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Boiler Water Treatment Considerations for Waste Heat Boilers in ammonia and ethylene plants

Francesco Tozzi

Presentation Overview

- General Boiler Water Treatment Goals
- Ammonia Plant Waste Heat Boilers
- Ethylene Plant Waste Heat Boilers
  - Transferline exchangers
- High Temperature Polymer – HTP2

General Boiler Water Treatment Goals

- Deposit Control
  - Feedwater Pretreatment
  - Boiler Internal Treatment Programme
    - Polymeric Dispersants plus buffered PO_4 solution
  - Boiler Blowdown
- Corrosion Control
  - Oxygen
  - Acid
  - Caustic
- Steam Purity

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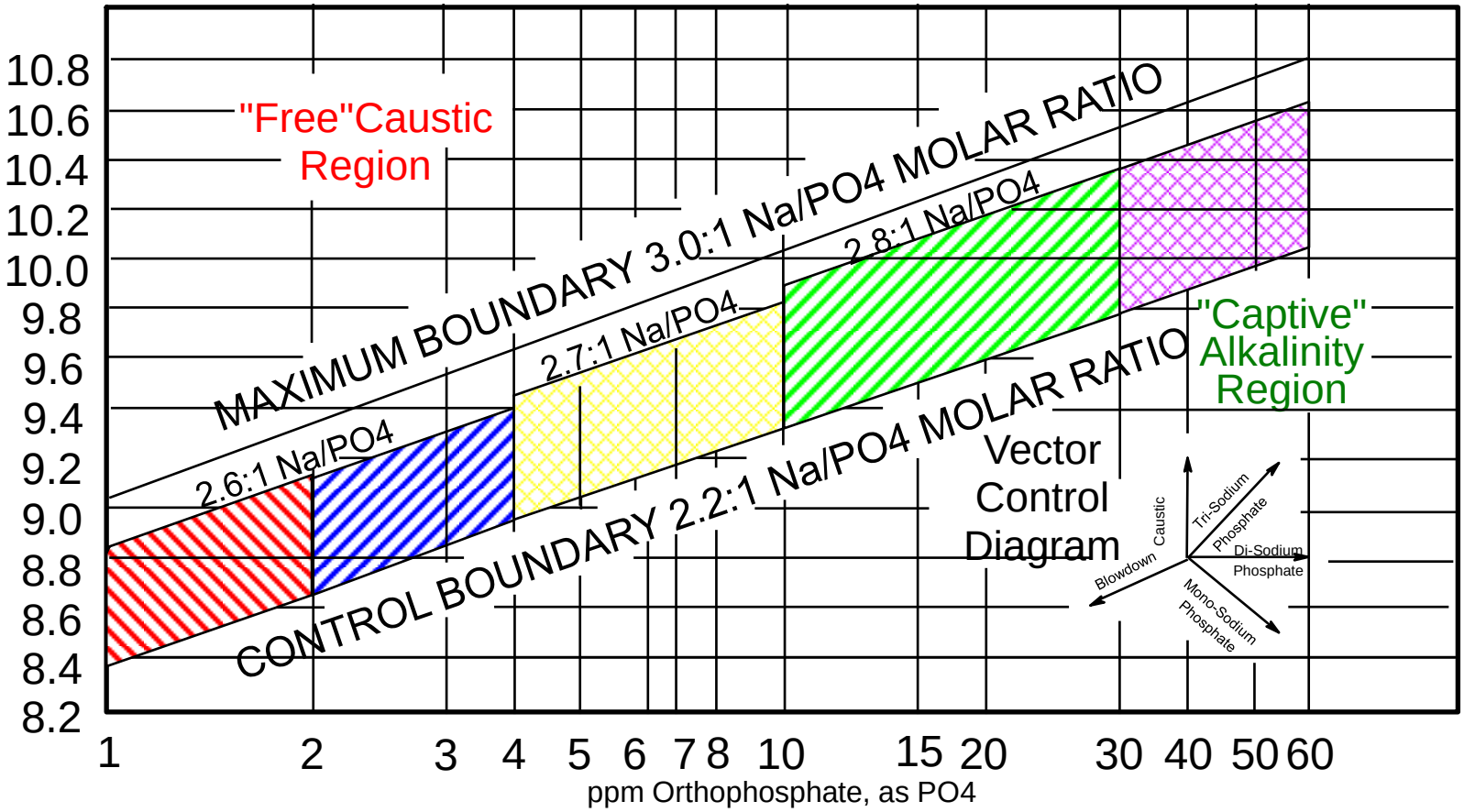
Coordinated pH Phosphate Control



Steam Purity

	GE	ABB	Westing-house
Sodium	<20	<10	<5
Cation Cond	<0.2	<0.2	<0.3
SiO2	<20	<20	<10

c

Steam Purity

- Maintain Steam Purifying Equipment in Good Condition
- Ensure Quality of Attemperation Water
- Maintain Proper Steam Drum Water Level

