Worldwide Pollution Control Association

WPCA-Duke Energy FGD Wastewater Treatment Seminar

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Causes & Impacts of WFGD ORP on Effluent Composition

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Overview

- Introduction into WWT for WFGD Blowdown
- Important Chemical Parameters for Wastewater Treatment
- Impact of ORP on WFGD Effluent Composition
- Causes of Variation in WFGD ORP Levels
- Mitigation Strategies for Improved Bleed Stream Composition
- Conclusions & Path Forward

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Introduction into WWT for WFGD Blowdown

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Mitigation Strategies for Improved Bleed Stream Composition

Conclusions & Path Forward

Technologies for Treatment of WFGD Effluent*

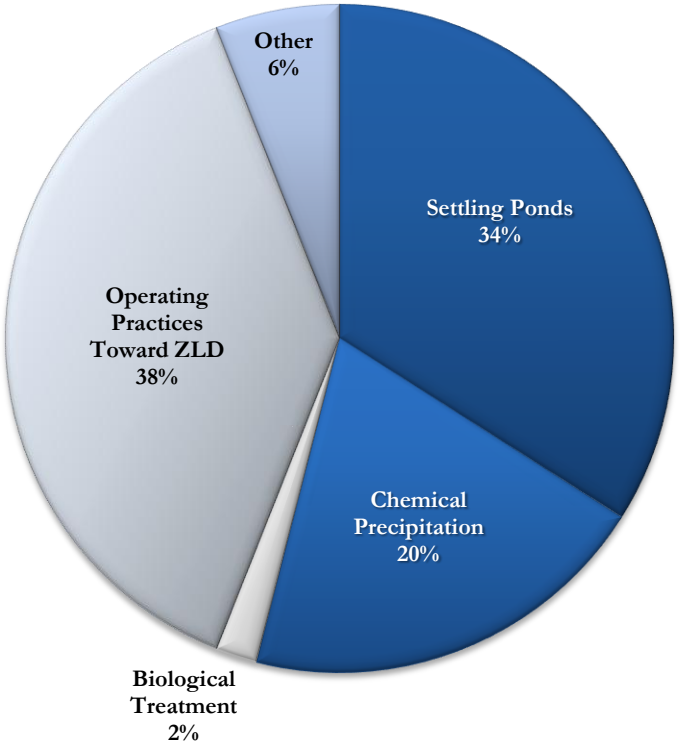
Settling Ponds
- Mostly to reduce suspended solids

Chemical Precipitation
- Targets mercury and arsenic removal

Biological Treatment
- Targets Selenium
- Also removes nitrates & sulfates

Operating Practices toward ZLD

Other
- Vapor-Compression Evaporation
  - 1 unit in US
- Clarifiers
- Constructed Wetlands
- Commingling with other wastewater
- Ash solidification



*As reported by the EPA in October 2009 report

Brine Concentrator Systems(BCS) Overview

For FGD, Typically Two Steps:

1. **Brine concentration using a falling film evaporator (FFE) with mechanical vapor compression (MVC)**
   - **Reduces the water content of the wastewater by ~90%**

2. **Forced Circulation Crystallization(FCC) using either steam or MVC as the energy source**
   - **Creates crystals by further evaporating water to concentrate the stream to a value above the solubility limits of the dissolved solids**
   - **Crystals are separated using a dewatering device such as filter press**

BCS Pre-Treatment

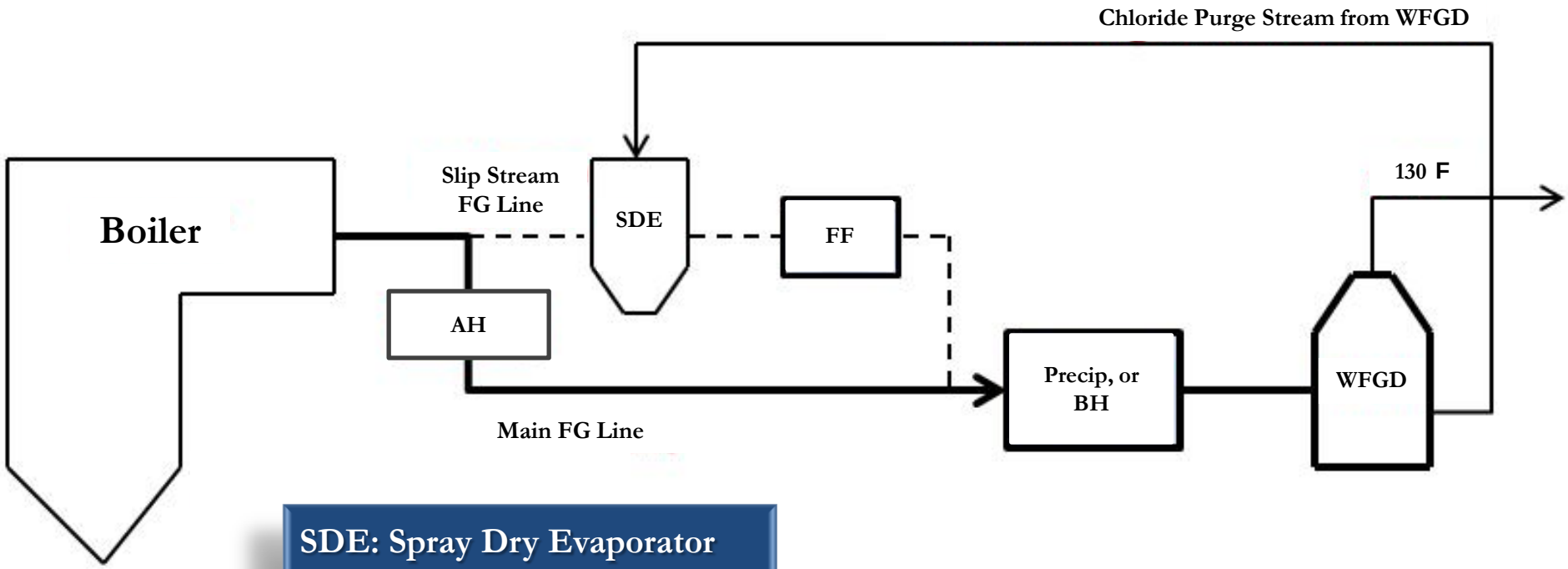
Typical chemical precipitation (CP) system

- **Used for gypsum de-saturation & heavy metals removal**
- **May prevent hazardous waste classification**

Complete removal of Calcium & Magnesium via soda ash softening is desirable from an operating standpoint

