REINHOLD ENVIRONMENTAL Ltd.

2013 APC Round Table & Expo Presentation

July 8-9, 2013, in St. Louis, MO / Hosted by Ameren

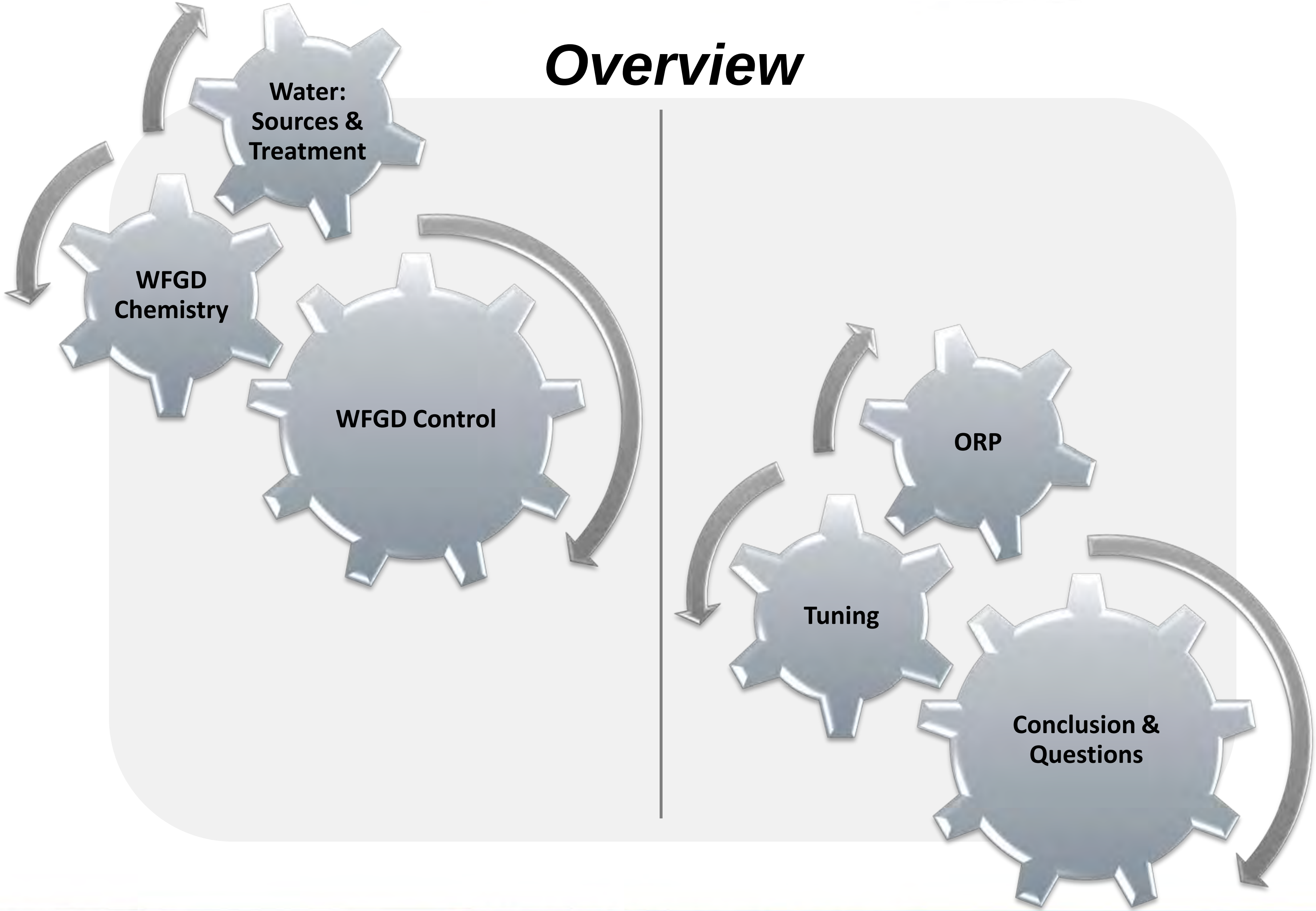
WFGD Chemistry, Tuning and Optimization for Improved Wastewater Characteristics and Treatment

2013 Reinhold APC Conference

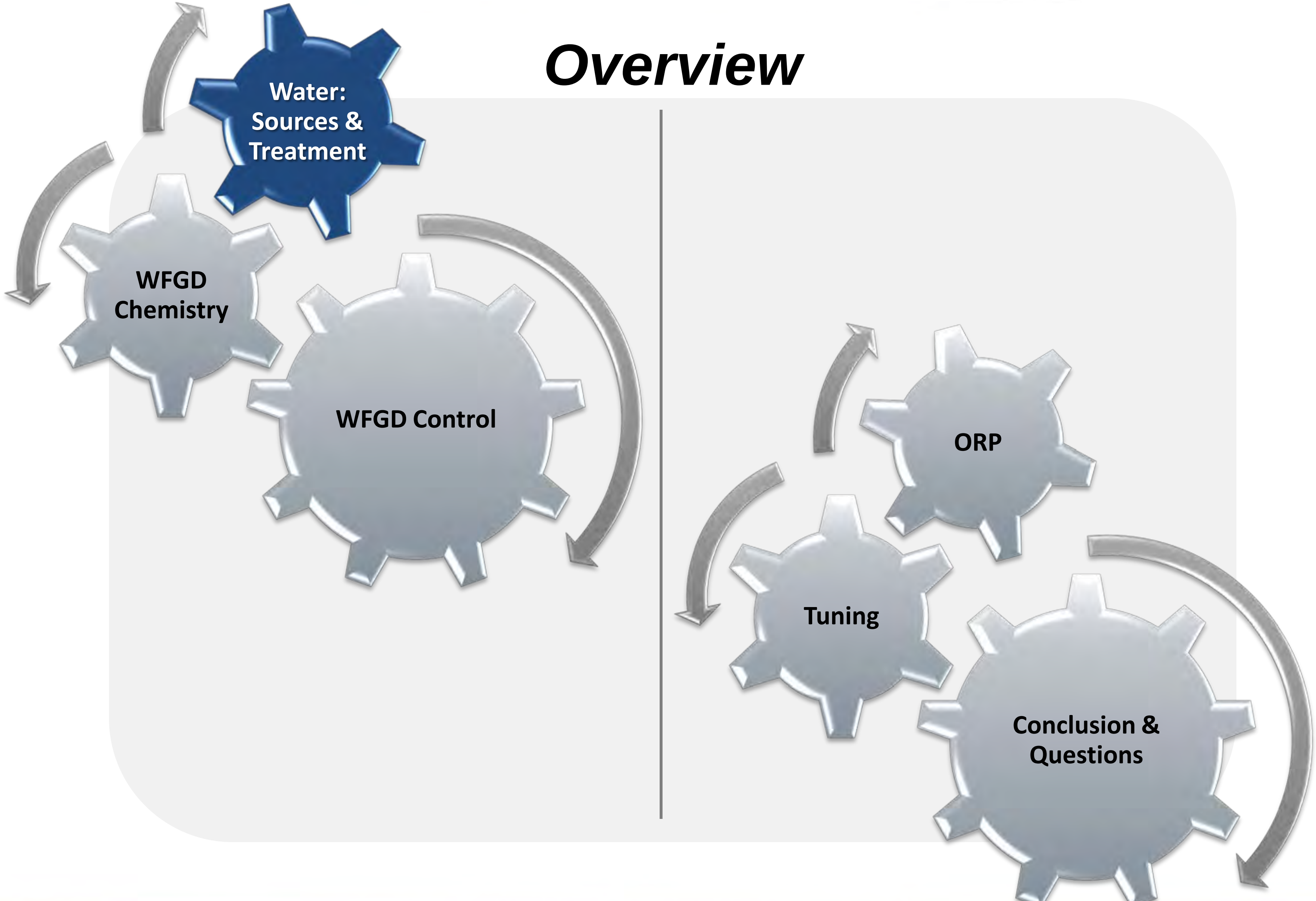
St. Louis, Missouri – July 8-9, 2013

Shannon R. Brown, *AQCS Engineer*
Daniel B. Johnson, P.E., *Field Service Engineer*

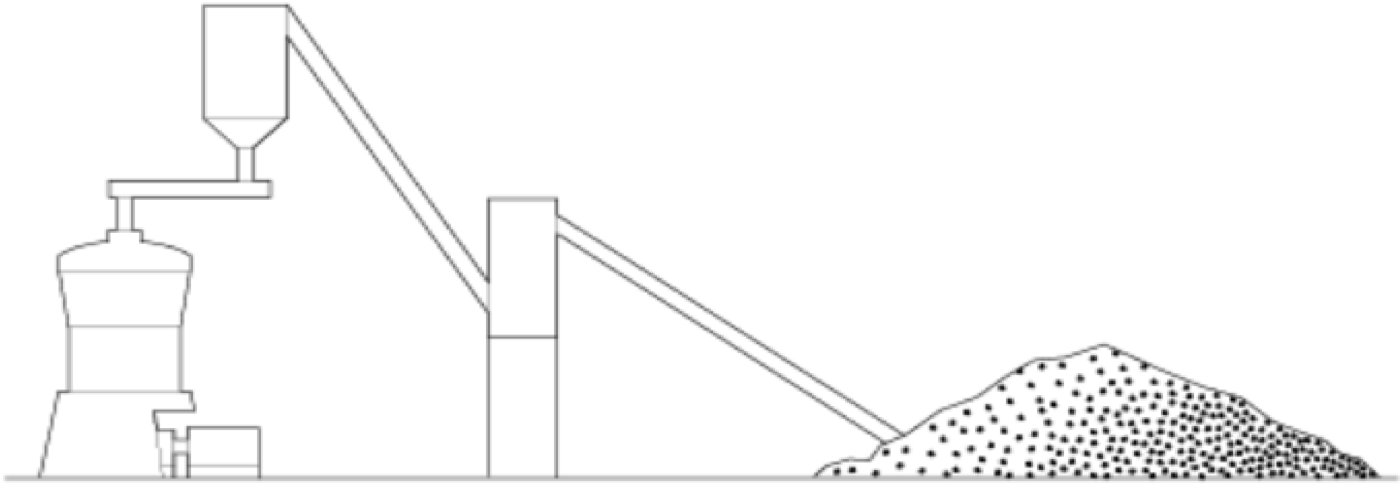
Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control
ORP
Tuning
Conclusion & Questions

Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control
ORP
Tuning
Conclusion & Questions

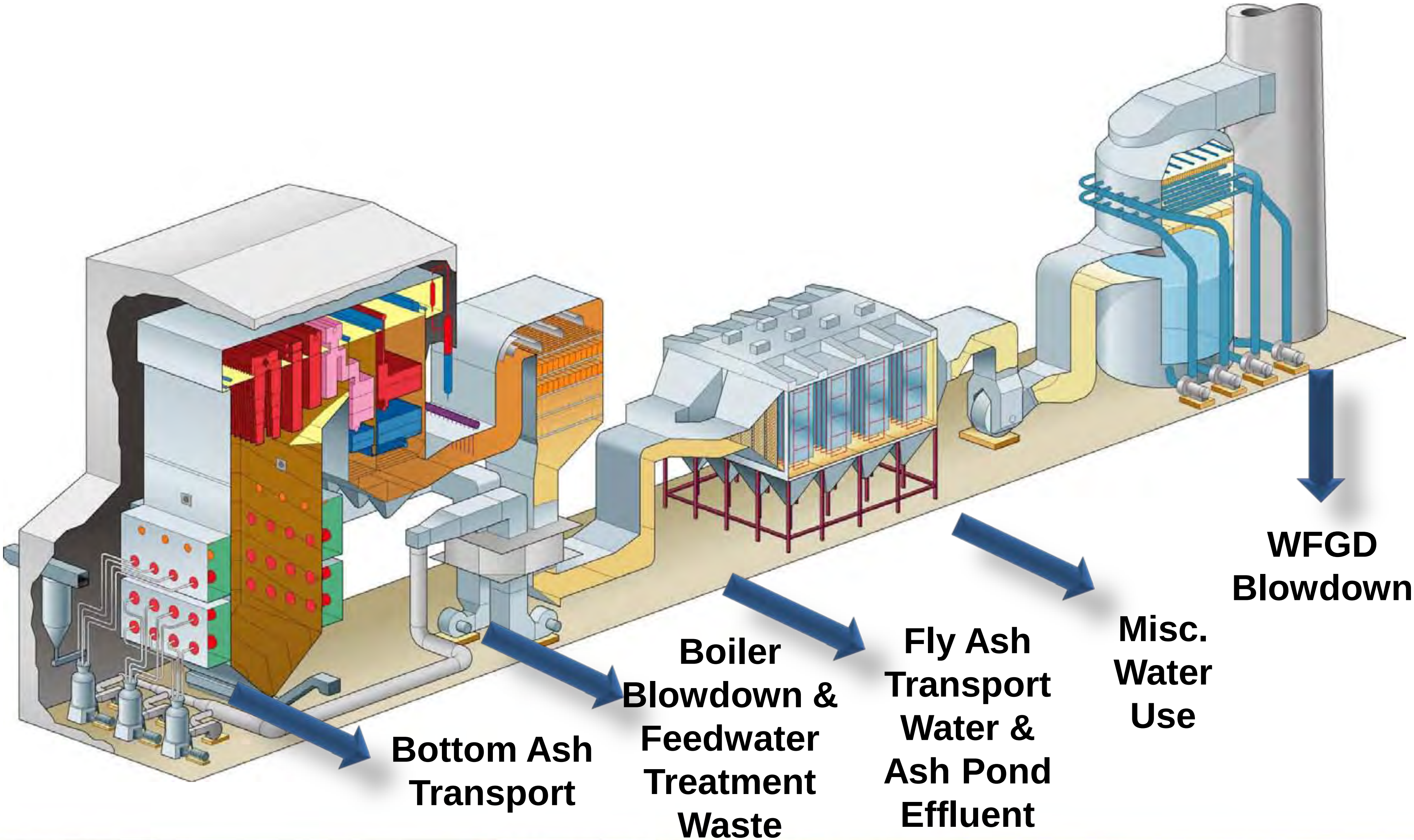
Systems Feeding to WWT


Coal Pulverization

Coal Supply

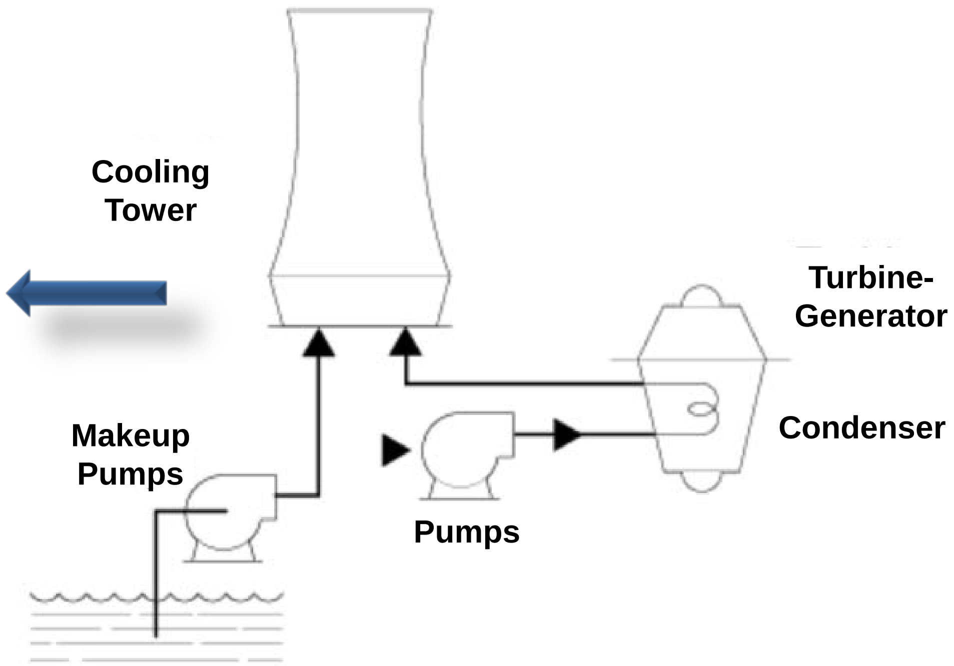
Coal Pile Runoff

Systems Feeding to WWT



Systems Feeding to WWT

Cooling Tower Blowdown



*Nominal Flowrates and Bulk Properties of Wastewater Streams in a Power Plant**

Water Source	Normalized Flow Rate (gpd/MW)	TSS (mg/L)	TDS (mg/L)
WFGD Blowdown	300	10,000	30,000
Boiler Blowdown	200	5	50
Cooling Tower Blowdown	3,600	20	2,000
Ash Pond Effluent	5,000	10	1,000