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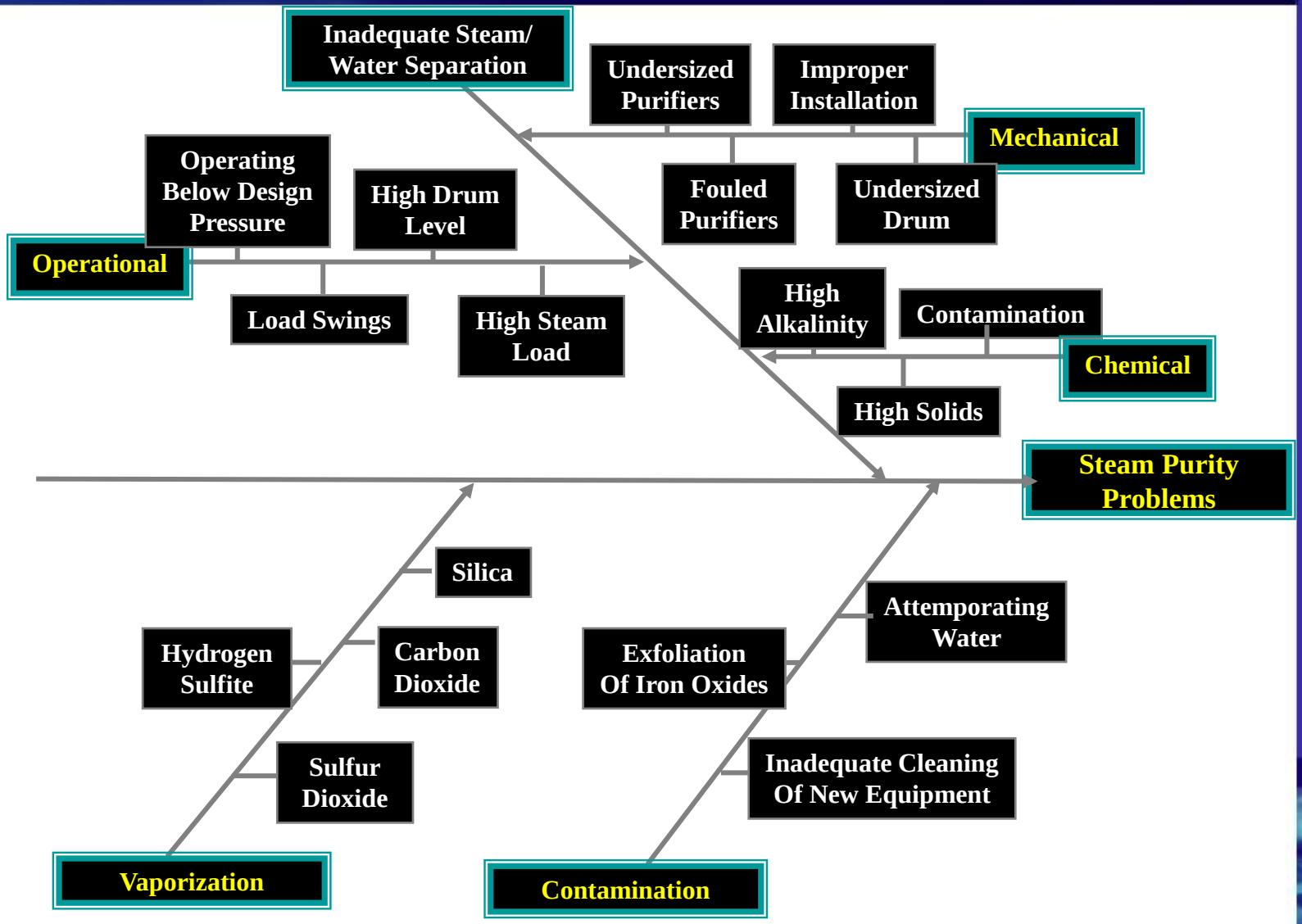
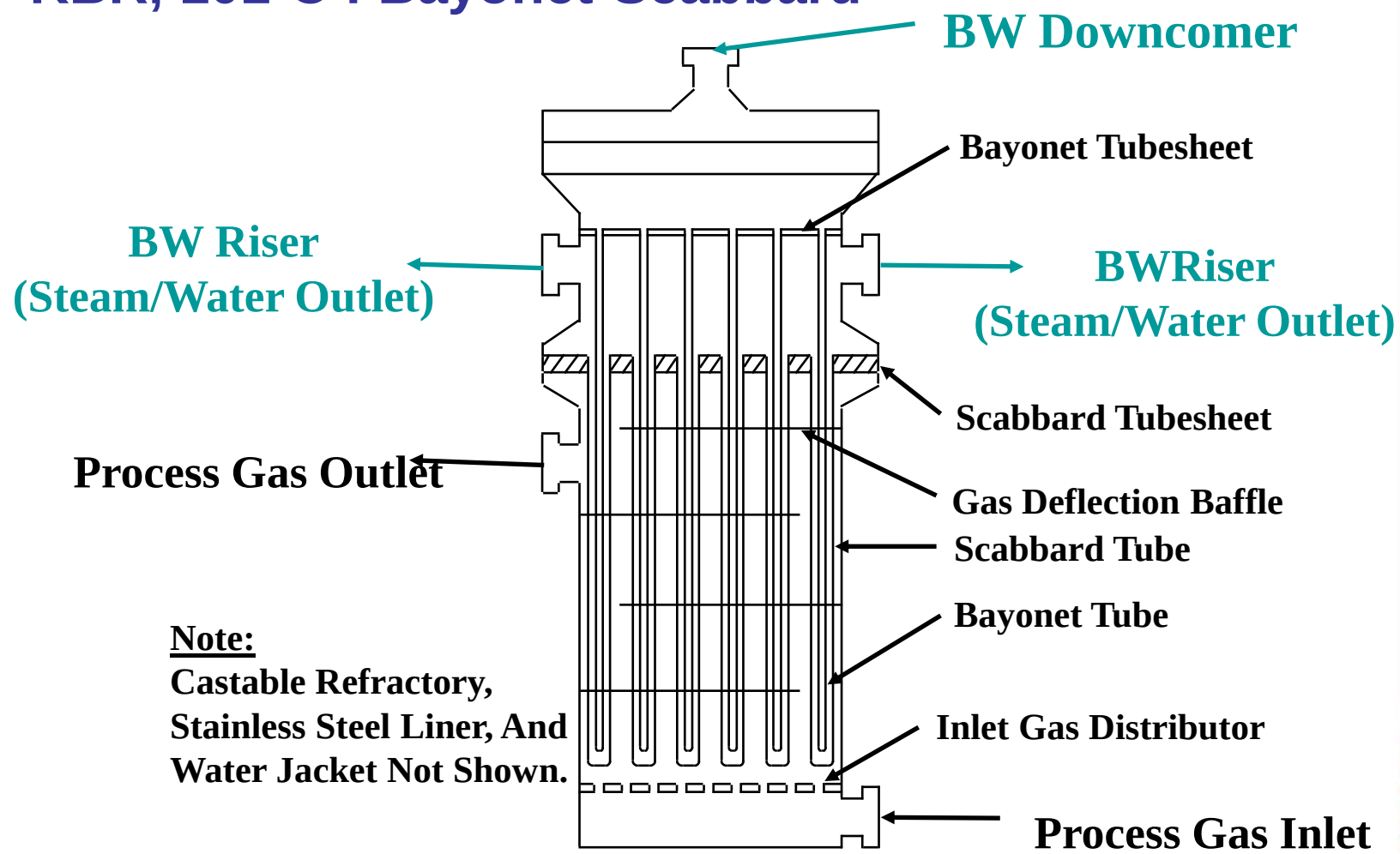


Ammonia Plant Waste Heat Boilers

- Kellogg, Brown and Root (KBR)
  - 101-C :
    - Secondary Reformer WHB
    - Inlet Process Temp : ~ 900 °C
    - Outlet Process Temp : ~ 500 °C
    - High Pressure Steam + 100 bar
    - Suspended Solids Tolerance is Zero

KBR, 101-C : Bayonet-Scabbard



Note:
Castable Refractory, Stainless Steel Liner, And Water Jacket Not Shown.

