Nalco AT ORP™ Sensor to Measure and Control Corrosion Stress and Corrosivity of Boilers Feed water Systems

Essential Expertise for Water, Energy and Air SM

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CONTROL OF CORROSION AND CORROSION PRODUCT TRANSPORT IN BOILERS CONDENSATE AND FEED-WATER SYSTEMS IS CRITICAL TO MAINTAINING RELIABLE, EFFICIENT OPERATIONS.

HIGH CORROSION RATES CAN LEAD TO A VARIETY OF SYSTEM PROBLEMS, WHICH INCLUDE LOCALIZED CORROSION AND FAILURE OF FEED-WATER HEATER TUBES, BOILER TUBE CORROSION AND FAILURES, BOILER DEPOSITS AND FREQUENT CLEANING

- ***Control of the corrosive environment through the use of passivator is a widely accepted practice and a part of the EPRI recommendation is to utilize oxidation-reduction potential (ORP) for passivator control in AVT-R programs.***
- ***However, the use of low-temperature ORP for monitoring and control of redox stress in the feed-water system has been quite problematic for most users as the low-temperature ORP systems cannot detect the true reduction/oxidation stress that is found under operating temperatures in feed-water systems.***

- ***There have been new developments in automation technology for boiler feed water treatment monitoring and control to help meet these challenges.***
- ***This paper discusses Nalco's best practice for boiler feed water treatment automation technology using AT ORP probe, with the 3DTrasar boiler technology.***

- ***Traditional FW REDOX stress management philosophy is to:***
- ***Feed an oxygen scavenger/reductent at a constant feed rate to the FW.***
- ***Analyze FW or boiler for residual levels of scavenger perhaps once per shift***
- ***Scavenger feed rate is adjusted accordingly to maintain a desired residual amount in the water.***

- ***The drawback to these REDOX stress management control scenarios is that they are incapable of true system REDOX stress control, because REDOX stress is not being measured and systems themselves rarely operate at steady state.***
- ***To address the need for improved monitoring and control of boiler FW REDOX stress events, Nalco Company in 2000 began a research effort to develop a technology that could measure the actual FW REDOX stress at the temperatures and pressures of the operating boiler systems.***

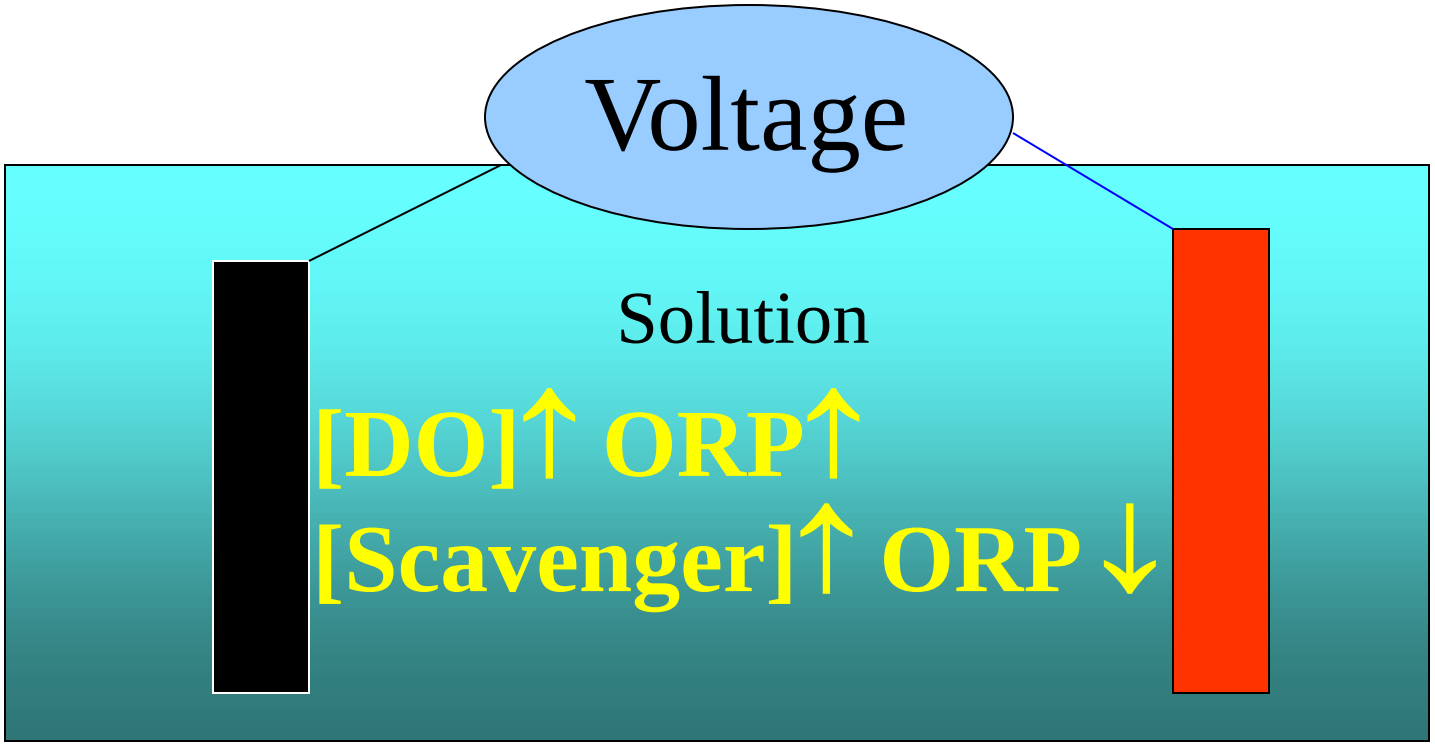
3D TRASAR TECHNOLOGY

DETECT DETERMINE DELIVER

- ***After 10 years extensive R&D effort we developed an innovative @T ORP™ sensor technology that measures the net oxidation-reduction potential (ORP) of the water at actual FW system temperatures and pressures***
- ***The @T ORP™ provides a quantum improvement in FW REDOX stress management greatly improving preboiler corrosion control with continuous, real-time monitoring and diagnostics***
- ***Measuring and reacting to the changing corrosivity of the system at actual operating conditions. The @T ORP technology automatically feeds chemicals on demand based on true at-temperature and pressure REDOX changes.***

- ***Nalco @T ORP™ provides a quantum improvement (and paradigm shift) in FW REDOX stress management by:***
  - ***greatly improving preboiler corrosion control***
  - ***with continuous, real-time monitoring and diagnostics***
  - ***by measuring and reacting to the changing corrosivity of the system at actual operating conditions.***
  - ***The @T ORP technology automatically feeds chemicals on demand based on true at-temperature and pressure REDOX changes.***

What is ORP?
Oxidation Reduction Potential (REDOX)



Type
Temp.

Noble Metal

Reference Electrode

$Ag + Cl^- \leftrightarrow AgCl + é$

EPBRE vs sat KCl

External Pressure Balanced Reference Electrode

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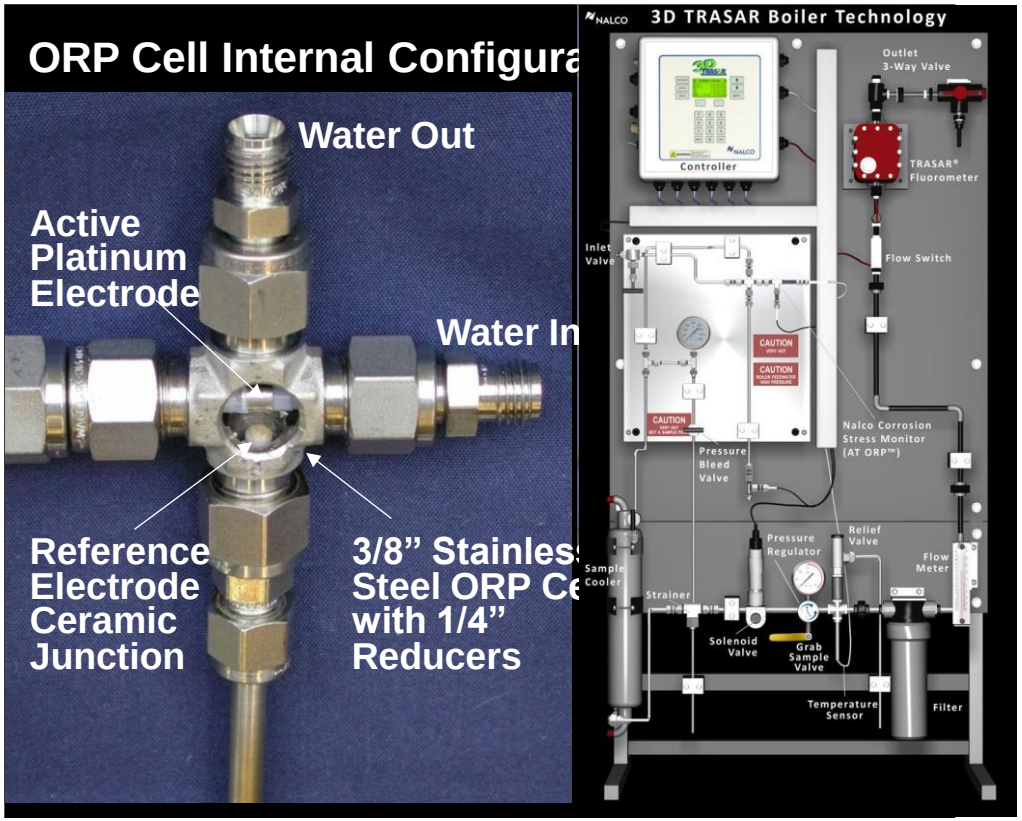
WHAT DOES AT ORP DO?