*As reported by the EPA in 2009 report, DOE/NETL in 2010 report

Water Balance

- **Boiler, Cooling Tower and WFGD use the most water within the plant.**
- **By reusing water within the overall process of the plant, less water intake is needed and less water is sent to wastewater treatment.**
- **Water can often be reused in the WFGD**

Water Reuse in The WFGD

- Not all “water” streams are created equal
  - Content of water added to the WFGD should be expected to impact overall chemistry
  - Total metal loading to WWT will still need to be treated, but may be more concentrated
  - Consider materials of construction as concentration increases
- Considerations for Reuse in WFGD
  - Many waters can be used for reagent prep
  - ME wash has a high capacity/flowrate, but ensure that waters added will not cause buildup on ME blades
  - Pump seal water should be pure
- Tighten water balance within the WFGD
  - OEM can make recommendations for tuning water use including ME wash frequency and/or blowdown operations

Technologies for Treatment of WFGD Effluent*

Settling Ponds
- Mostly to reduce suspended solids

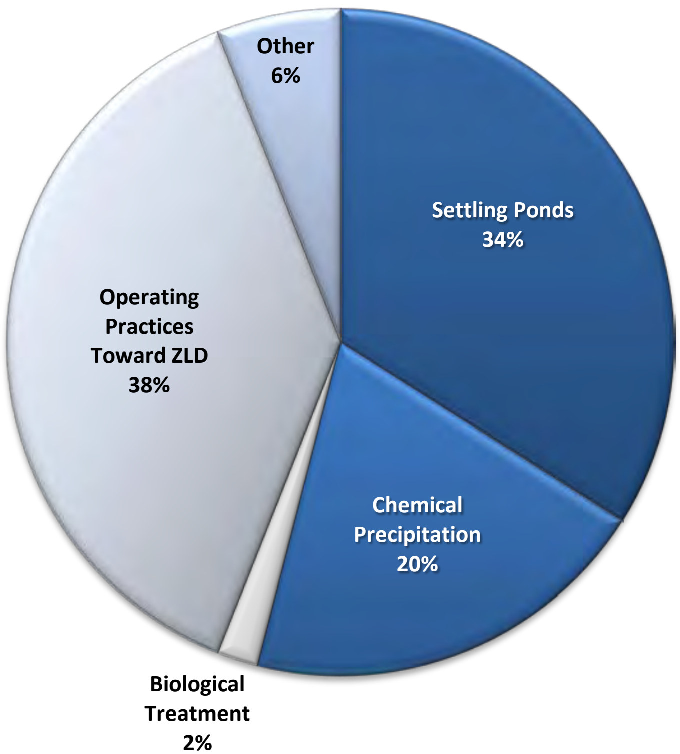
Chemical Precipitation
- Targets mercury and arsenic removal

Biological Treatment
- Targets Selenium
- Also removes nitrates & sulfates

Operating Practices toward ZLD

Other
- Vapor-Compression Evaporation
- Clarifiers
- Constructed Wetlands
- Commingling with other wastewater
- Ash solidification

B&W is researching reclaiming water from ZLD systems for reuse in boiler pretreatment, etc



*As reported by the EPA in October 2009 report

Brine Concentration & Crystallization

Pre-Treatment

- Chemical precipitation (CP) system
- Used for gypsum de-saturation & heavy metals removal
- Complete removal of Ca & Mg (by soda ash softening) desirable but expensive

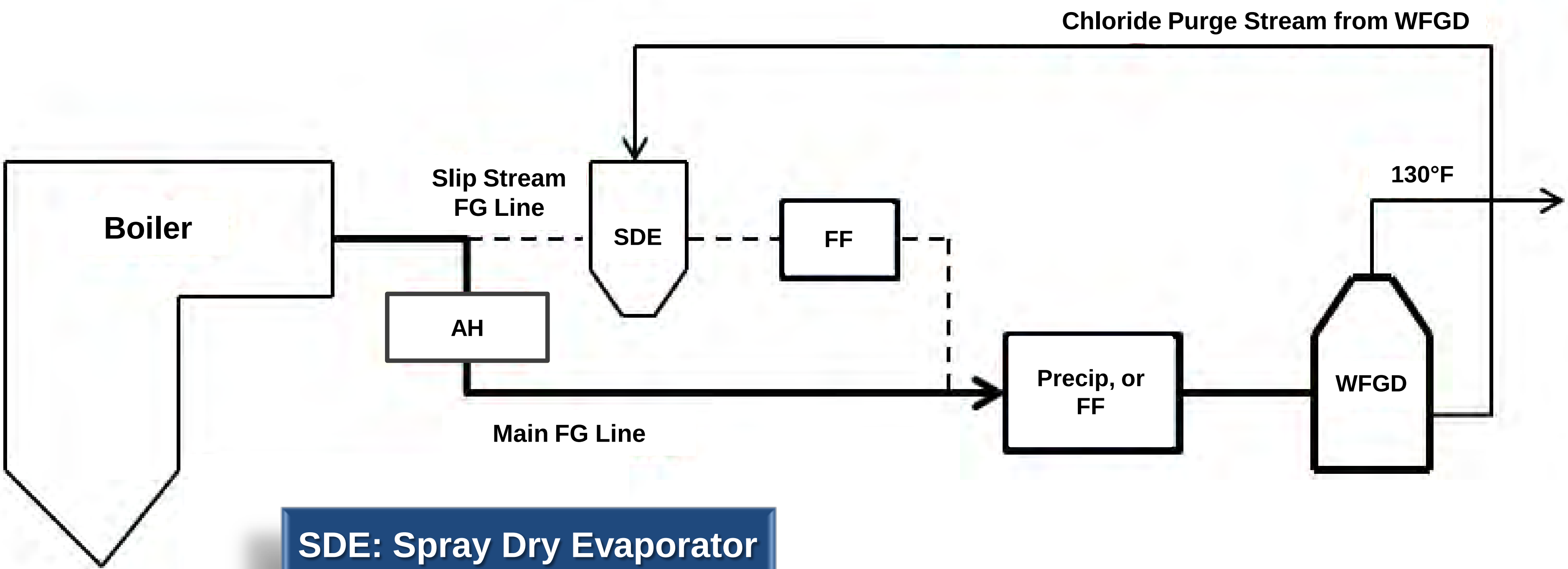
Brine Concentration

- Falling film evaporator (FFE) with mechanical vapor compression (MVC)
- Reduces the water content of the wastewater by ~90%

Forced Circulation Crystallization (FCC)

- 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
- Generally uses either steam or MVC as the energy source

Spray Dryer Evaporation Process Flow Diagram



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

WFGD Chemistry sets the Difficulty of Effluent Treatment

WFGD Bleed to Dewatering

- Solids removed as gypsum product
- Filtrate split between WFGD reclaim and waste water treatment
- Control of TDS set by dilution of Reaction Tank

Recycle

- Primary Hydroclone tuning for gypsum purity & optimal gypsum moisture
- Secondary Hydroclone tuning for TDS tuning, fines removal and WWT optimization

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:

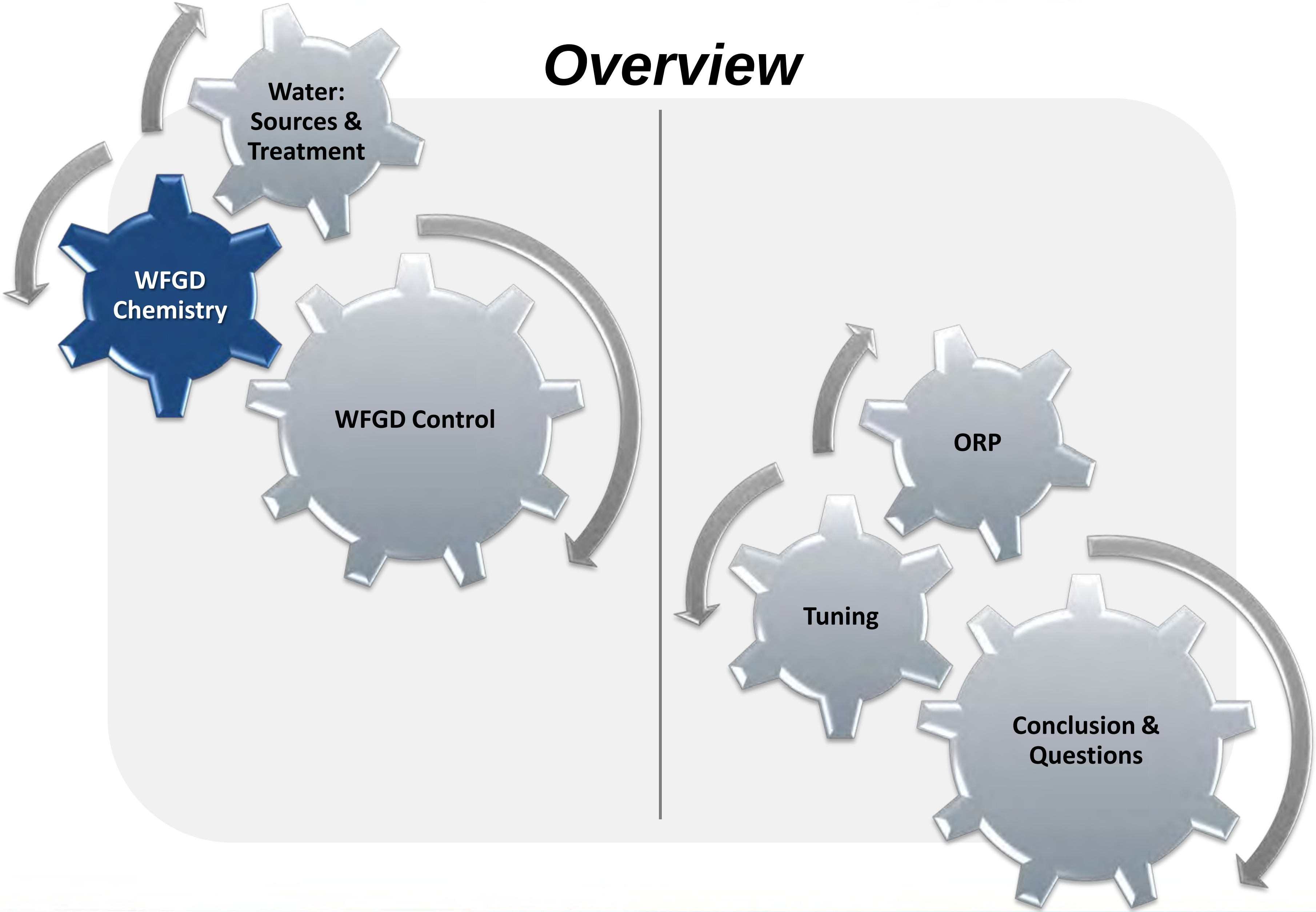
- **High in Halogens**
- **High TDS**
- **Selenite (IV)/Selenate (VI)**
- **Mercury**
- **Boron**

Significant variation exists with WFGD absorber slurry samples

- **TDS std. dev. of 15,000 mg/L**

*As reported by the EPA in October 2009 report

Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control
ORP
Tuning
Conclusion & Questions

WFGD Chemistry: Characterization

Online Measurement
- Can be fed into process controls
- Real time

Grab Samples
- Measure more species
- Significant time lag from time of sampling

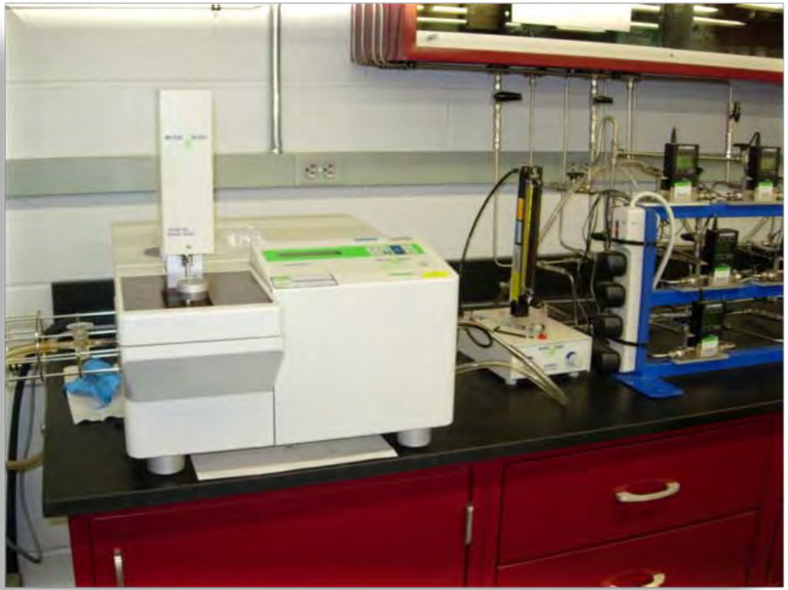
Characterization

- Online process measurement afford the means to trend, predict and control process chemistry
  - Flowrate
  - Density
  - pH
  - ORP
- Ideally, measure pH and ORP at process effluent & WWT influent points
- As many WFGD systems are kinetically controlled, reactions may continue downstream of the effluent point.

Characterization

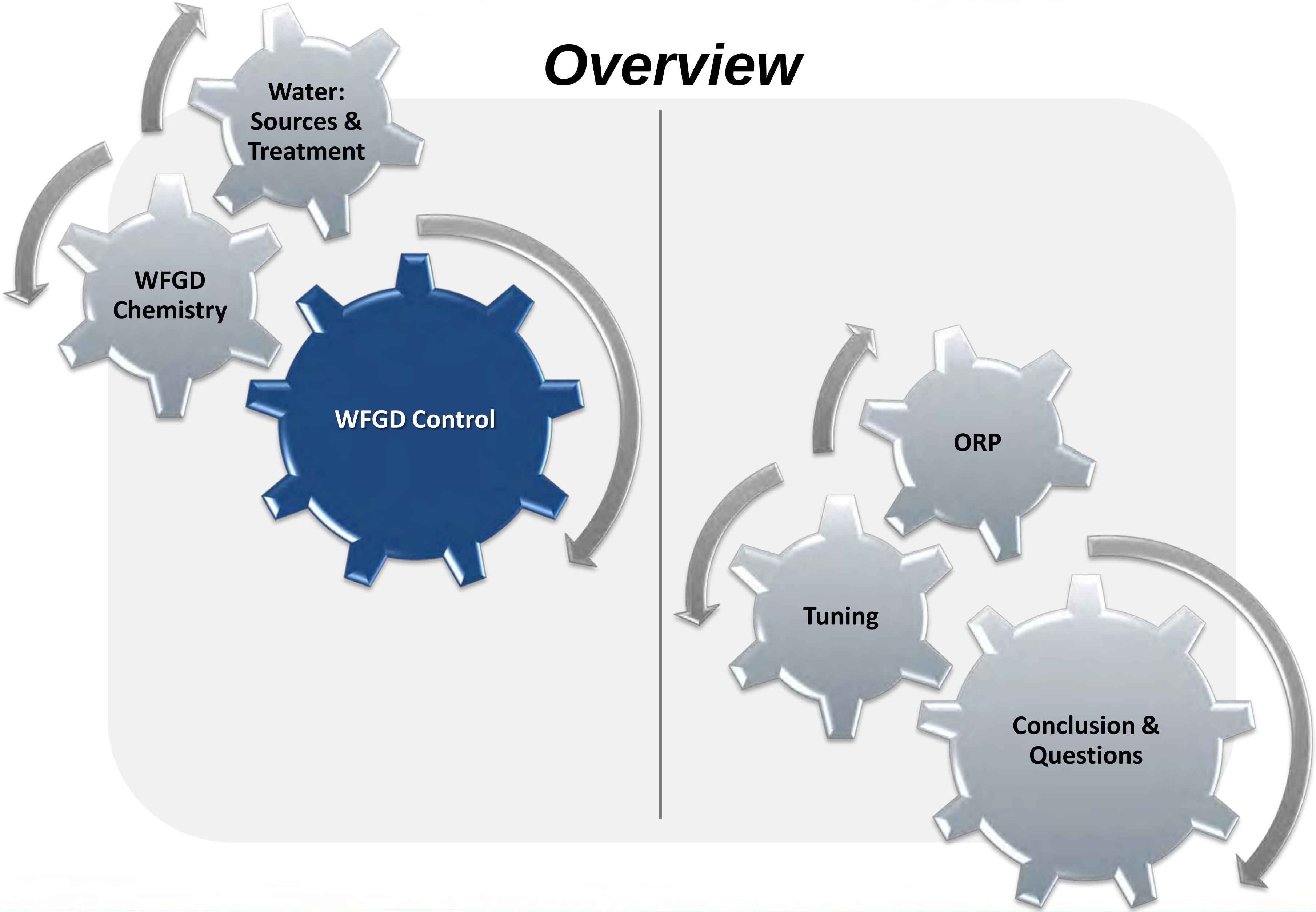
- **Grab samples are needed for advanced chemical analysis**
  - **TSS**
  - **TDS**
  - **pH**
  - **ORP**
  - **Chloride content**
  - **Gypsum Purity**
  - **Total, Speciated Anions**
    - **Ion-Chromatography (IC)**
  - **Full Metal Scan of Speciated Metals (Cations)**
    - **Inductively Coupled Plasma (ICP) Spectroscopy**
  - **Specific Testing for Current Regulated Metals**
    - **Speciated Hg and Speciated Se**