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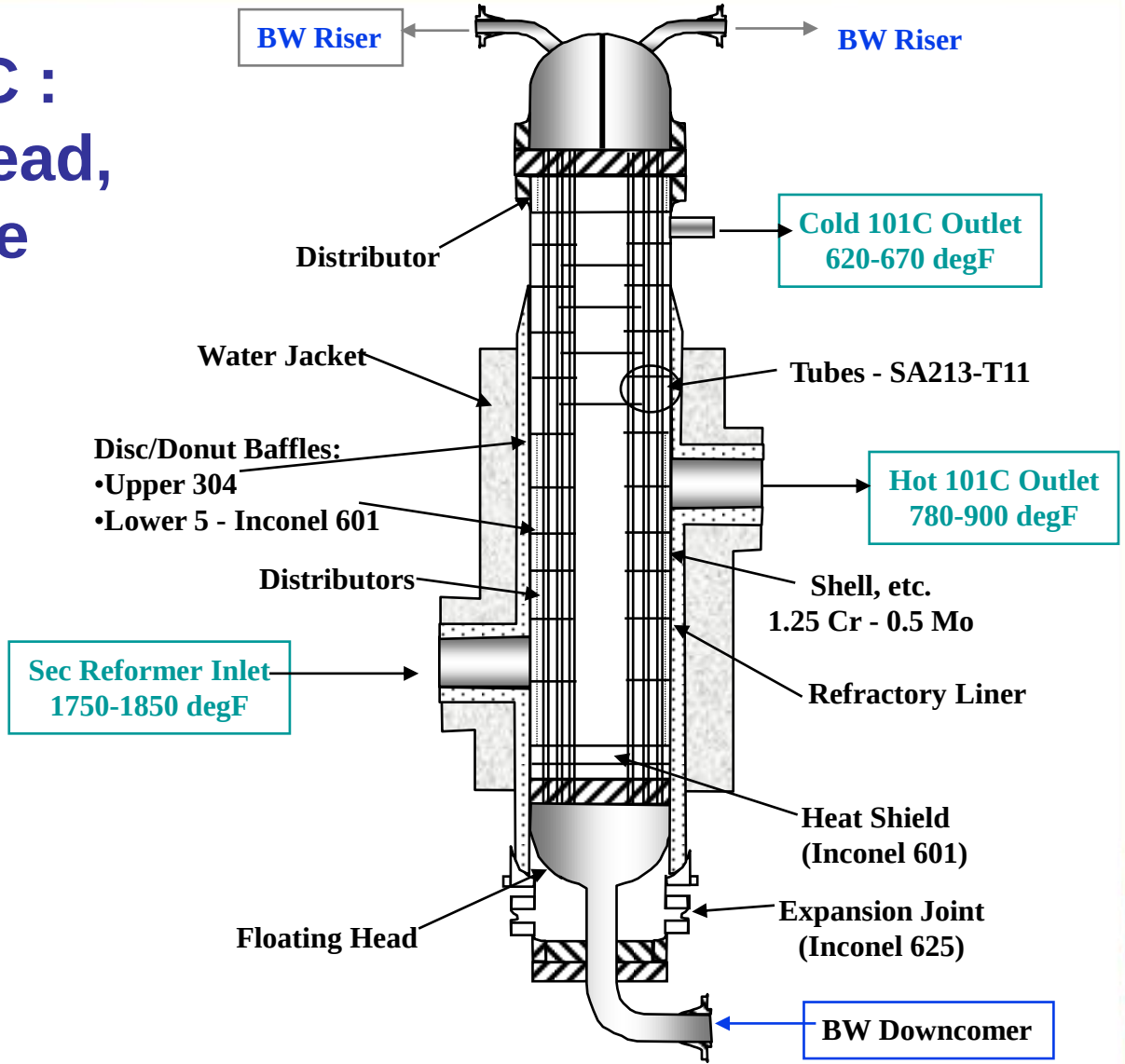
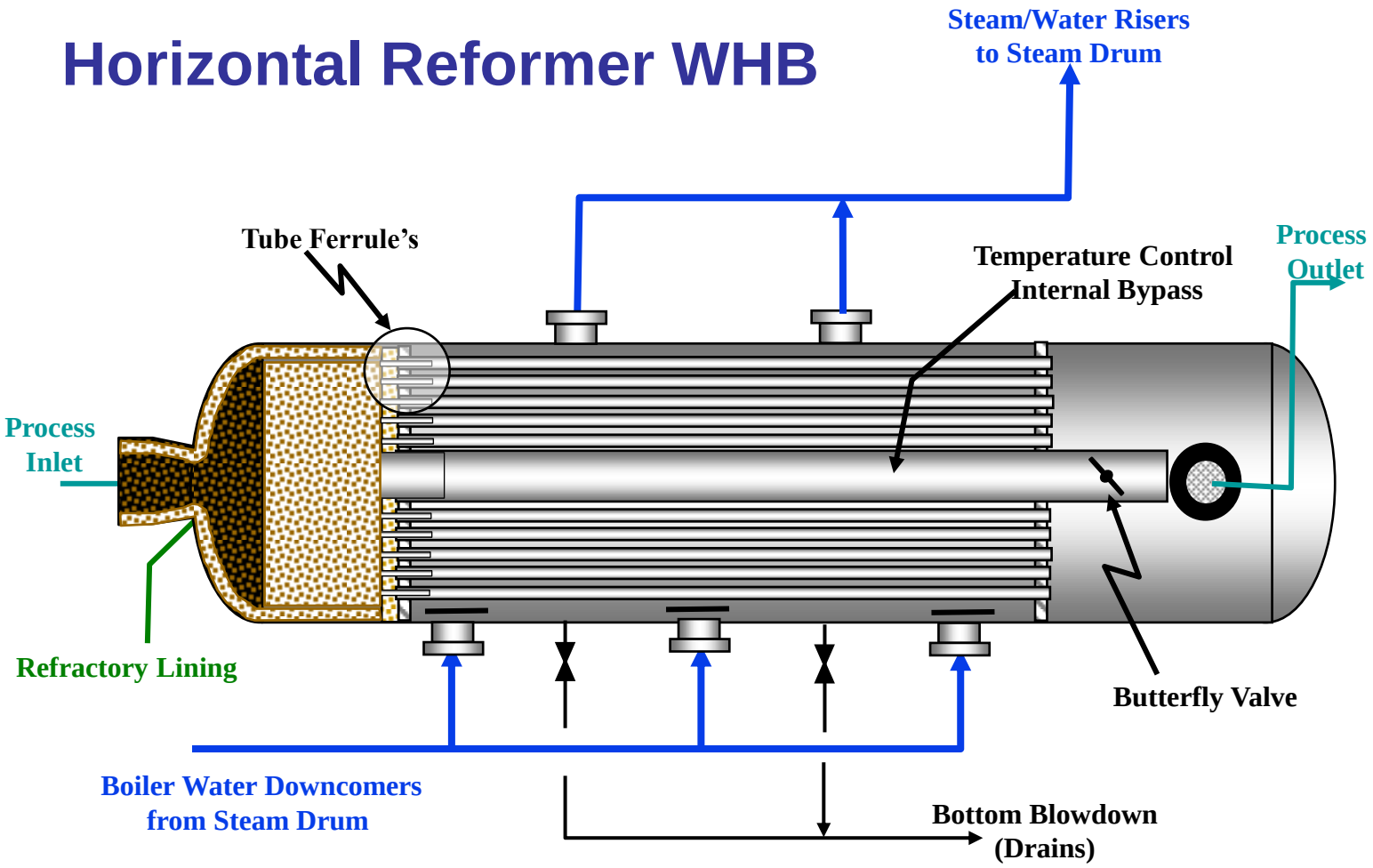
KBR, 101-C : Floating Head, Single Tube