NCSM with AT ORP technology: Provides a paradigm shift in corrosion stress measurement, understanding and control



- The AT ORP program feeds reductant to maintain the system in an AT ORP control zone
- It responds to AT ORP stress, which correlates with system corrosion events
- The AT ORP probe responds quickly and with the appropriate magnitude / sensitivity to the actual redox stress event
- Action is taken immediately 24/7 to resolve the issue within the MOC constraints of the plant
- Chemistry is fed on demand

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NCSM - A Custom-Built ORP Analyzer

- ORP → **O**xidation **R**eduction **P**otential
- Considerations:
  - Corrosion is linked to REDOX potential
  - REDOX potential is indicated by ORP voltage (mV)
  - ORP voltage can be used to assess bulk FW corrosivity
- FACT: Reducing conditions, as indicated by more negative ORP values, tend to result in lower corrosion. Oxidizing conditions, similarly, tend to be more corrosive.

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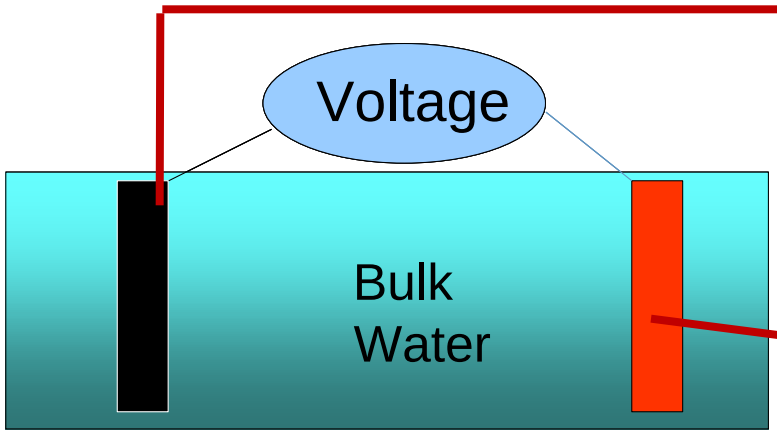
NCSM: How does it work?

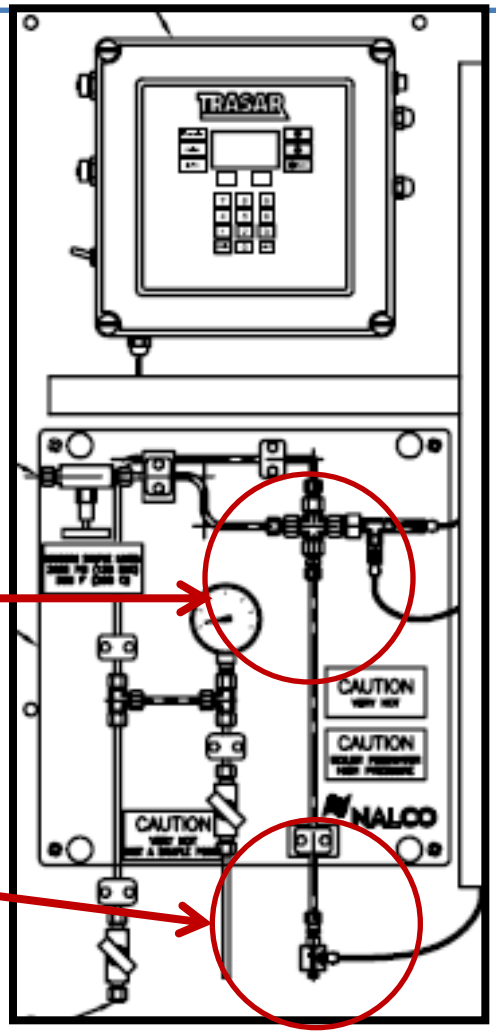
The NCSM compares a reference electrode (EPBRE) to an inert, platinum electrode.

The inert electrode does not participate in any corrosion reactions , unlike a corrator probe.



Inert Metal (Pt)

External Pressure Balanced Reference Electrode (EPBRE)



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ORP indicates the potential for water to corrode

Corrosion = REDOX Reactions

REDOX Reactions = Electron Flow

Electron Flow = ORP (mV) (Oxidation Reduction Potential)

ORP = bulk FW corrosivity

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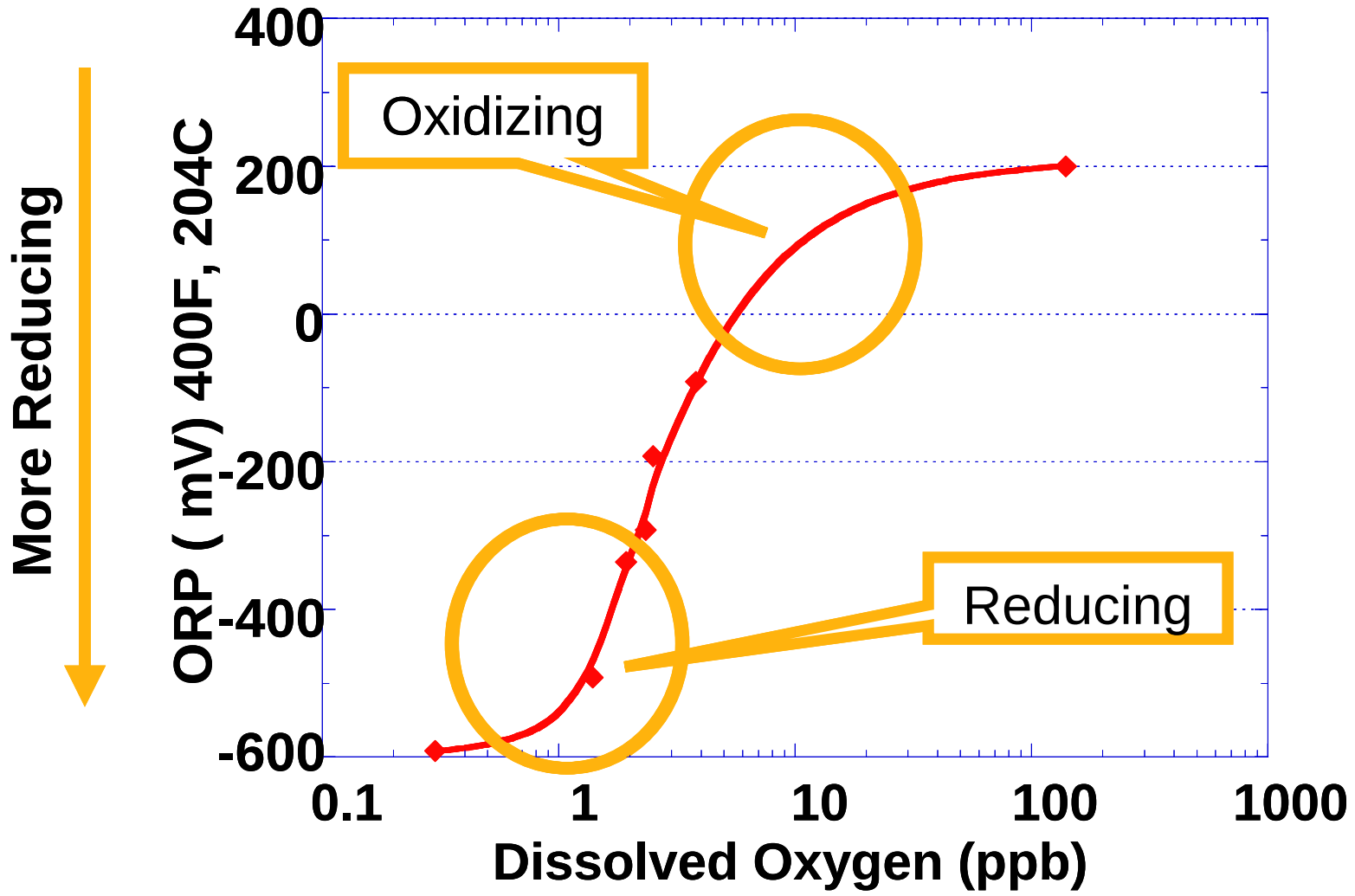
Reducing conditions minimize corrosion (more negative ORP)



How does NCSM control corrosion stress?

