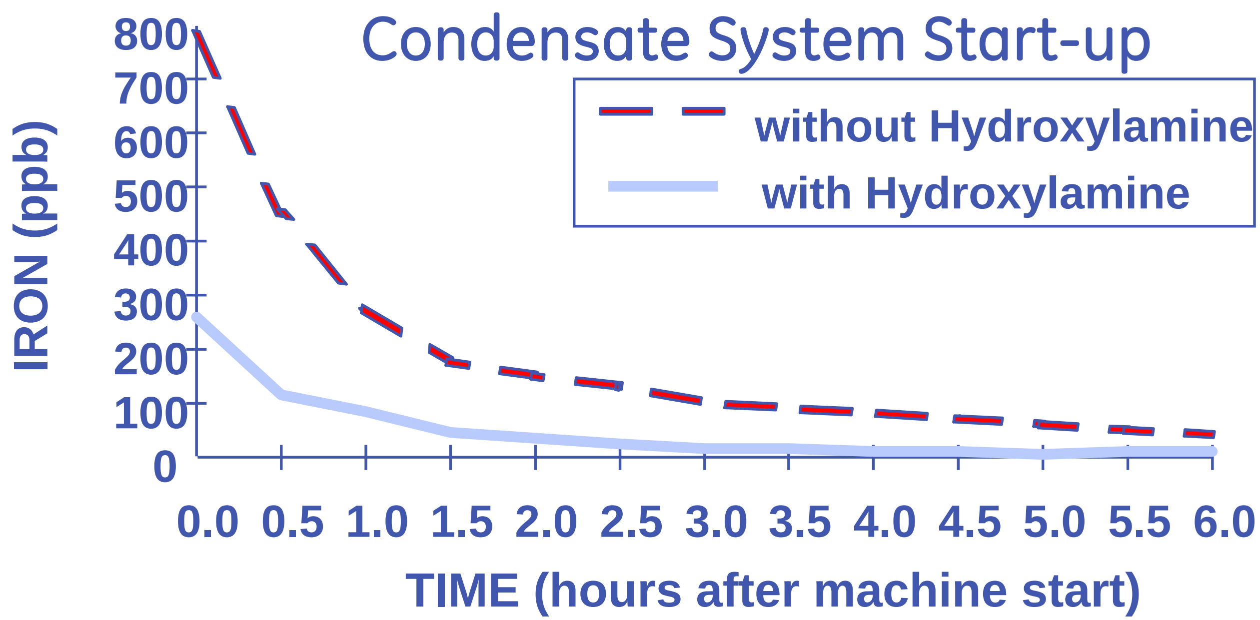
Polarization curve for 1010 mild steel at 25ºC in the presence of hydrazine and diethylhydroxylamine under laminar flow conditions at pH 8.0 relative to a blank.

DEHA is confirmed as better pasivation agent from polarization curves

imagination at work

NACE JUBAIL

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

imagination at work

NACE JUBAIL

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**

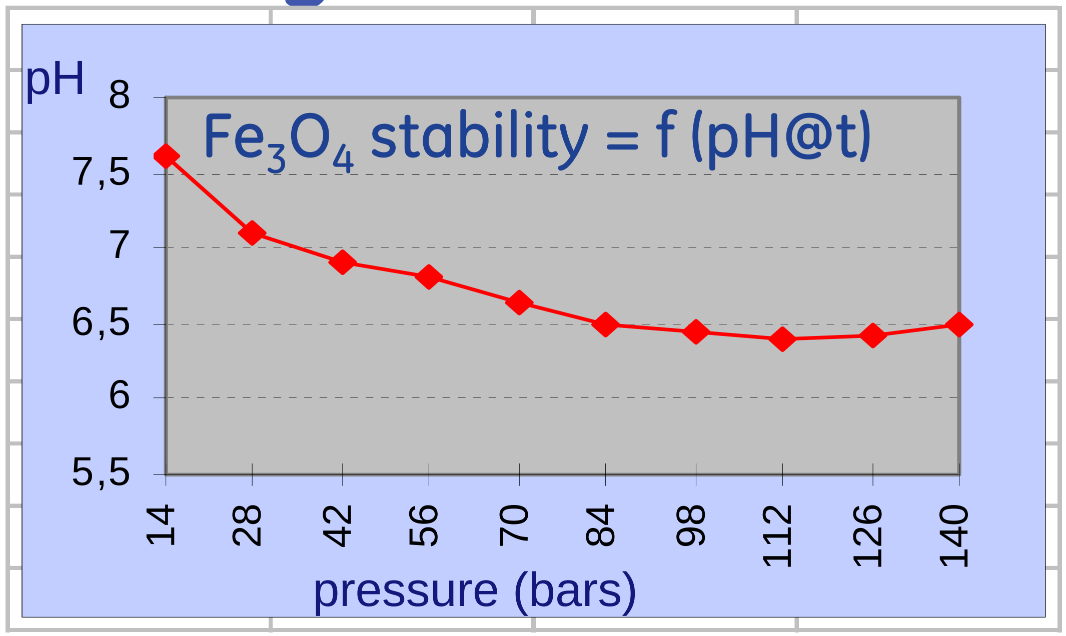
  Amine treatment, some mineral alkalinity from demi water