Notes about WFGD Characterization

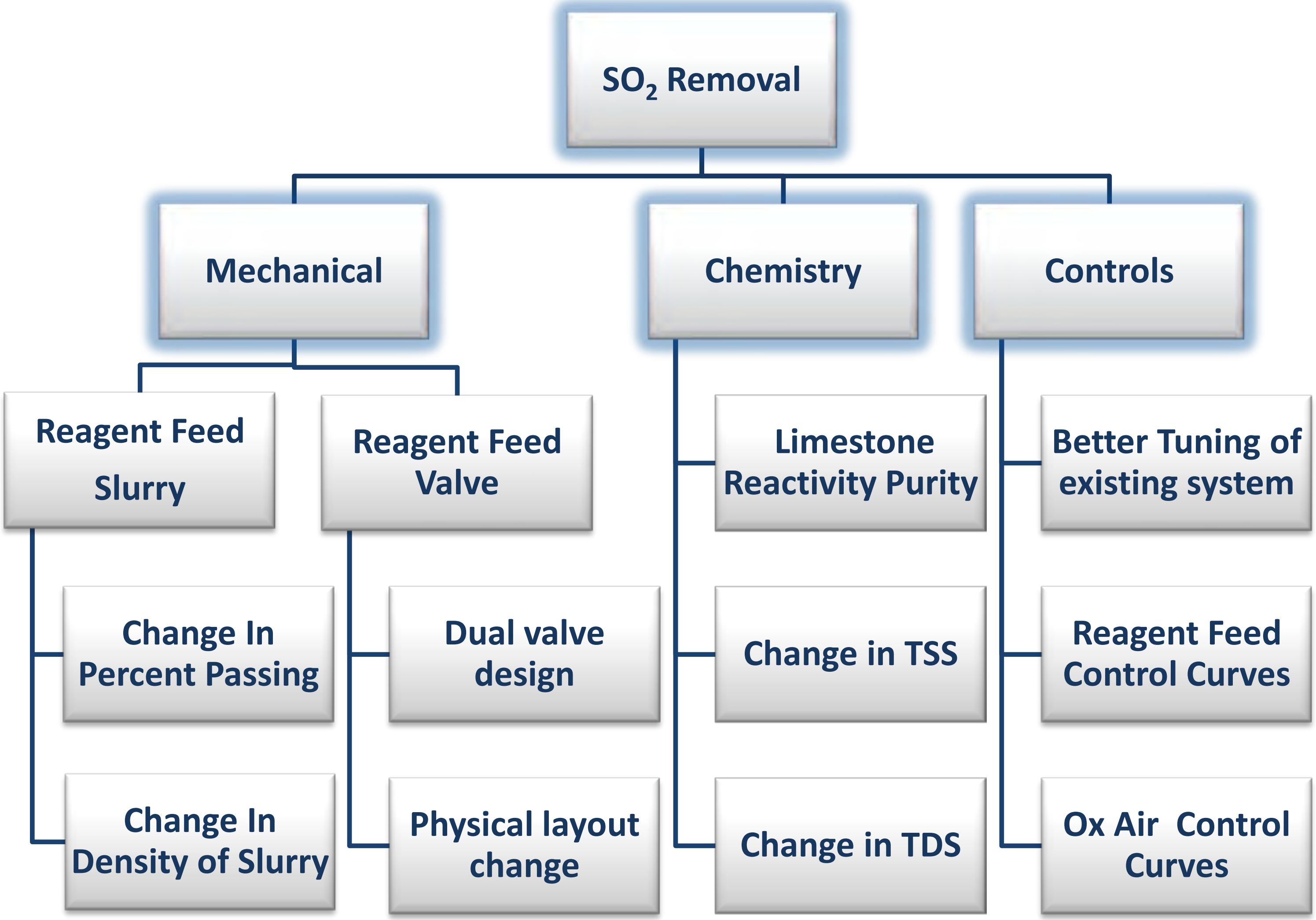


- **Perform routine calibration and verification of online monitoring instrumentation**
  - **You can't control to bad data**
- **Use proper sampling techniques for grab samples**
  - **Mercury needs to be collected in glass**
  - **Some analysis is time sensitive**
- **Validate laboratories**
  - **Due diligence in making sure results reported are accurate and repeatable**
  - **Certification**

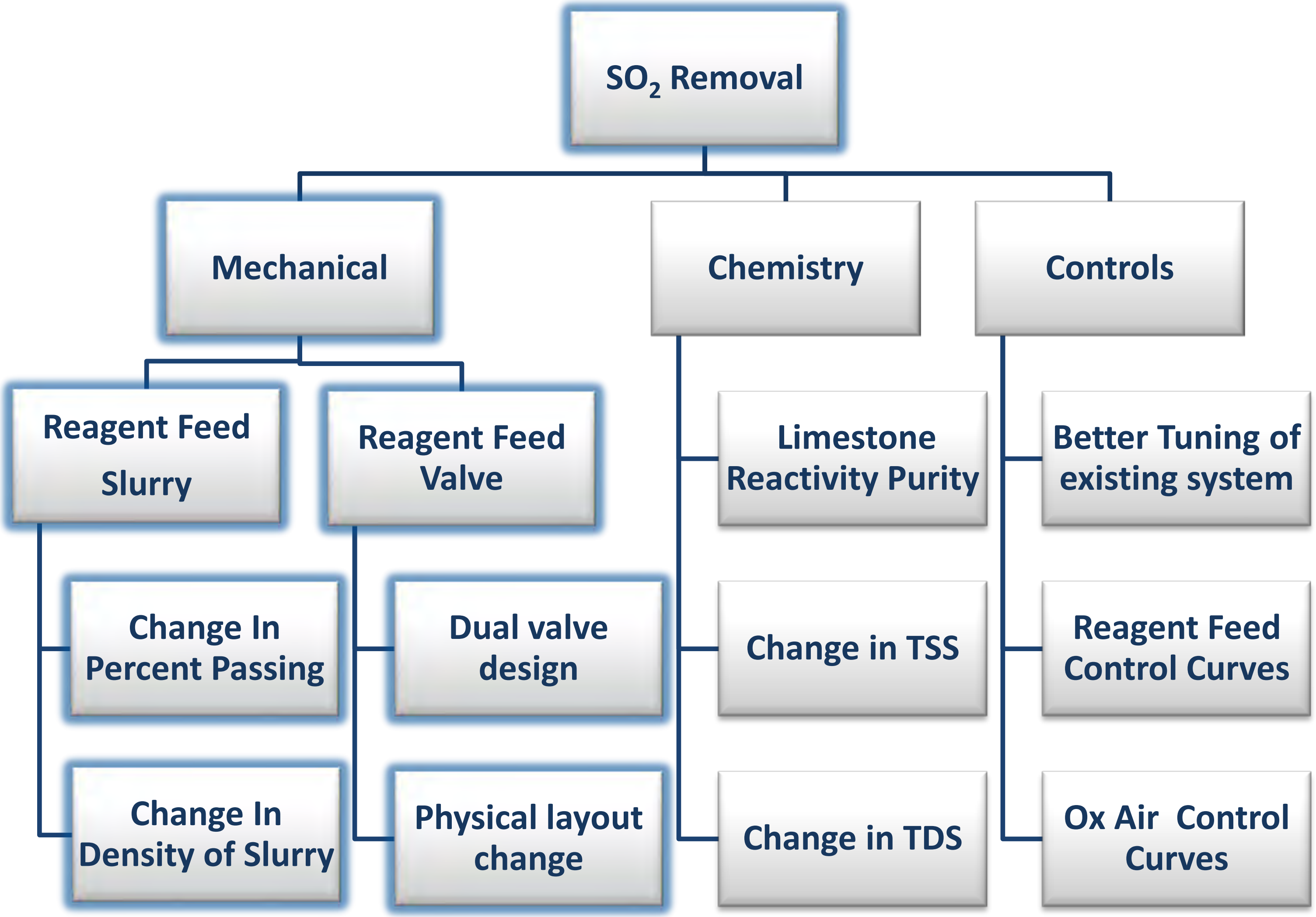
Overview


Water:
Sources &
Treatment
WFGD
Chemistry
WFGD Control
ORP
Tuning
Conclusion &
Questions

WFGD System Control



WFGD System Control



Reagent Feed System

Reagent Feed System

- **Why is Reagent Feed Important for Bleed Optimization**
  - **Control of excess carbonates and gypsum purity**
  - **Proper control of SO2 removal and pH operating band**
  - **Reduce risks of limestone blinding by proper pH control, and particle size**
  - **Smoother operation prevents batch feeding of reagent**
- **Control Parameters for Optimization of Reagent Feed**
  - **Limestone Reactivity – B&W Design Standard**
  - **Limestone Grind – usual standard is 95% passing 325 mesh**
  - **Limestone Density – usual standard is 28%**
  - **Limestone Purity – control fines in dewatering and excess metal entry into system**
- **ORP Levels vs. Reagent Feed**
  - **High ORP levels can cause the system to lower pH**
  - **pH control system will add limestone due to acid liberate by oxidizer rxns, not SO_2 demand**
  - **Kinetic vs. Thermodynamic control of WFGD chemistry**
  - **Limestone major contributor to reaction rate**

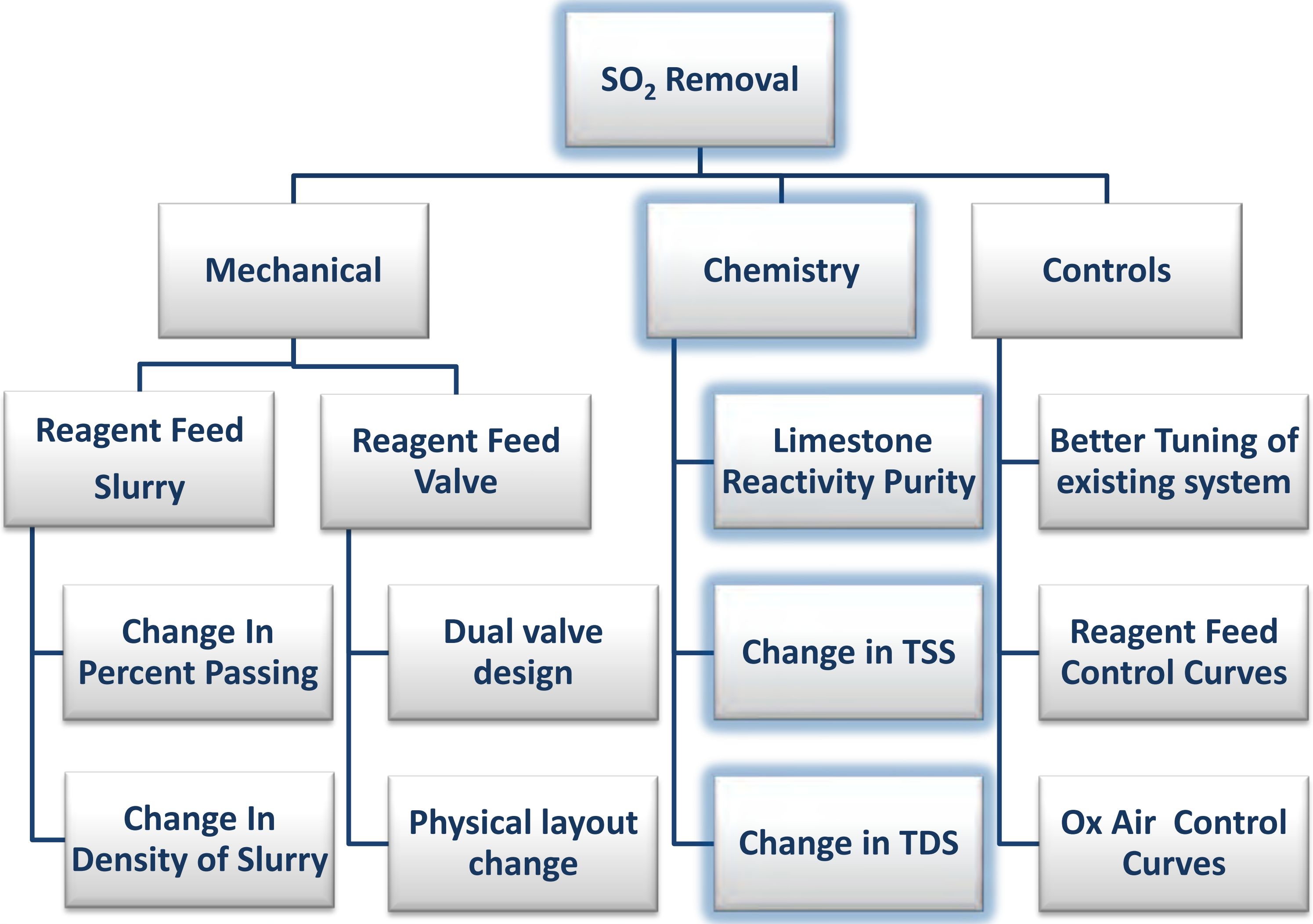
Tuning Reagent Feed System

- **Ball Mill Tuning**
  - **Percent passing may be raised by decreasing the feed of limestone**
  - **Rate of dissolution is dependent upon the percent passing**
    - **Open spray towers this becomes a more critical parameter**
  - **Change Reagent Feed Density**
    - **Reagent feed valve in it's correct Cv/GPM range**
    - **Change in input of makeup water for TDS control**
- **Reactivity**
  - **In less reactive limestone, use a finer grind to maintain the same [Ca^{2+}] and [CO_3^{2-}]**
  - **B&W has experience with determination of limestone reactivity**

Reagent Feed System
Feed Control Valve

- **Dual Valve Design**
  - **High/low load operation**
  - **Helps maintain minimum velocity through pipe**
  - **More continuous reagent flow**
- **Physical Layout Change**
  - **Allows for gravity draining of pipe**
  - **Lower (GPM) minimum flow rates**
  - **Minimum open position of valve is changed**

WFGD System Control



SO_2 to $CaSO_4$ Conversion Basic Equations

- **Basics of conversion**
  - **The conversion from $SO_{2\,(g)}$ to $CaSO_{3\,(aq)}^{-}$ occurs in the spray zone of the tower**
  - **The conversion causes the slurry to become acidic, which is the cause for the drop in pH**
  - **The acidic slurry causes the limestone slurry, $CaCO_3$, to disassociate. This allows for the formation of the calcium sulfite, $CaSO_3$**
  - **Oxidation to $CaSO_4$ in ART**

Equations:

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$HSO_3^- + Ca^{2+} + \tfrac{1}{2}H_2O \rightarrow CaSO_3 \bullet \tfrac{1}{2}H_2O + H^+$$

$$2CaSO_3 \bullet \tfrac{1}{2}H_2O + O_2 + 3H_2O \rightarrow 2CaSO_4 \bullet 2H_2O$$

SO_2 to $CaSO_4$ Conversion at Higher ORP Levels

- **Effects of Higher ORP Levels**
  - **Strong Oxidizers react with halogen species in the slurry**
  - **Higher ORP levels may have an effect higher gypsum purity**
  - **Associated drop in pH from interaction**
  - **Postulated formation of gypsum directly without oxidation air**

Equations:

$$S_2O_8^{2-} + 2Cl^- + 2Ca^{2+} + 5H_2O \rightarrow 2CaSO_4 \bullet 2H_2O + Cl^- + 2H^+ + ClO^-$$

$$S_2O_8^{2-} + 2Br^- + 2Ca^{2+} + 5H_2O \rightarrow 2CaSO_4 \bullet 2H_2O + Br^- + 2H^+ + BrO^-$$

$$S_2O_8^{2-} + 2I^- + 2Ca^{2+} + 5H_2O \rightarrow 2CaSO_4 \bullet 2H_2O + I^- + 2H^+ + IO^-$$

SO_2 to $CaSO_3^-$ Conversion Function of Absorber Trays

Absorber Trays

- Perforated plate(s) allowing for a froth formation. The liquid froth layer on the tray increases residence time
- The trays function as bubbling bed that forces the gas through the slurry spray from above
- Provides for better distribution of gas flow
- The absorber can be equipped with a single tray or two trays

