Worldwide Pollution Control Association

WPCA-Duke Energy FGD Wastewater Treatment Seminar

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Optimization and Control of AQCS Systems for Optimal Bleed Stream Chemistry

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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)

Overview

Basics of WFGD Control

- Reagent Feed
- SO_2 to $CaSO_4$ conversion
- Oxidation Air
- Bleed/Blow Down System

Bleed Stream Chemistry

- Chloride Purge
- ORP

System Optimization for WWT

- Water Balance
- Hydroclone Tuning
- ORP Control

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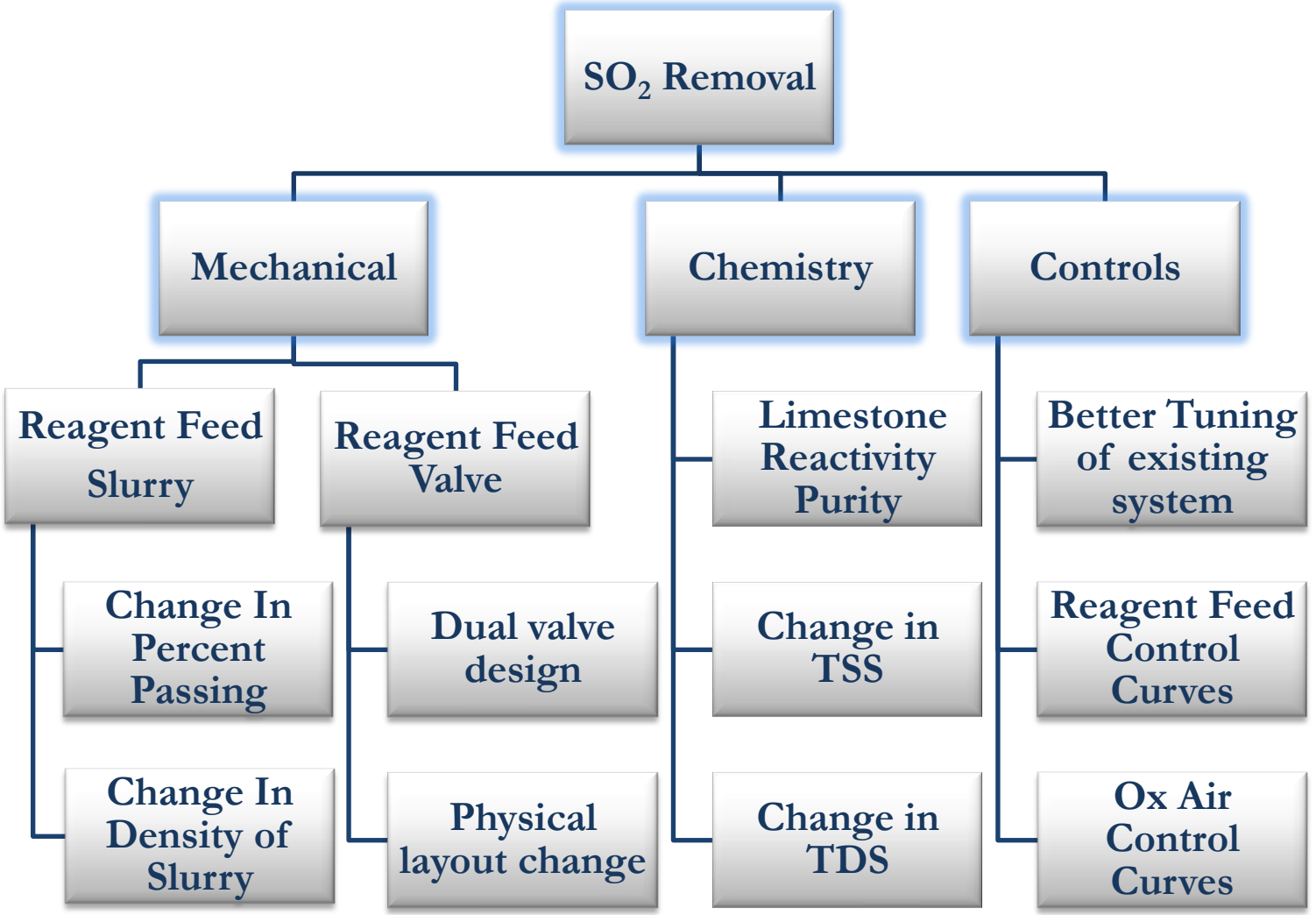
WFGD System Control