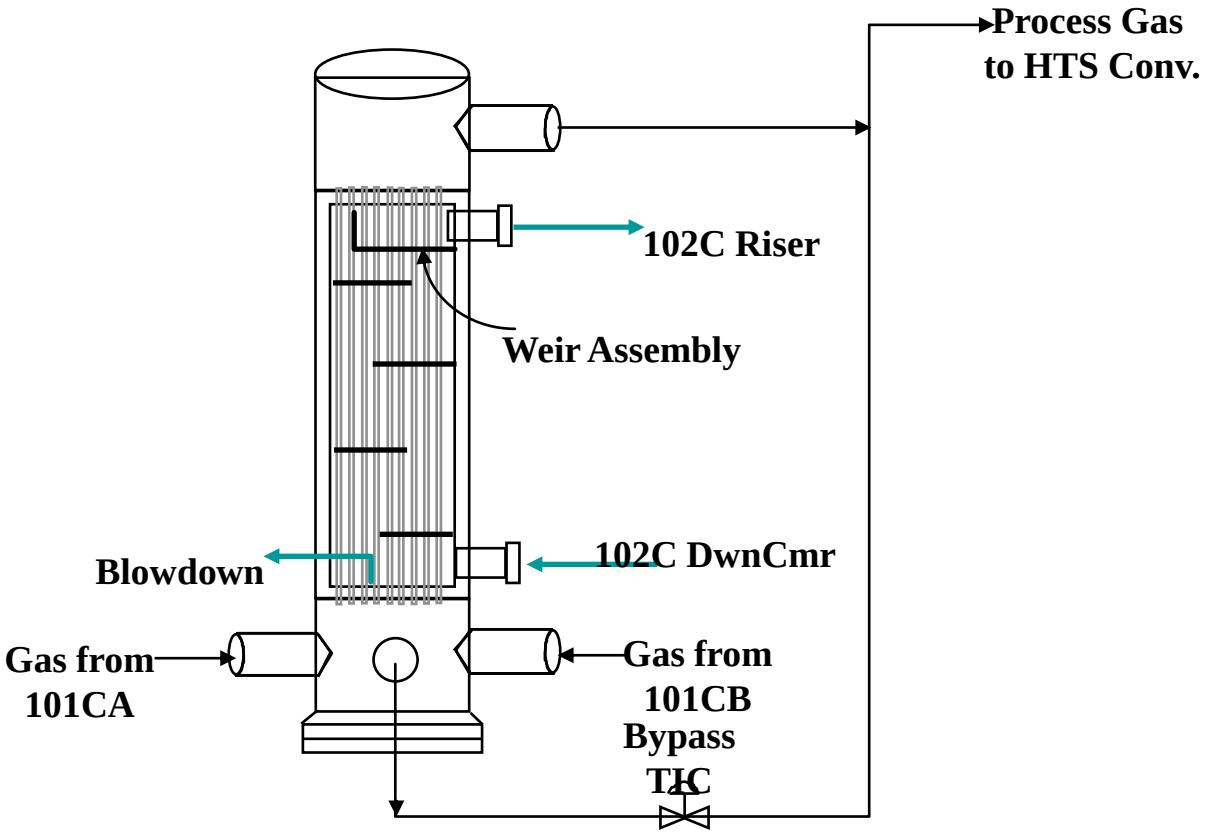
Horizontal Reformer WHB



Kellogg, Brown and Root

- 102-C
  - Receives Cooled Process Gases from 101-C : ~ 500 °C inlet
  - Cools Process Gas to ~ 370 °C
  - High Pressure Steam +100 bar
  - Vertical WHB
    - Tube Plate Cooling issue / Magnetite Formation
    - Intermittent Blowdown
  - Bypass for Temperature Control

KBR, 102-C


Process Gas
to HTS Conv.
102C Riser
Weir Assembly
Blowdown
102C DwnCmr
Gas from
101CA
Gas from
101CB
Bypass
TIC

Ammonia Plant Waste Heat Boilers

- Deposition control :
  - **“pure” water requirement**
    - **Condensate quality requires polishing**
      - **Cation polishing**
      - **Mixed Bed polishing**
  - **Polymeric dispersant - HTP2**
  - **“limited” blowdown facility**
- Boiler Feedwater Spec’s (ASME)
  - **Dissolved Oxygen : < 0.007 ppm O_2**
  - **Total Iron : < 0.010 ppm Fe**
  - **Total Copper : < 0.010 ppm Cu**
  - **Total Hardness : Not Detectable**
  - **pH range : 9 – 9.6**

Ammonia Plant Waste Heat Boilers

- Corrosion Control
  - Under deposit corrosion
  - Design factors / avoiding film boiling
  - pH / PO_4 coordination
  - Ammonia adjusted Control Boxes
- Boiler Water Spec's (ASME)
  - Silica : < 1 ppm SiO_2
  - Total Alkalinity : not specified
  - Free hydroxide : not detectable
  - Spec. Cond. : < 80 µS/cm