- Detects REDOX stress in a boiler feed water system (ORP at operating T & P)
- Determines correct response to REDOX stress
- Delivers the correct amount of scavenger to minimize the corrosivity of boiler feed water

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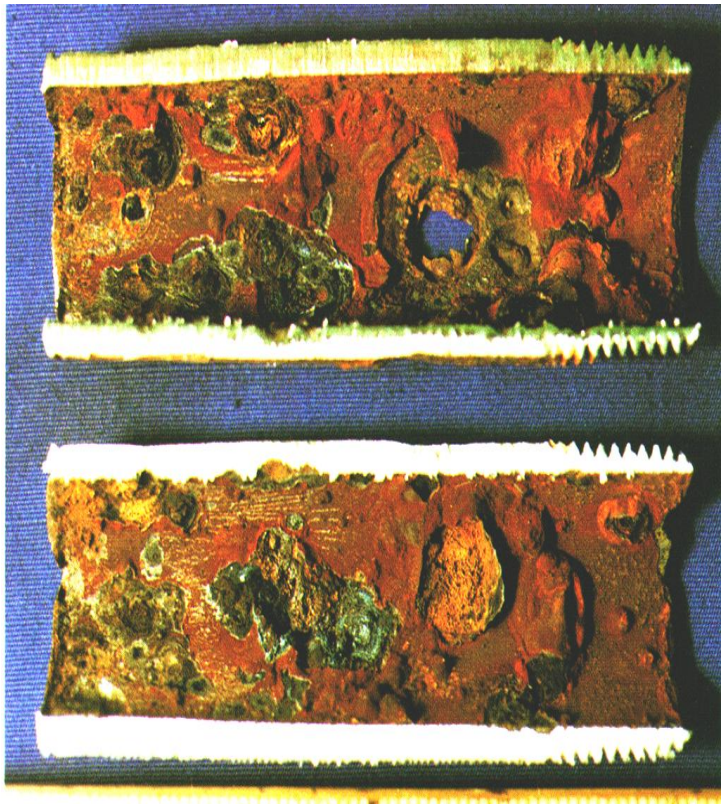
Oxygen Corrosion Control

- Mechanical Deaeration
  - primary means of O2 removal
- Chemical Oxygen Scavenging
  - removal of trace amounts of O2 remaining after deaeration
- Maintain Reduced Conditions
  - minimize corrosivity
  - promote passivation



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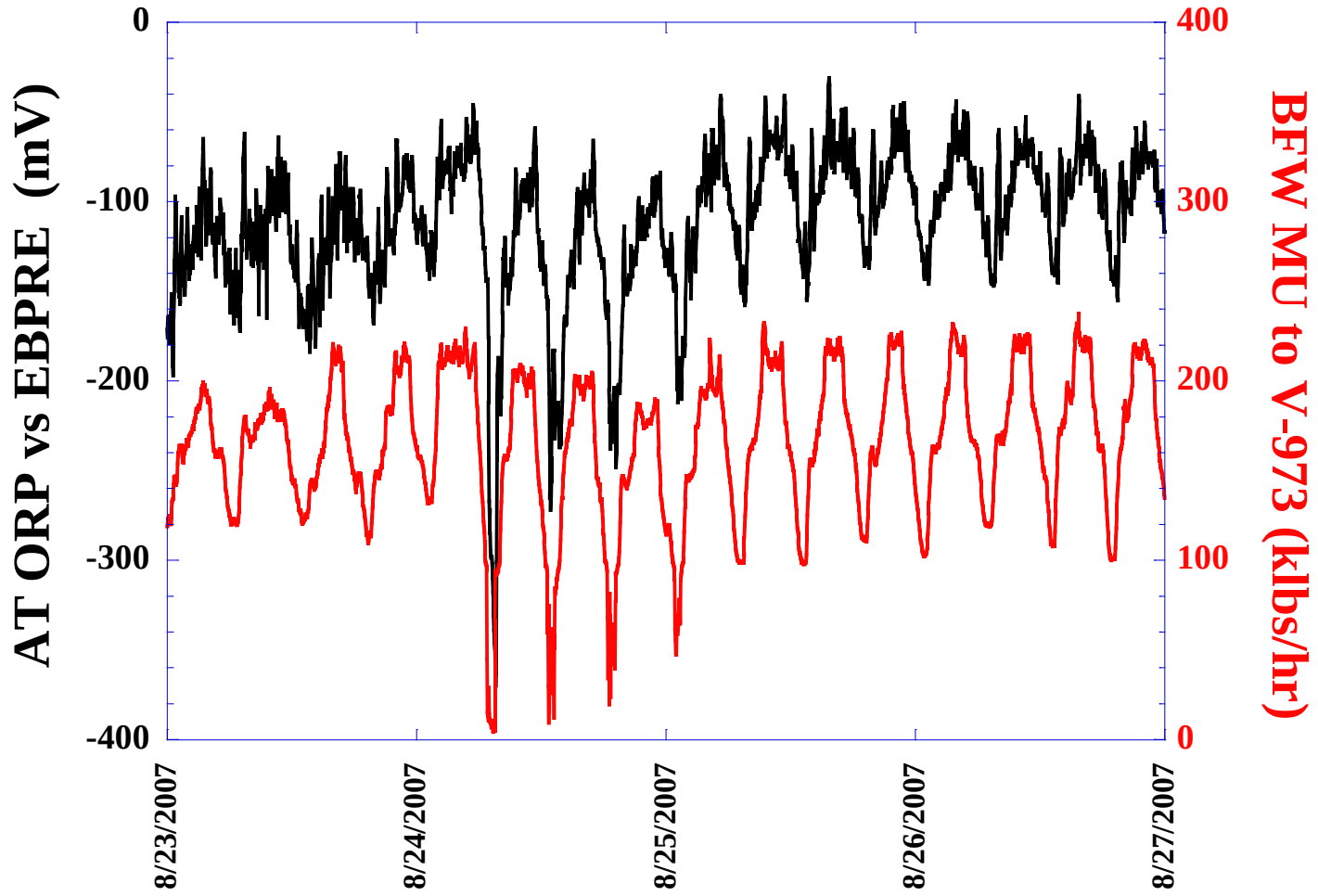
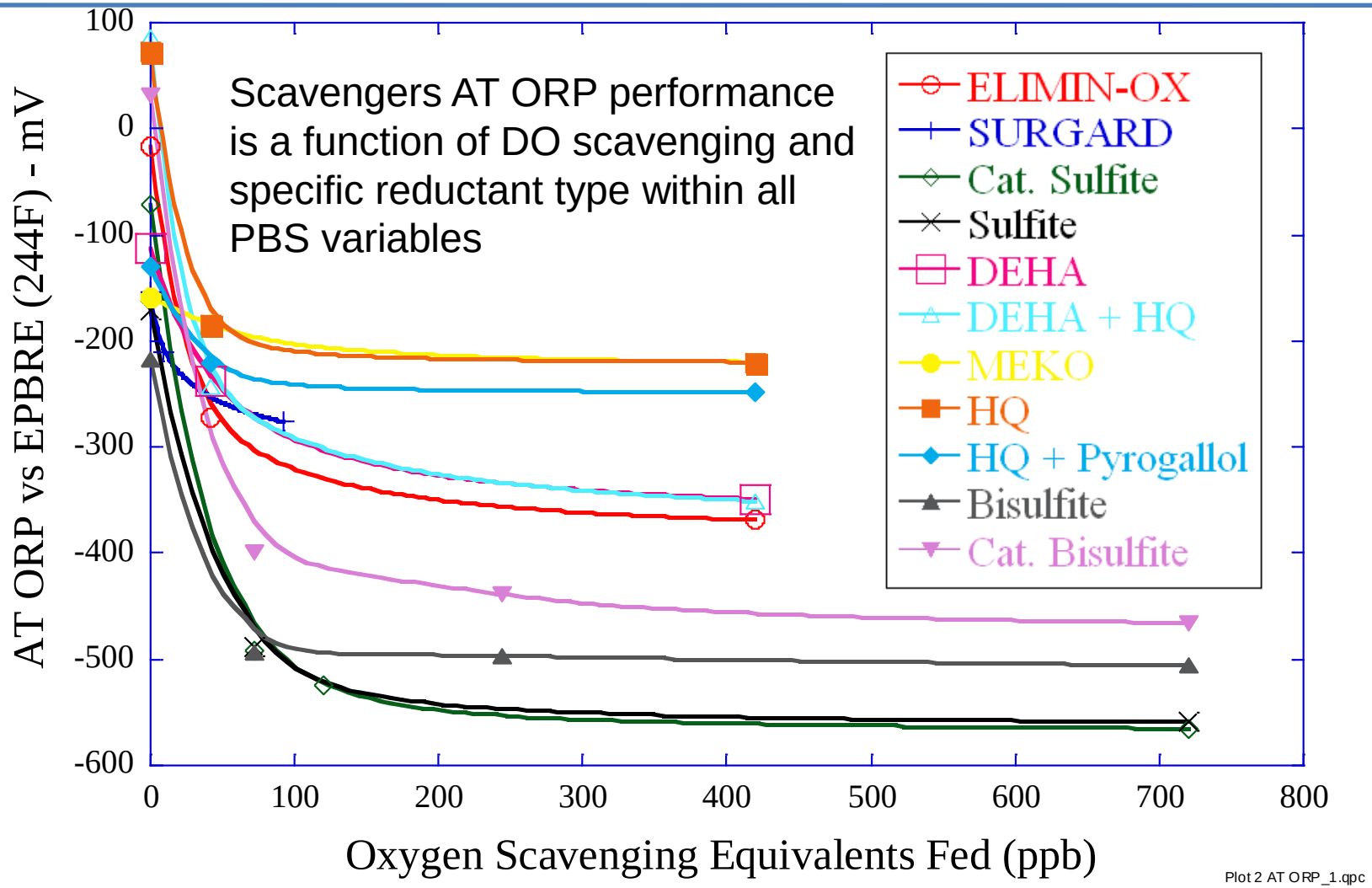
MU water flow variations and their effect on REDOX stress

