Particle Measurement for Iron Transport and Iron Analysis

2015 Air Cooled Condenser Users Group

Gettysburg, PA

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Air Cooled Condenser Users Group

OBJECTIVES

- Introduction to FAC Monitoring
- Alternatives for monitoring corrosion product transport in the steam cycle
  - On-line surrogate method (suspended iron)
  - Grab sample method (total iron)
  - Millipore filter pad (suspended)
- Data from plants with ACCs

Overview

Flow Accelerated Corrosion (FAC):

- a chemical and mechanical corrosion mechanism which steadily erodes the inside of piping and other carbon steel components.

- identified as the cause of several power plant accidents & deaths

- is extremely expensive in terms of mechanical failures

- is particularly problematic for plants using air cooled condensers

FAC Overview

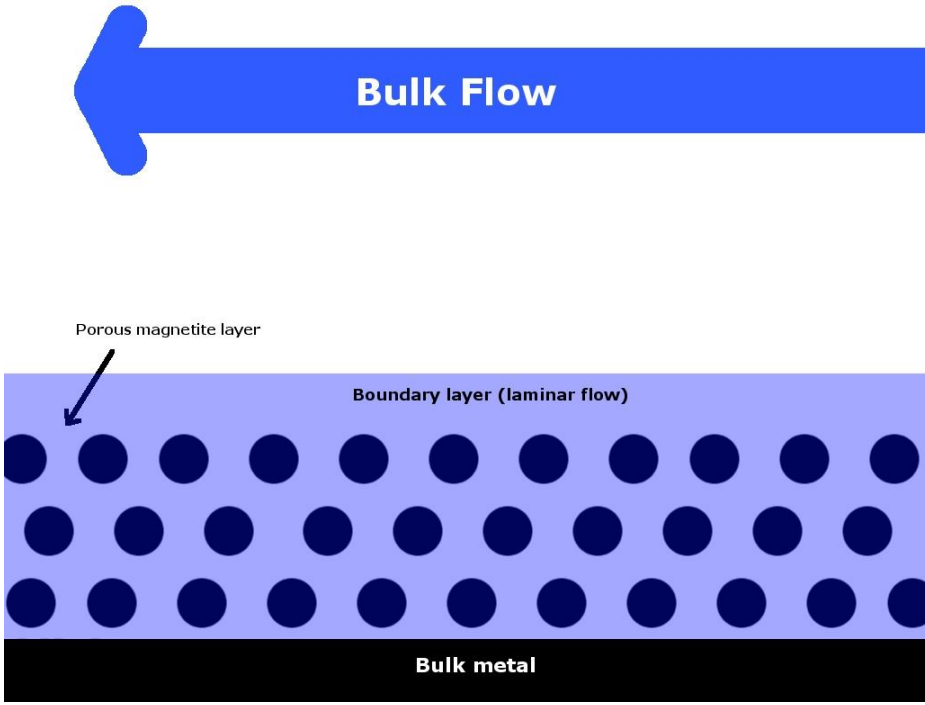
Protective Magnetite

Reducing with laminar flow

Soluble ferrous iron is transported from the bulk metal to the boundary layer

Ferrous iron creates a porous protective layer of particulate magnetite, Fe_3O_4.

Magnetite layer protects the bulk metal



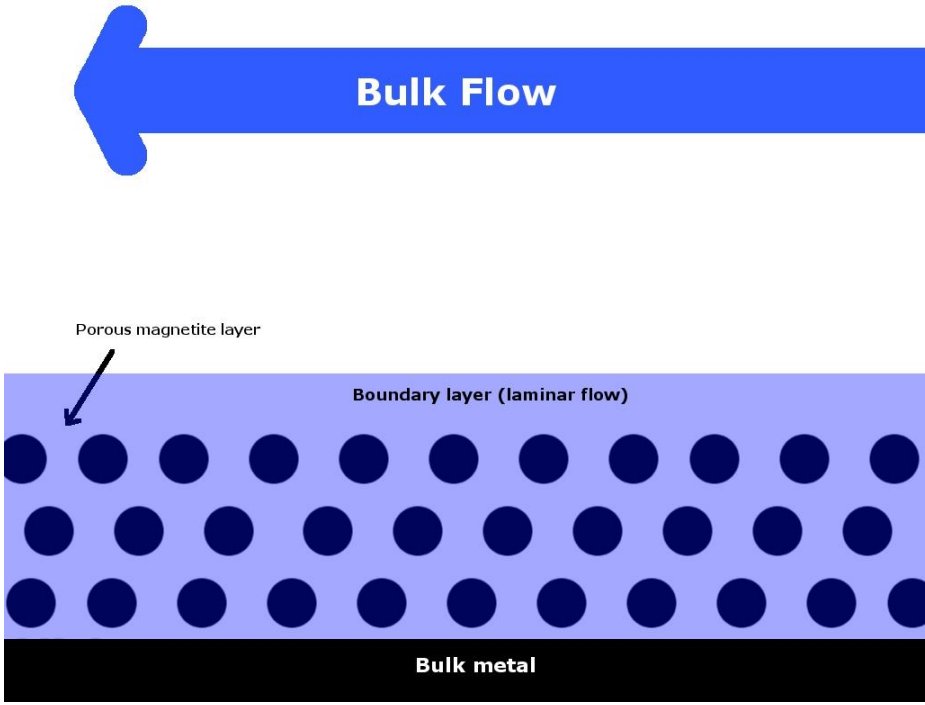
FAC Overview

Protective Hematite

Oxidizing conditions

Ferrous iron ions oxidize & combine with oxygen to form hematite

Hematite particles distribute throughout the porous magnetite lattice forming a strong protective layer



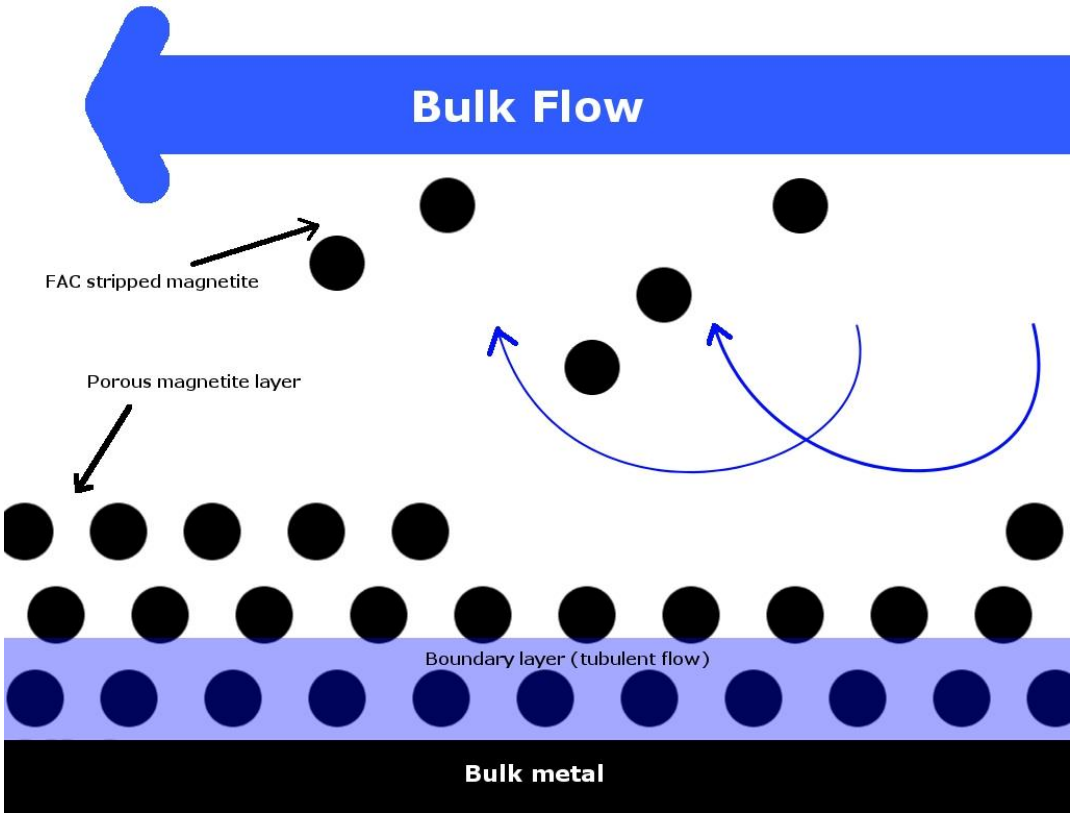
FAC Overview

Magnetite Stripping

Turbulent flow strips the protective magnetite layer from the metal surface

Metal is thinned and weakened

Magnetite is re-deposited in other areas



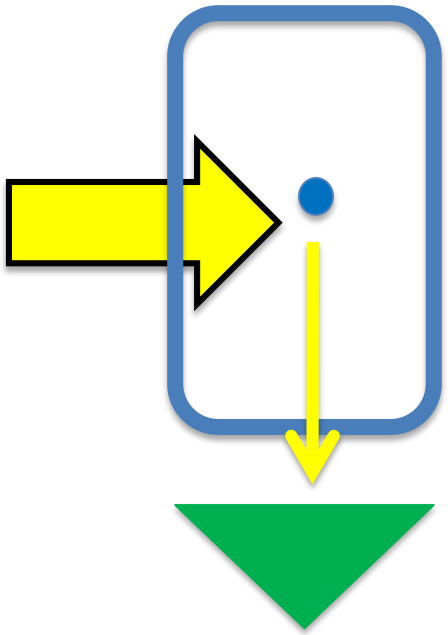
Traditional Sampling Methods

- Inductively Coupled Plasma
  - Optical Emission Spectrometry (ICP-OES)
  - Mass Spectrometry (ICP-MS)
- X-Ray Flourescence (XRF)
- Particle Counters & Monitors
- Colorimetric (lab) – very limited

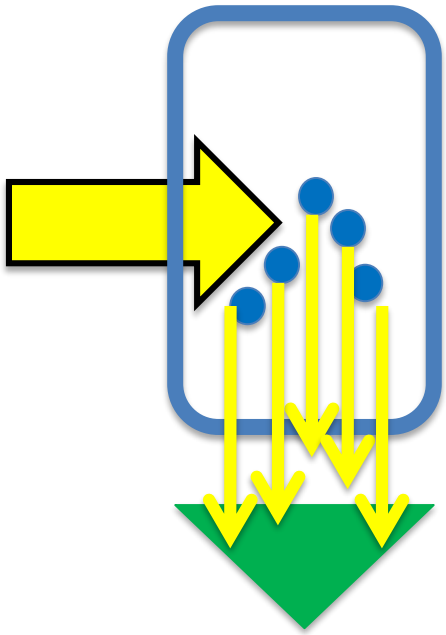
Filter Pad Monitoring

- Provides a total Fe picture *after* the fact
- Averaging produces a deceptive picture of the real corrosion environment