- **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

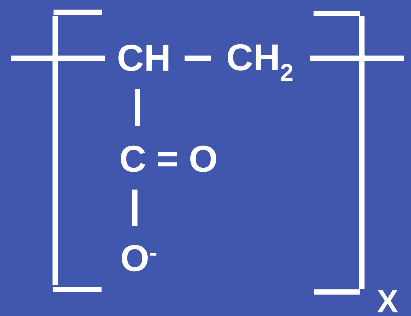


- Pressures <120 bars, all will benefit from polymer dispersants
  - ✓ ***High Temperature Polymers to prevent iron oxide deposition - HTP***
  - ✓ ***Long boiler water retention times. High Boiler cycles 100***
  - ✓ ***Allowing APT-pH-PO4 programs***

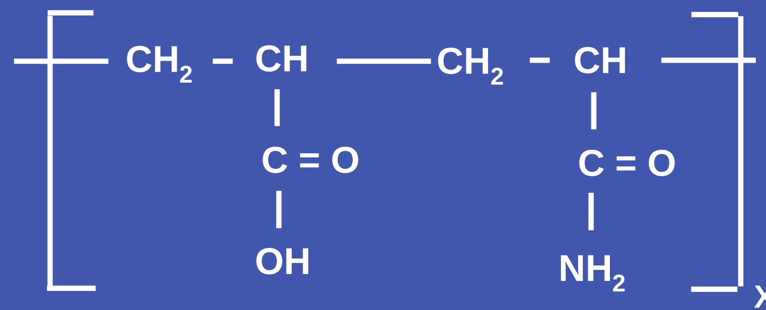
imagination at work