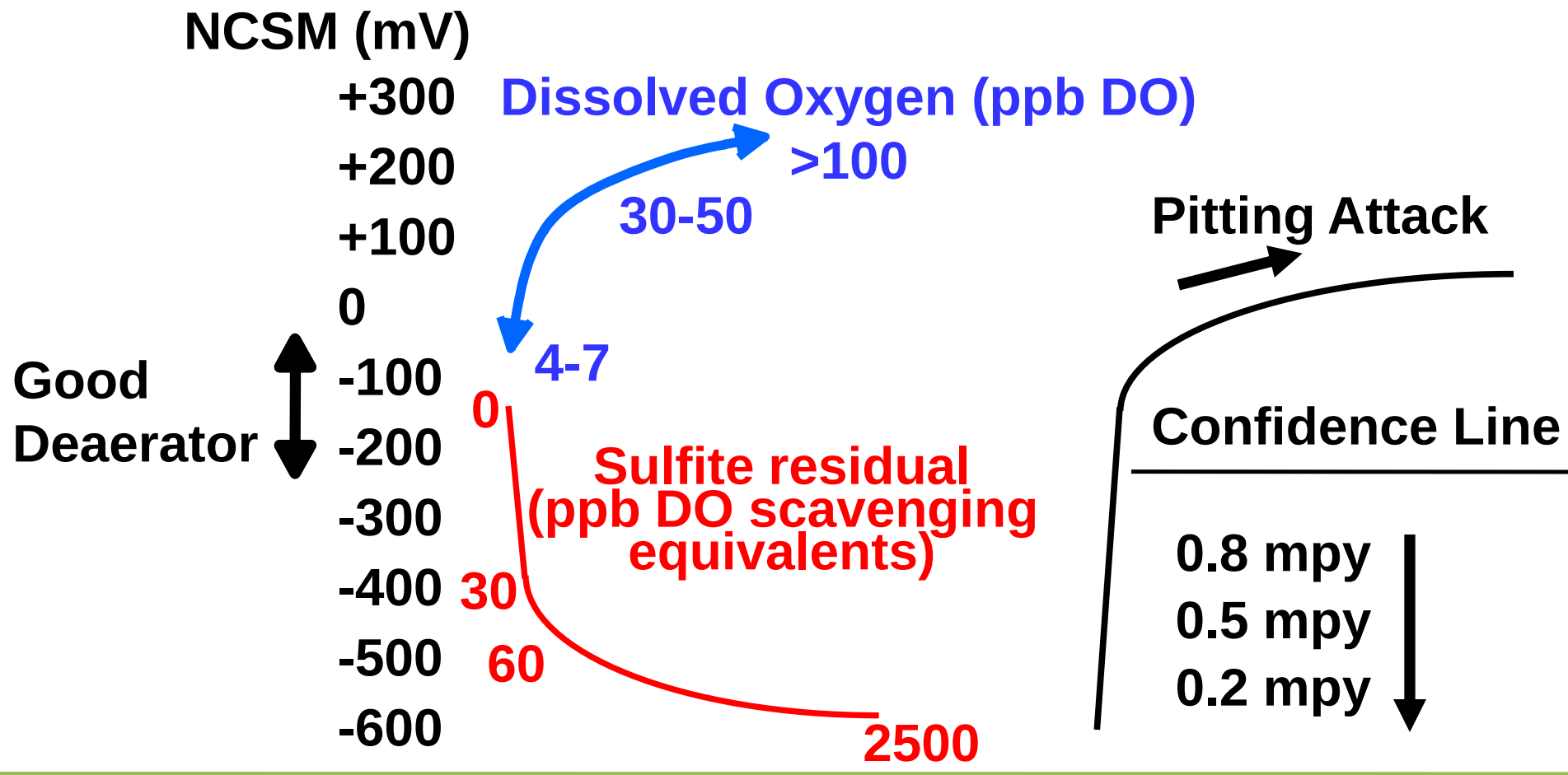


AT ORP on Scavenger addition

(Deaerated DIW: DO_i = 6 ppb)



Example of NCSM operating ranges for sulfite & carbon steel system (400F)



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Current Oxygen Corrosion Monitoring

- Check mechanical deaeration
  - Plume
  - Dome & Storage Section Temperature Differential
- Monitor & Control product residual in BW
- Oxygen Testing
  - Online DO Analyzer
  - Chemets
- Total Fe & $Fe^{+}2$ Testing

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Corrosion & @T ORP Correlations

- ***Corrosion***
  - ***Higher, more positive @T ORP***
  - ***Soluble species such as Fe_2O_3***
- ***Lower Corrosion***
  - ***Lower @T ORP***
  - ***Soluble species such as Fe_2O_3 minimized***
  - ***Low oxygen, reduced state***
- ***Lowest Corrosion - Passivation***
  - ***Lower @T ORP with higher pH***
  - ***Solid phases such as Fe_3O_4***
  - ***Solid, protective oxide film inhibits further metal dissolution***
  - ***Corrosion will be minimized***