SO_2 to $CaSO_3^-$ Conversion Liquid to Gas Ratio

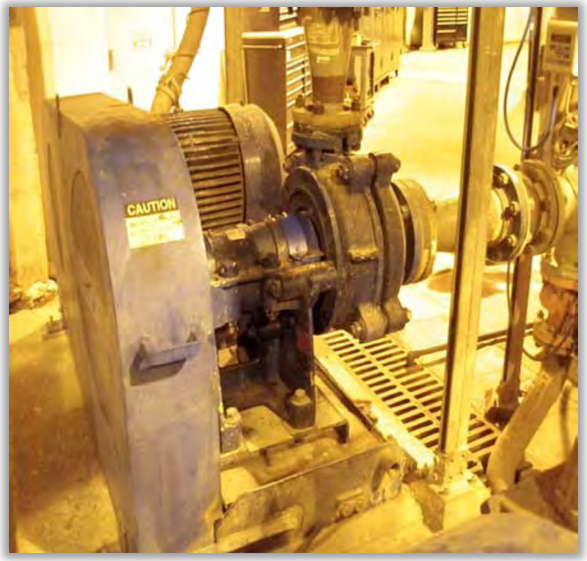
L/G Ratio

- **Interspatial Spray Patterns**
- **Combines two sprays into one level**
- **At lower load operations, a decrease in spray flux is possible**

Bleed System

Function:

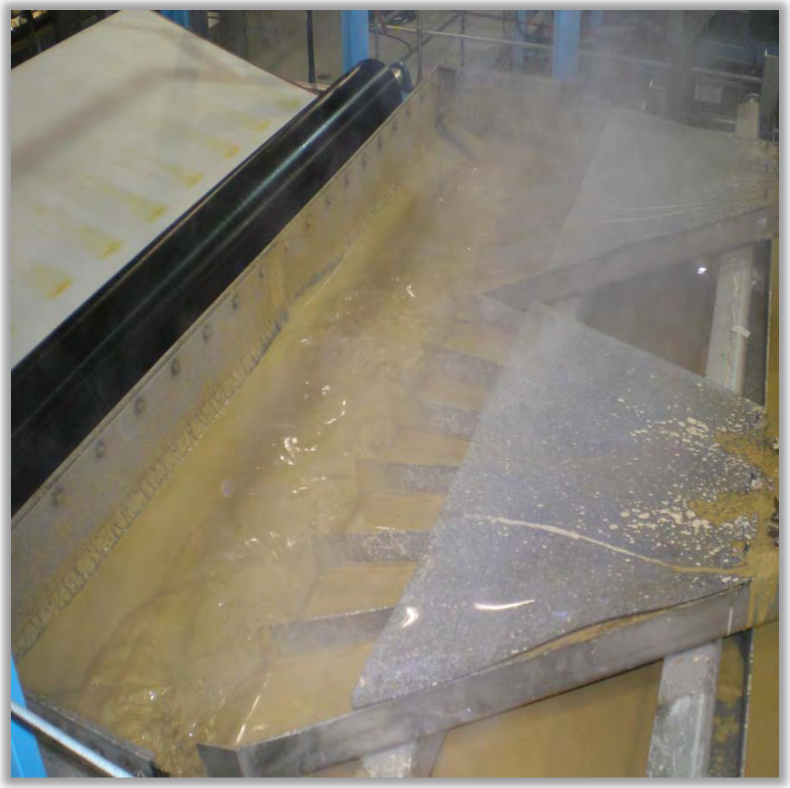
- **Control Total Suspended Solids, TSS**
  - **Gypsum Production**
- **Control Chloride Concentration in the absorber tower, TDS**
  - **Secondary Dewatering System Overflow**



Bleed System

Adjustment of TSS/TDS

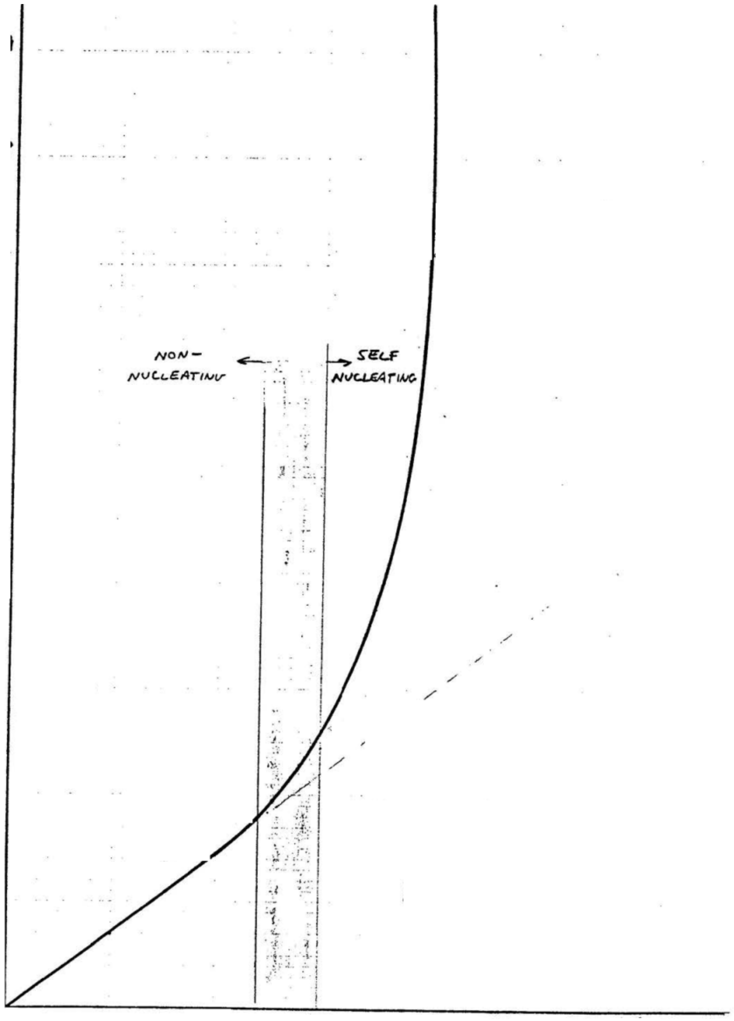
- **A higher TSS has been shown to help increase removal of SO_2**
  - **Sluggish Controls**
  - **Pump Vibration increase**
  - **Decrease the blow down rates**
- **Variation of TSS may be one control parameter for relative saturation**
  - **Control parameter of gypsum crystal growth**
- **Secondary Dewatering**
  - **Allows for control of TDS will maintaining a constant TSS level**
  - **Fine tuning of blowdown for consistent TDS feed to WWT**



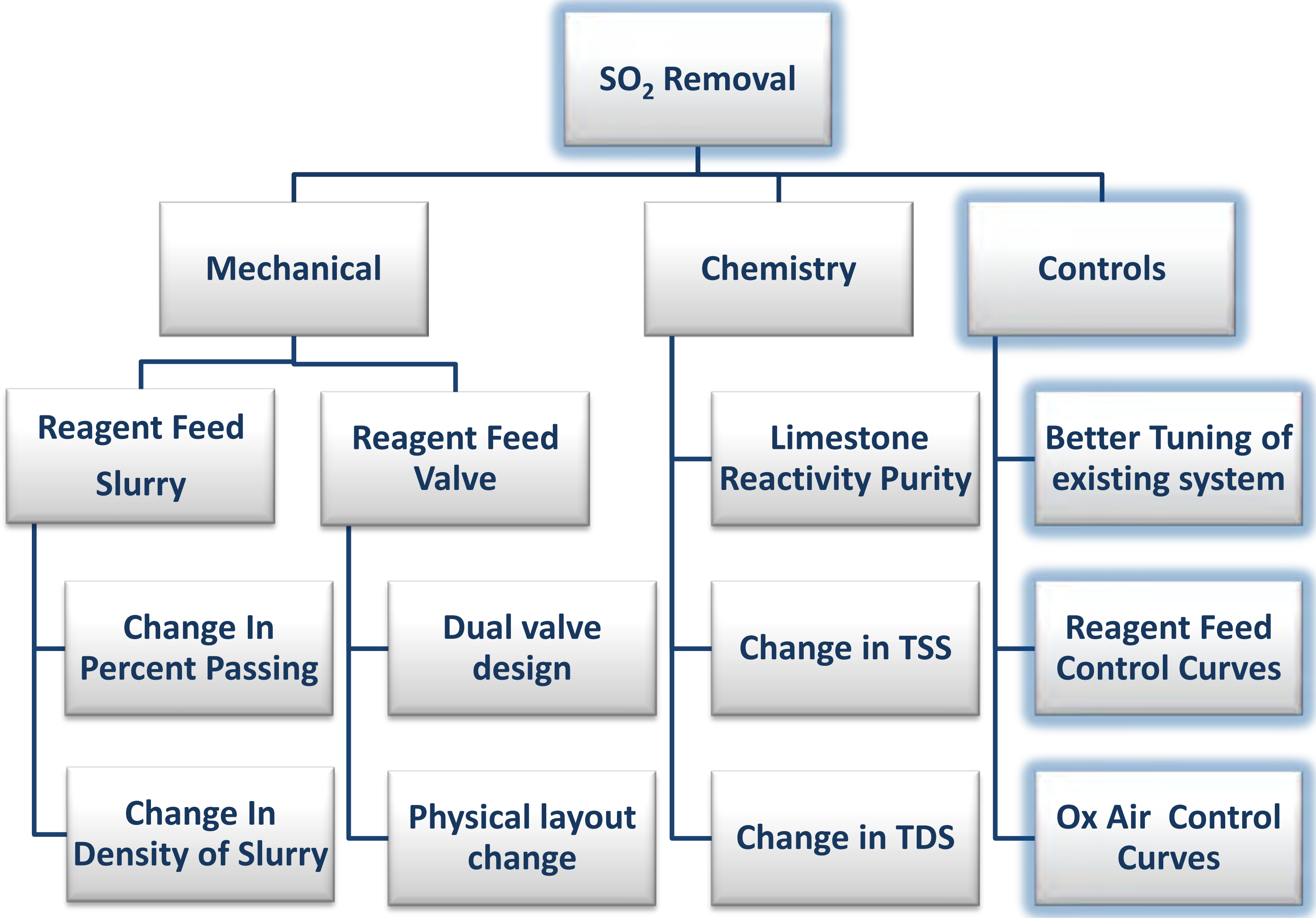
Relative Saturation Level

Control of Gypsum Crystal Growth

- Self-Nucleating Zone has uncontrolled growth
- Non-Nucleating Zone linear growth pattern
- Ratio of Calcium to Sulfate concentrations



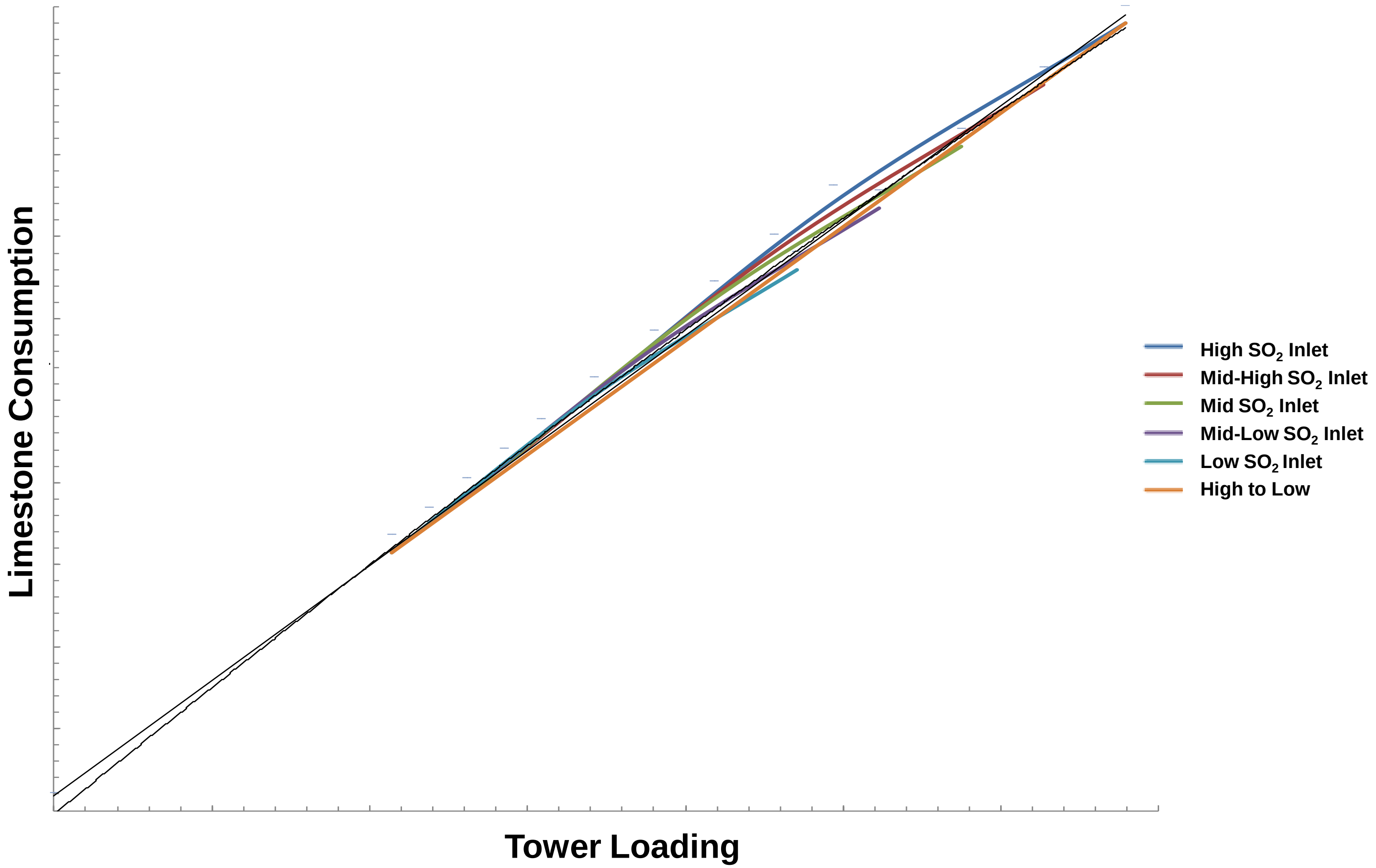
WFGD System Control



Why Tuning/Controls?