Light Scattering Propagation of Submicron Particles



Non-detectable



Detectable

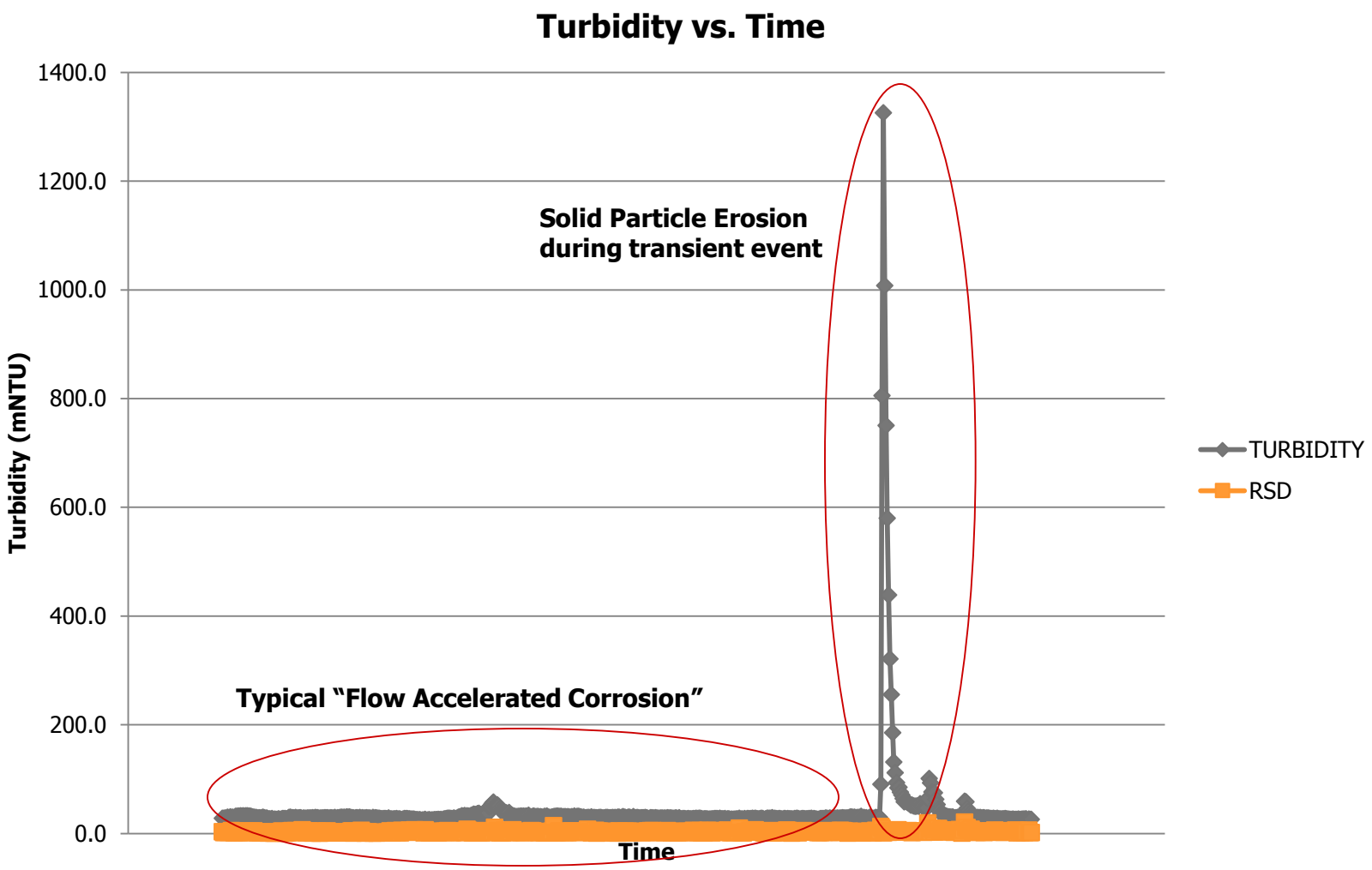
Laser Nephelometry

Potential solution for detection of insoluble iron:

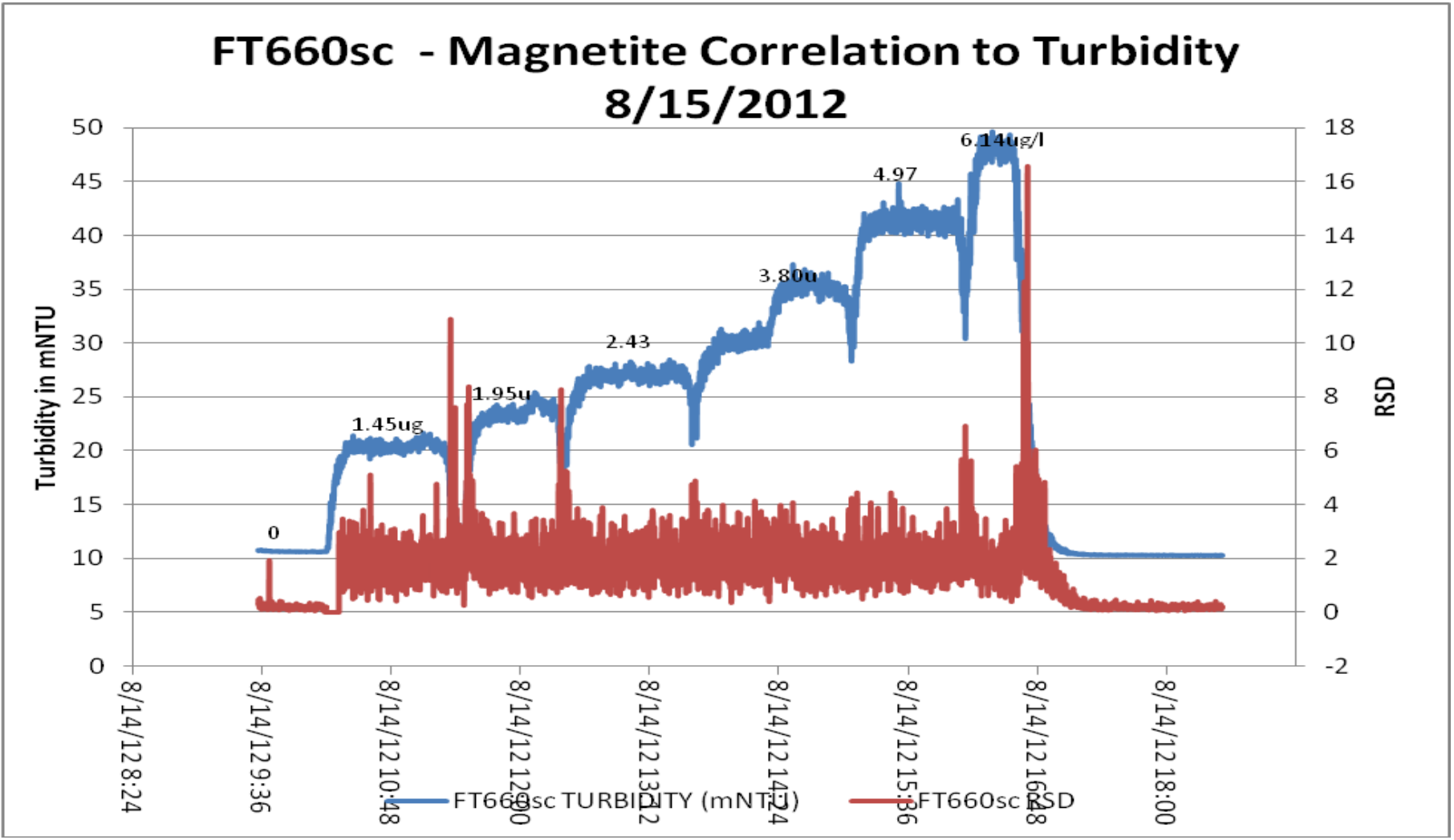
- Theoretically 1 mNTU = 1 ppb total solids (kaolin)
- LOD is 0.3 mNTU
- Particle sizes <1 micron are detected when concentration of particles is such that the sum reflectance can increase photodetector response above 7 mNTU.

A reference bench method (FerroZine) has been developed to support the on-line research

Corrosion Product Monitoring



Magnetite


FT660sc - Magnetite Correlation to Turbidity
8/15/2012
Turbidity in mNTU
RSD
0
1.45ug
1.95u
2.43
3.80u
4.97
6.14ug/l
50
45
40
35
30
25
20
15
10
5
0
18
16
14
12
10
8
6
4
2
0
-2
8/14/12 8:24
8/14/12 9:36
8/14/12 10:48
8/14/12 12:00
8/14/12 13:12
8/14/12 14:24
8/14/12 15:36
8/14/12 16:48
8/14/12 18:00
FT660sc TURBIDITY (mNTU)
FT660sc RSD

Correlation Data – MAGNETITE

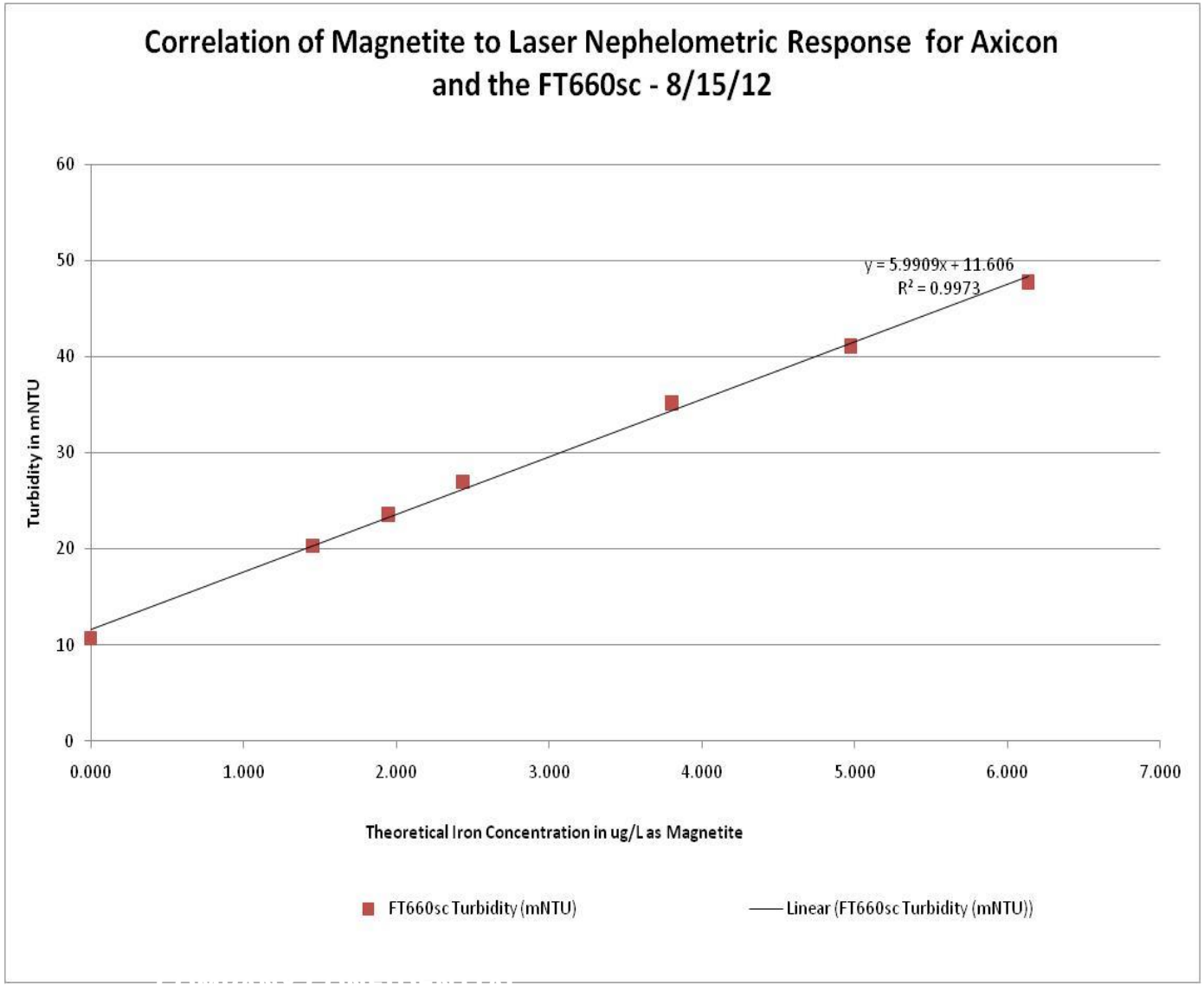
Insoluble Iron Detection

Laser Nephelometry Performance (Magnetite)