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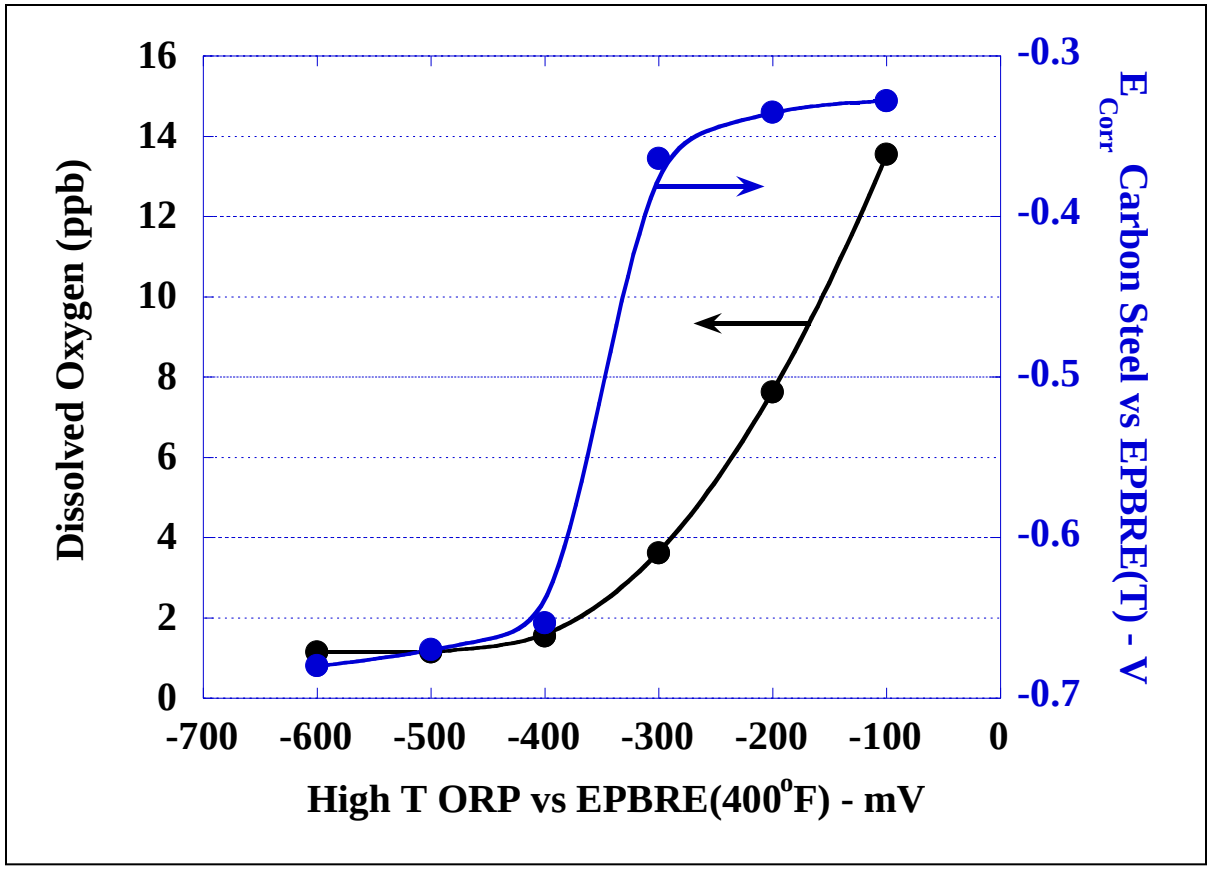
Example: Engineering Alloys and Corrosion Potentials



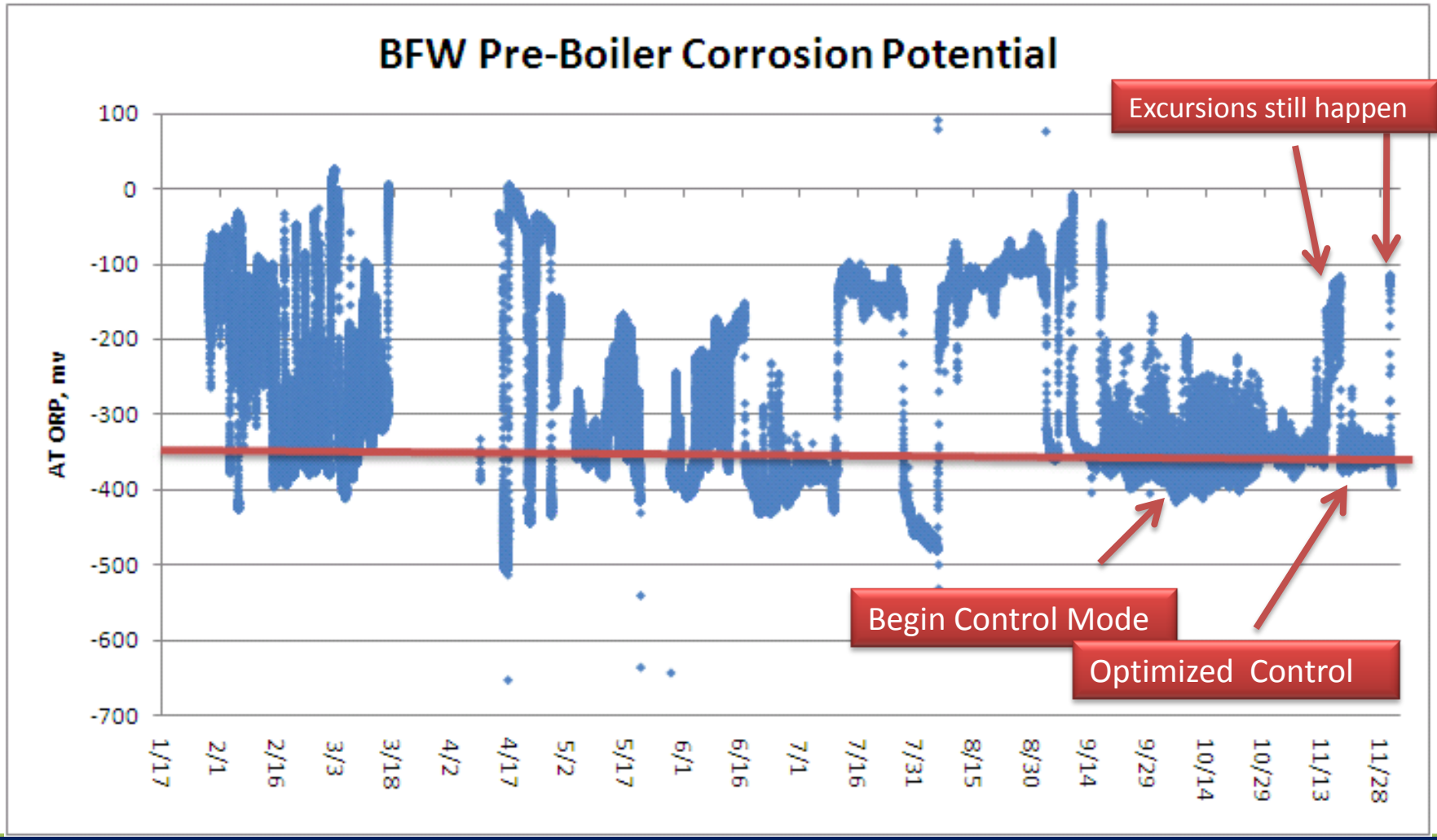
In this case notice how the corrosion potential of carbon steel declines as oxygen is removed from the system with the oxygen scavenger erythorbic acid. The data is plotted with the @T ORP data at 400F.