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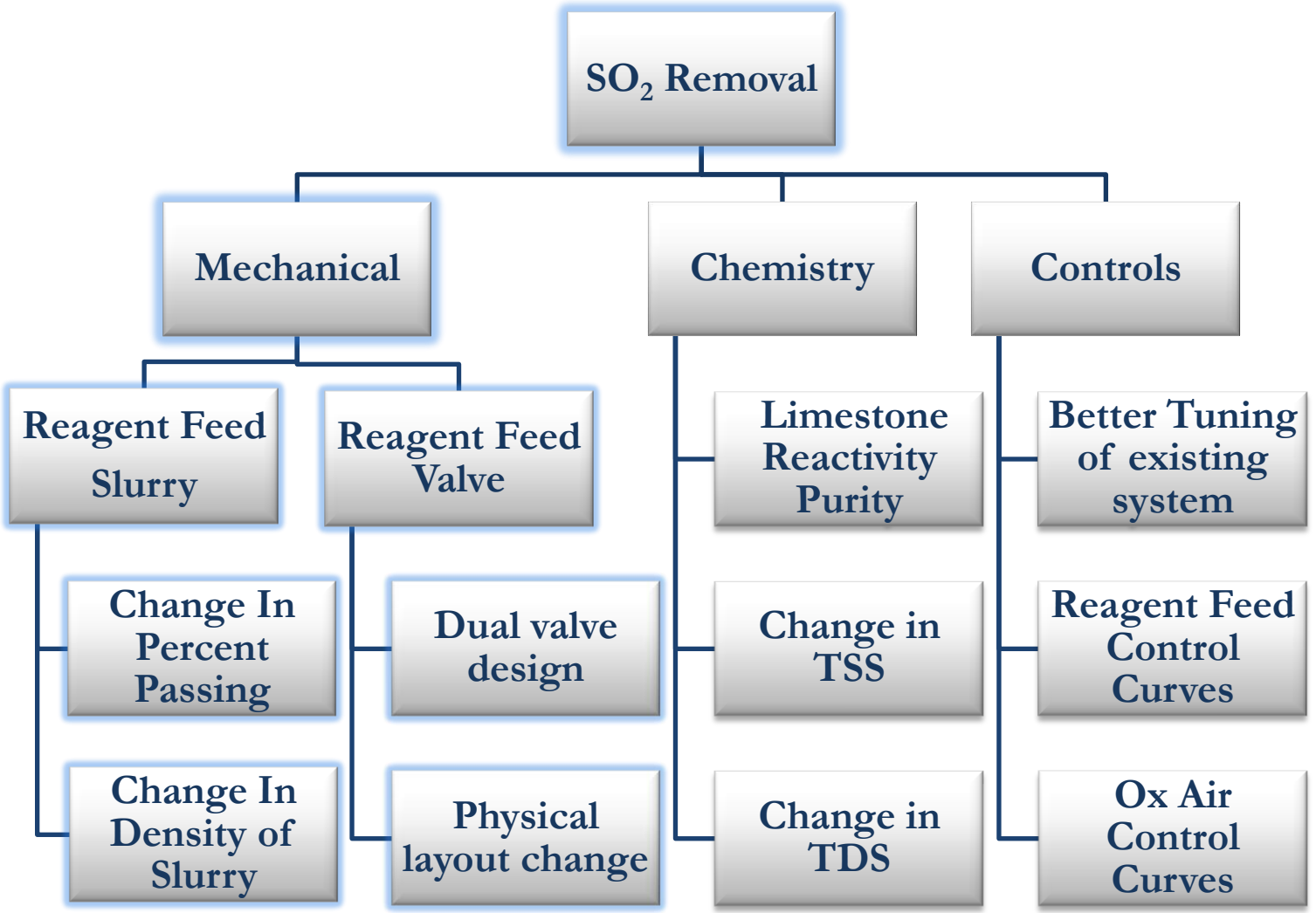


Reagent Feed System

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
- 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