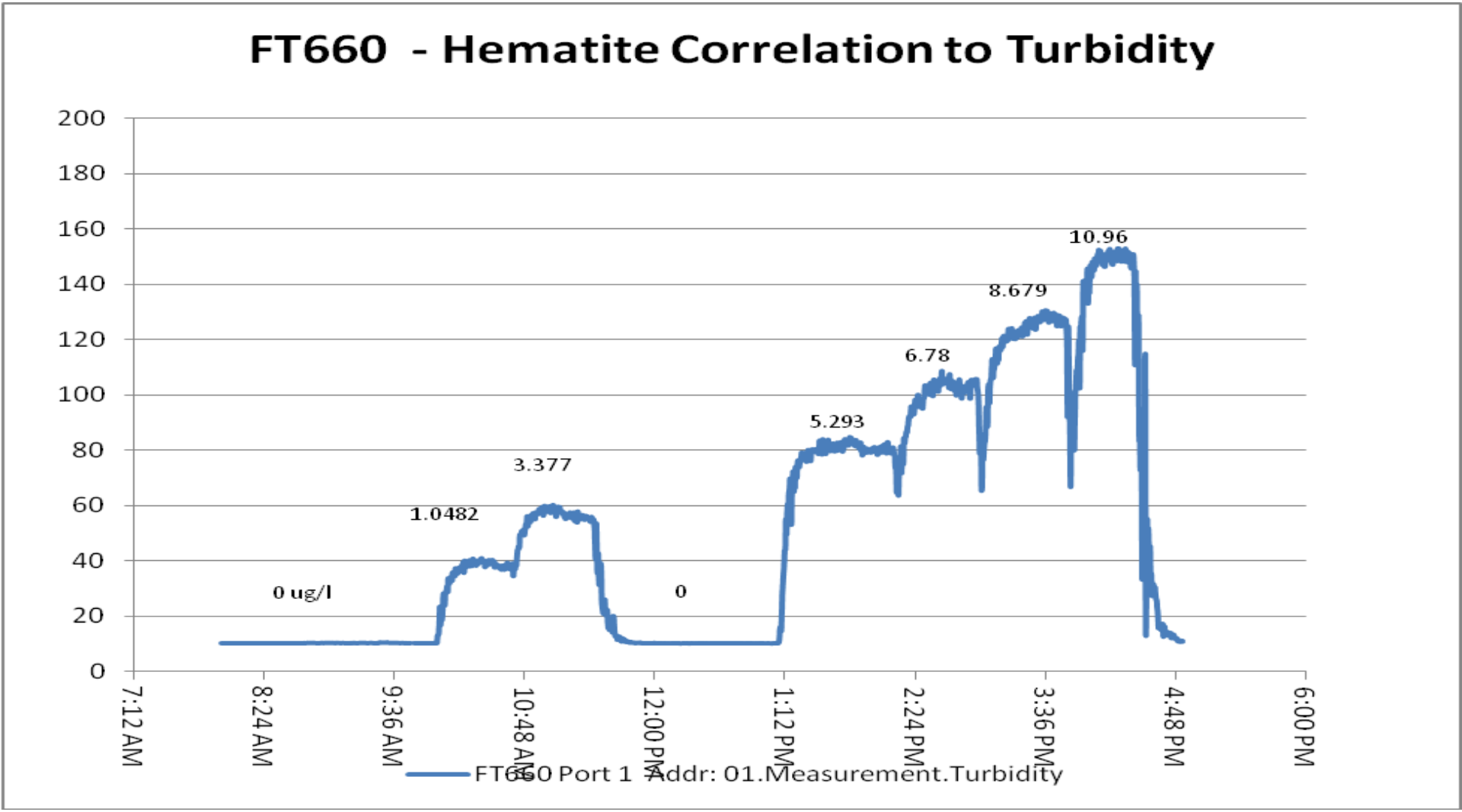
An increase of 1-ppb iron results in an increase of 6 mNTU

Linear response curve

Detection limit 50 ppt range



Hematite


FT660 - Hematite Correlation to Turbidity
200
180
160
140
120
100
80
60
40
20
0
0 ug/l
1.0482
3.377
0
5.293
6.78
8.679
10.96
7:12 AM
8:24 AM
9:36 AM
10:48 AM
12:00 PM
1:12 PM
2:24 PM
3:36 PM
4:48 PM
6:00 PM
FT660 Port 1 - Addr: 01.Measurement.Turbidity