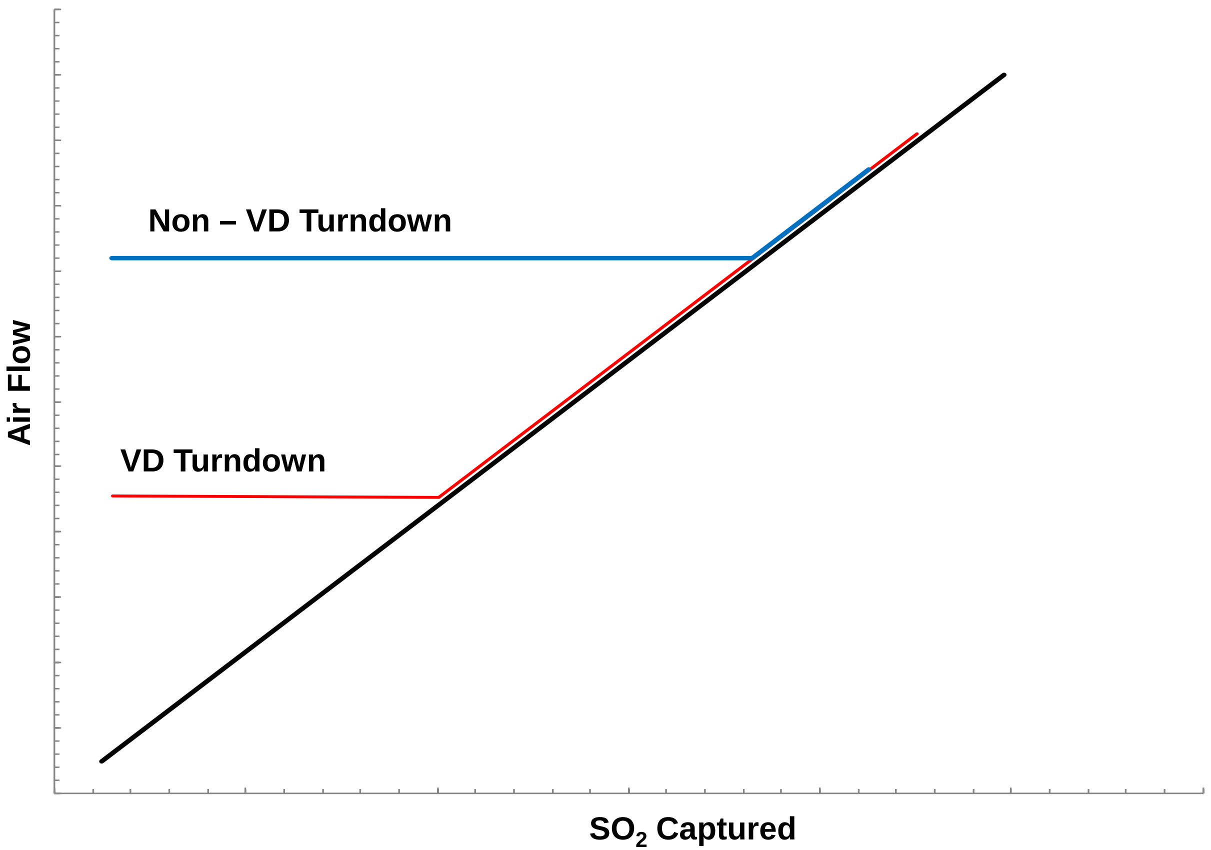
- **Tuning of AQCS chain for tailored bleed stream composition and loading eliminates or decreases the need for costly additives**
- **Decreased operating cost**
- **Improved response to load swings**
- **Improves wastewater treatment unit operation performance, ensuring compliance**

Reagent Feed System
New Control Curve for SO_2 removal

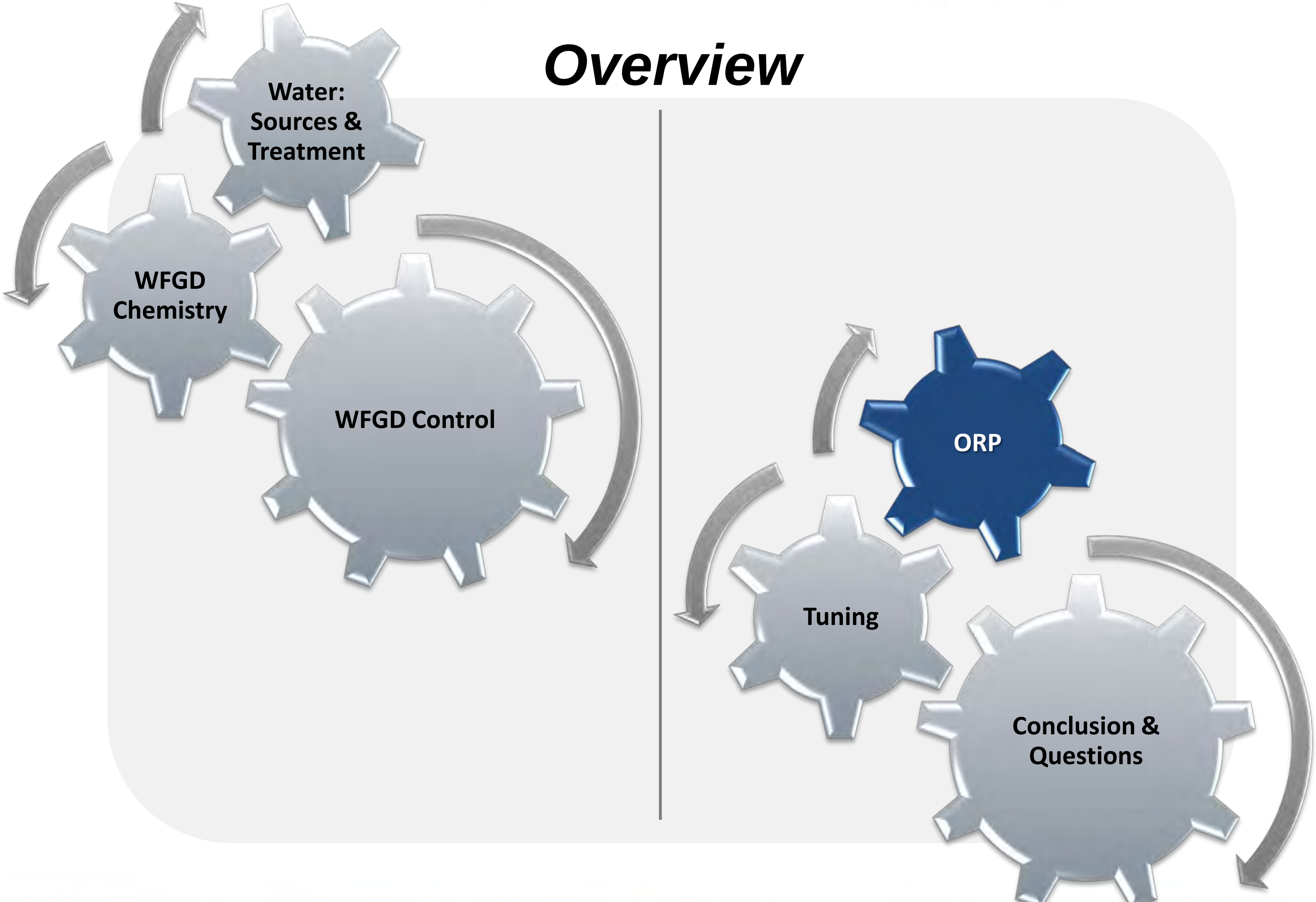


Oxidation Air System

Oxidation Air
Example Oxidation Air Flow Control Curve



Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control
ORP
Tuning
Conclusion & Questions

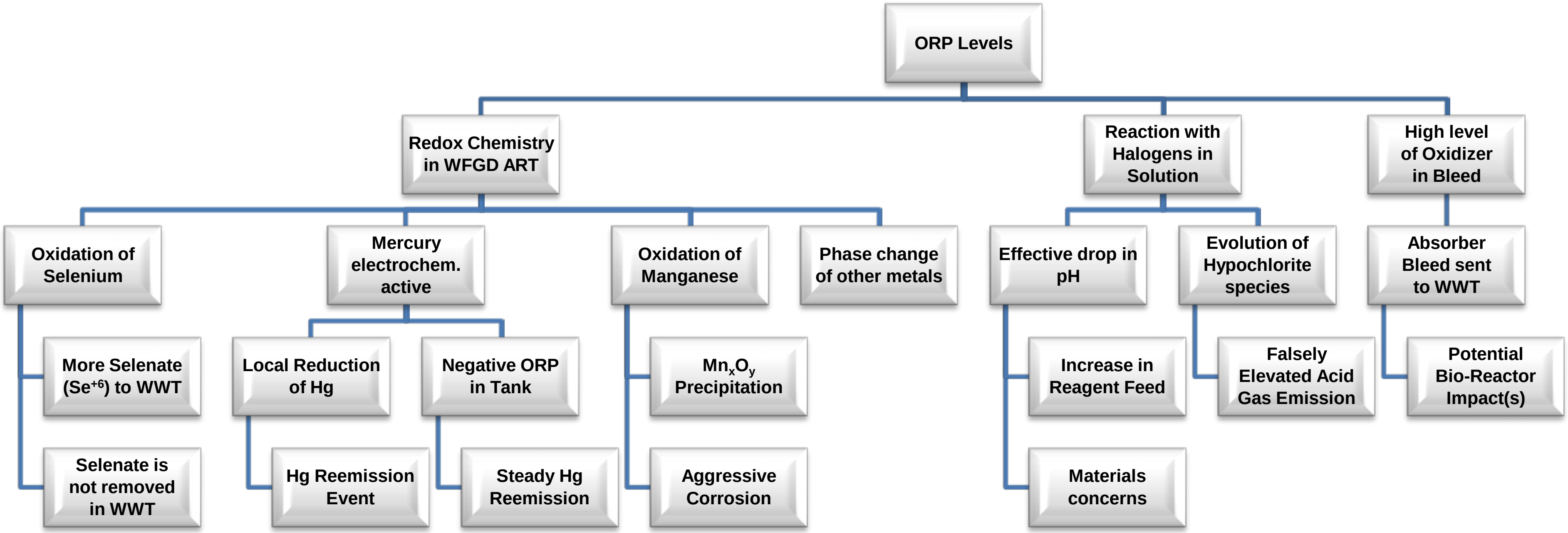
What is ORP?

- 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
    - Can lead to reduction of mercury to elemental state and reemission

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***
- **Oxidation state often controls solubility & phase partitioning of many species**

Impacts of ORP on WFGD Chemistry & Blowdown

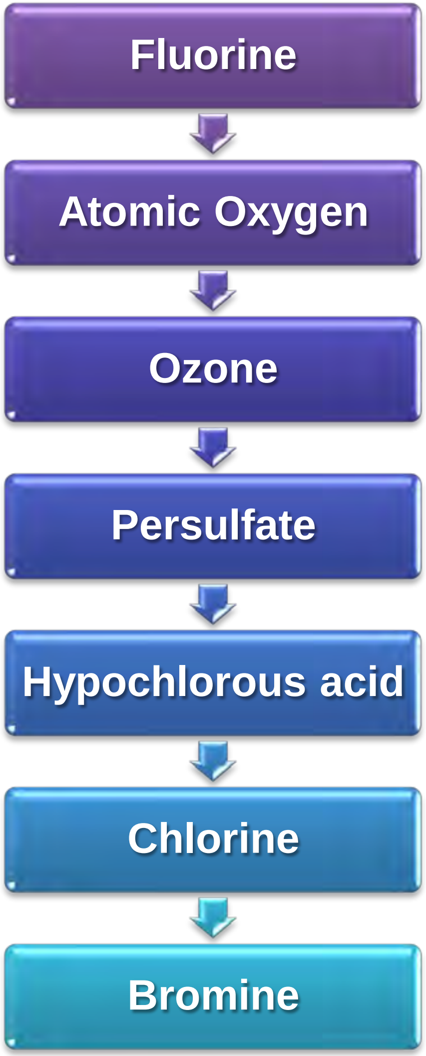


Redox Chemistry within the WFGD

The Relationship Between ORP and Strong Oxidizer Concentration

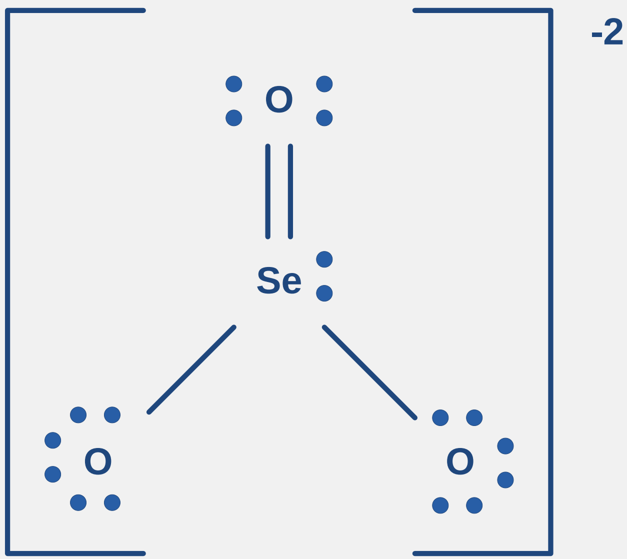
Total Oxidizer Titration Results		
Unit	**ORP Profile**	**Oxidizer (ppm)**
1	High ORP	1680
2	High ORP	1592
3	High ORP	1574
4	High ORP	1571
5	Low ORP	227
6	Low ORP	169
7	Low ORP	50
8	Low ORP	29
9	Low ORP	27
10	Low ORP	19
11	Low ORP	10
12	Low ORP	<2

Strength of Oxidizers



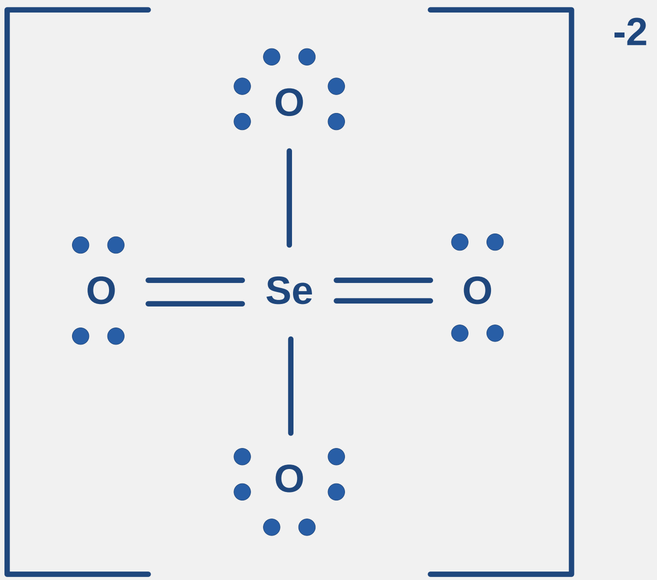
Selenium Chemistry

Selenite



- Selenium in +4 oxidation state
- $Se^0 \rightarrow Se^{+4} + 4e^-$

Selenate



- Selenium in +6 oxidation state
- $Se^0 \rightarrow Se^{+6} + 6e^-$

Selenium

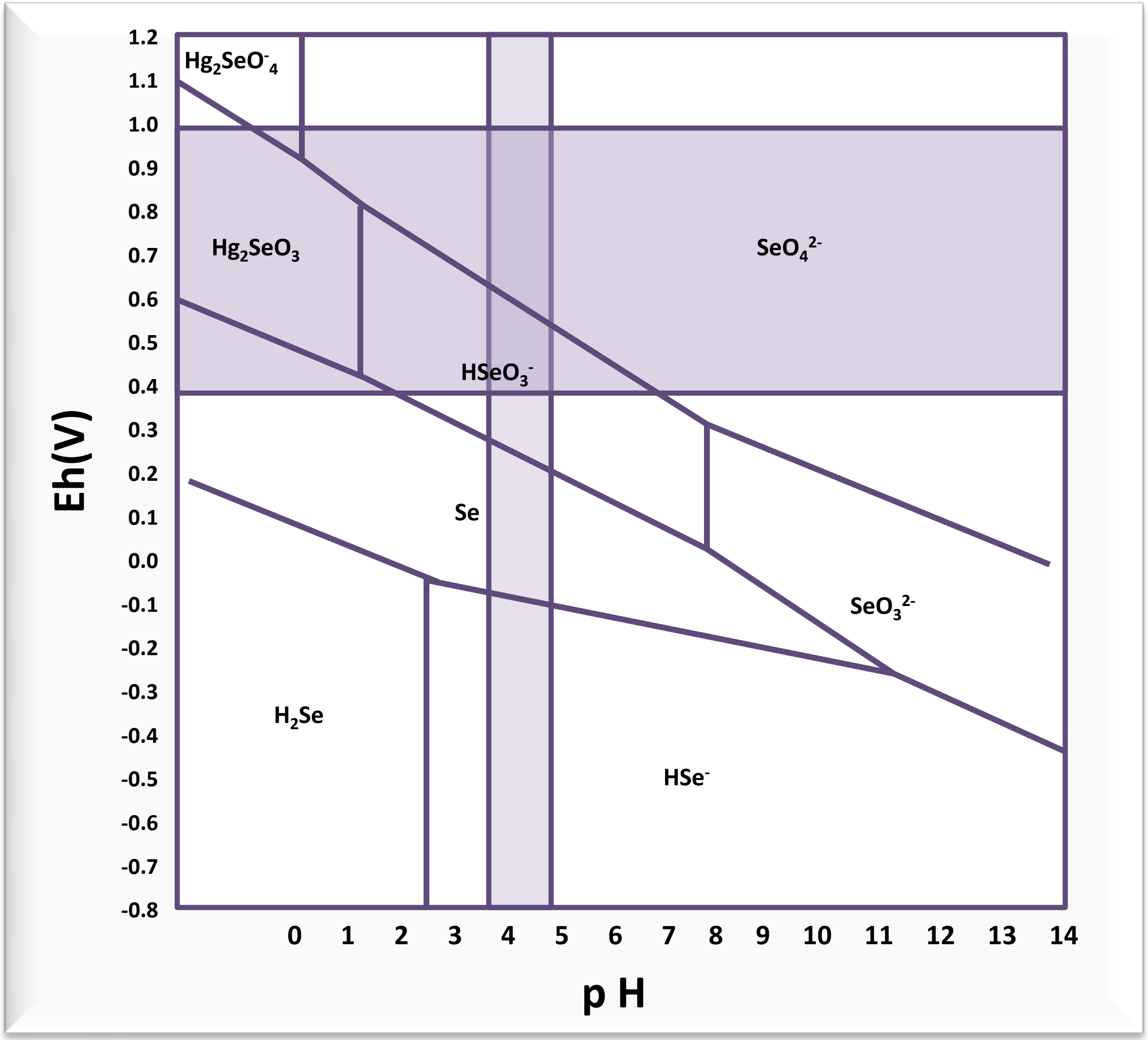
In a ORP environment < 300 mV

- Selenite, Se^{+4} will be the dominant form
- Selenium removal is optimal for waste water treatment
- Solid phase