NACE JUBAIL

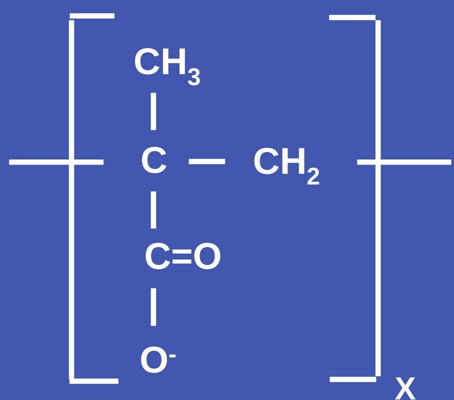
Traditional Polymer Structures



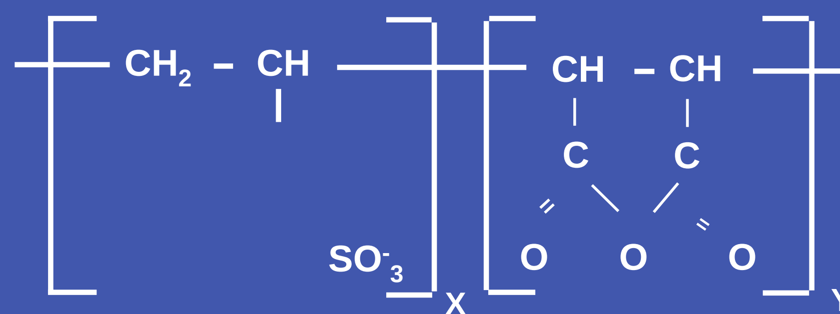
POLYACRYLATE



ACRYLATE-ACRYLAMIDE COPOLYMER

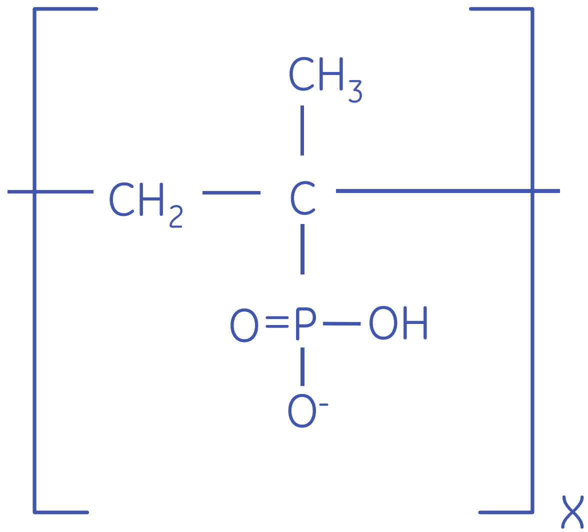


POLYMETHACRYLATE



SULFONATED STYRENE-MALEIC ANHYDRIDE COPOLYMER

High Temperature Polymers HTP-2



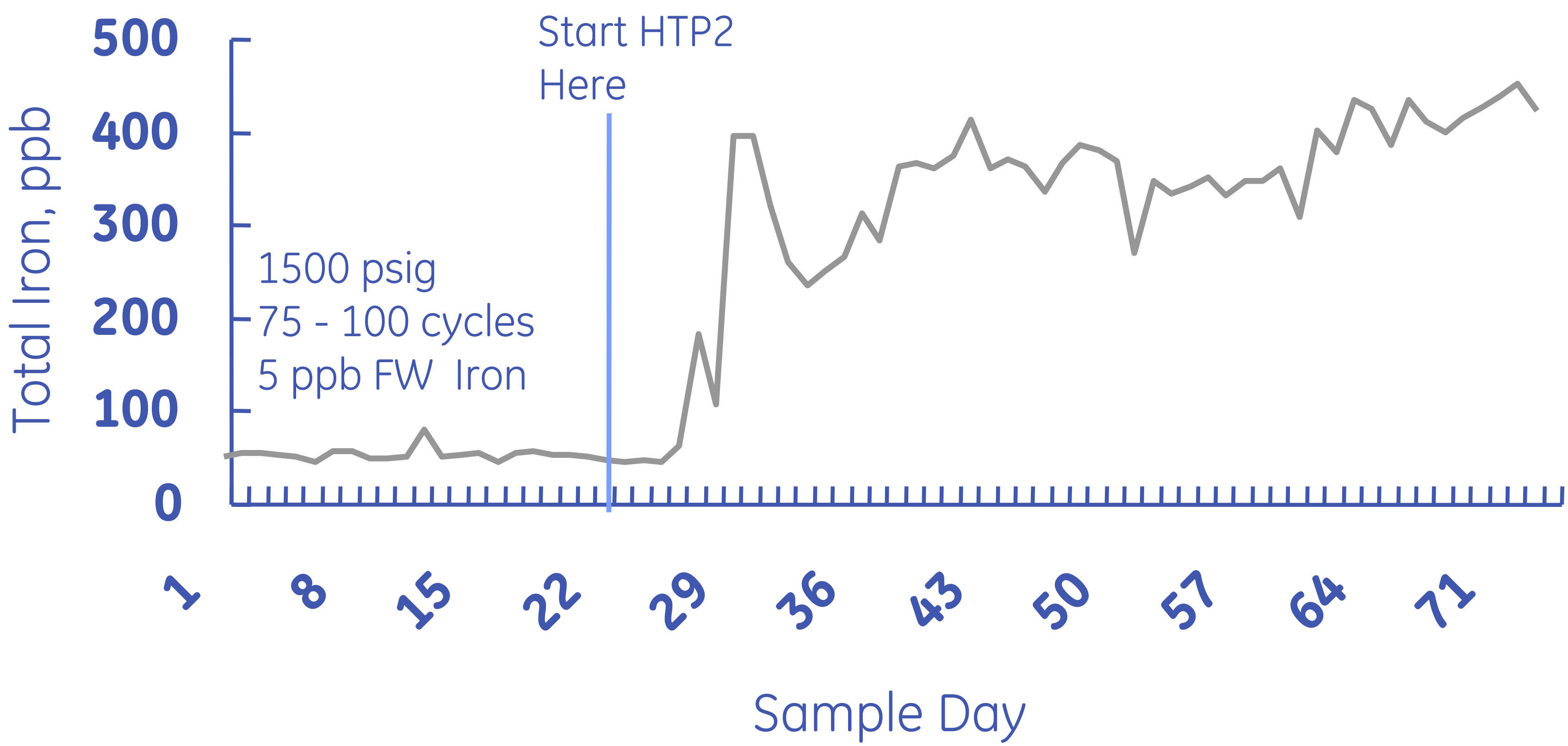
Poly (isopropenyl phosphonic acid) . . . PIPPA