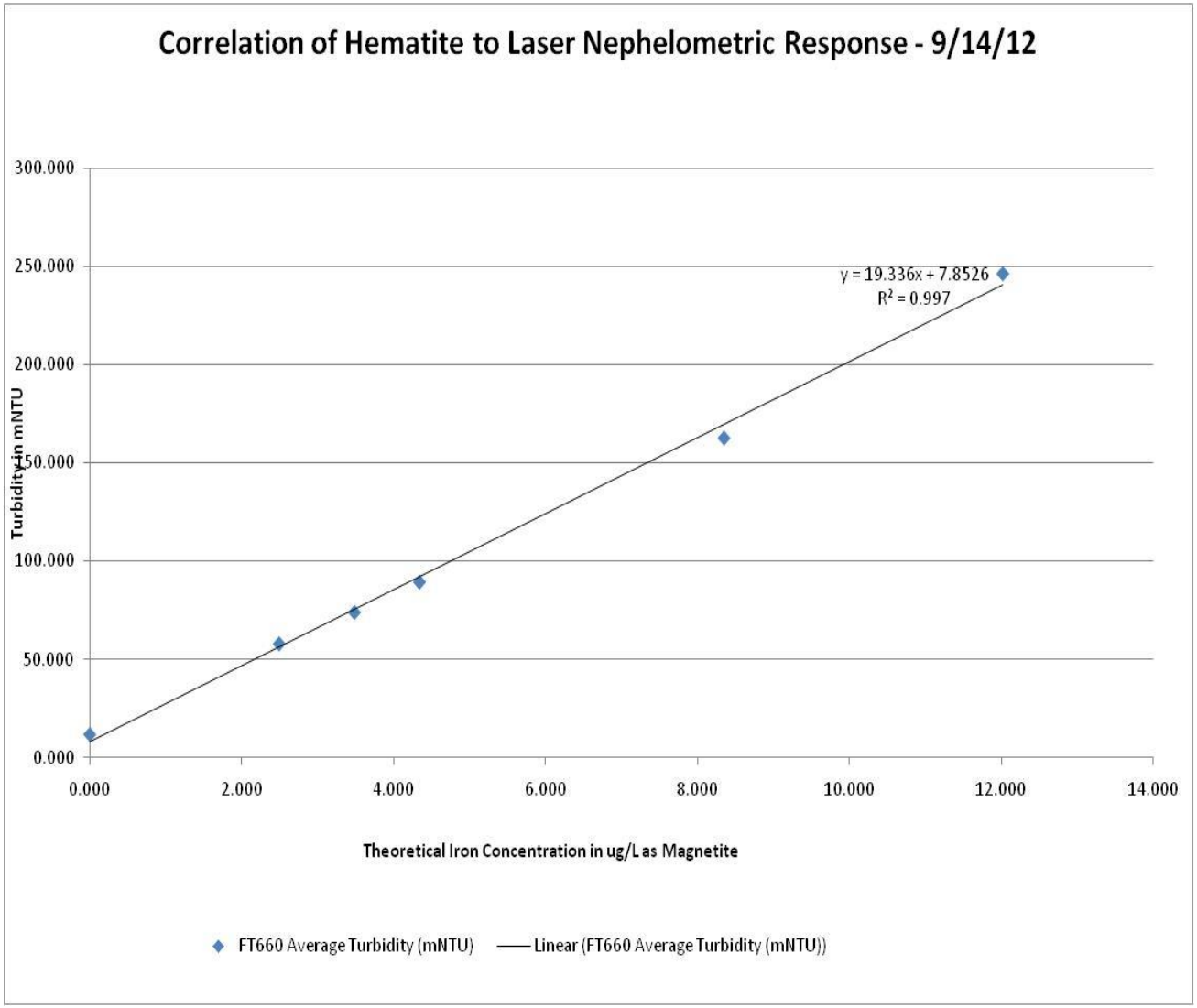
Correlation Data – HEMATITE

Insoluble Iron Detection

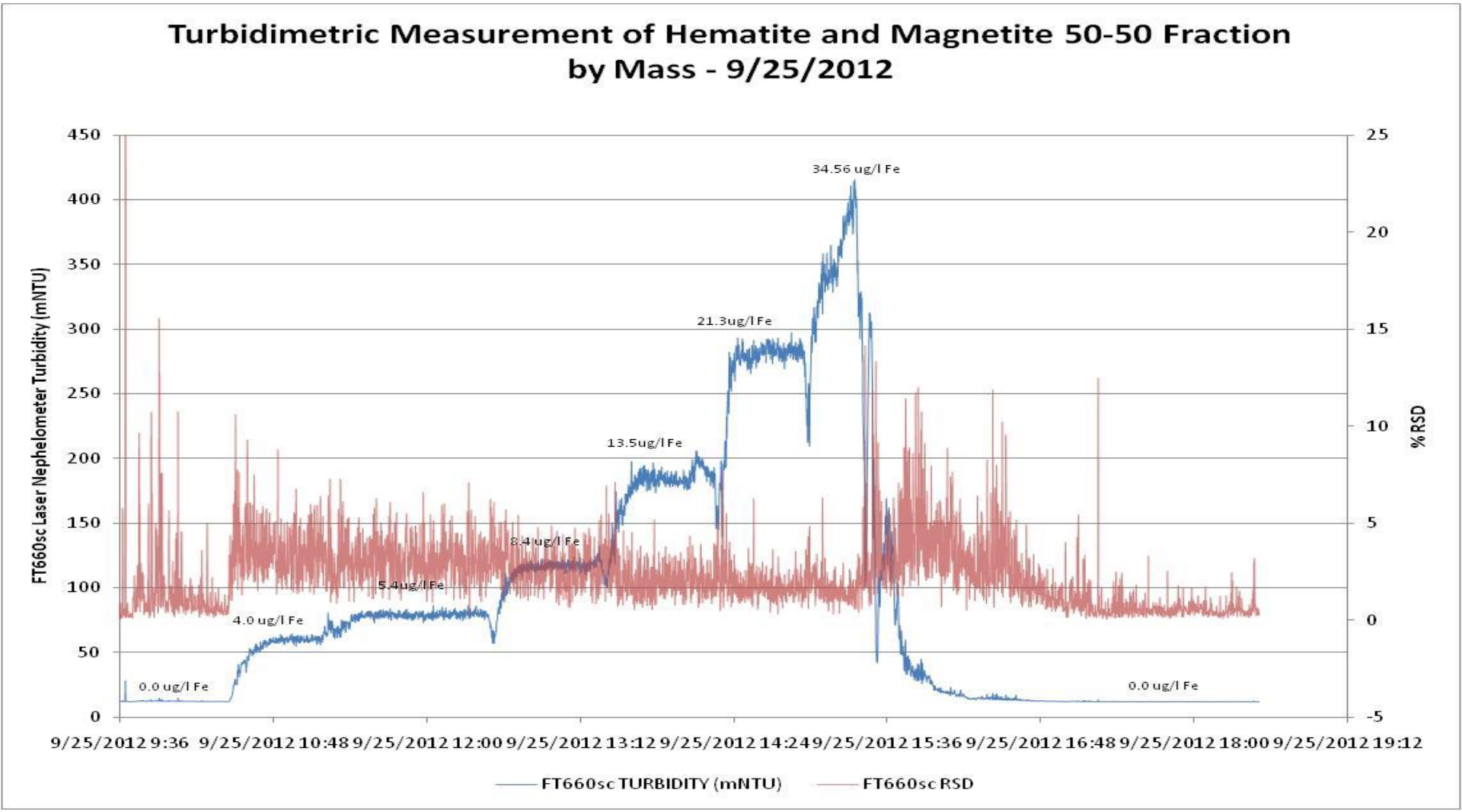
Laser Nephelometry Performance (Hematite)

An increase of 1-ppb iron results in an increase of 20 mNTU Linear response curve.

Detection limit 15 ppt range



50:50 Mixture



Correlation Data – 50:50

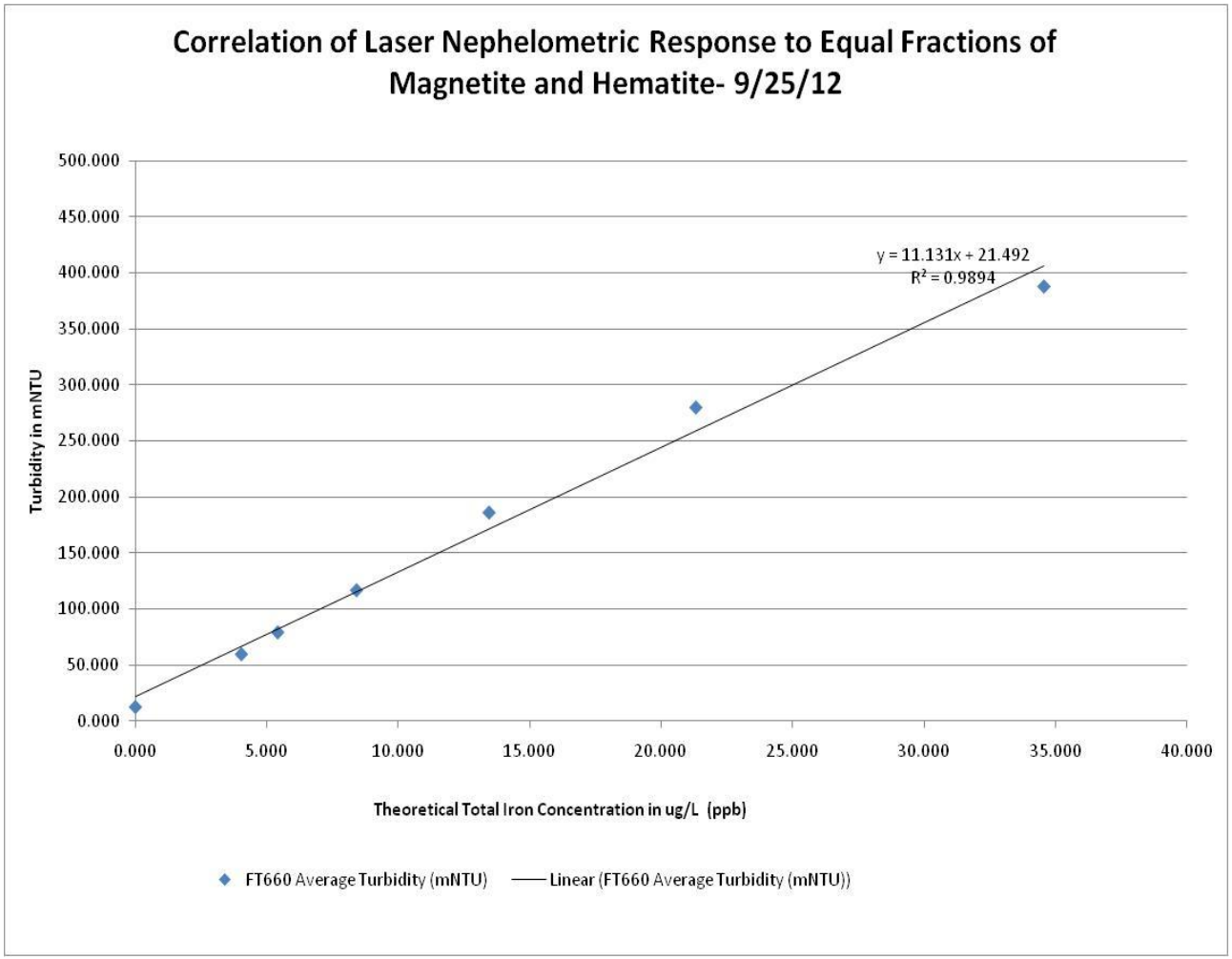
Insoluble Iron Detection – Magnetite – Hematite 50:50 Mass Fraction

Laser Nephelometry Performance

An increase of 1-ppb iron results in an increase of 11 mNTU (FT660)

Linear over the tested range

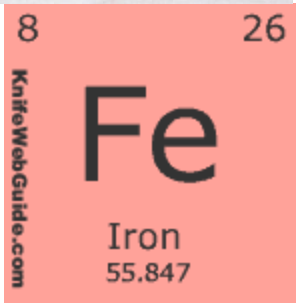
Detection limit 27 ppt range as total iron



Determination of Total Iron

(Bench Method)

- Analytical Objective
  - Measure total iron in the plant at <2.0 µg/L
  - Analysis to be convenient to perform at plant level
    - Multiple analysts able to perform test
  - Measure soluble and total iron including particulate.
    - Ferrous and ferric
    - Magnetite
    - Hematite
- Tactical Objective
  - In-plant analysis of iron
  - Correlation of iron to laser turbidity