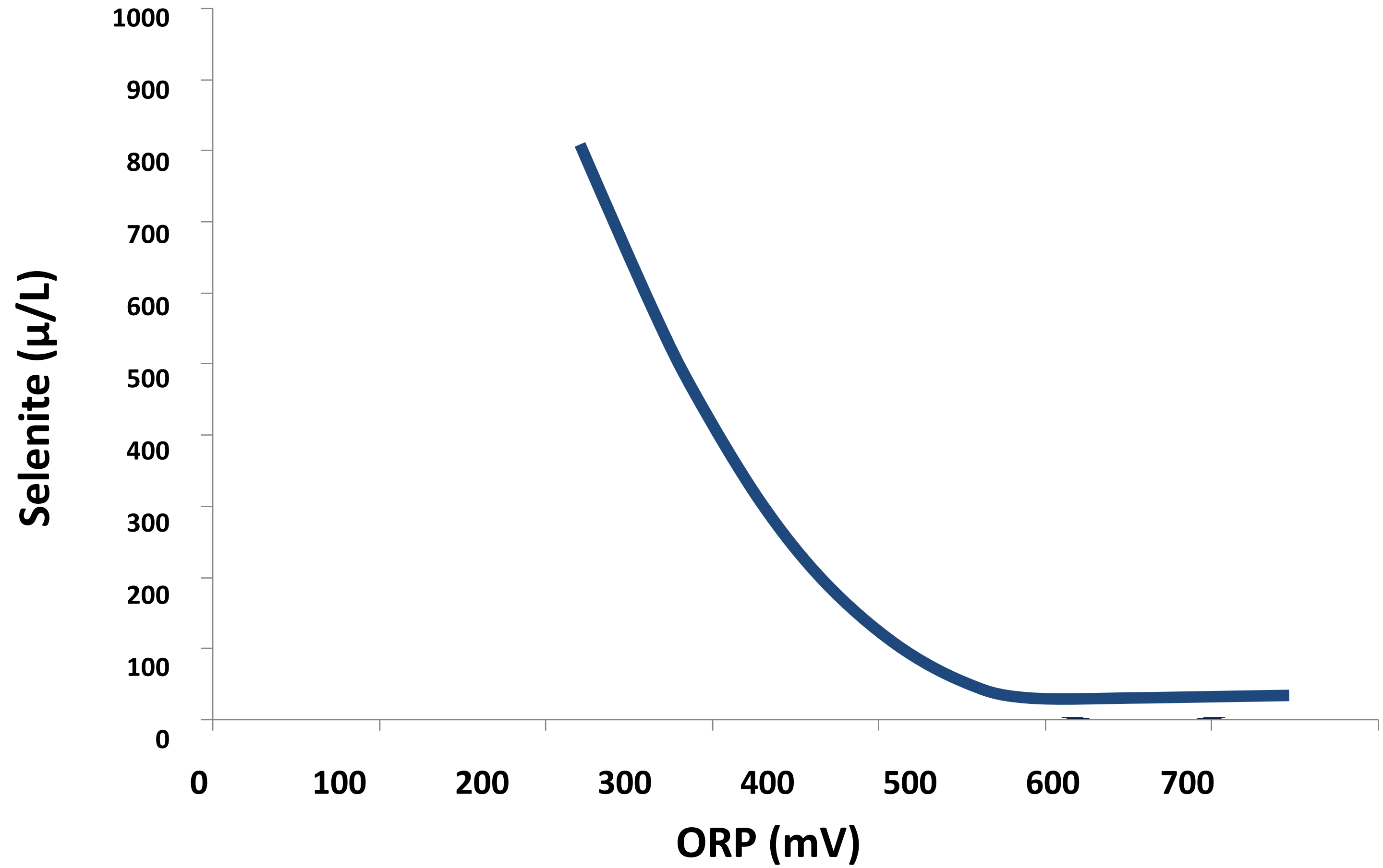
In a ORP environment > 300 mV

- Selenate, Se^{+6} will be dominant form
- Selenium will pass through wet-lands
- Dissolved phase
- Difficult to remove by chemical precipitation

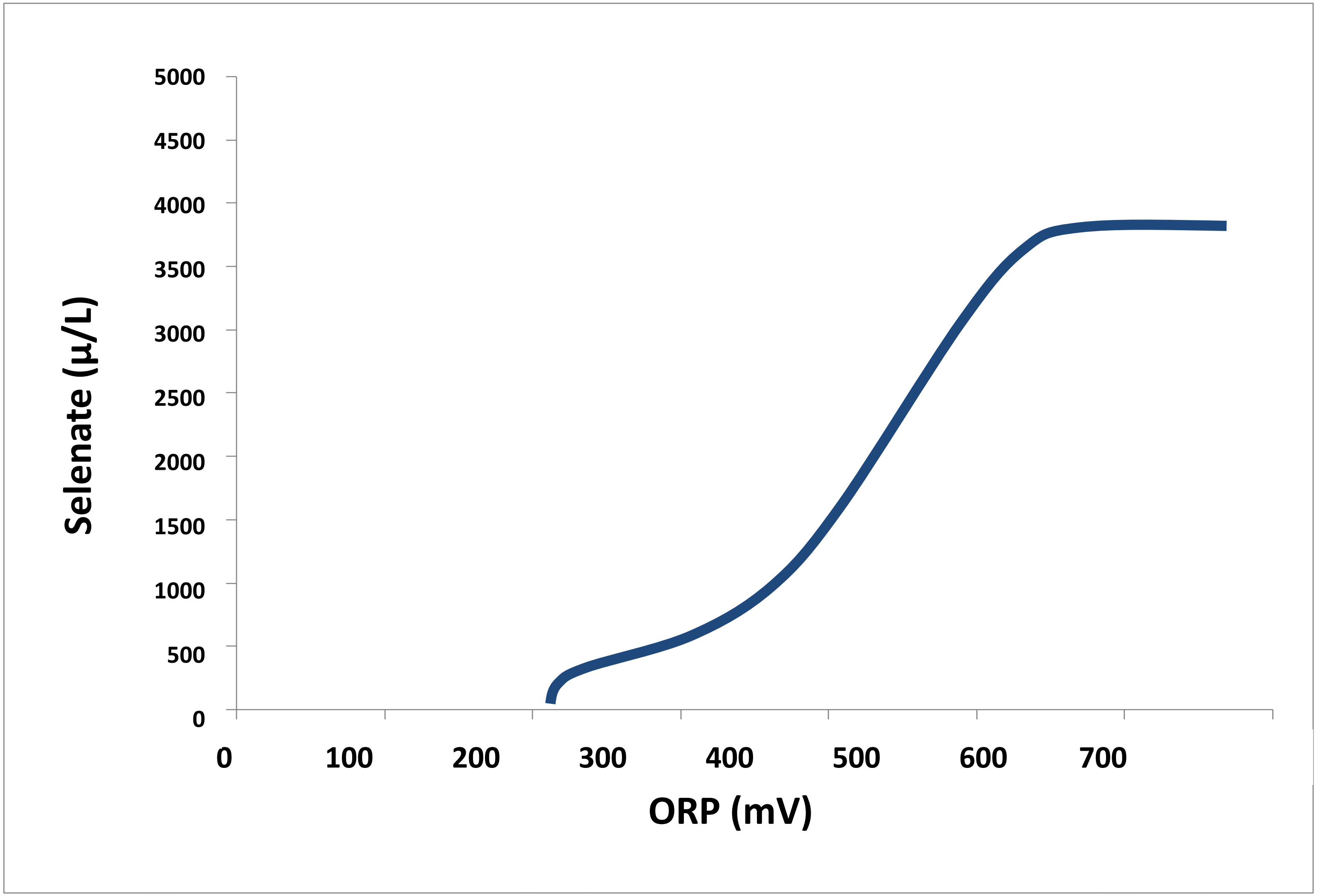
Phase Partitioning– Selenium



Selenite vs. ORP in WFGD ART Slurry



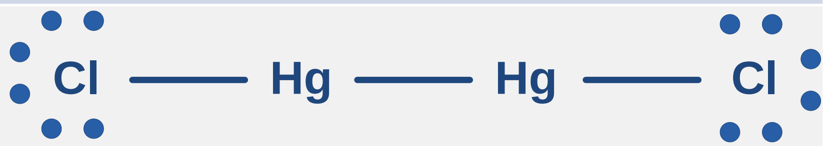
Selenate vs. ORP in WFGD ART Slurry



Mercury Chemistry

First Ionization

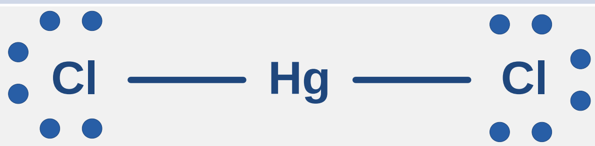
$Hg^0 \rightarrow Hg^{+1} + e^-$



- $HgCl$, Hg_2Cl_2
- Mercury in +1 oxidation state
- Less Stable

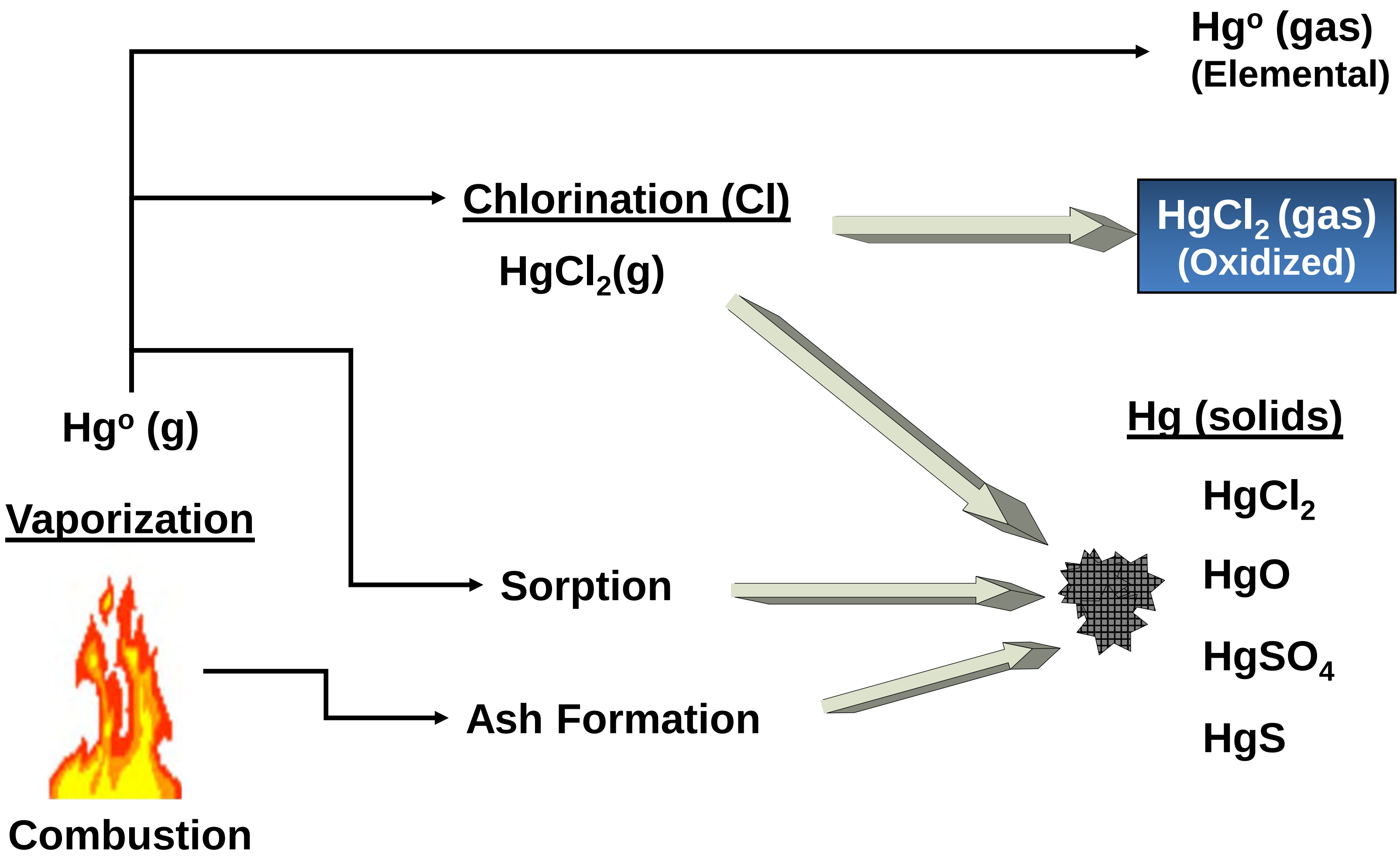
Second Ionization

$Hg^0 \rightarrow Hg^{+2} + 2e^-$



- $HgCl_2$
- Mercury in +2 oxidation state
- More Stable

Speciation of Hg During Coal Combustion



ORP Impacts on Mercury

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

Overall Reactions:

1. $HgCl_2 + HSO_3^- + H_2O \rightarrow Hg^o\uparrow + SO_4^{2-} + 3H^+ + 2Cl^-$
2. $2Me^{2+} + Hg^{2+} \rightarrow Hg^o\uparrow + 2Me^{3+}$

Mercury

Within the bleed stream Mercury state is:

- Particle Bound
- Dissolved Ionic Salt
- Precipitated

ORP levels ~500 mV dissolved Hg^{2+} increases

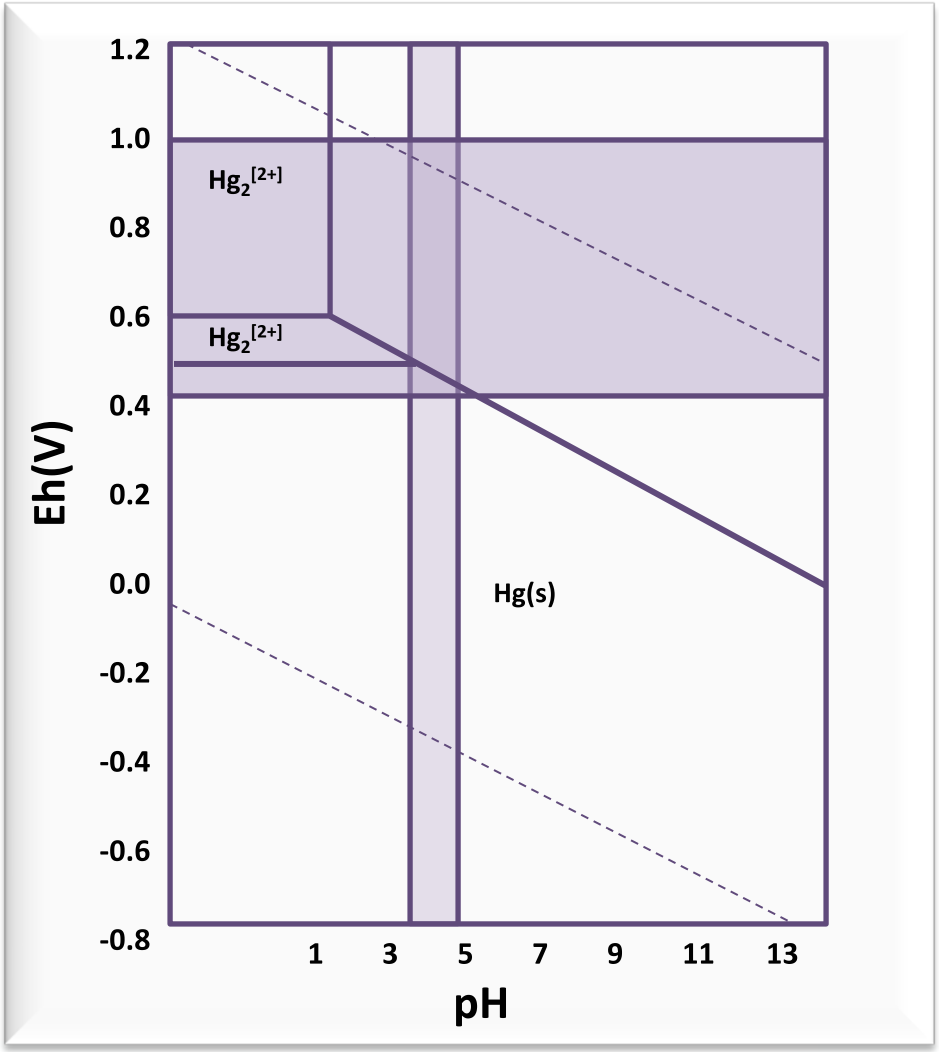
Emission of dissolved Mercury from the tanks