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.

imagination at work

NACE JUBAIL

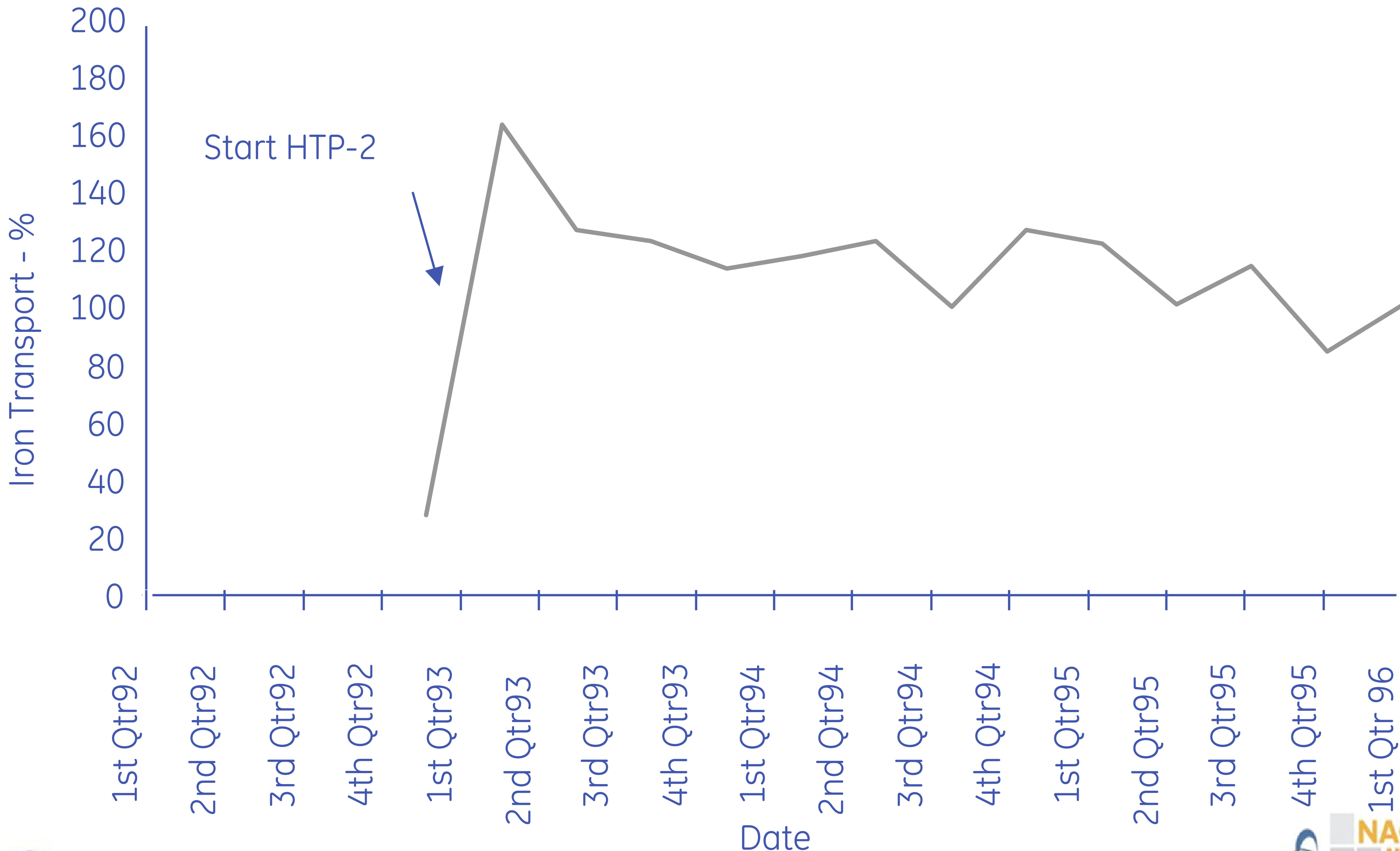
Blowdown Iron



Measured hydrogen levels on steam slightly declined when HTP2 was introduced

imagination at work

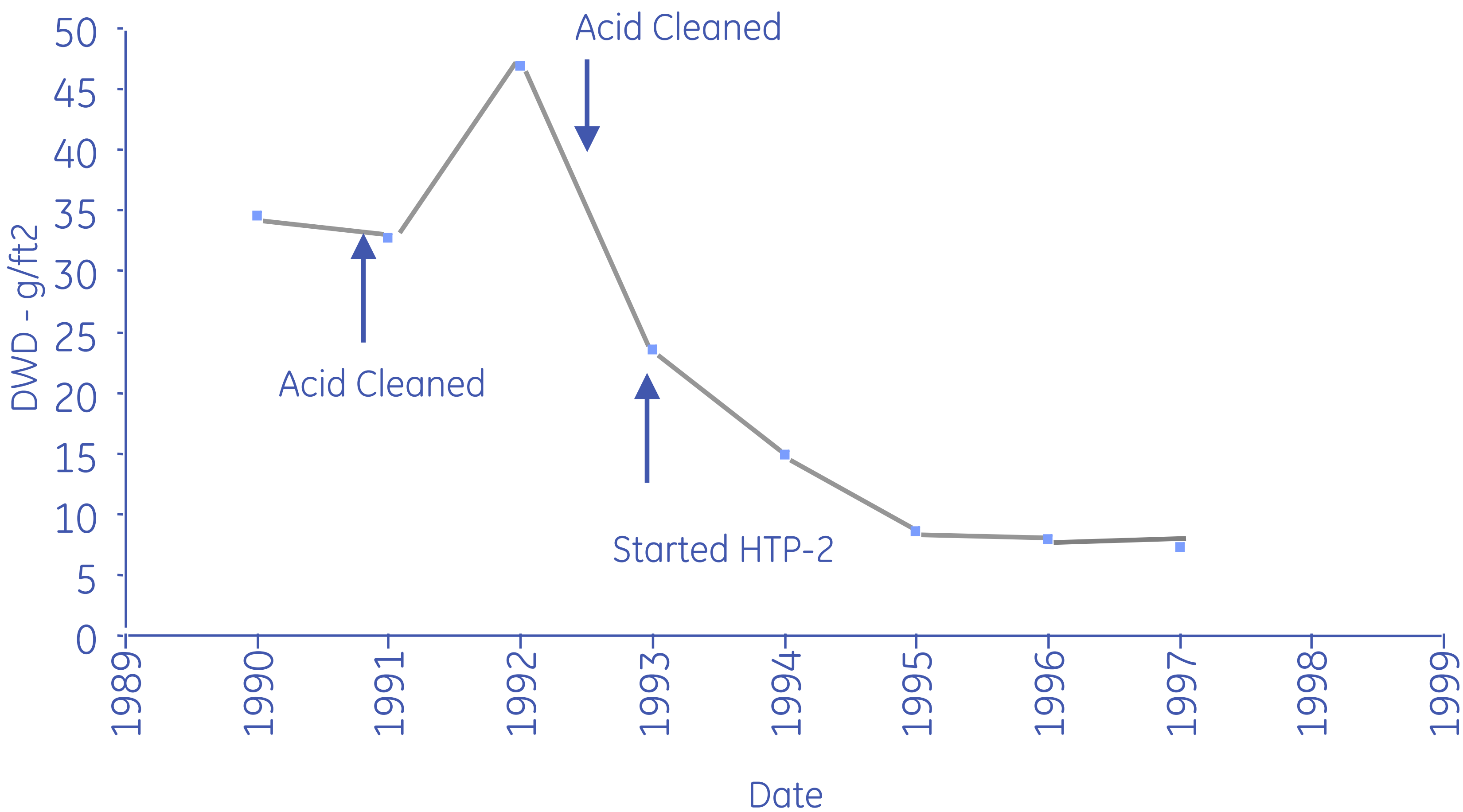
1,500 psig boiler
Boiler Iron Transport



imagination at work

NACE JUBAIL

Boiler Deposit Weight Density Data



High iron transport and on line cleaning performance when used at higher dosages

imagination at work

NACE JUBAIL

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