Case Study #1

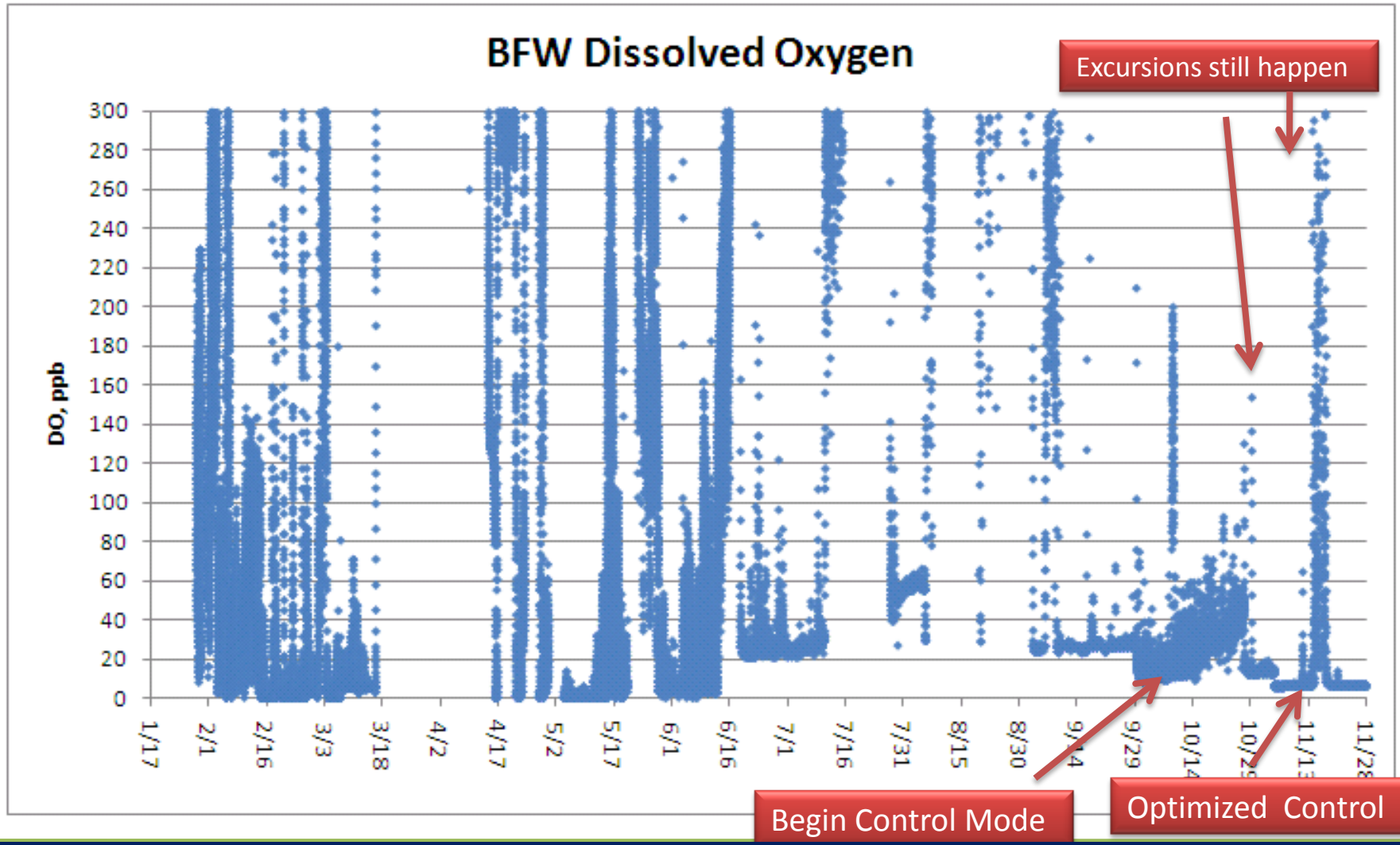
Gulf Coast Refinery

- Utilities Unit
  - NaZ MU
  - 600# Boilers

3D TRASAR Pre-Boiler Corrosion Control with the NCSM (AT ORPTM)



Dissolved Oxygen Before & After Automatic Control



Dissolved Oxygen
Before & After Automatic Control

	Before	After
# data points	86,837	8,825
average	172.0	31.5
min	0.0	5.8
max	2091.3	520.4
-3 std dev	-942.5	254.4
+3 std dev	1286.5	-191.5

% in control	59%	89%

Summary

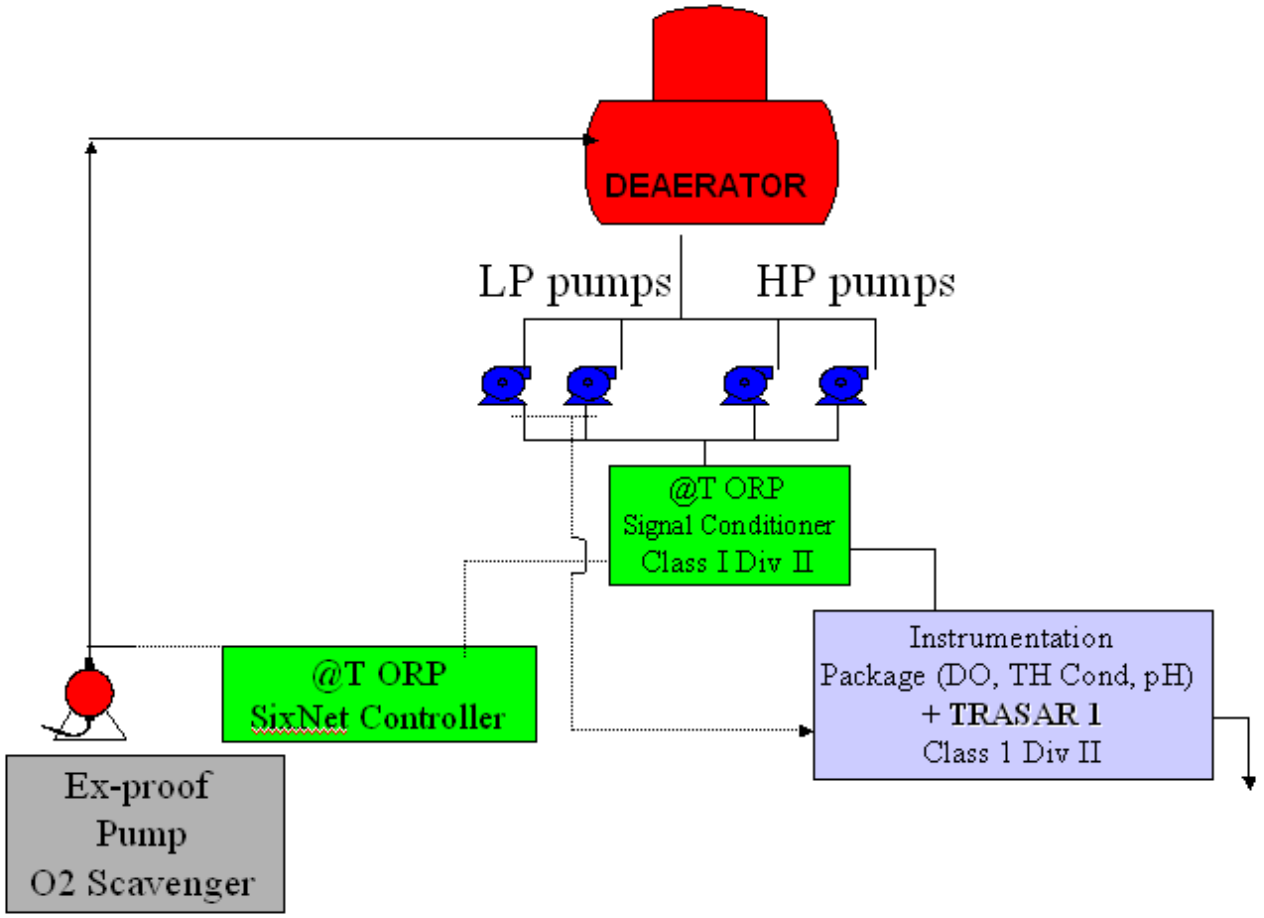
- Poor operating Graver unit results in *excessively* high FW DO levels which cause severe corrosion stress conditions
- NCSM AT ORP detects & responds immediately to changes in BFW REDOX/corrosion stress conditions caused by poor operating DA
- Manual feed of scavenger provides poor BFW corrosion stress control
- The use of AT ORP to automatically control feed of EliminOx significantly reduces the DO & corrosion stresses
- Feeding EliminOx instead of sulfite reduces the overall solids loading on the boiler
- Opex Reduction: chemical oxygen scavenger spend ~ $75K
- **Net Result – Improved Reliability**
  - **Decreased potential for pitting corrosion**
  - **Decreased potential for super heater tube fouling**