- **But very expensive with costs over 50 cents per pound of calcium removed and $1 per pound of magnesium removed.**

Spray Dryer Evaporation Process Flow Diagram



SDE: Spray Dry Evaporator
FF: Fabric Filter
FG: Flue Gas
AH: Air Heater

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WFGD Chemistry sets the Difficulty of Effluent Treatment

WFGD Bleed to Dewatering

- Solids removed as gypsum product
- Filtrate split between WGFD reclaim and waste water treatment

Recycle

- Hydroclone tuning and split is important for water balance, gypsum purity & chloride level

Wastewater Treatment

- WWT operations needs to treat the bleed stream as it comes, including phase partitioning of regulated metals

WFGD Effluent Composition

Nominal WFGD Effluent Stream Composition	
Species	mg/L
Boron	300
Calcium	5,000
Magnesium	2,000
Sodium	1,000
Chloride	11,000
Sulfate	5,000
TDS	25,000

Typical WFGD Blowdown Streams Pose Challenges:

- High in Halogens
- High TDS
- Selenite (IV)/Selenate (VI)
- Mercury
- Boron

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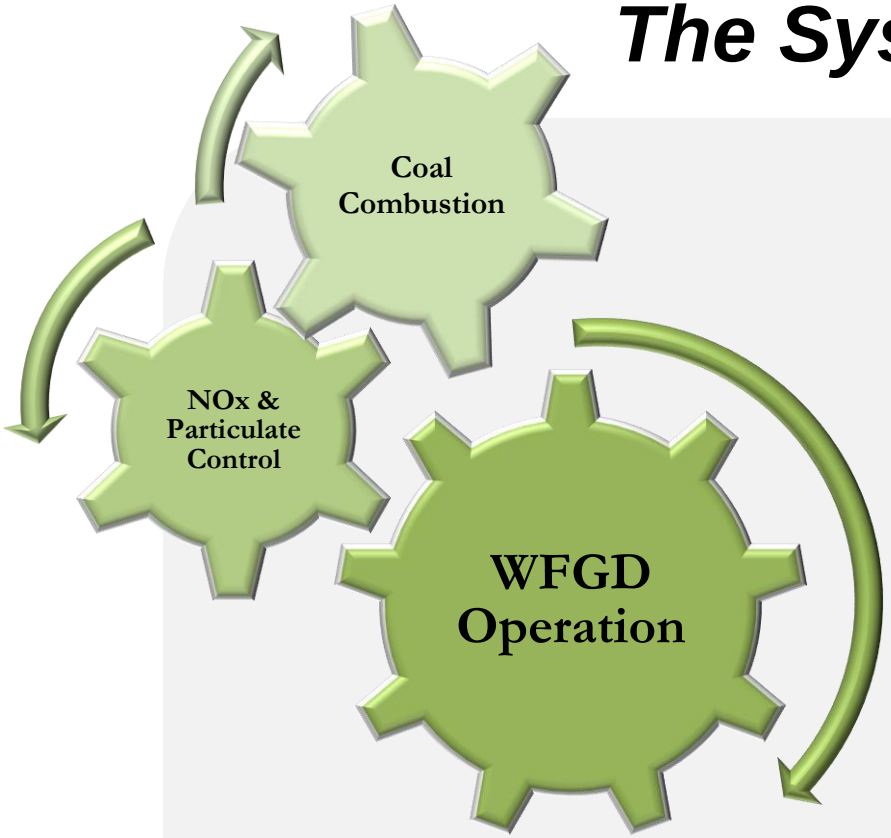
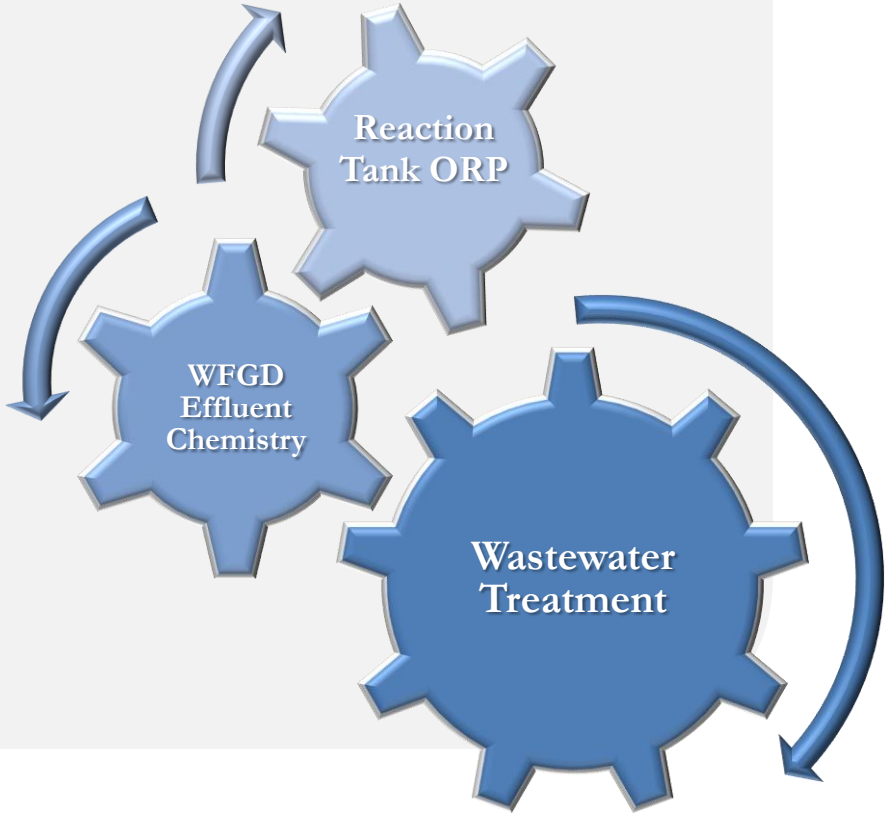
The System View