- Kinetic vs. Thermodynamic control of WFGD chemistry
  - Limestone major contributor to reaction rate
- High ORP levels can cause the system to pH to lower
- pH control system will add limestone due to lower pH from ORP, not SO_2 demand

Tuning Reagent Feed System

Ball Mill Tuning

- Percent passing may be raised by decreasing the feed of limestone
- Rate of dissolution are dependent upon the percent passing
  - Open spray towers this becomes a more critical parameter

Density

- Operation below the designed tower load and reagent system design
- 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 lower 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

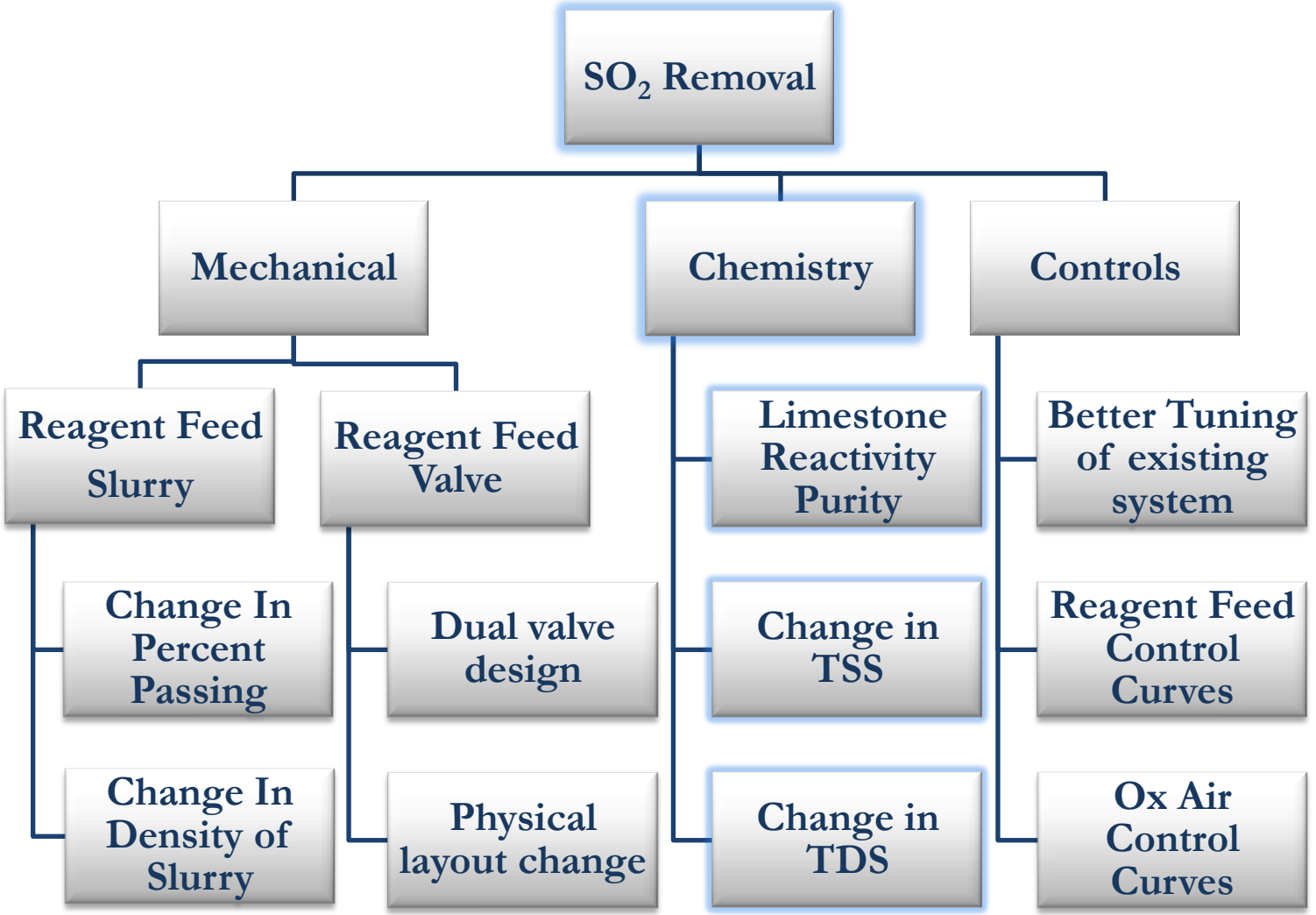
Dual Valve Design