- Stagnant water may lead to stratification of ORP levels
- Mixing of stratified layers may change bulk ORP, impact seen if sent to WFGD due to gas stripping
- Keep circulation of fluid in tanks

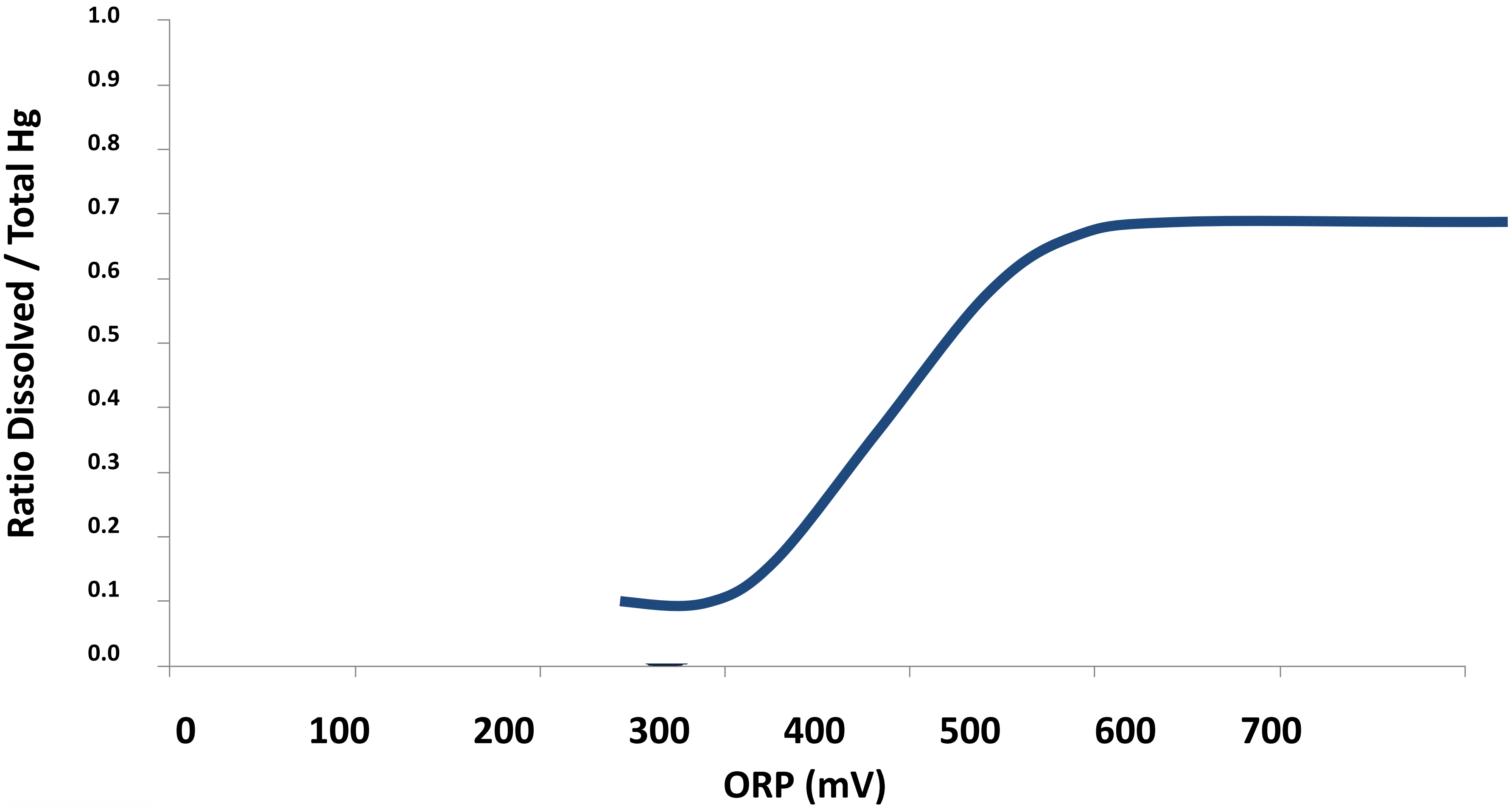
Chloride Levels in the Slurry

- May aid in the oxidation of the Mercury

Phase Partitioning– Mercury



Dissolved Mercury vs. ORP in WFGD ART Slurry



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**
  - **After buffering solids are removed, pH could decrease downstream**

$S_2O_8^{-2}$ and pH Drop

$$S_2O_8^{-2} + 2Cl^- + 2Ca^{+2} \rightarrow 2CaSO_4 + Cl_2$$

$$S_2O_8^{-2} + 2Br^- + 2Ca^{+2} \rightarrow 2CaSO_4 + Br_2$$

$$S_2O_8^{-2} + 2I^- + 2Ca^{+2} \rightarrow 2CaSO_4 + I_2$$

High ORP levels

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + ClO^-$$

$$Br_2 + H_2O \rightarrow 2H^+ + Br^- + BrO^-$$

$$I_2 + H_2O \rightarrow 2H^+ + I^- + IO^-$$

Hypochlorite formation & lower pH

Impact Downstream

Bioreactor and oxidizer

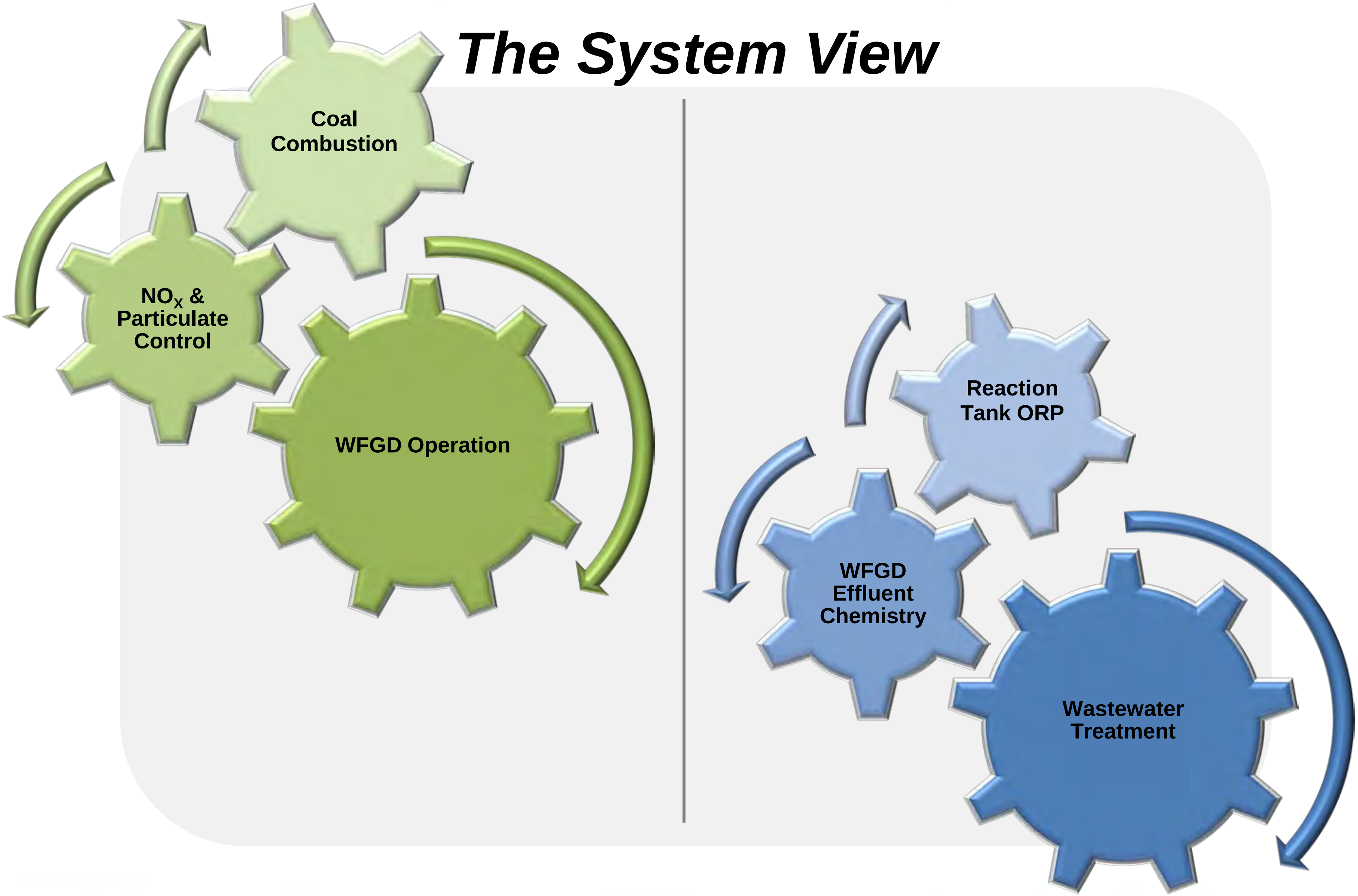
- **Strong oxidizer in the effluent stream**
- **Microbes can weakened**

pH drop with high ORP

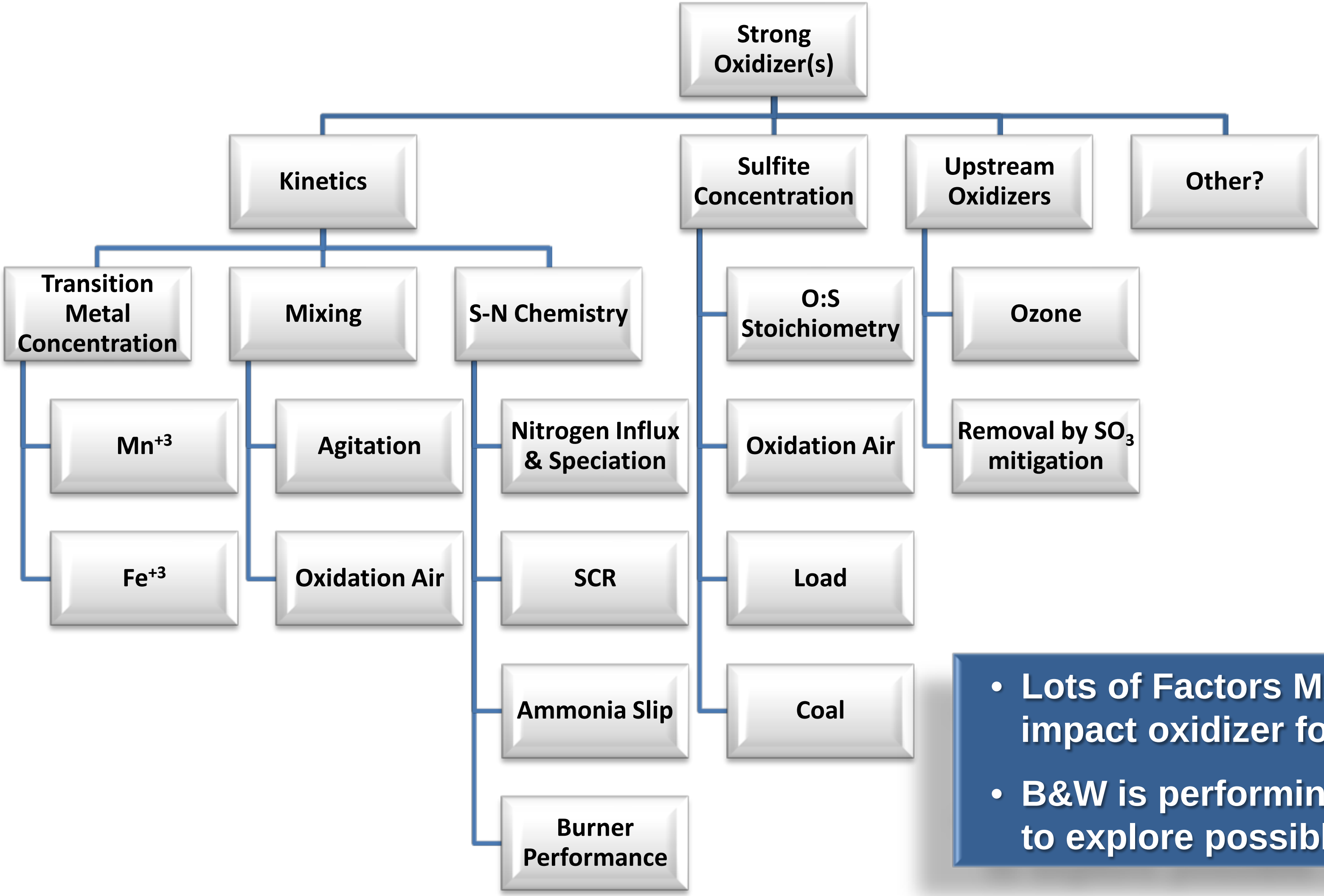
- **Buffer capability of slurry removed from dewatering**
- **Low pH may be fed to Wastewater Treatment**

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + ClO^-$$

The System View



Strong Oxidizer Formation



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

Potential Mitigation Strategies

System Impact

- Integrated control & tuning of AQCS chain

Fine Adjustment

- Optimization of WFGD Chemistry & Control
- Reduced Oxidation Air

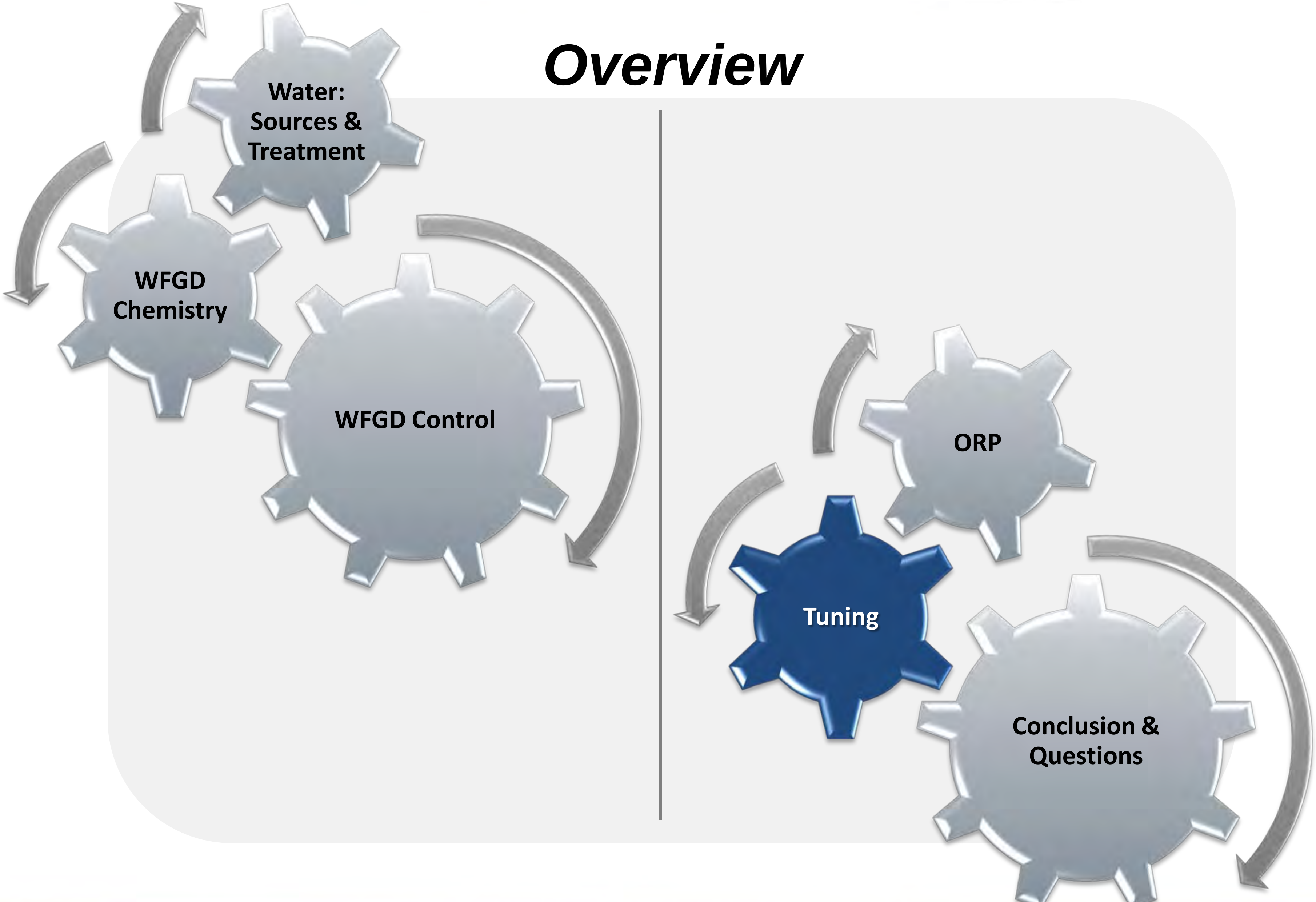
Medicine

- Injection of Reducing Agents

?