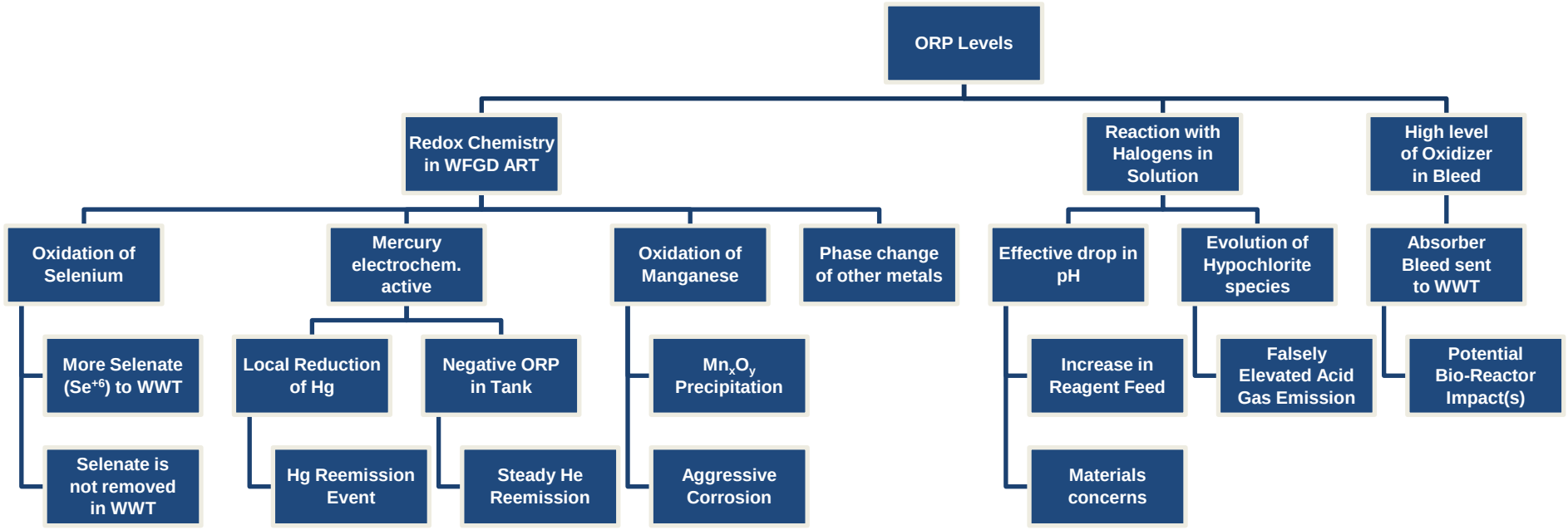
What is ORP?

- **Oxidation Reduction Potential (ORP)**
  - **A single voltage measurement against a reference electrode**
    - **Measurement technique similar to pH**
    - **Can be monitored on-line**
  - **The strength of oxidizers and reducers in a solution in relation to their respective concentration**
  - **The more positive the voltage, the more strongly a solution would oxidize (attract electrons from) other sources**
    - **Oxidizers accept electrons, reducers lose electrons.**
  - **ORP can be negative**

Why is ORP important?

- **ORP control the oxidation of slurry constituents**
  - **Knowledge of Slurry ORP, in combination with pH and chloride level, can be used to predict WFGD chemistry**
  - ***Think of ORP as a threshold value. Comparing the ORP to the electronegativity and other known parameters, one can make estimations of the thermodynamically preferred and most likely state for each slurry constituent***
    - **At high ORP slurry constituents are oxidized**
    - **At low ORP slurry constituents are in lower oxidation states**
- **Oxidation state often controls solubility & phase partitioning of many species**
- **WFGD Slurry ORP often follows and S-shaped curve, rapidly escalating from 50-150 mV to >500 mV**

Impacts of ORP on WFGD Blowdown



Redox Chemistry within the WFGD

ORP

Selenium
- As ORP ↑ Selenate (Se^{+6}) is dominant
- At lower ORP, Se^{+4} is dominant

Mercury
- As ORP ↑ Mercury seems to shift from the particle bound to the dissolved phase
- Swinging or negative ORP may cause reemission

Other Metals
- Solubility & phase partitioning of many metals, such as manganese & cobalt may also be predicted

pH & Oxidizer Content
- Unreacted oxidizer(s) in the bleed stream may disrupt downstream WWT
- pH may drop due to oxidizer reactions