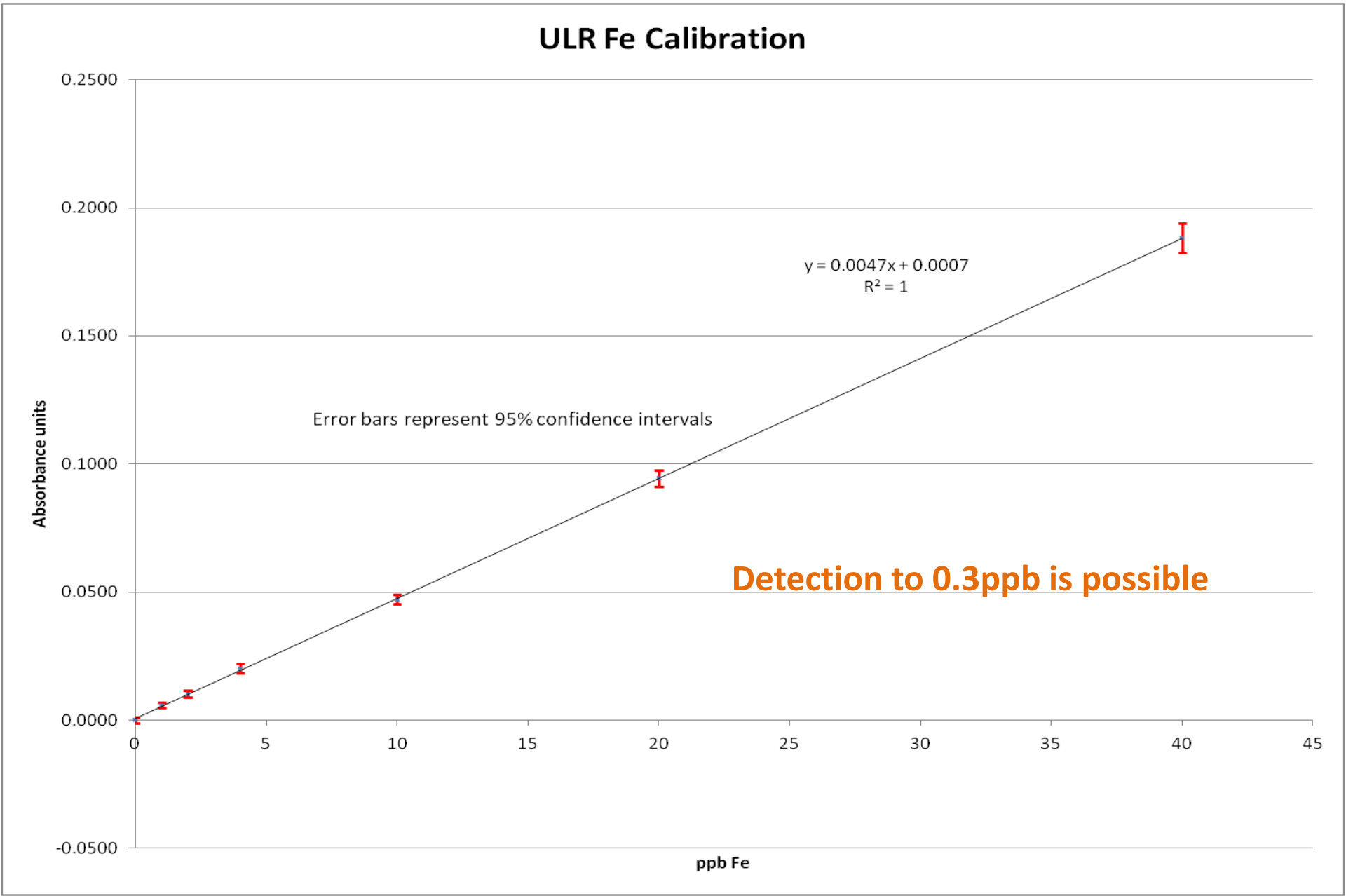


ULR FerroZine Method

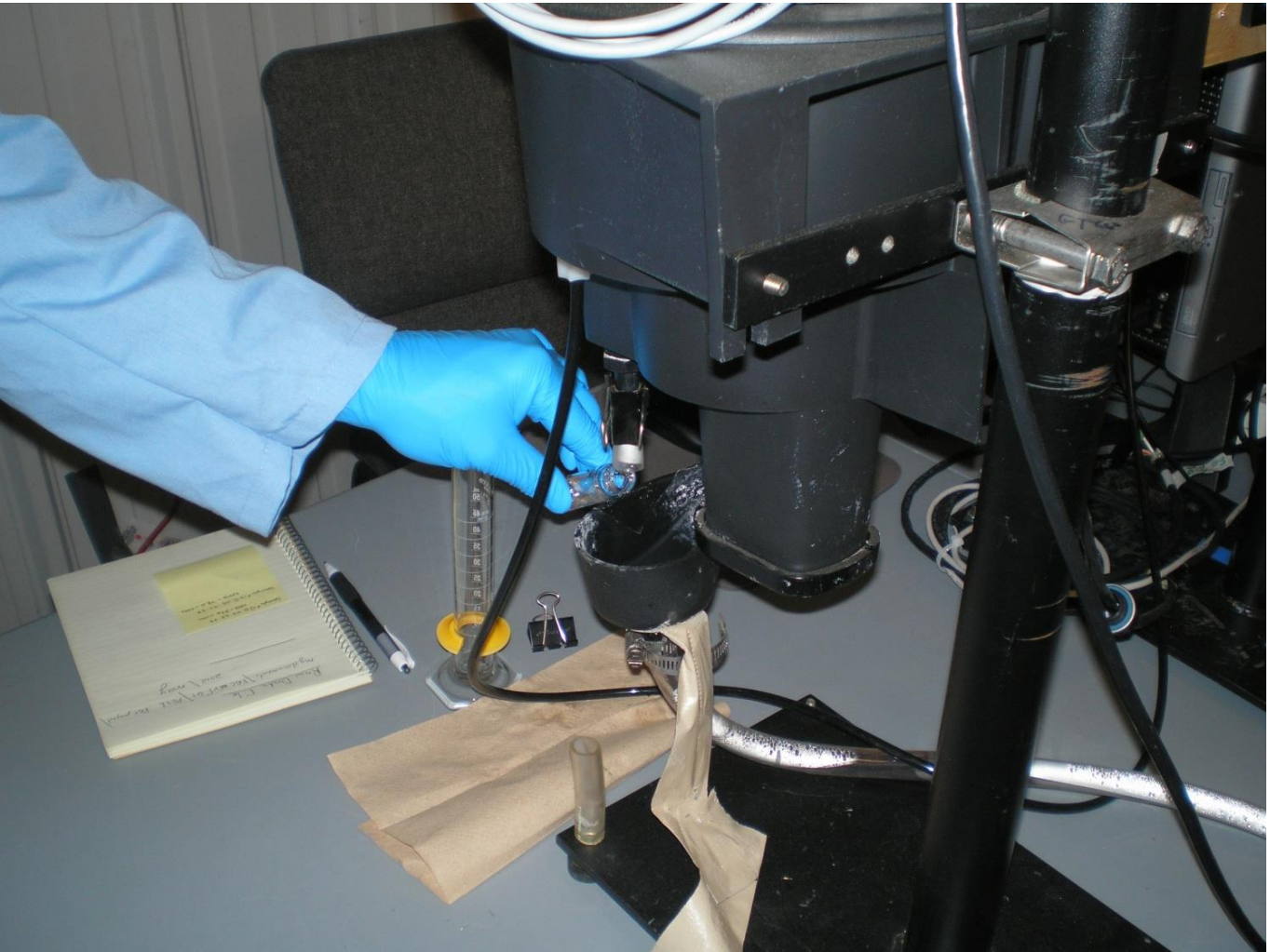
- *Combination* reagent - FerroZine + TGA
  - TGA is responsible for digestion
  - FerroZine creates the color
- Reduces *all Fe* including magnetite & hematite
- 150°C digestion for 30 mins

Designed for low ppb range

Ultra Low Range Iron Analysis



Sample Acquisition



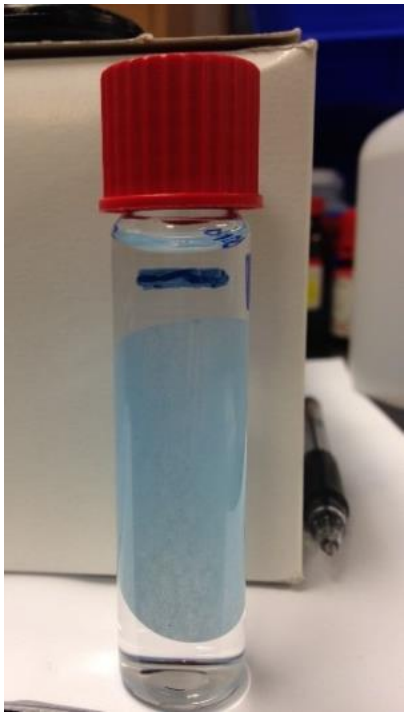
Attention to technique and method is critical

Addition of Reagents

FerroZine + TGA (Thioglycolic acid)

Dissolution

Using a digestion block at 150°C for 30 minutes

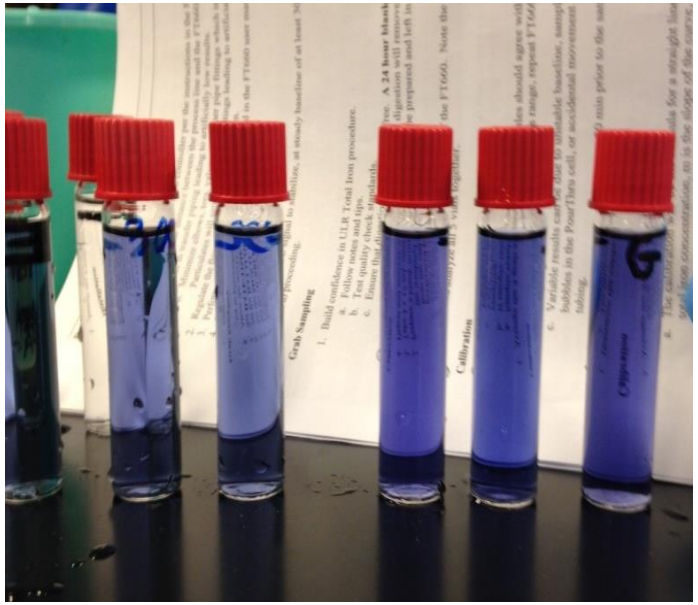


Measurement

Spectrometer must have high quality optics

Filter Pad Procedure

- Place the filter pad into vial containing 15ml of DI water
- Add 10 drops of FerroZine and digest for 30 mins at 150°C
- Dilute sample into analytical range
- Add 8 drops of FerroZine to the diluted sample
- Run in spectrophotometer
- Calculate iron on the filter pad



NOTE: *ALL* vials should initially be cleaned by heating 10 drops of FerroZine in 15 ml H_20 for 24 hrs to extract Fe from the glassware

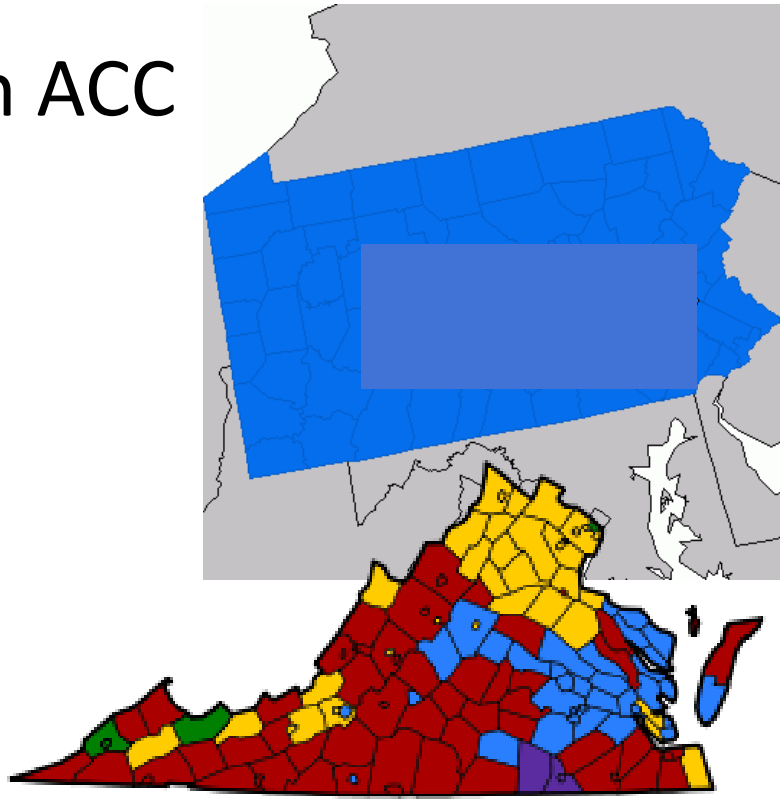
Example

If the diluted concentration is 0.900 mg/L, and the sample was diluted 1 mL/500 mL, then the total mass of Fe on the filter pad is:

$$\frac{0.900\frac{mg}{L} \times 500mL \times 0.015L}{1\ mL} = 6.75\ mg$$

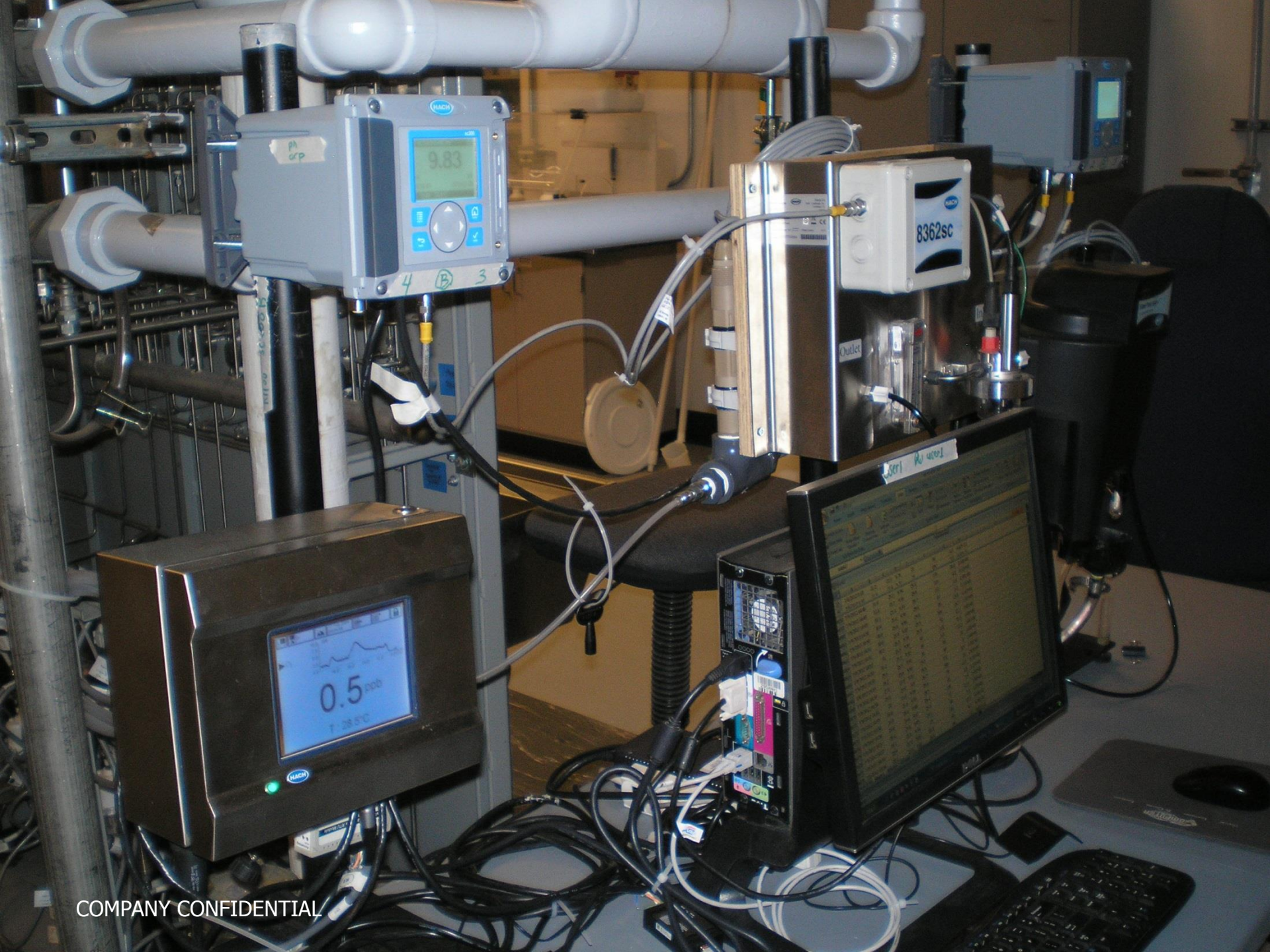
Plant Studies

- California HRSG with ACC
- Virginia HRSG with ACC
- Pennsylvania HRSG with ACC

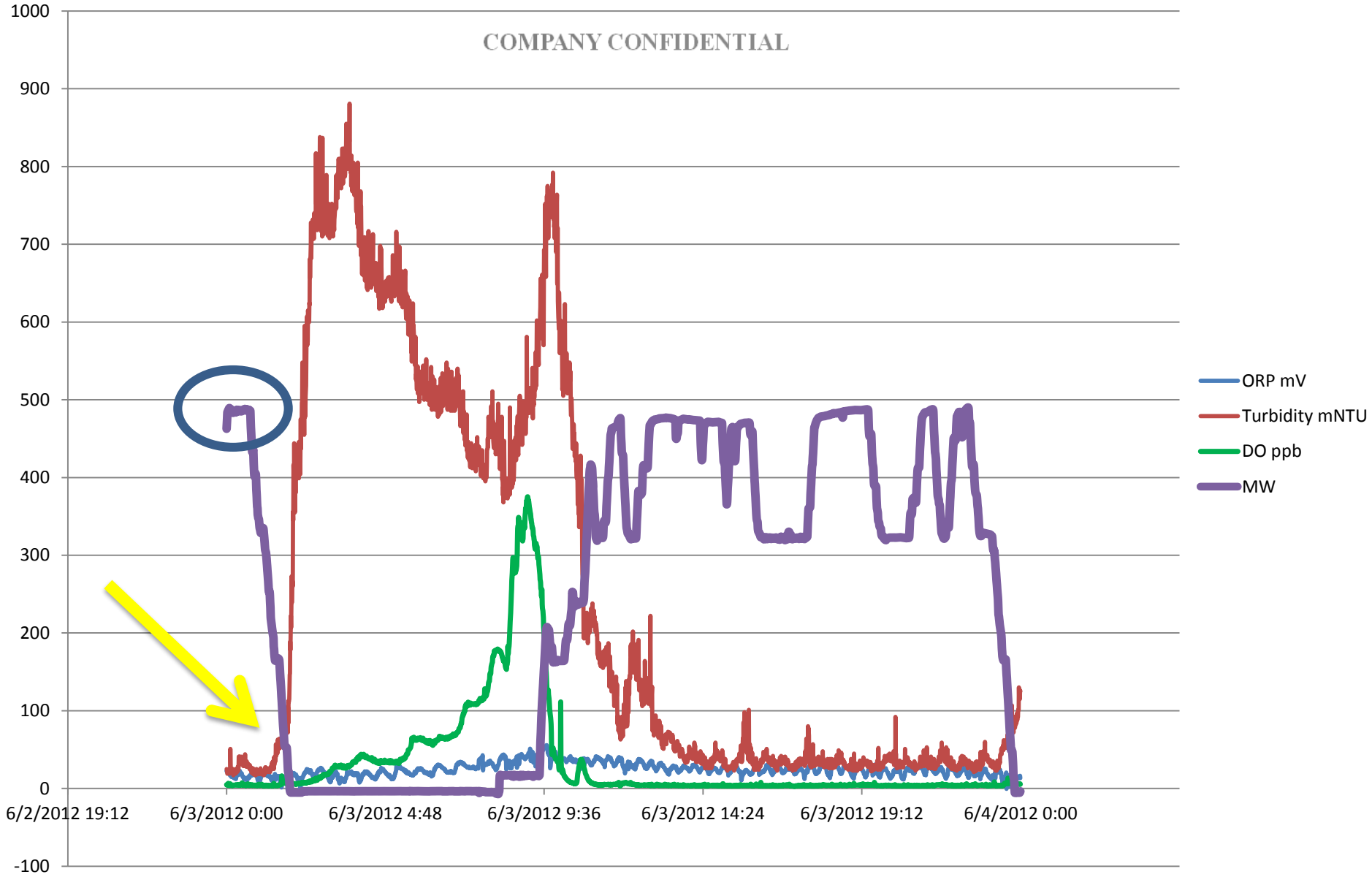


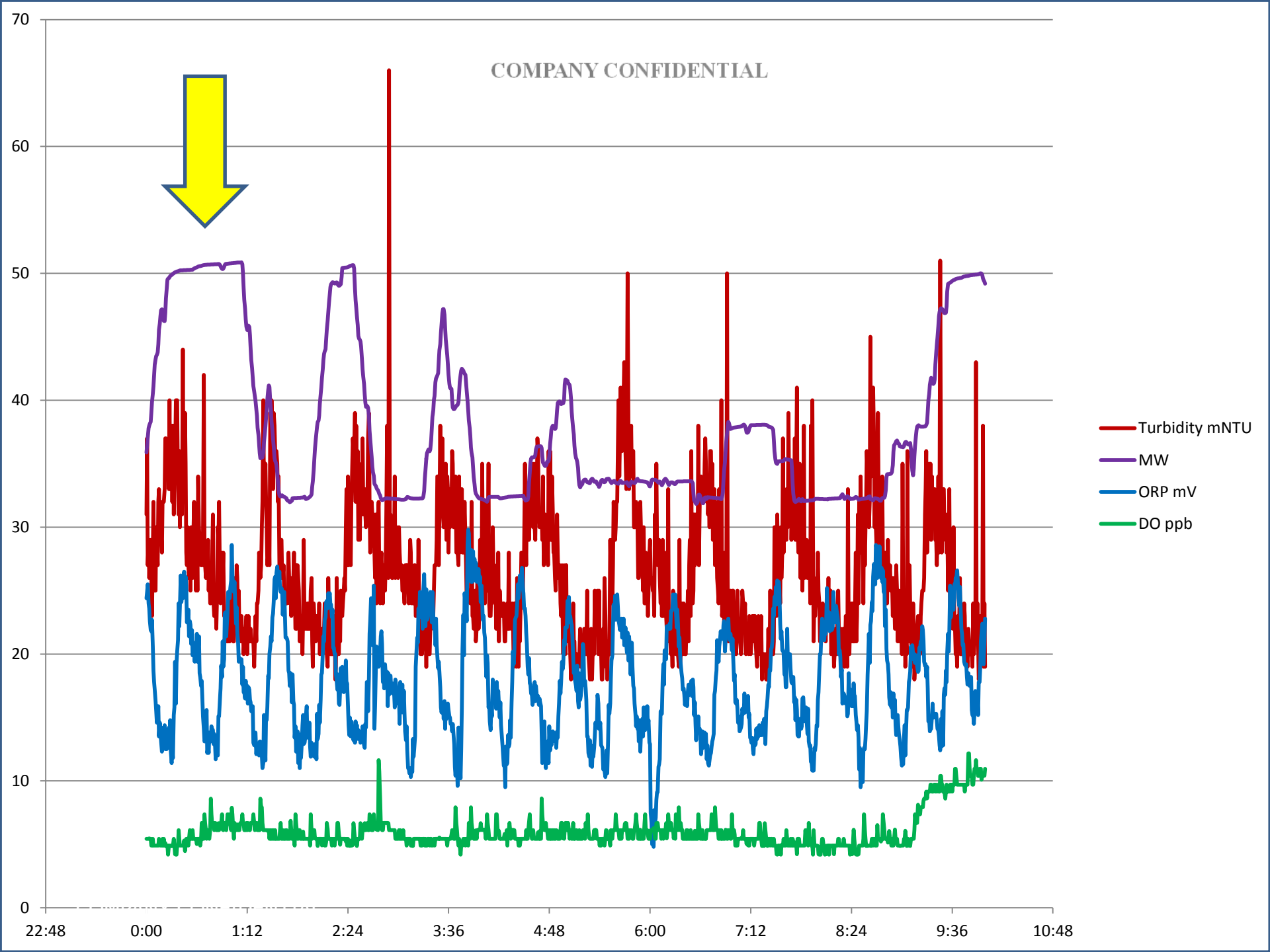
California Study: 5/12 – 8/12

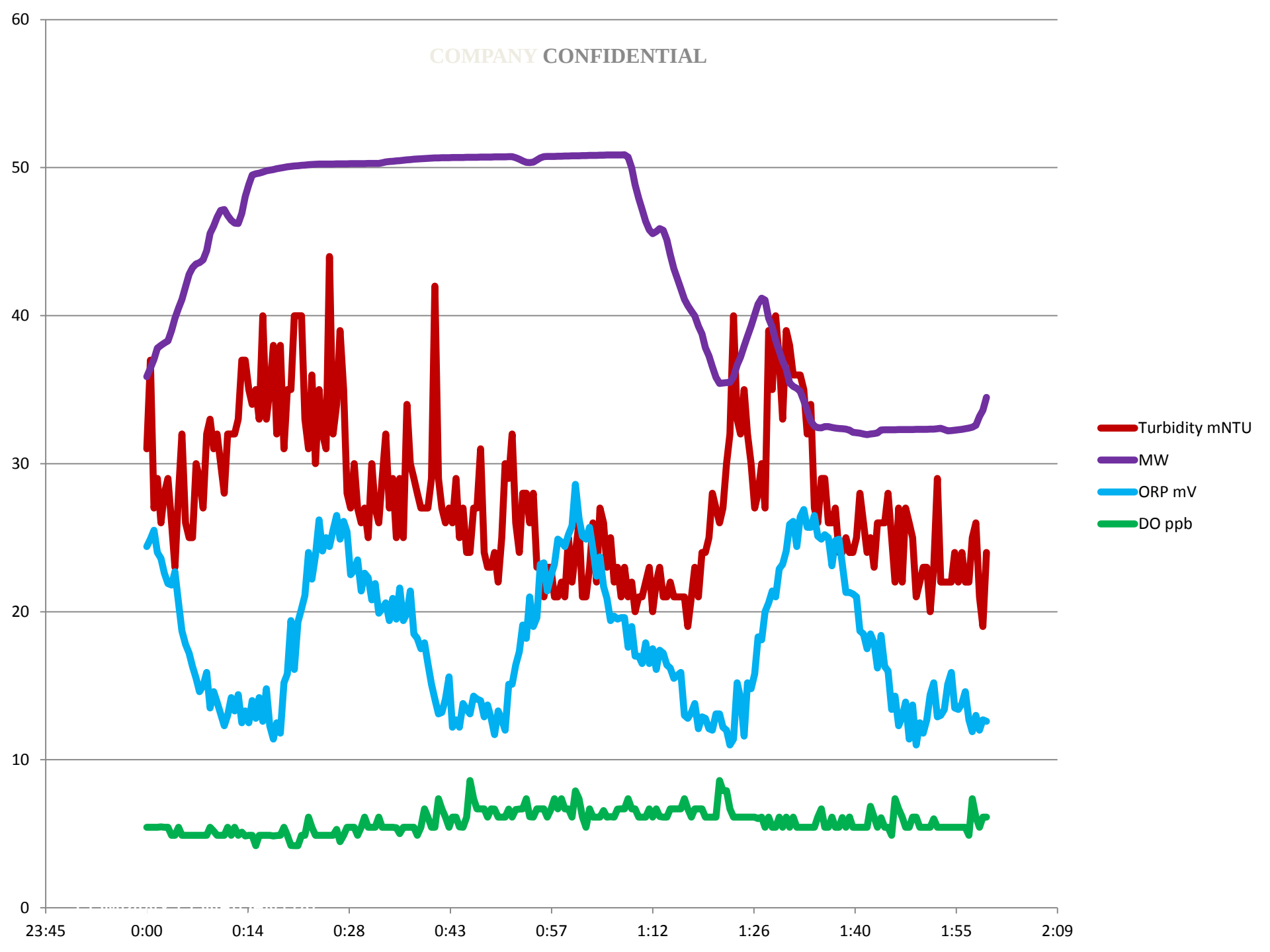
- HRSG Plant
  - 2X1
  - 600 MW
  - ACC
- Continuous Monitoring of Condensate:
  - Laser Turbidity (mNTU)
  - pH
  - ORP
  - DO
  - Temperature
- Continuous data is logged to computer every 30 seconds.


9.83
8362sc