- Other

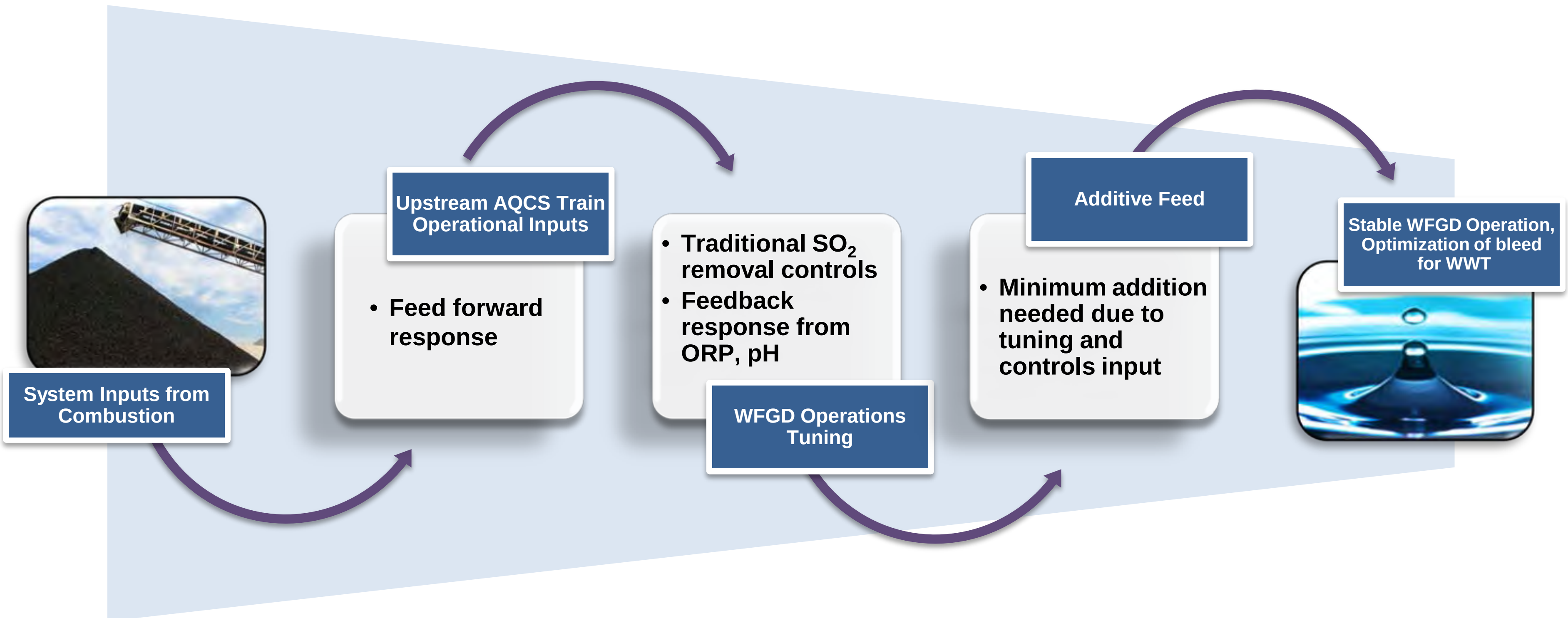
Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control
ORP
Tuning
Conclusion & Questions

Purpose of Process Controls Tuning

- ✓ **Tuning of AQCS chain for tailored bleed stream composition and loading eliminates or decreases the need for costly additives**
- ✓ **Decreased operating cost**
- ✓ **Improved response to load swings**
- ✓ **Improves wastewater treatment unit operation performance, ensuring compliance**

Process Controls Tuning



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**
    - **The same results have been observed 14 times since the testing on the operating units**
  - **Results are under review**
- **Potential for control of WFGD chemistry through tuning**

Process Controls Tuning: Status

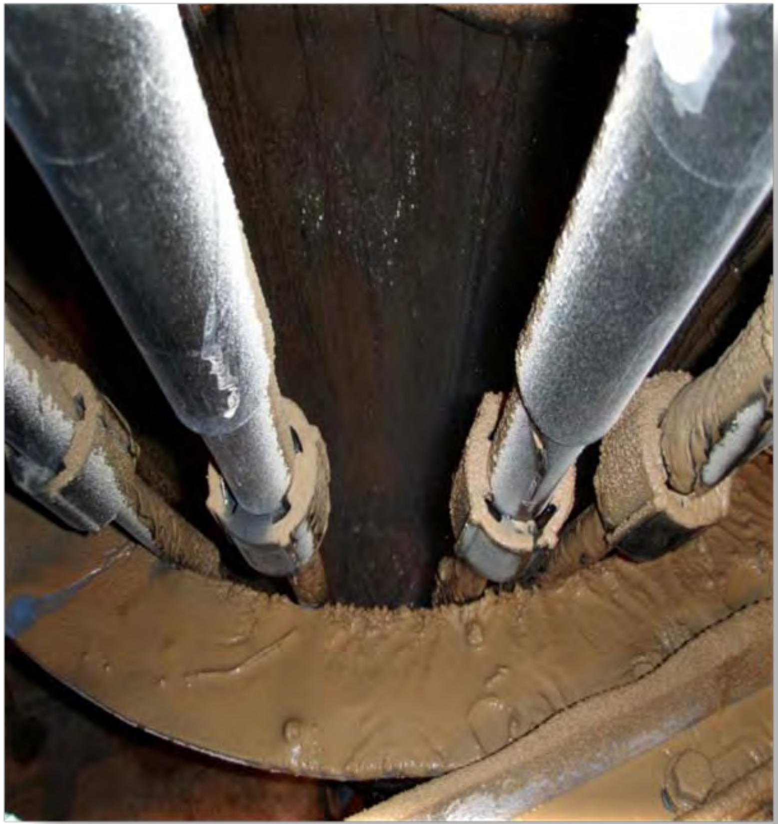
- Tuning of the WFGD alone in terms of SO_2 removal, pH, reagent flow and water balance is readily done.
- WFGD system chemistry (ORP) tuning for WWT
  - Controls parameters under review
  - Focus of current R&D
  - Will involve response to upstream AQCS train operations
- Control of different unit operations at plants often treated independently with systems that do not communicate

Development of an optimizer that will link data communication of systems within the plant and provide ability for WFGD chemistry control in progress (B&W patent-pending)

Chloride Purge Stream

Control of Chloride Level

- Function of secondary dewatering
- Slip-stream
- Allowable levels are function of alloy
- Control of other dissolved solids
    - ORP levels effect phase-partitioning and oxidation state
- Optimization of WWT



Optimization – Water Balance

Control of TDS going to Waste Water Treatment

Decrease of TDS in Absorber

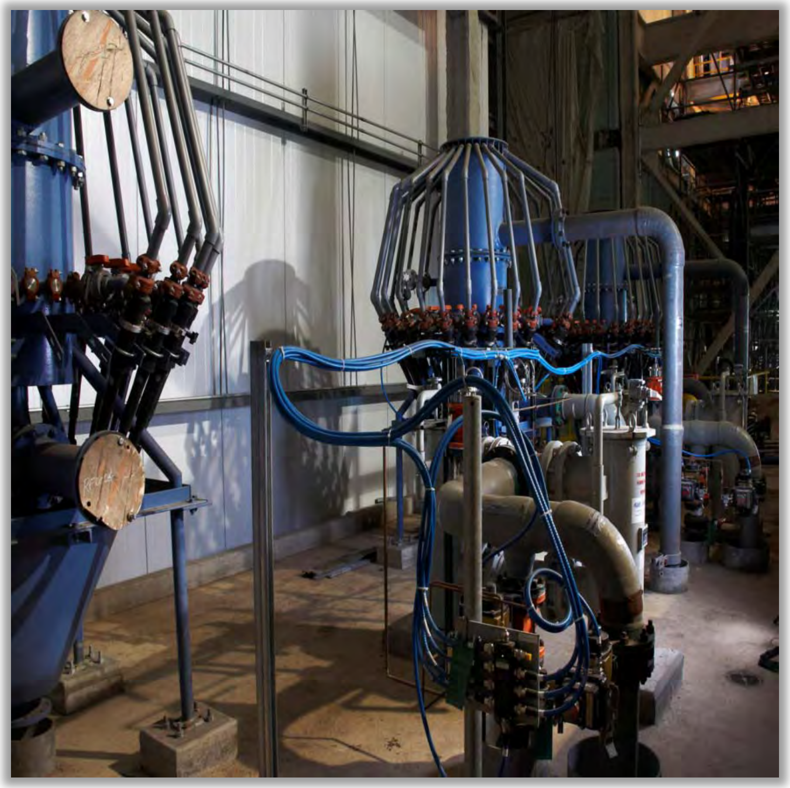
- **Increase blow down rates**
- **Larger volume/lower concentration**
- **Increased Make-up Water**

Increase of TDS in Absorber

- **Decrease blow down rate**
- **Corrosion Potential increased**
- **Possible decreased reactivity**

Chloride Concentration Increase

- **Possible increase in oxidized Hg**
- **Increased dissolved Hg species**



Optimization – Dewatering

Hydroclone Tuning

- Improved split between gypsum and wastewater
- Removal of excess water from gypsum slurry
- Improved operation of filter system

Operational Strategy for tank management

- Switch from batch to continuous
- Constant flow rates to WWT
- Ease of tank level management
- Constant dilution water to absorber

Optimization with Varying Load

Tuning for a steady state ORP number

- Possible (Re)Emission control of Hg
- Control of phase-partitioning of metals
- WWT
- Corrosion control

Optimization of effluent stream for future ZLD system

ORP Control

- Additives
- PAPs systems
- B&W Patent Pending Optimization Control System

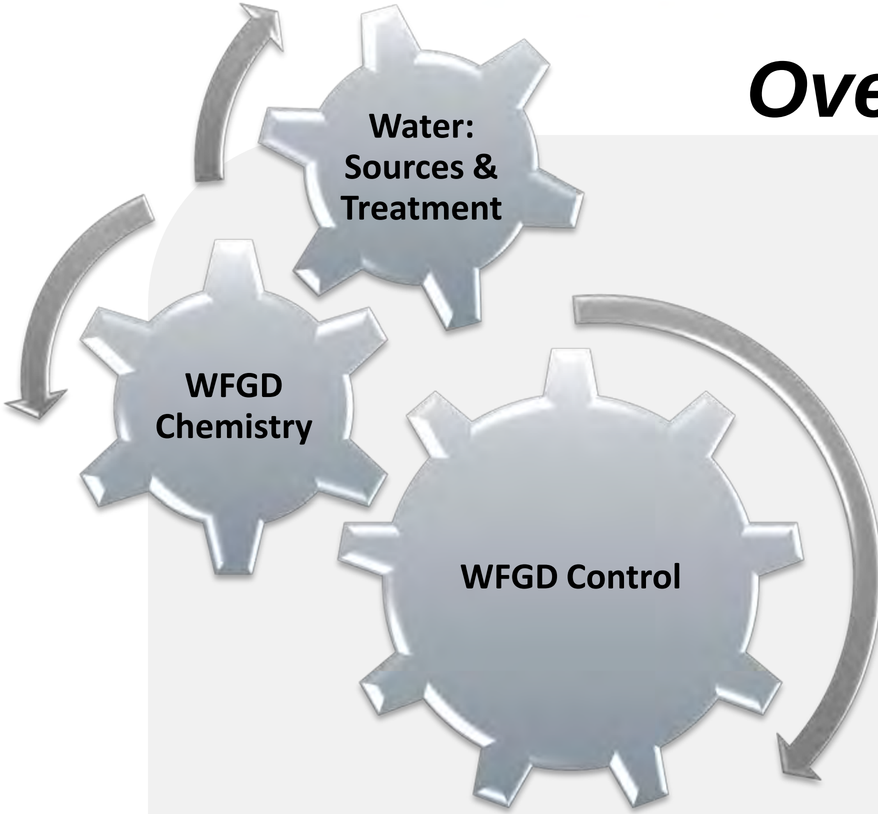
TDS Control

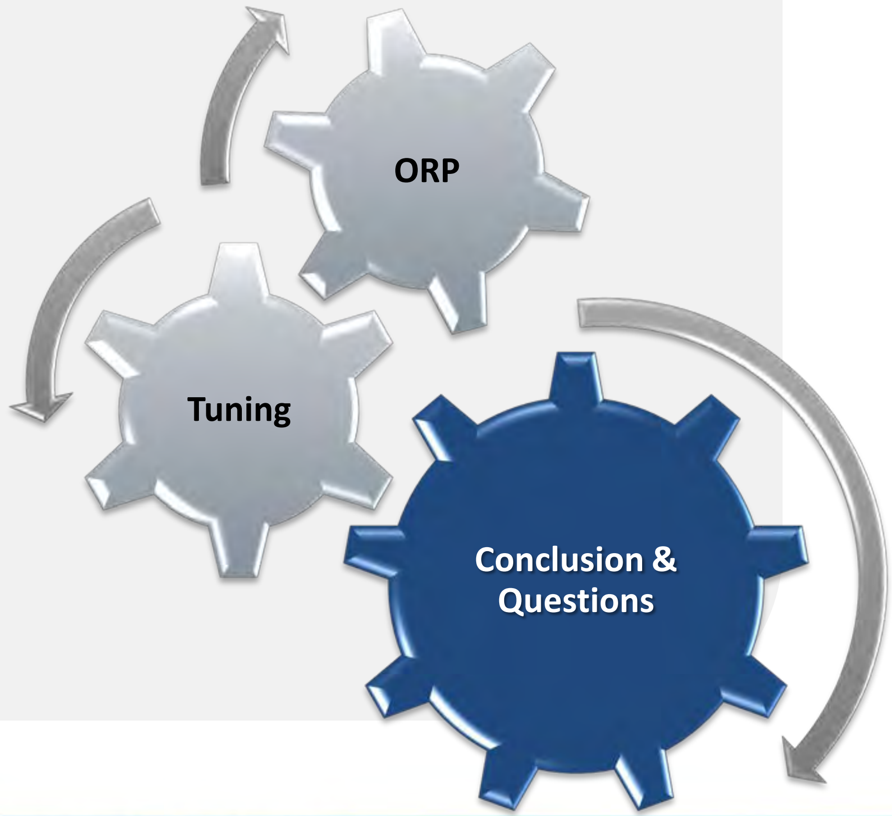
- Adjustment of blow down rates
- Variation in dilution rates
- Batch to continuous mode

ZLD System

- Effluent System may be tuned for specific parameter requirements of system
- Ability to maintain parameters with system variation

Overview


Water: Sources & Treatment
WFGD Chemistry
WFGD Control


ORP
Tuning
Conclusion & Questions

Solutions for Wastewater

Opportunities for Success

Bleed Stream Composition
- **Selenium Speciation**
- **Hg Speciation and Reemission**
- **Other Trace Metals**
- **Chlorides**
- **Oxidizer Content**

Water Balance
- **TSS and TDS**

Economics
- **Controls vs. Chemicals**

Tuning Parameters

Integrated AQCS Controls

WFGD Performance Tuning
- **SO_2 Removal**
- **Reagent Feed**
- **Oxidation Air**
- **Dewatering**
- **Dilution/Tank Balance**

Post-Bleed Mitigation
- **Additives (reducing/oxidizing agents)**

Conclusions

- **Absorber System can be controlled for better results on variation of loads**
- **WFGD Bleed Streams can be tuned for optimal bleed stream composition and flow rate. The WFGD Bleed stream composition is important to performance of wastewater treatment operations.**
- **By tuning the Bleed Stream, performance of WWT unit operations is consistent or enhanced**
    - **Oxidation state and phase partitioning of metals (Se, Hg, etc...)**
    - **pH, ORP, Dissolved halogen content (F-, Cl-, Br-, I-)**
- **Optimization can accomplished by:**
    - **Integrated control of the AQCS chain**
    - **Integrated control of combustion systems**
    - **Optimizing the WFGD (tuning)**
    - **Chemical Additives**
- **Industry thought process change**

power generation group

WFGD Chemistry, Tuning and Optimization for Improved Wastewater Characteristics and Treatment

2013 Reinhold APC Conference
St. Louis, Missouri – July 8-9, 2013

THANK YOU. QUESTIONS?

Shannon R. Brown, *AQCS Engineer*
srbrown@babcock.com

Daniel B. Johnson, P.E., *Field Service Engineer*
dbjohnson@babcock.com