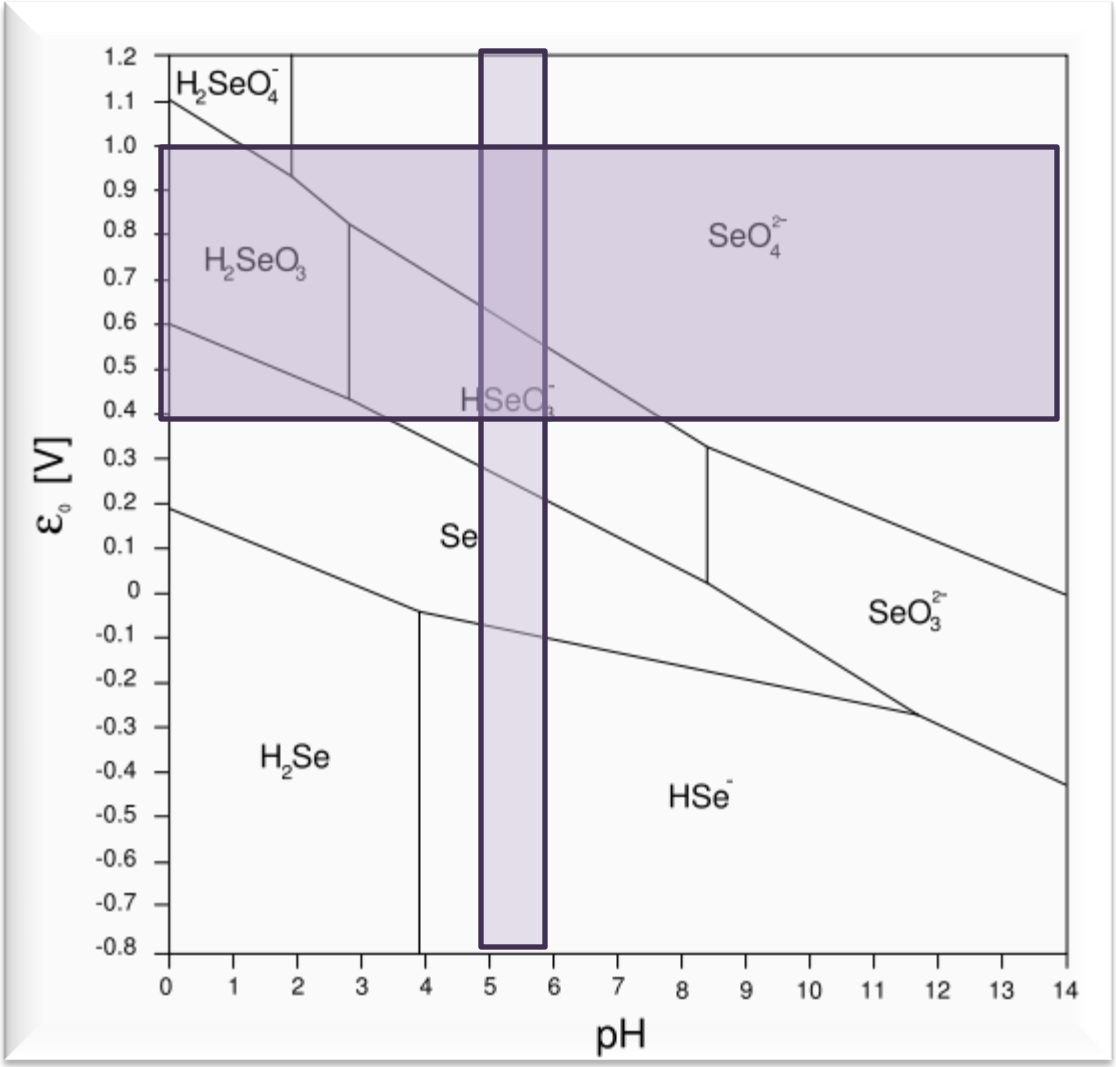
Selenium

Selenite (IV) and Selenate (VI) are dominant forms in FGD waters

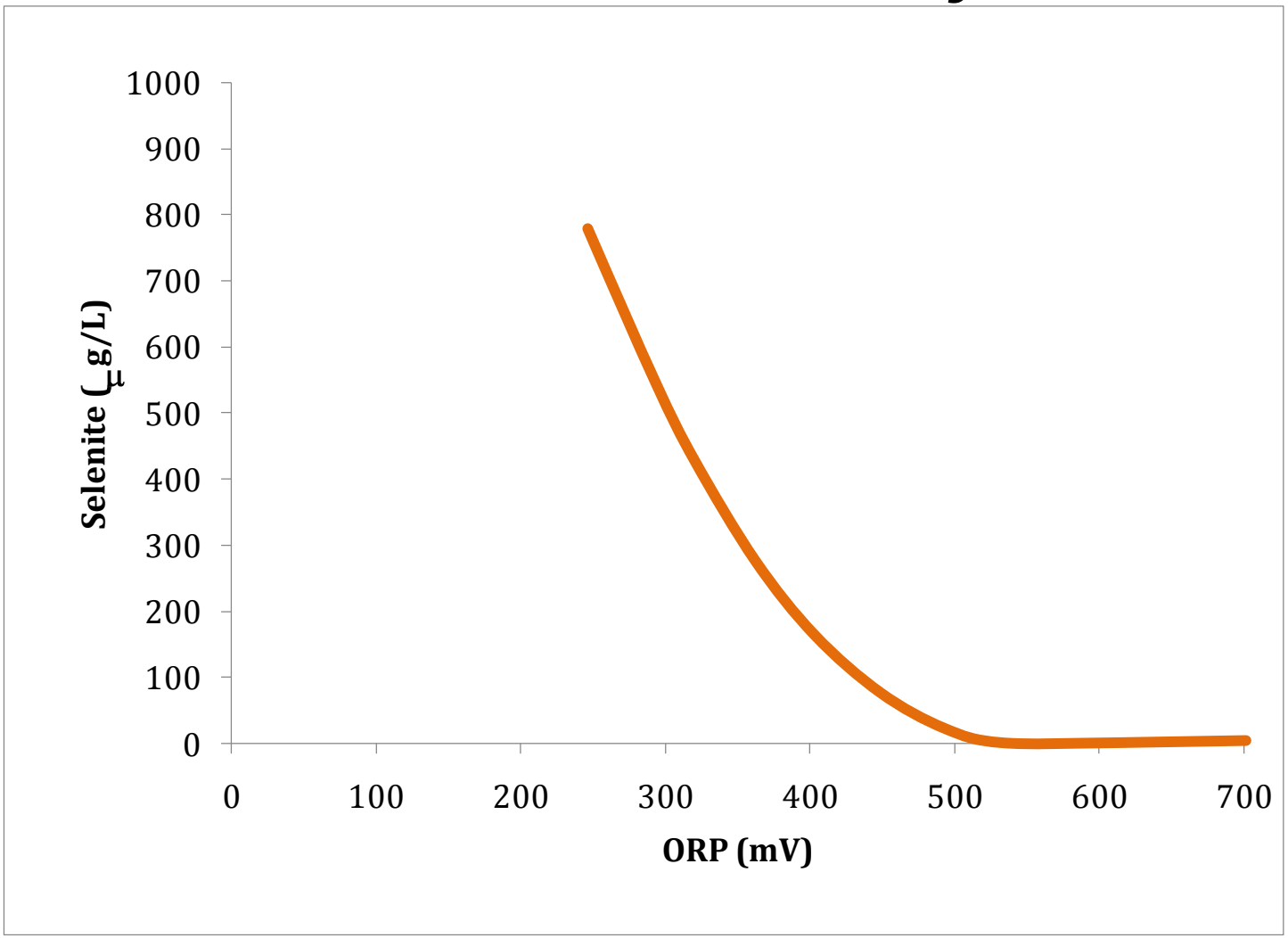
Selenate formation is problematic

- **Inability to be removed via chemicals**
- **Removal via biological remediation**