Outlet
0.5
COMPANY CONFIDENTIAL

June 3 00:00 – 24:00




COMPANY CONFIDENTIAL
70
60
50
40
30
20
10
0
22:48
0:00
1:12
2:24
3:36
4:48
6:00
7:12
8:24
9:36
10:48
Turbidity mNTU
MW
ORP mV
DO ppb


COMPANY CONFIDENTIAL
60
50
40
30
20
10
0
23:45
0:00
0:14
0:28
0:43
0:57
1:12
1:26
1:40
1:55
2:09
Turbidity mNTU
MW
ORP mV
DO ppb

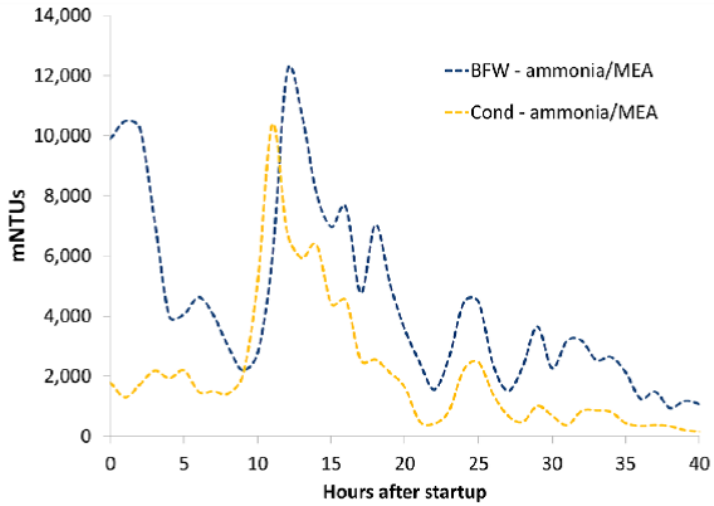
Virginia Study: 7/13 – 6/15

- Coal Plant
  - 600 MW
  - ACC
- Feeding Polyamine

Cold start w/ ammonia:MEA AVT

Turbidity peaked ~12K mNTU

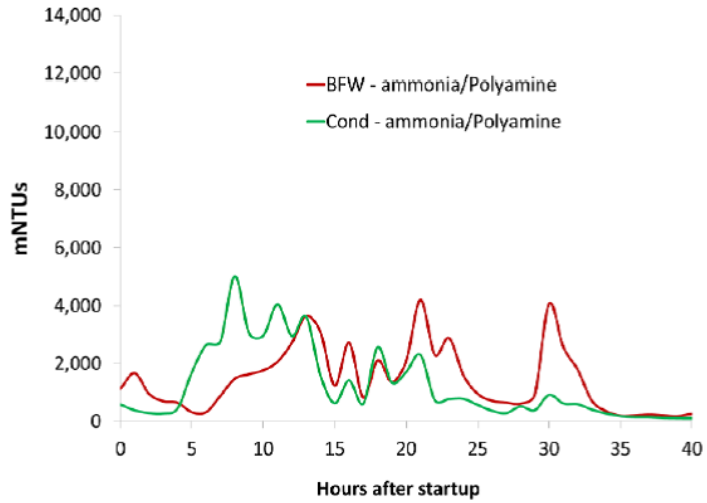
Condensate turbidity in 2-10K mNTU range