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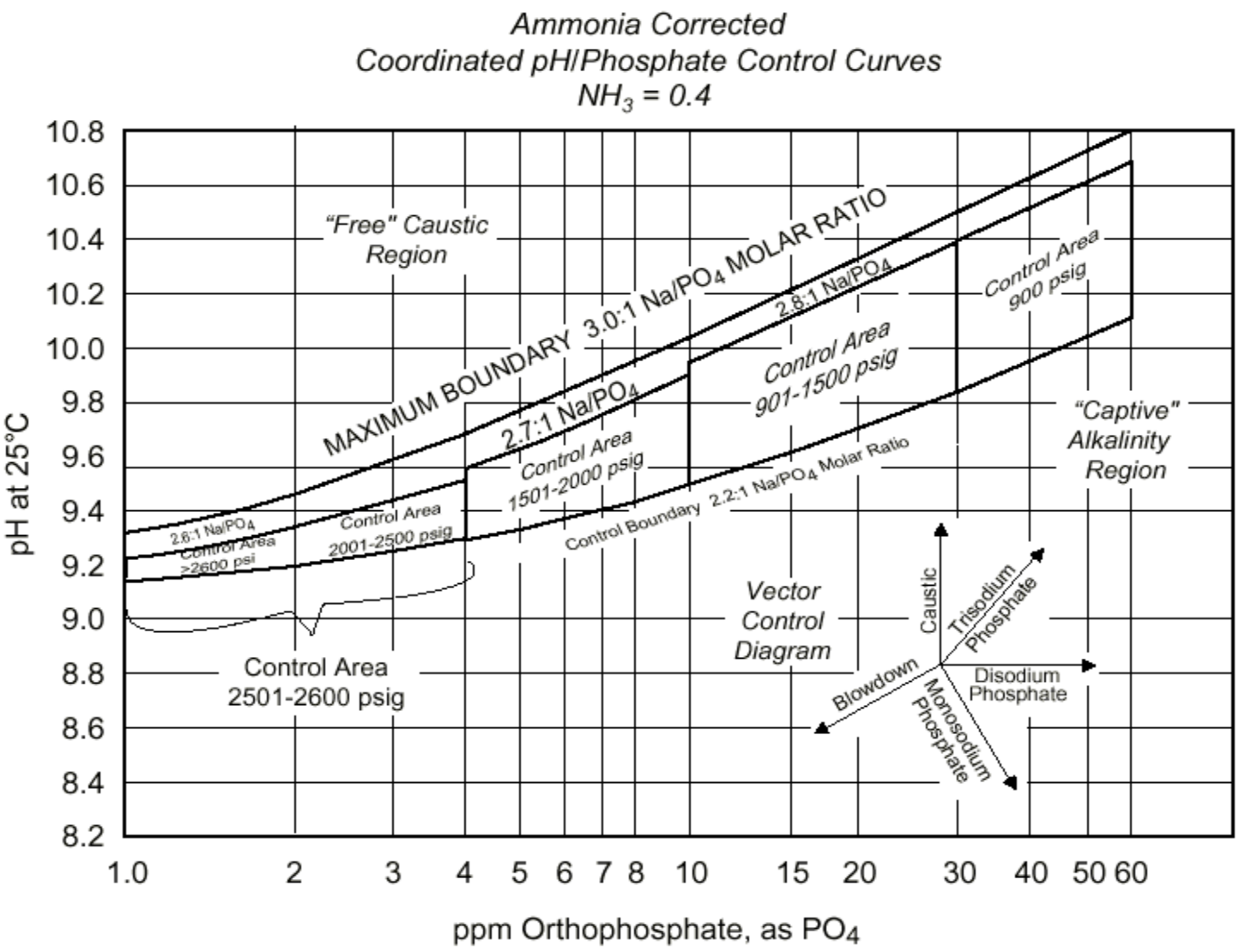
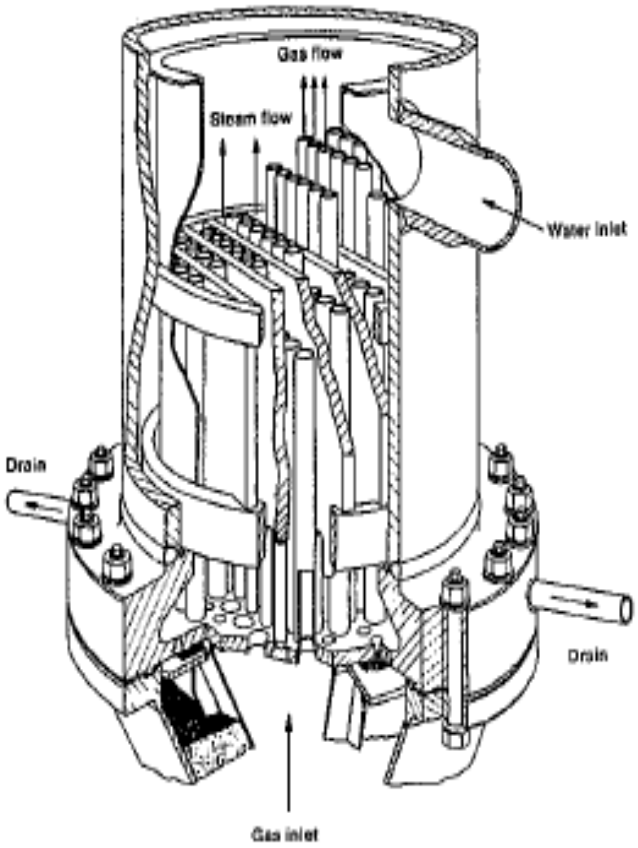
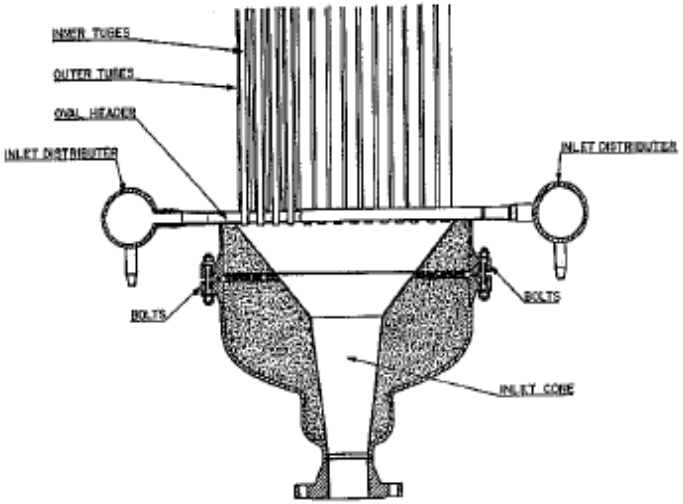


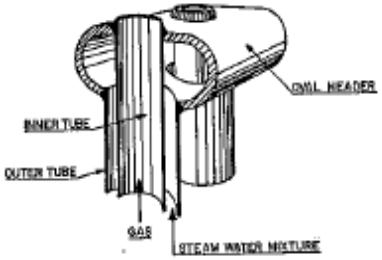
Waste Heat Boilers in Ethylene Plants

- Transferline Exchanger
  - Rapid Cooling of Cracked Gases
  - Inlet Temperature : 760 – 890 °C
  - Outlet Temperature : 400 – 500 °C
  - Very High Heat Flux : > 230 kW/m^2

Transferline Exchanger







Transferline Exchanger Deposition Control

- Mixed Bed Make-Up
- Condensate Polishing
- Feedwater Spec's (VGB)
  - pH > 9
  - Fe (total) < 20 ppb
  - Cu (total) < 3 ppb
- Polymeric Dispersants - **HTP2**
- Limited Blowdown Facilities

Transferline Exchanger Corrosion Control

- pH/PO_4 coordination
- Boiler Water Spec's (VGB)
  - PO_4 : 2 – 6 ppm PO_4
  - pH : 9 – 9.6
  - Specific Conductivity : < 50 µS/cm
  - Silica : < 1.2 ppm (pressure dependant)

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Characteristics of HTP-2

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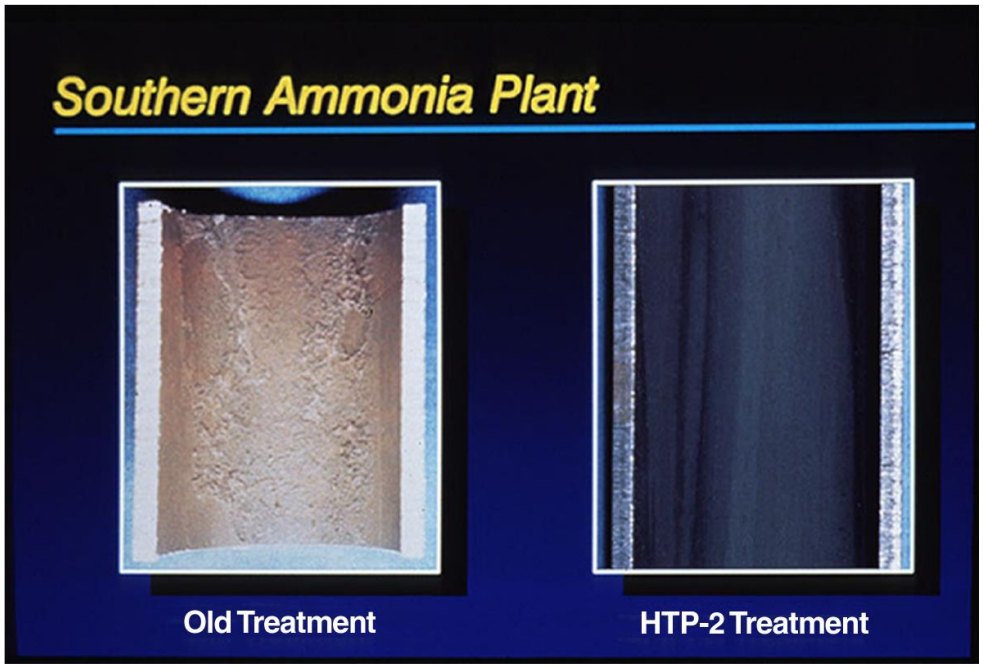
HTP 2

- A unique new phosphorylated boiler polymer
- Particularly effective on iron
- Demonstrated clean-up ability
- Designed for high purity/high cycles systems
- Suitable for use up to 125 kg/cm²

OptiSperse HTP2

- Before and after boiler inspection video stills on the same boiler tube after 3 months on ***OptiSperse HTP2***.