Phase Partitioning– Selenium



Selenite vs. ORP in WFGD ART Slurry



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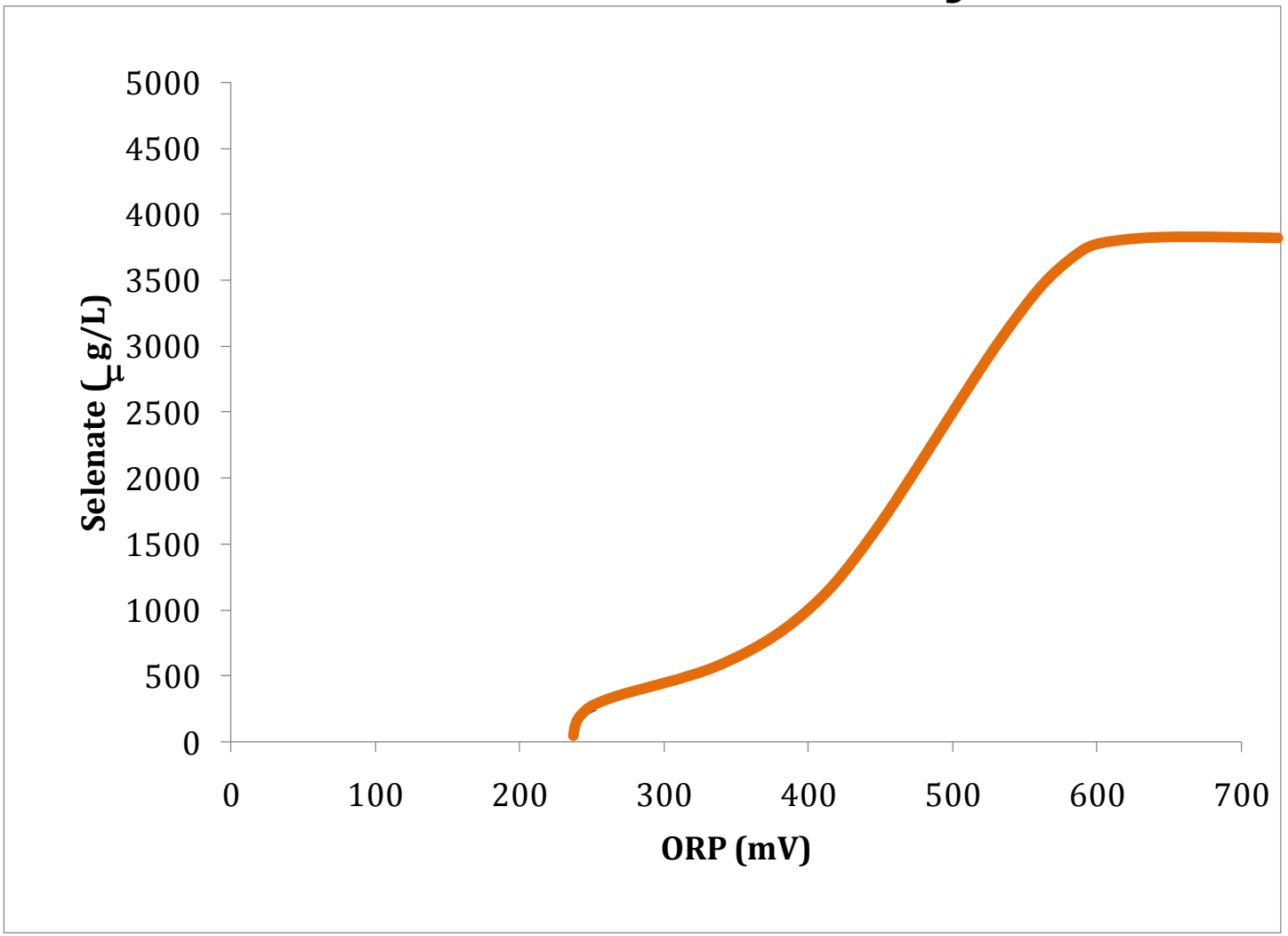
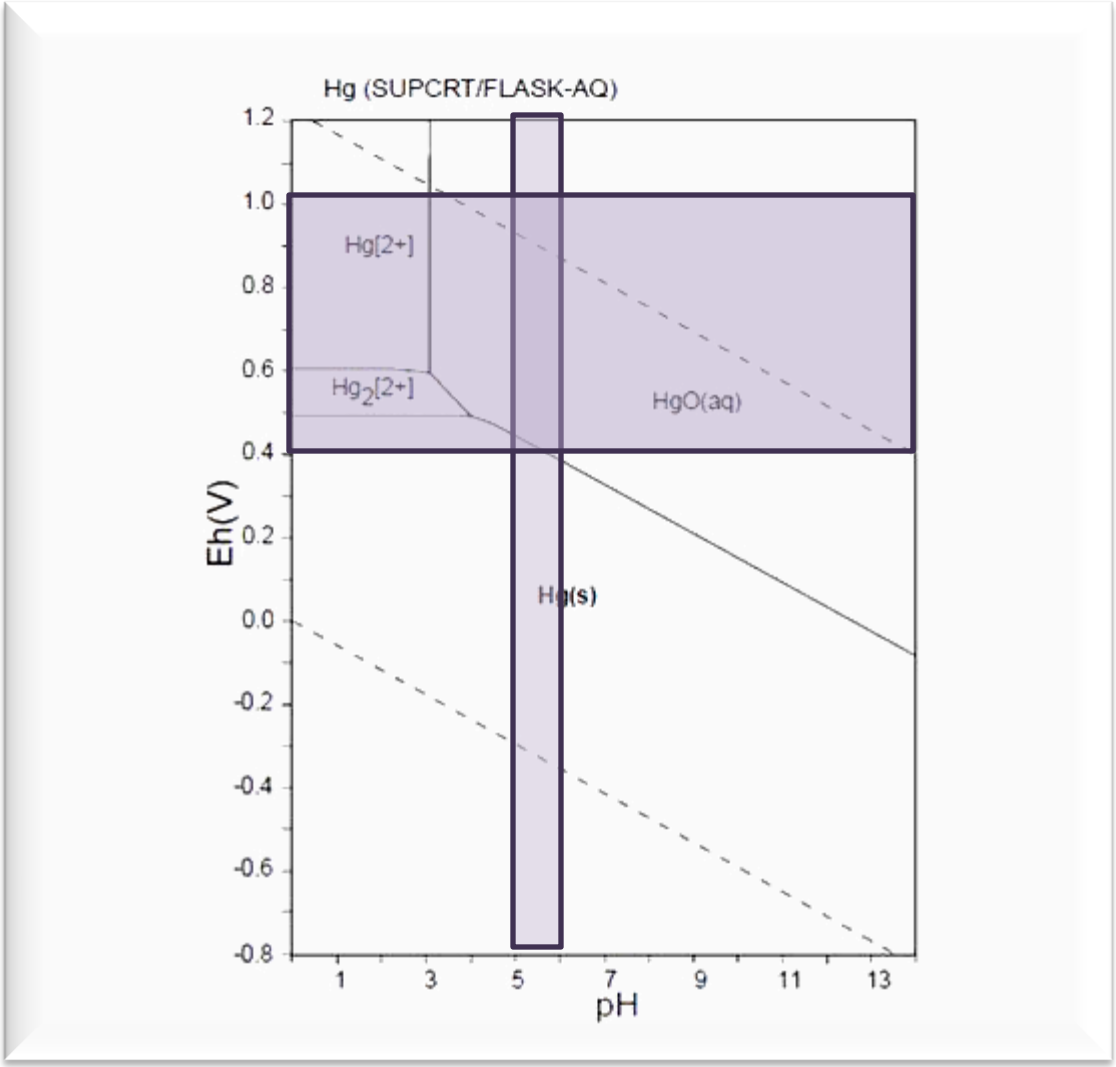