Case Study #3

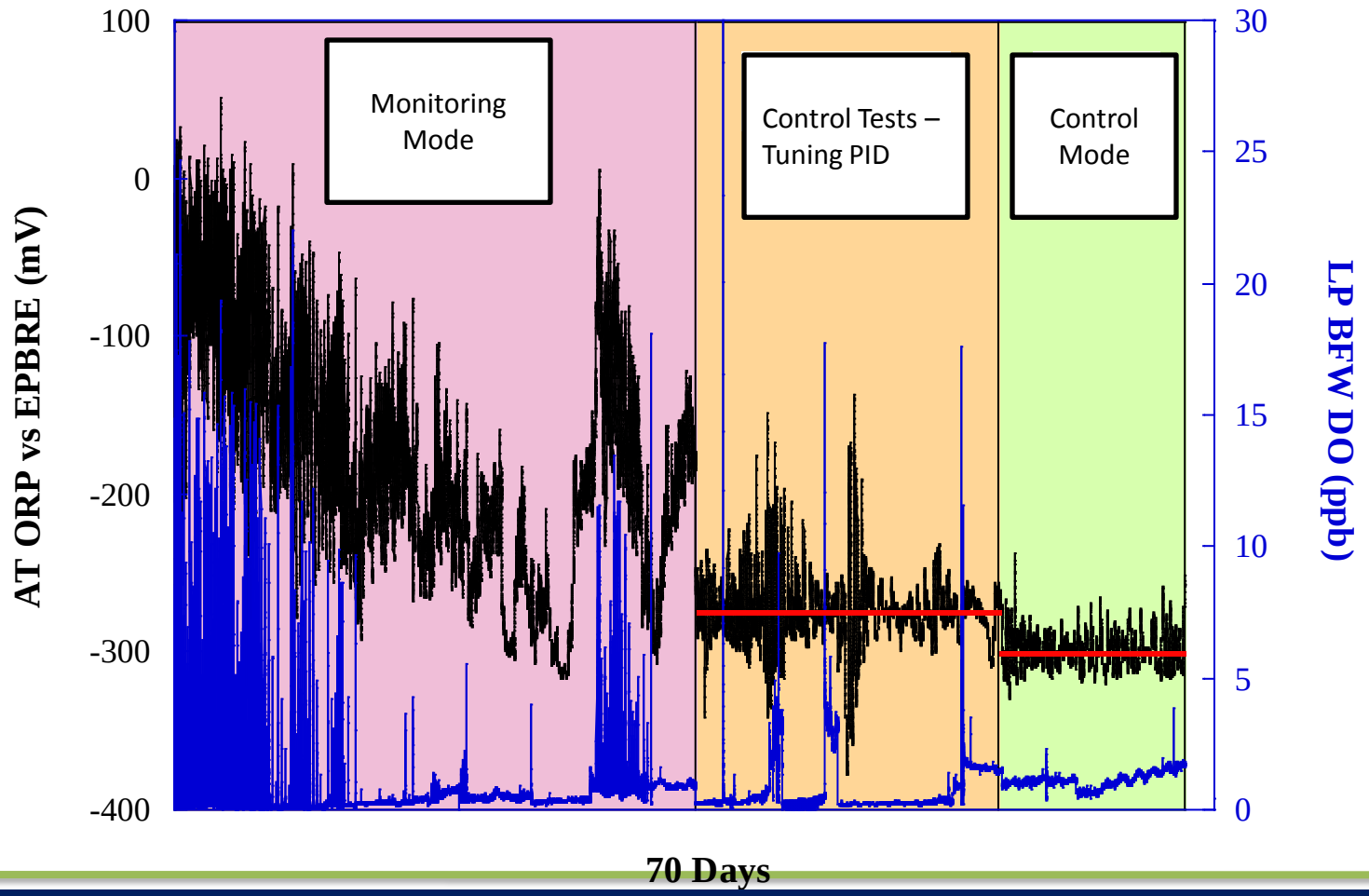
West Coast Refinery

- #600 WHBs at Isomerization Unit
- RO & Condensate MU

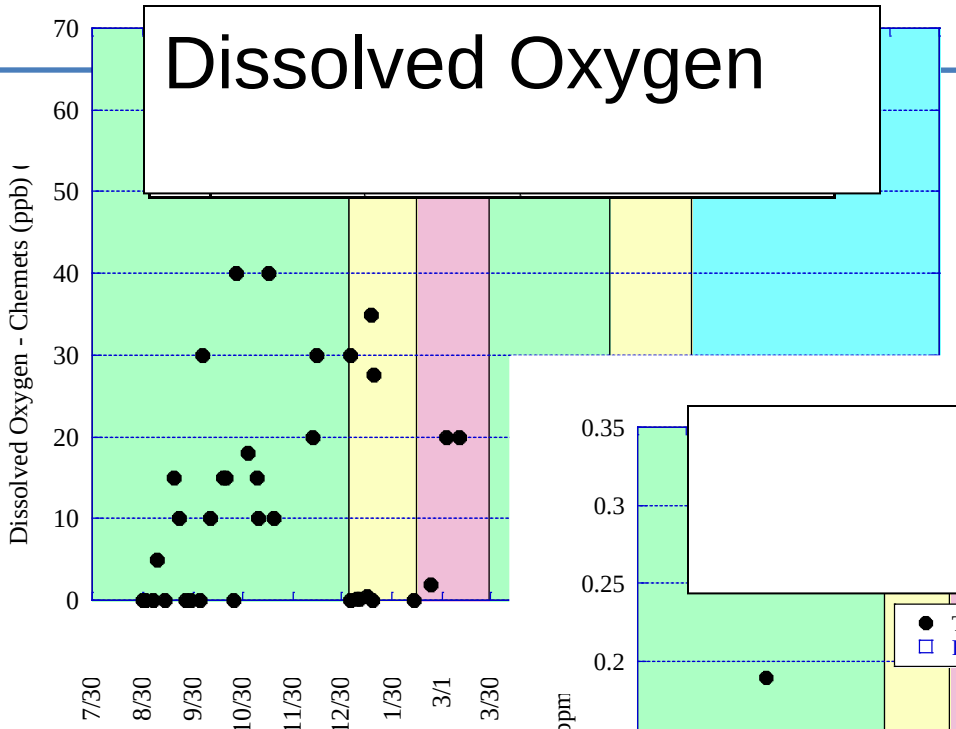
System Layout

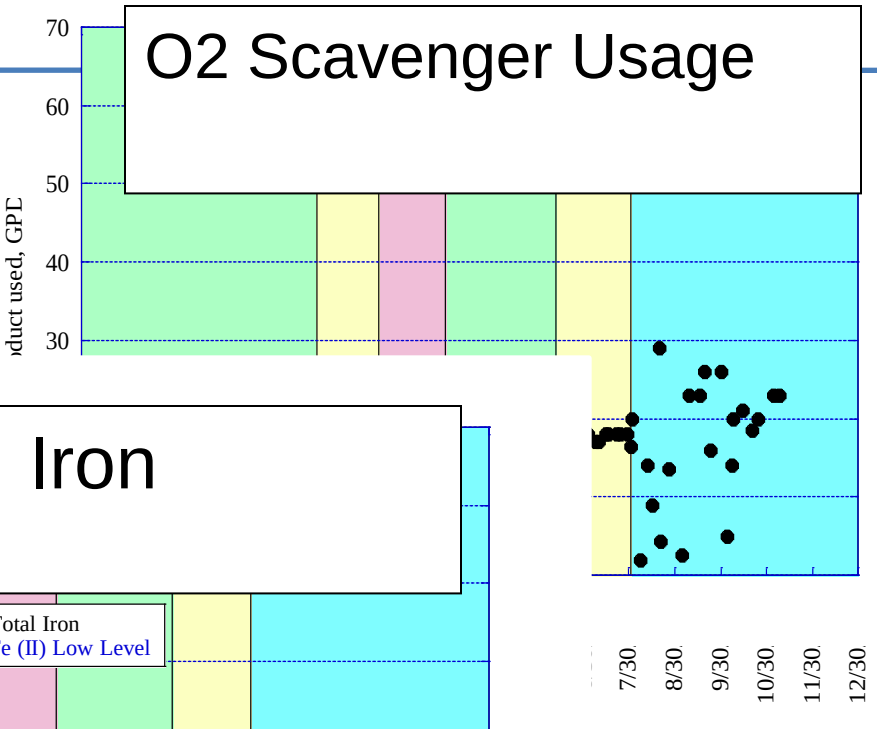


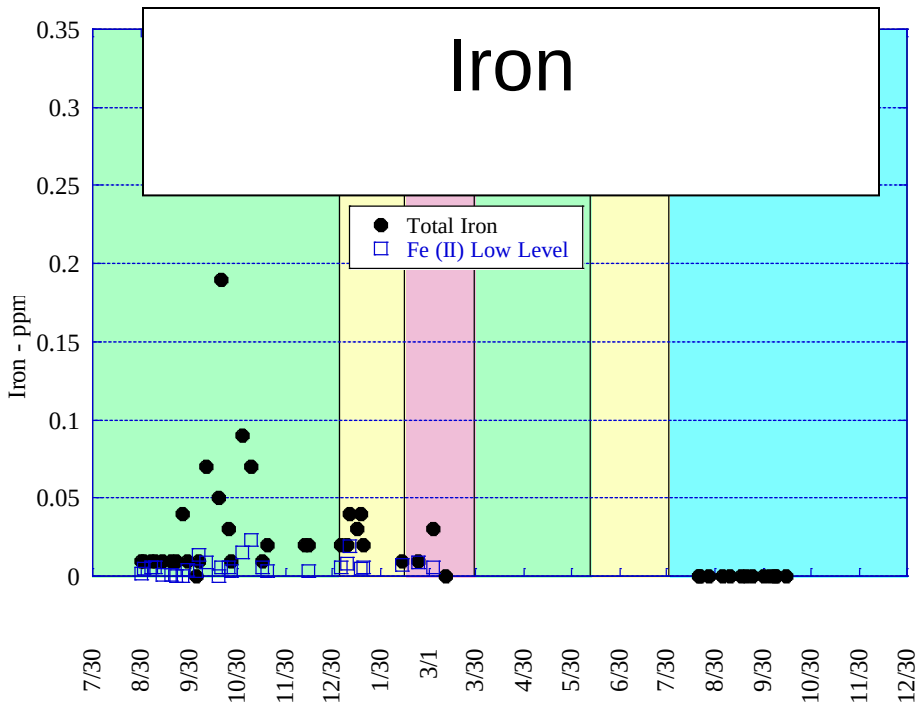
Results


AT ORP and DO for Monitoring and Control Tests
Monitoring Mode
Control Tests – Tuning PID
Control Mode
AT ORP vs EPBRE (mV)
LP BFW DO (ppb)
100
0
-100
-200
-300
-400
30
25
20
15
10
5
0
70 Days

Results- Grab Samples

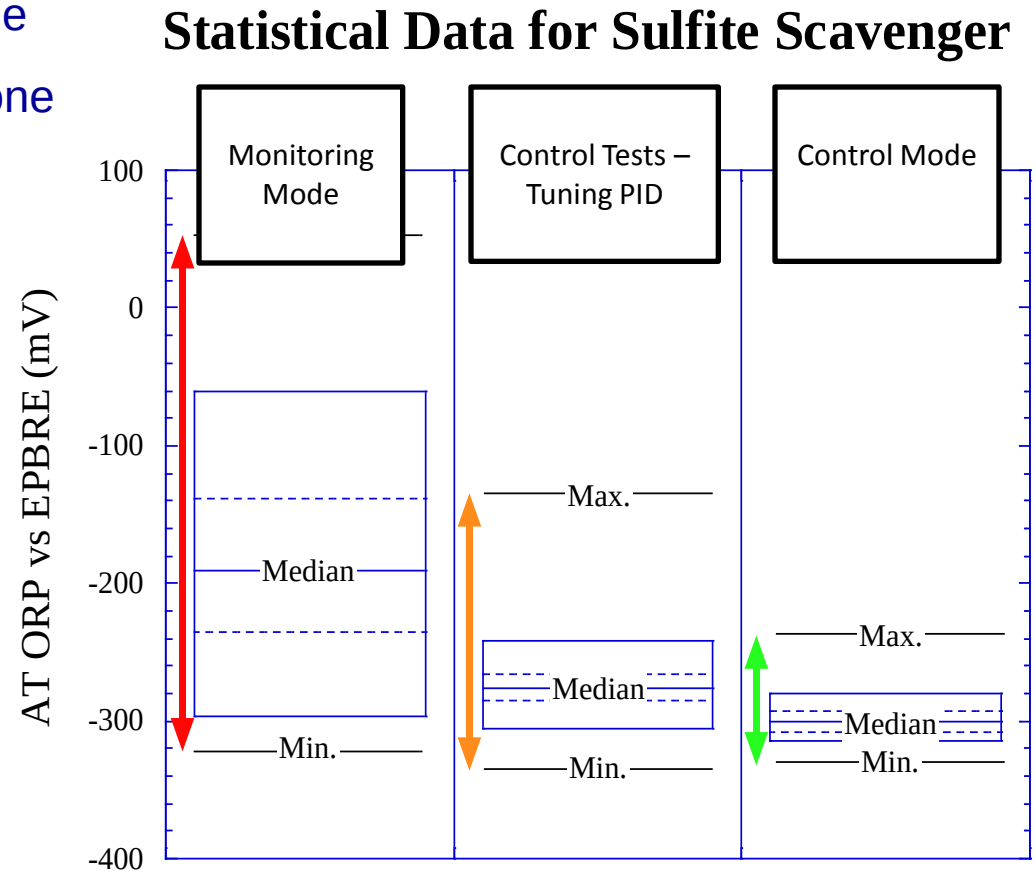






Results

- ✓ Best System Specific Scavenger found & utilized
- ✓ Determined Optimum AT ORP Zone
- ✓ Ability to **Stay** in Optimum ORP Zone
- ➢ Minimize Pre-Boiler Corrosion



3D TRASAR Corrosion Control

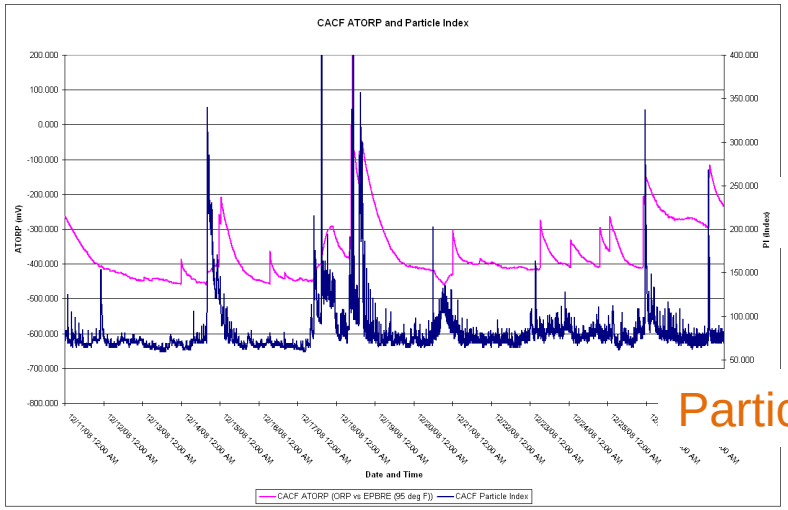
3D TRASAR Boiler Automation with AT ORP
helped the refinery:

- Understand the system stresses
- Diagnose & troubleshoot during upset conditions
- Determine the optimum REDOX operating zone to minimize pre-boiler corrosion potential
- Pro-actively feed the optimum amount of chemical regardless of system stresses