OptiSperse HTP2

- ***OptiSperse HTP2*** was designed to specifically react with metal oxides since they are the primary contaminate in high purity boiler water systems. It is constructed to maintain effectiveness under the higher pressure, longer residence times these systems operate under.

- While the typical users of ***OptiSperse HTP2*** are high-pressure installations, this technology can be used in lower pressure boilers that have high-purity feedwater**.** Metal oxides are the contaminants that need to be controlled, regardless of the system pressure.

OptiSperse HTP

Graph from a 1,500 psig boiler that underwent acid cleanings every 12 to 18 months before ***OptiSperse HTP2***.

It's been six years since the boilers have been cleaned now that ***OptiSperse HTP2*** is in use. Internal cleanliness is remarkable.

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1,500 psig boiler
Boiler Deposit Weight Density Data

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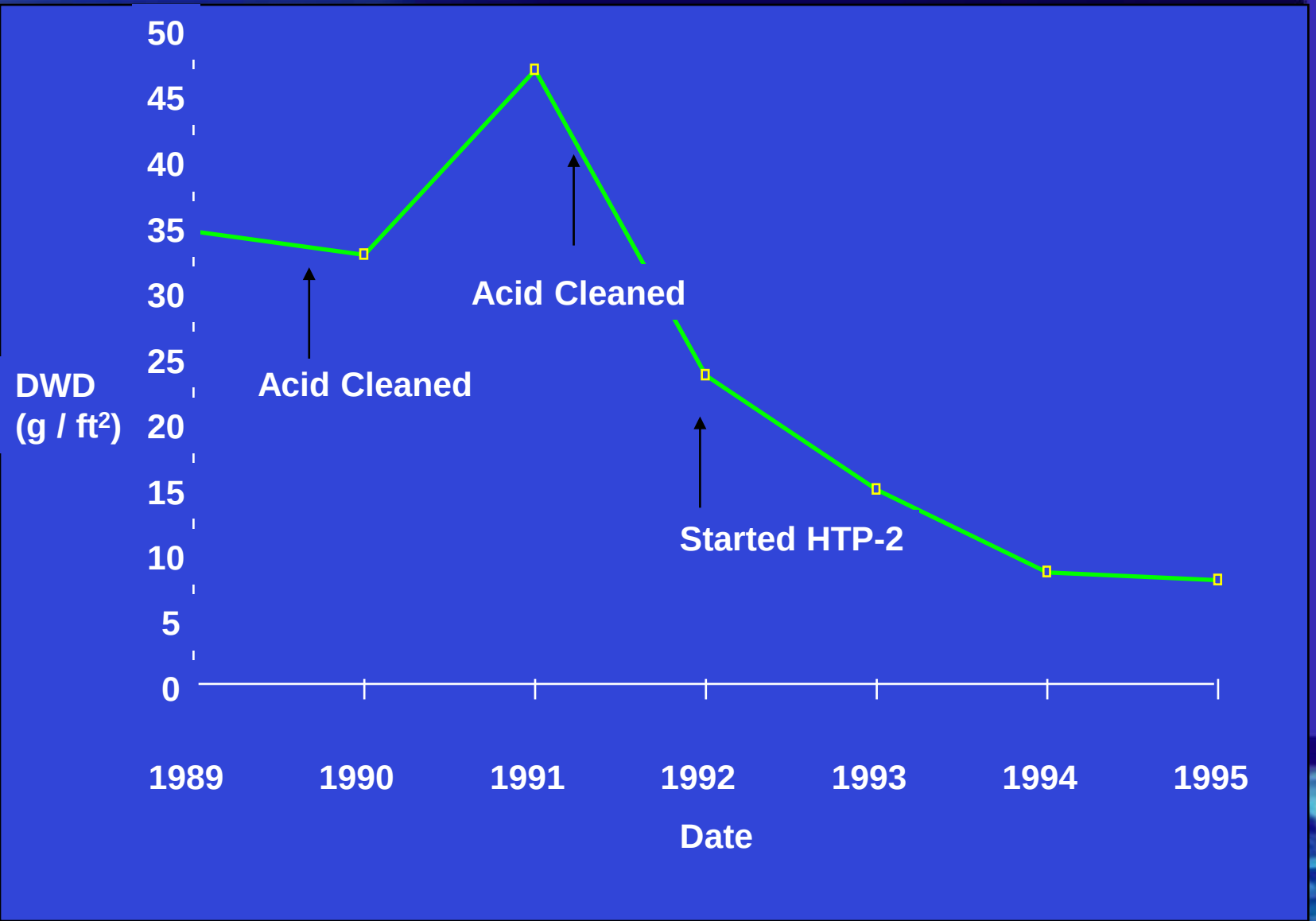