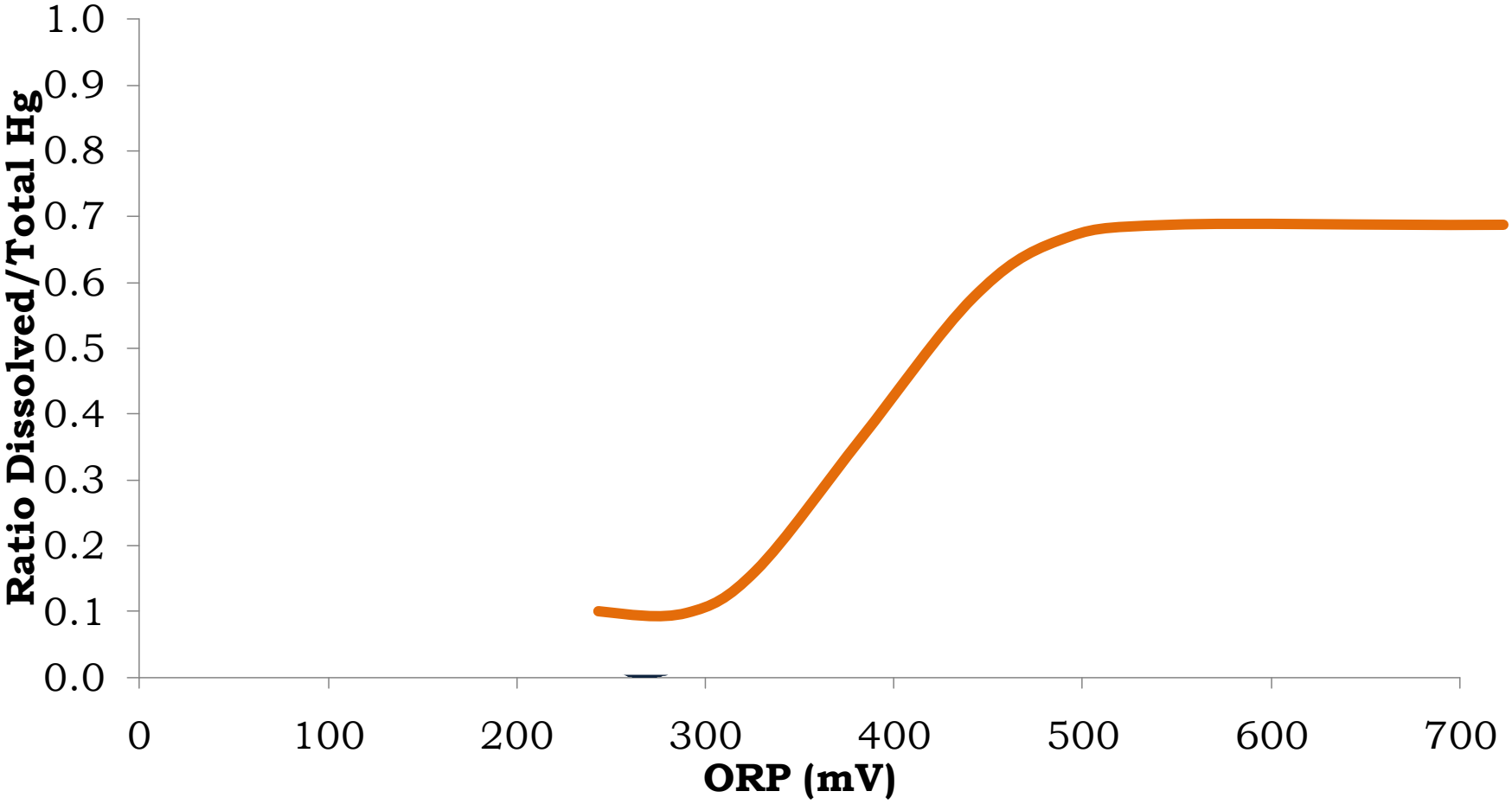
Mercury Re-emission

- **ORP effects mercury emission in WFGD absorbers**
- **Strongly reducing conditions within the scrubber will cause Hg^{+2} to be reduced to Hg^{0} and re-emitted**
- **Mercury is a very electrochemically active species**
- **Transitions in ORP have been implicated in Hg re-emission events**