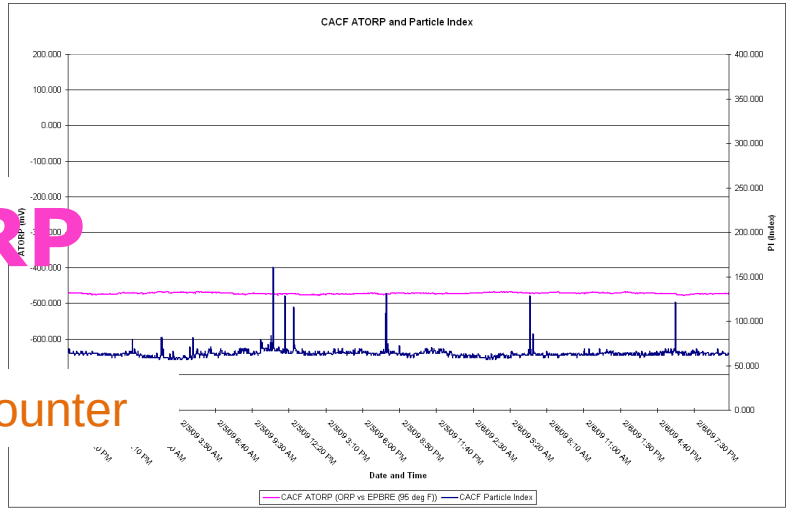
Improve Boiler System Reliability!

Less corrosion, less corrosion product

Traditional feed/control before NCSM



After NCSM control



ORP

Particle Counter

ORP measurements made with the NCSM correlate tightly with measurements made with a particle counter.

NCSM-based control of scavenger feed delivers less variability and less corrosion product generation.

3D TRASAR TECHNOLOGY

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Understanding the benefits of AT-ORP™ - We Expect:

- The deferral of feed water heater replacements
- Cleaner boilers, less tube damage and lowered cleaning costs
- Cleaner superheaters, reheaters and turbines with reduced repairs
- Better plant availability (e.g. thermal loading limited on startup) and longer plant life
- Better recognition of and response to feed water system mechanical and chemistry problems
- Reduced treatment chemical wastage
- Continued growth in the understanding of our systems
- Potential savings of millions of dollars each year and millions more in unit life extension
-

THANK YOU!