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Blowdown Iron

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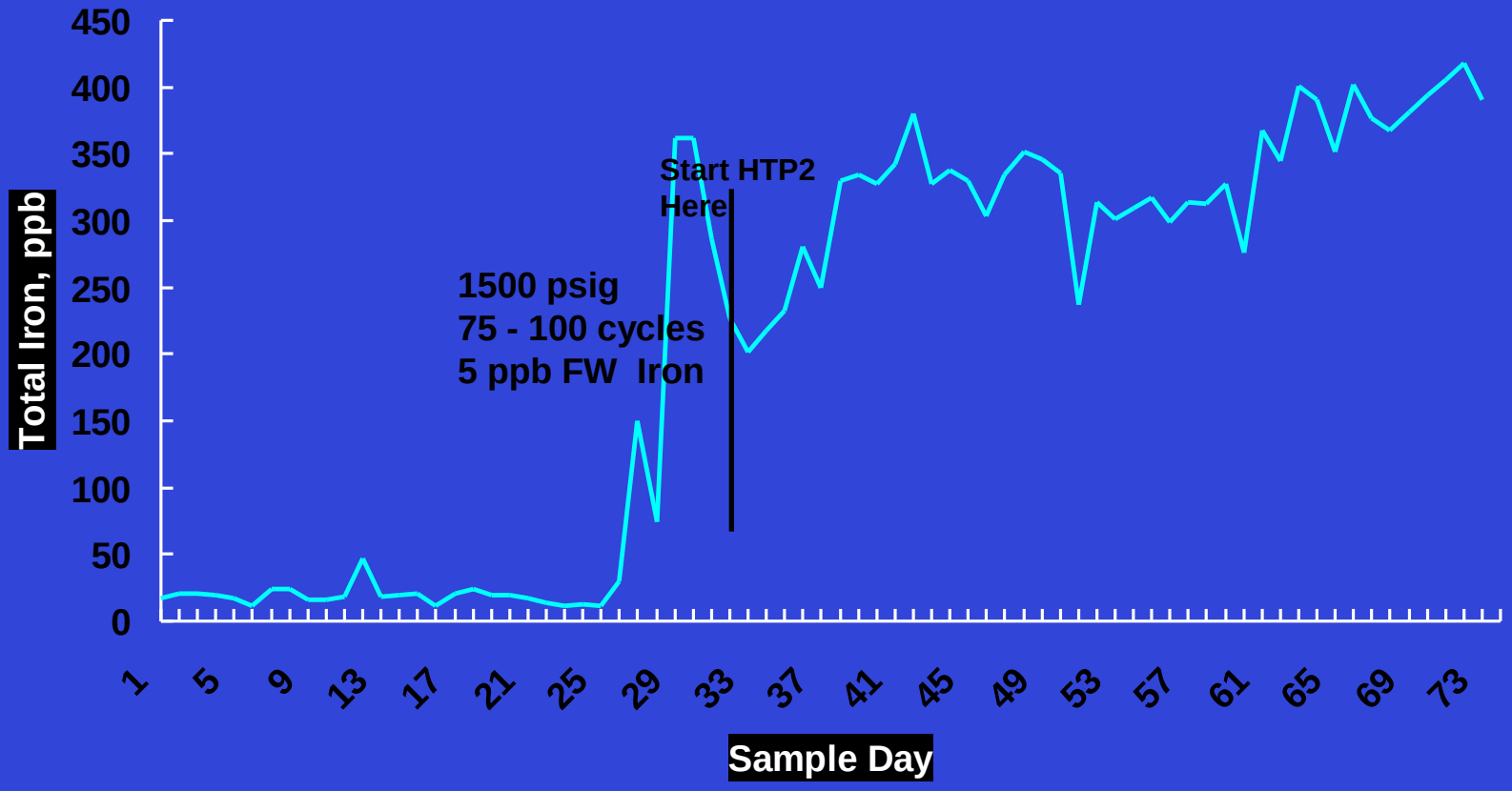

OptiSperse HTP2

- The product has been effectively and safely used in all major industry segments, including paper, chemical, refining, manufacturing, and utility installations.
- It can be used in accounts that require approval for producing paper that contacts food. It is currently not approved for direct food contact.

Paste contacts with Borsig ,TLE makers, confirmed ***OptiSperse HTP2*** as the only allowed into their 1,500 psig boilers.

OptiSperse HTP2

- What makes ***OptiSperse HTP2*** so effective?
  - Prior to ***OptiSperse HTP2,*** all dispersants were based on carboxylate chemistry. These are good, all purpose dispersants for hardness and metal oxides deposit control, but they have limitations under higher stress situations, such as those found in high pressure boilers.

OptiSperse HTP2

- ***OptiSperse HTP2*** was designed by molecular modeling using a phosphate backbone. This enabled the optimum polymer structure to be produced. Phosphate is a known metal oxide dispersant. The products containing this molecule do not lose their performance under higher pressures and longer residence times.

Traditional Polymer Structures

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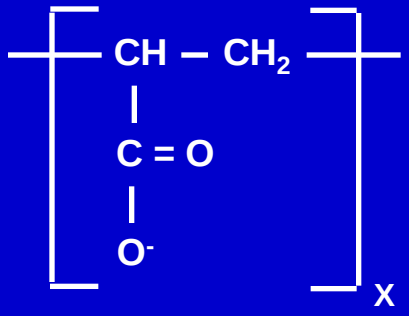
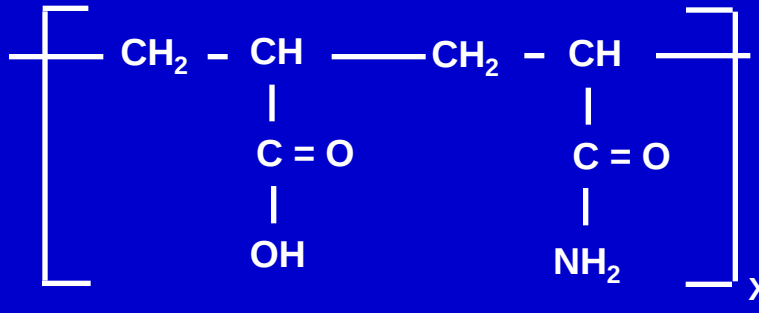
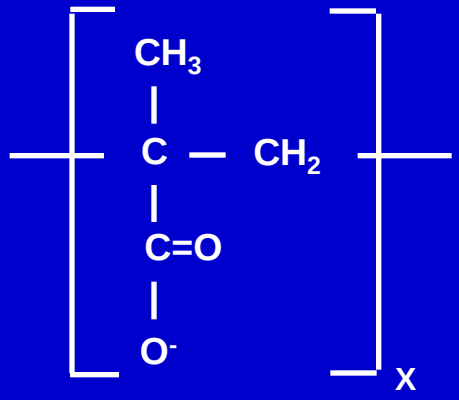