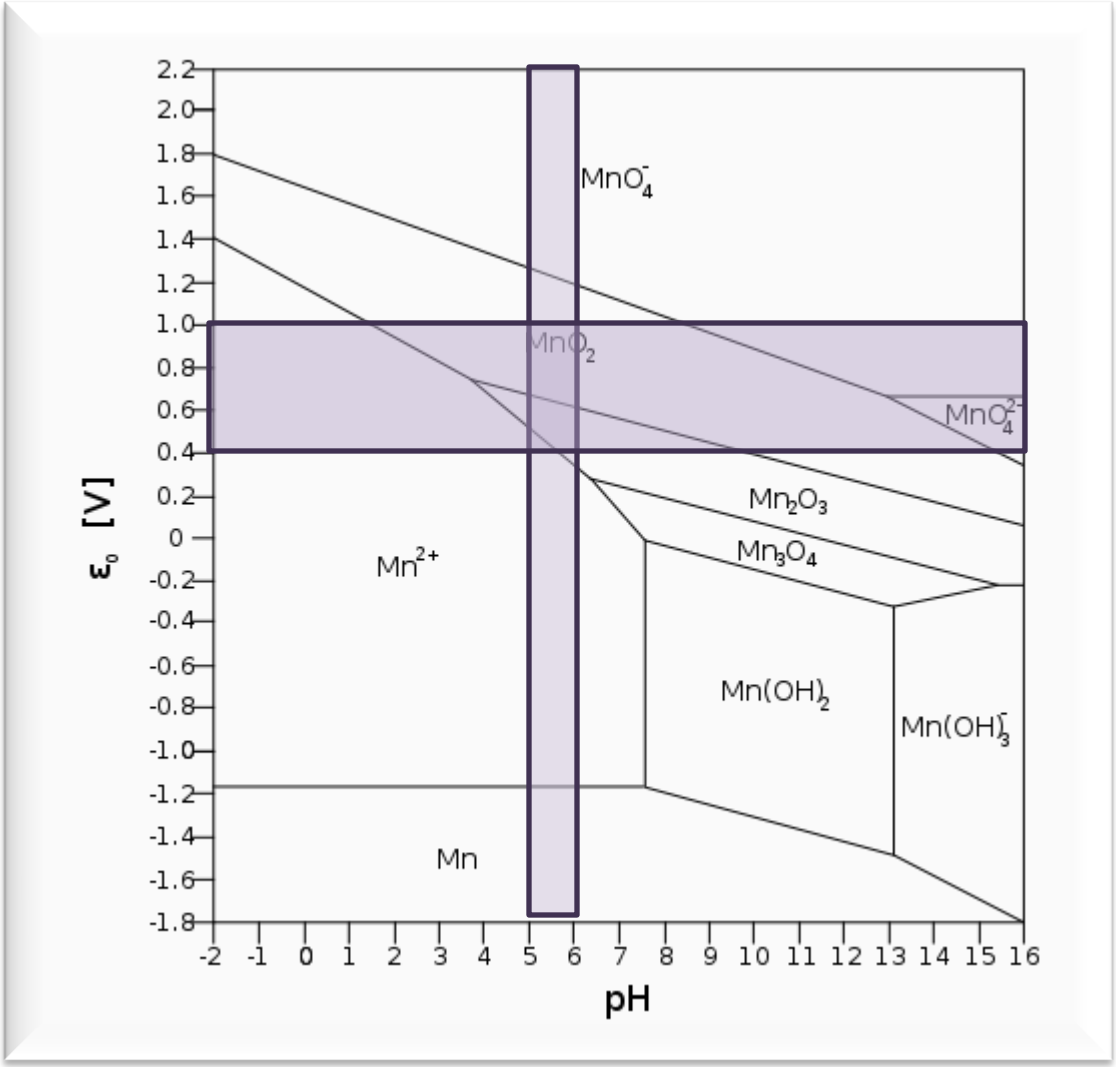
Phase Partitioning– Mercury



Dissolved Mercury vs. ORP in WFGD ART Slurry



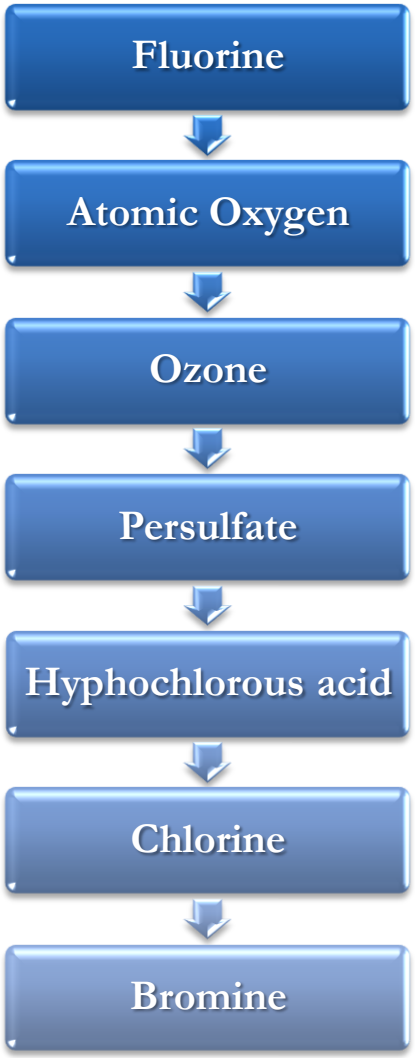
Phase Partitioning– Manganese



High ORP & pH Drop

- **High ORP results from a high concentration of strong oxidizers**
- **Oxidizers will continue to react with stream constituents until equilibrium is reached.**
- **WFGD absorber slurries are NOT at thermodynamic equilibrium at the time of bleed**
- **Strong oxidizers will react with the halogens in solution**
  - **liberating halogen containing gas**
  - **releasing hydronium ions in solution**
- **pH would be lowered within the ART, but reagent buffers this reaction**
  - **After buffering solids are removed, pH could decrease downstream**

Strength of Oxidizers



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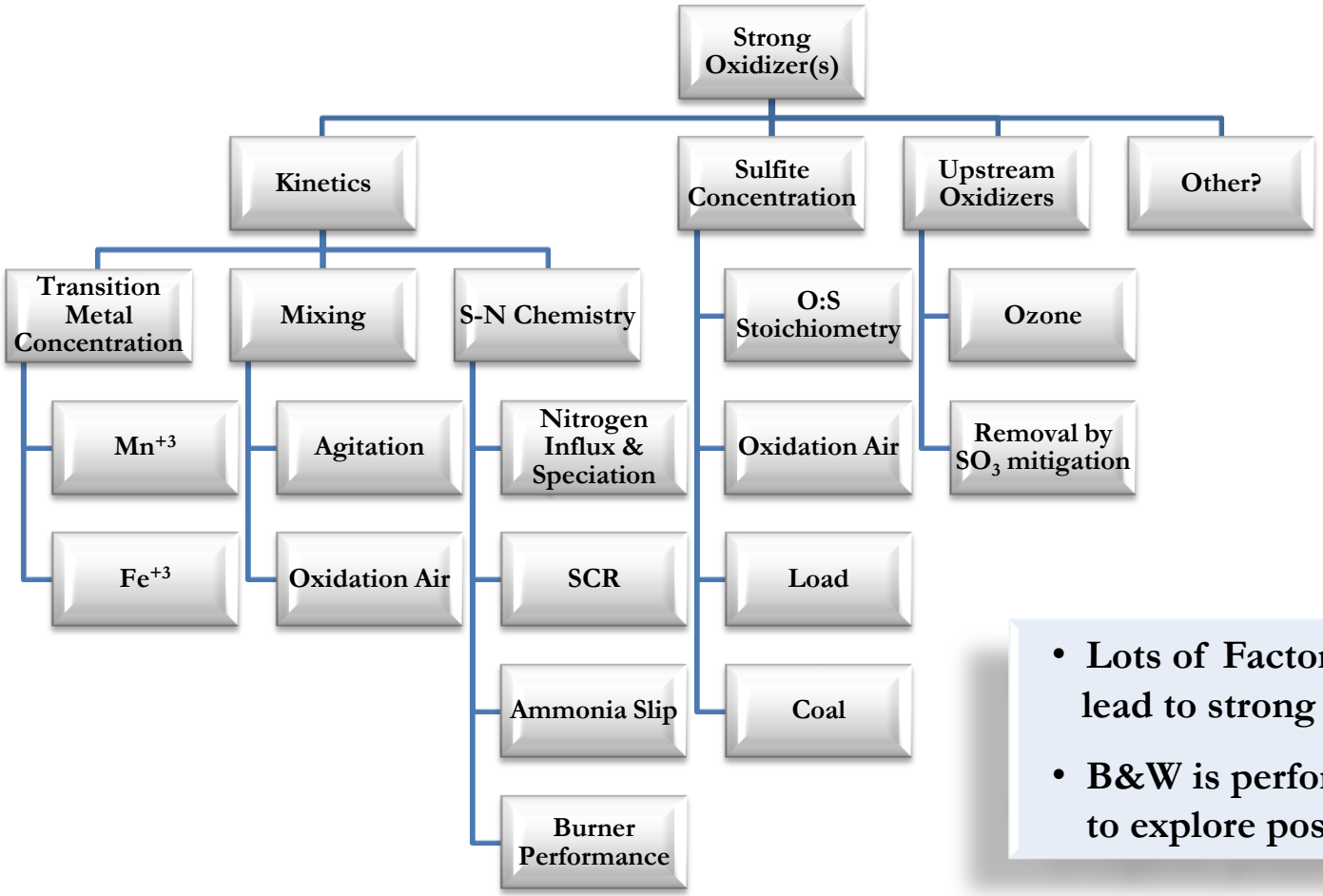
The Relationship Between ORP and Strong Oxidizer Concentration