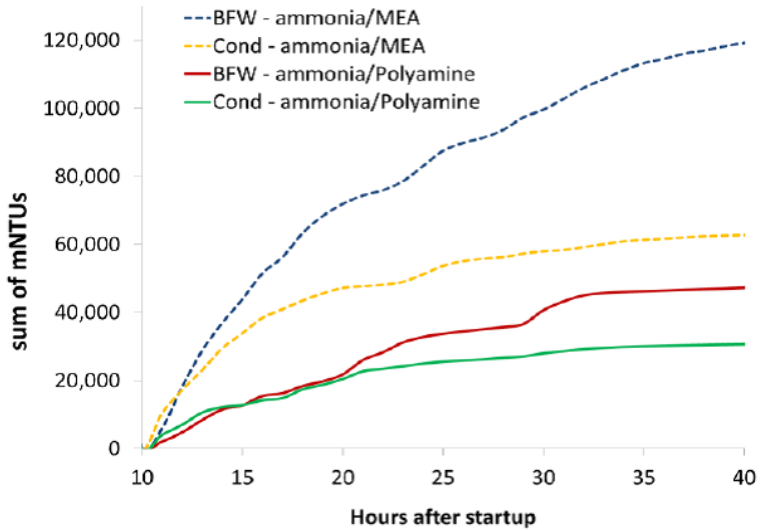


Cold start after Polyamine addition

Turbidity peaked ~5K mNTU

Condensate turbidity in 1-5K mNTU range



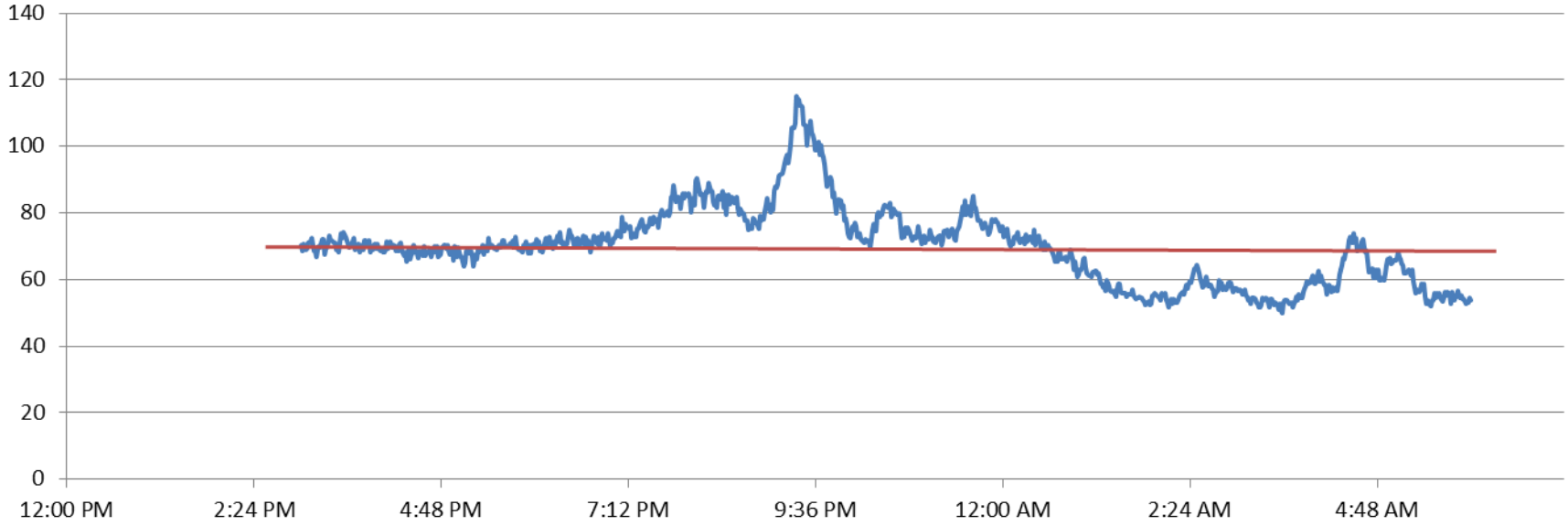


Courtesy GE Power & Water

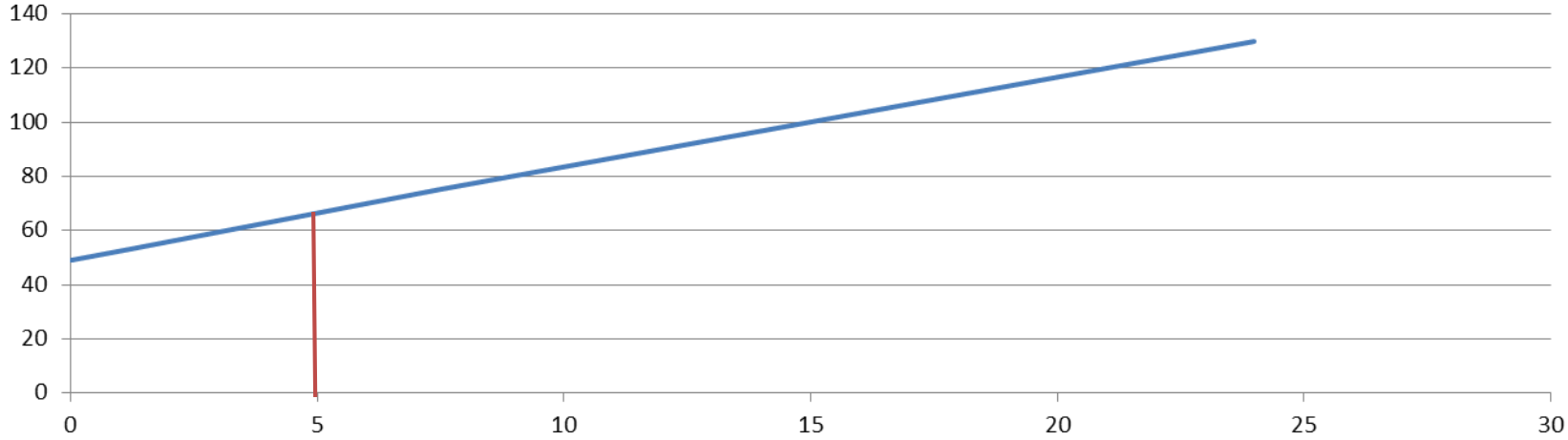
Pennsylvania Study: 8/15 - Present

- Combined Cycle
  - 900 MW
  - ACC

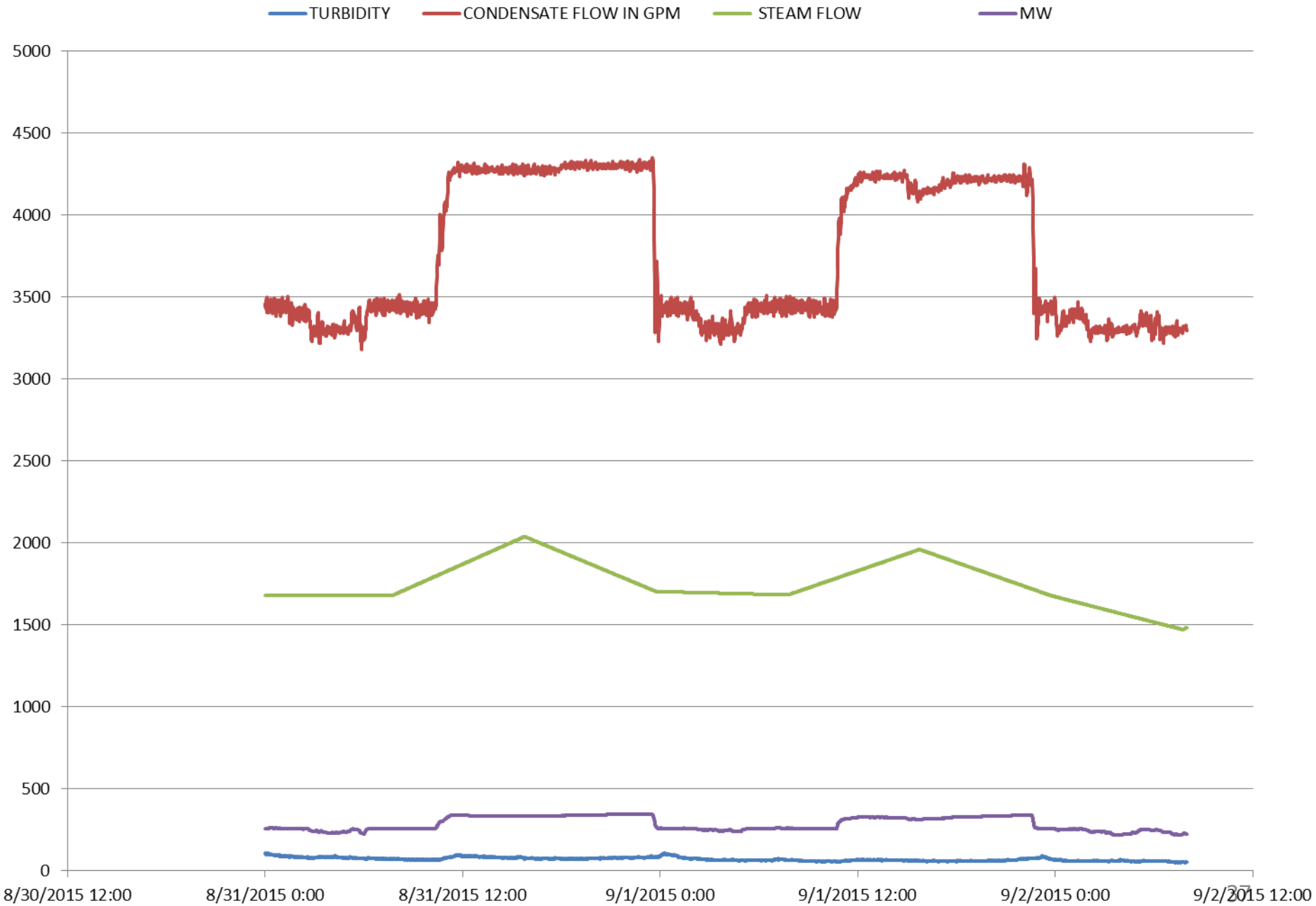
NRG Hunterstown - Condensate Iron (8/25 - 8/26)

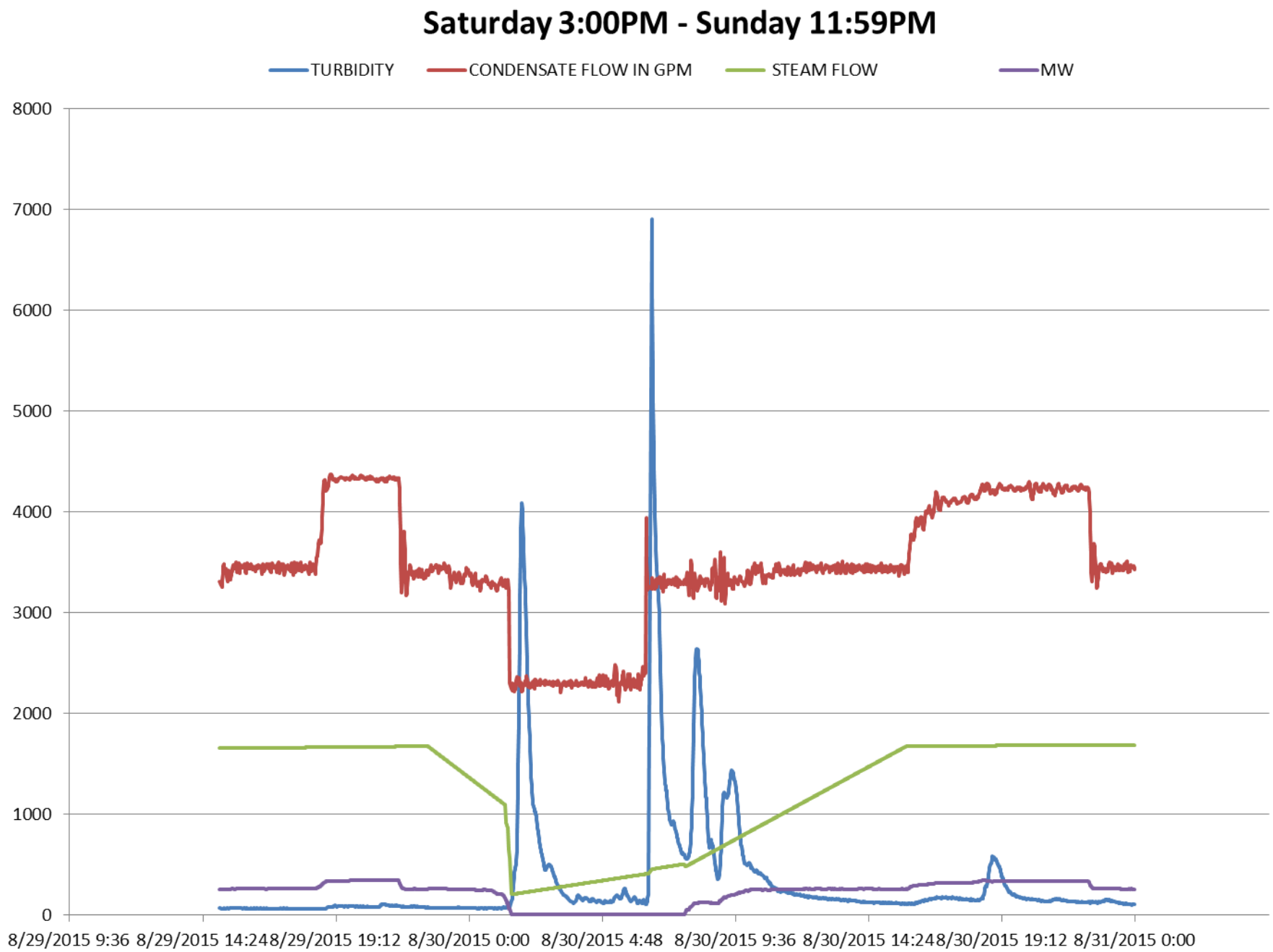


Correlation Curve



Monday 8/31 - Wednesday 9/2




Saturday 3:00PM - Sunday 11:59PM
TURBIDITY
CONDENSATE FLOW IN GPM
STEAM FLOW
MW
8000
7000
6000
5000
4000
3000
2000
1000
0
8/29/2015 9:36
8/29/2015 14:24
8/29/2015 19:12
8/30/2015 0:00
8/30/2015 4:48
8/30/2015 9:36
8/30/2015 14:24
8/30/2015 19:12
8/31/2015 0:00

TAKE AWAY!

- Surrogate methods have now been validated for monitoring iron continuously
- Total iron methods have been improved for grab samples to levels down to 1 ppb

Questions