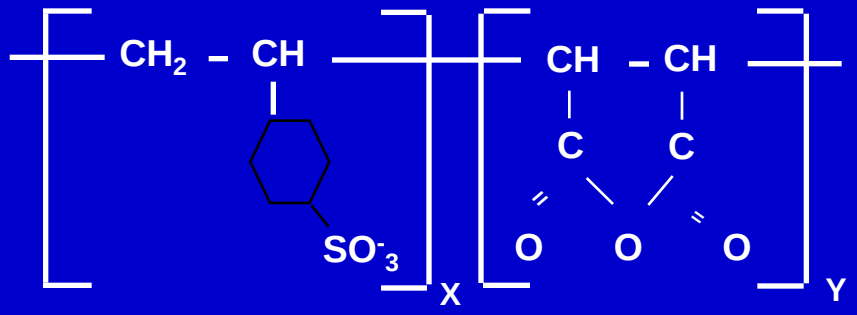
POLYACRYLATE



ACRYLATE-ACRYLAMIDE COPOLYMER



POLYMETHACRYLATE



SULFONATED STYRENE-MALEIC ANHYDRIDE COPOLYMER

GE Betz HTP-2 Polymer Structure

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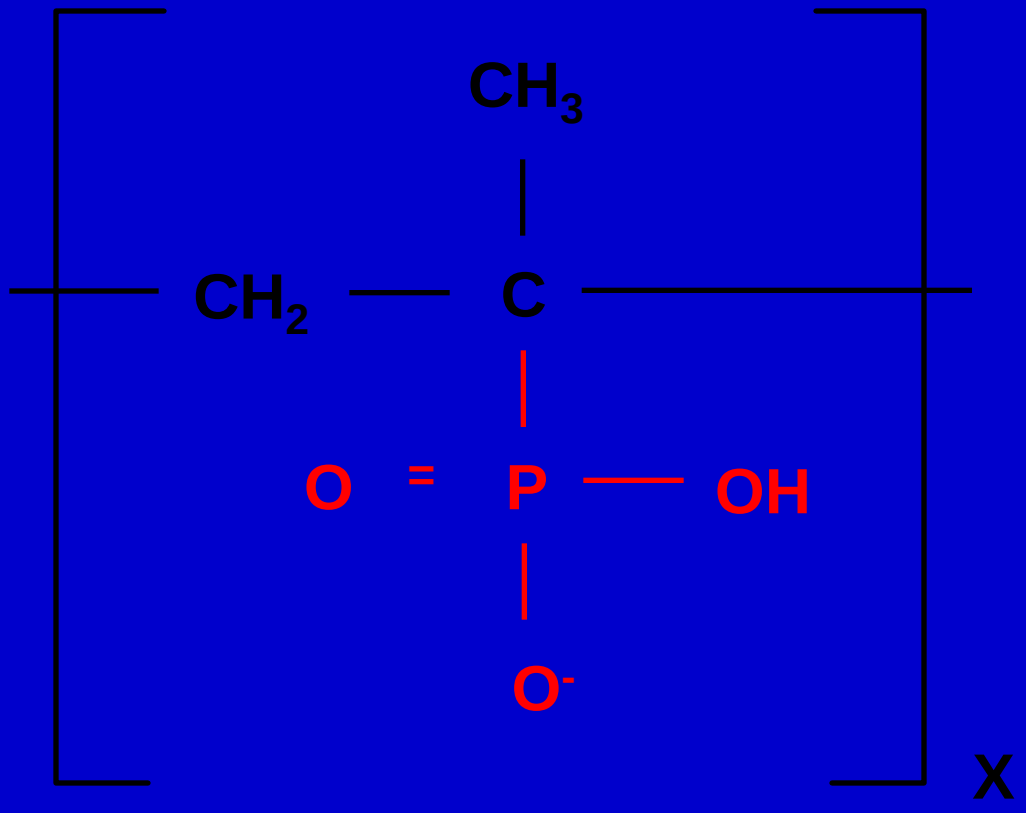

Poly (isopropenyl phosphonic acid)

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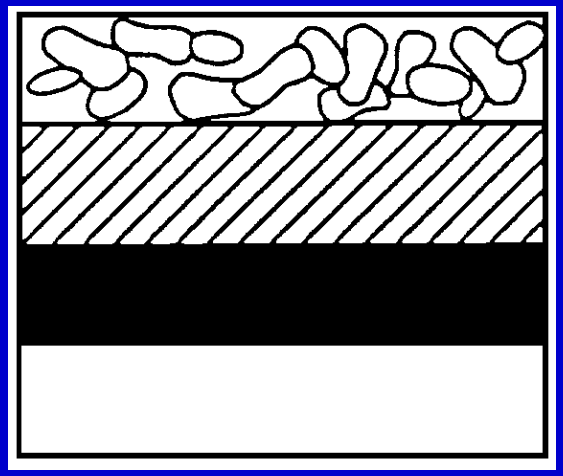
Iron Chemistry - Magnetite Formation

TWO DISTINCT MAGNETITE LAYERS



Particulate Deposition

Outer Layer

Inner Layer

Base Metal

Magnetite Formation

Inner Layer

$$3\,Fe^{\circ} + 4\,H_2O \longrightarrow Fe_3O_4 + 4H_2$$

iron — water — magnetite — hydrogen

- self limiting, tenacious, protective oxide
- does not impede heat transfer

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Magnetite Formation

Outer Layer

- Formed from Fe^{+2} diffusion through inner layer
- Porous, less tenacious, non-protective
- Contributes to deposit weight density (DWD)
- Does impede heat transfer

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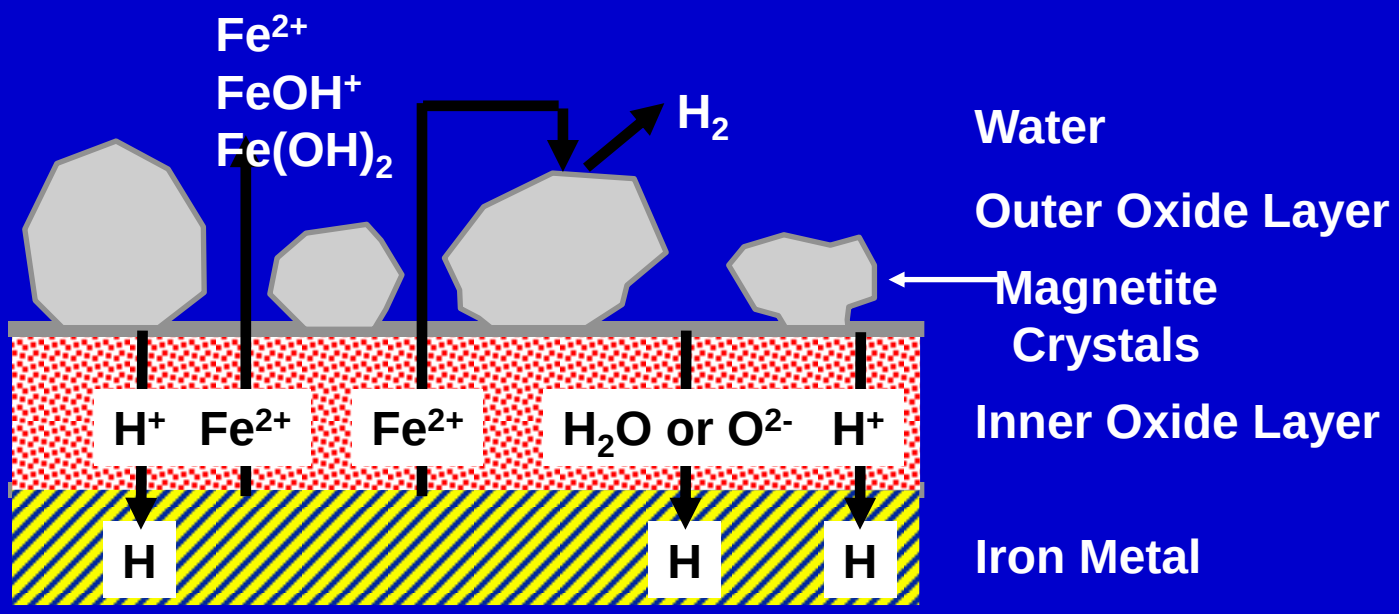
MODEL OF OXIDE LAYERS ON IRON / WATER INTERFACE



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Deposition Layer

- Deposited particulate material
- Typically iron (in high purity systems)
- Porous, loose and non-protective
- Contributes to DWD
- Impedes heat transfer

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How Boiler Polymers Function on Existing Deposition

- Boiler polymers are surface/particle active
- Some polymers show clean-up activity on particle deposition and the outer porous magnetite layer
- Polymers have no impact on the tenacious inner magnetite layer

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Water & Process Training – Rome, june 2003

Thank you for your Attention

Francesco Tozzi