Total Oxidizer Titration Results		
Unit	**ORP Profile**	**Oxidizer (ppm)**
1	High ORP	1680
2	High ORP	1592
3	High ORP	1574
4	High ORP	1571
5	Low ORP	227
6	Low ORP	169
7	Low ORP	50
8	Low ORP	29
9	Low ORP	27
10	Low ORP	19
11	Low ORP	10
12	Low ORP	<2

Prior to Testing:
What We Knew About Strong Oxidizer Formation



- Lots of Factors MAY lead to strong oxidizer formation
- B&W is performing testing to explore possible causes

Full Spectrum Gas and Slurry Field Testing

- **3rd Quarter 2012**
- **Test Parameters:**
  - **Coal Type**
  - **O:S stoichiometry**
  - **ESP Operation**
  - **SCR Performance**
- **Data Obtained**
  - **Full Spectrum Gas Analysis**
    - **FTIR, Inlet Velocity & SO_3 Traverse, Speciated Mercury Testing**
  - **Full Spectrum Analysis of the Slurry for Metals**
    - **IC, ICP-MS, Speciated Se & Hg**

Preliminary Results of Field Testing

- **Able to cause ~300mV increase in scrubber ORP, raising ORP to over 500 mV**
  - **Change occurred rapidly (~1 hour), as is observed in industry cases**
  - **ORP came down in a decay expected of a residence time distribution after test parameter returned to normal**
  - **Test replicated 3 times with same result**
  - **Results are under review**
- **Results to be verified through testing with another Utility**
- **Potential for control of WFGD chemistry through tuning**

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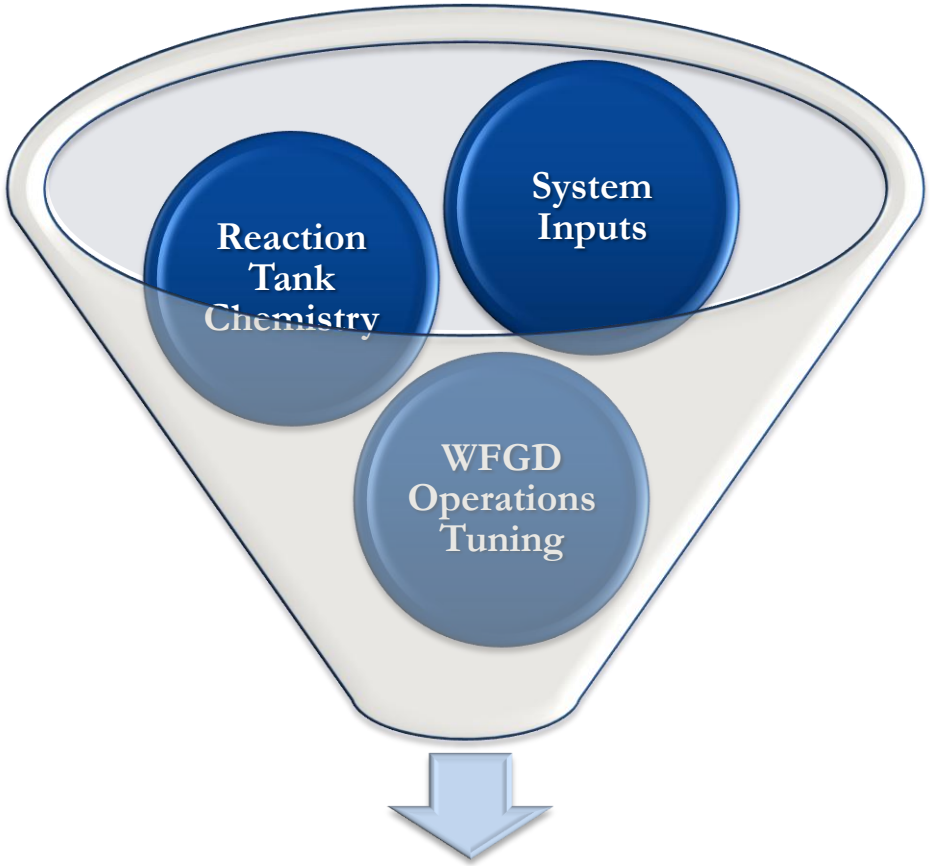
System Tuning



WFGD Bleed Stream Optimization for WWT

Potential Mitigation Strategies

System Impact

- Integrated control & tuning of AQCS chain

Fine Adjustment

- Optimization of WFGD Chemistry & Control
- Reduced Oxidation Air

Medicine

- Injection of Reducing Agents

?

- Other

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Conclusions & Path Forward

- **Implementation of holistic control of the AQCS system may provide tailored effluent stream composition(s)**
  - **Operation of upstream parameters impact WFGD ORP and composition**
  - **WFGD design and operation also changes bleed stream chemistry**
  - **WWT performance optimization may thus be obtained by controlling these parameters**
- **WFGD Bleed stream composition is important to performance of wastewater treatment operations**
  - **Oxidation state speciation and phase partitioning of metals (Se, Hg, etc...)**
  - **pH, ORP, Dissolved halogen content (F^-, Cl^-, Br^-, I^-)**
- **Further Research into how upstream changes impact downstream chemistry**

Questions