- 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
Higher ORP Levels

Effects of Higher ORP Levels

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

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

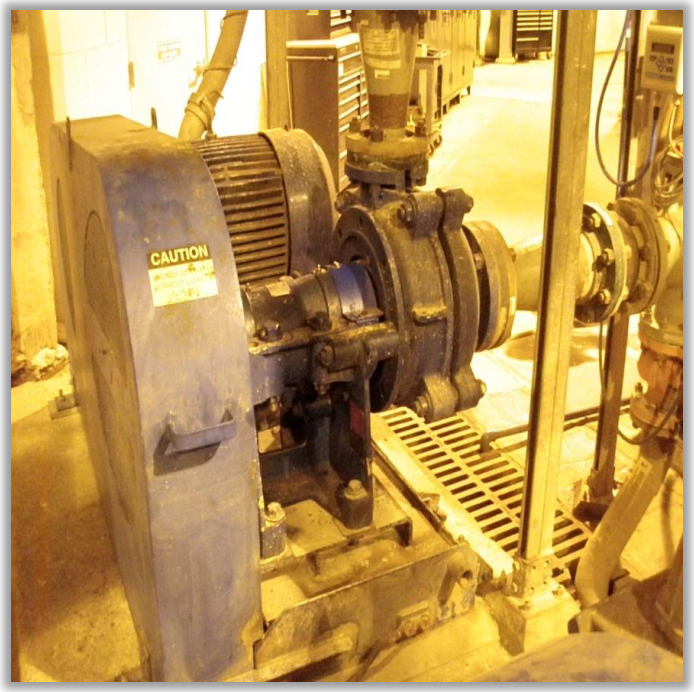
L/G Ratio

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

Bleed System

Function

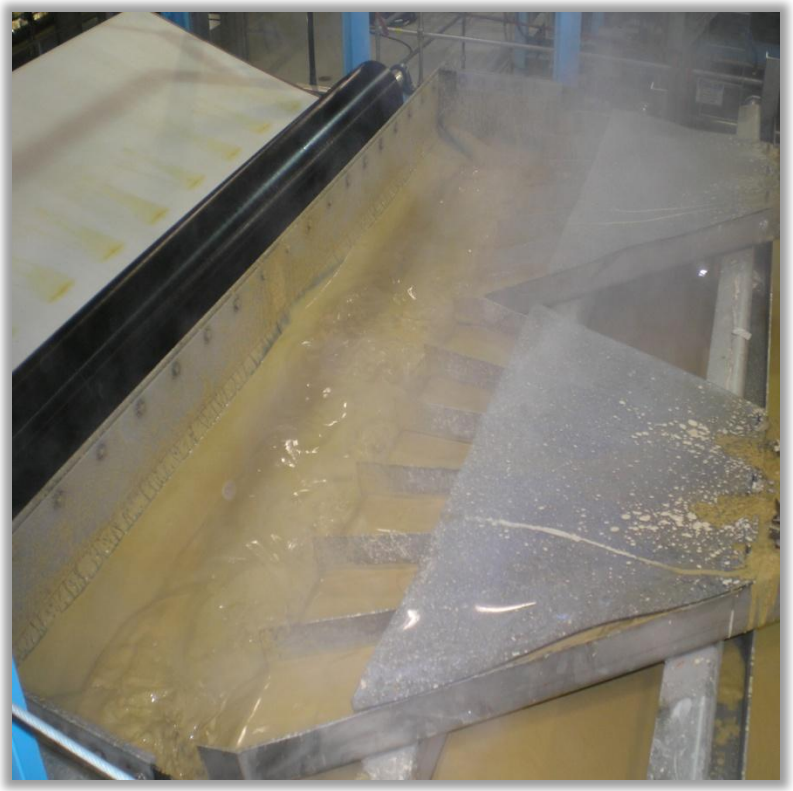
- Control Total Suspended Solids, TSS
  - Gypsum Production
- Control Chloride Concentration in the absorber tower, TDS
  - Secondary Dewatering System Overflow



Bleed System

Adjustment of TSS

- 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
- In sites without Secondary Dewatering, TSS adjustment will regulate TDS



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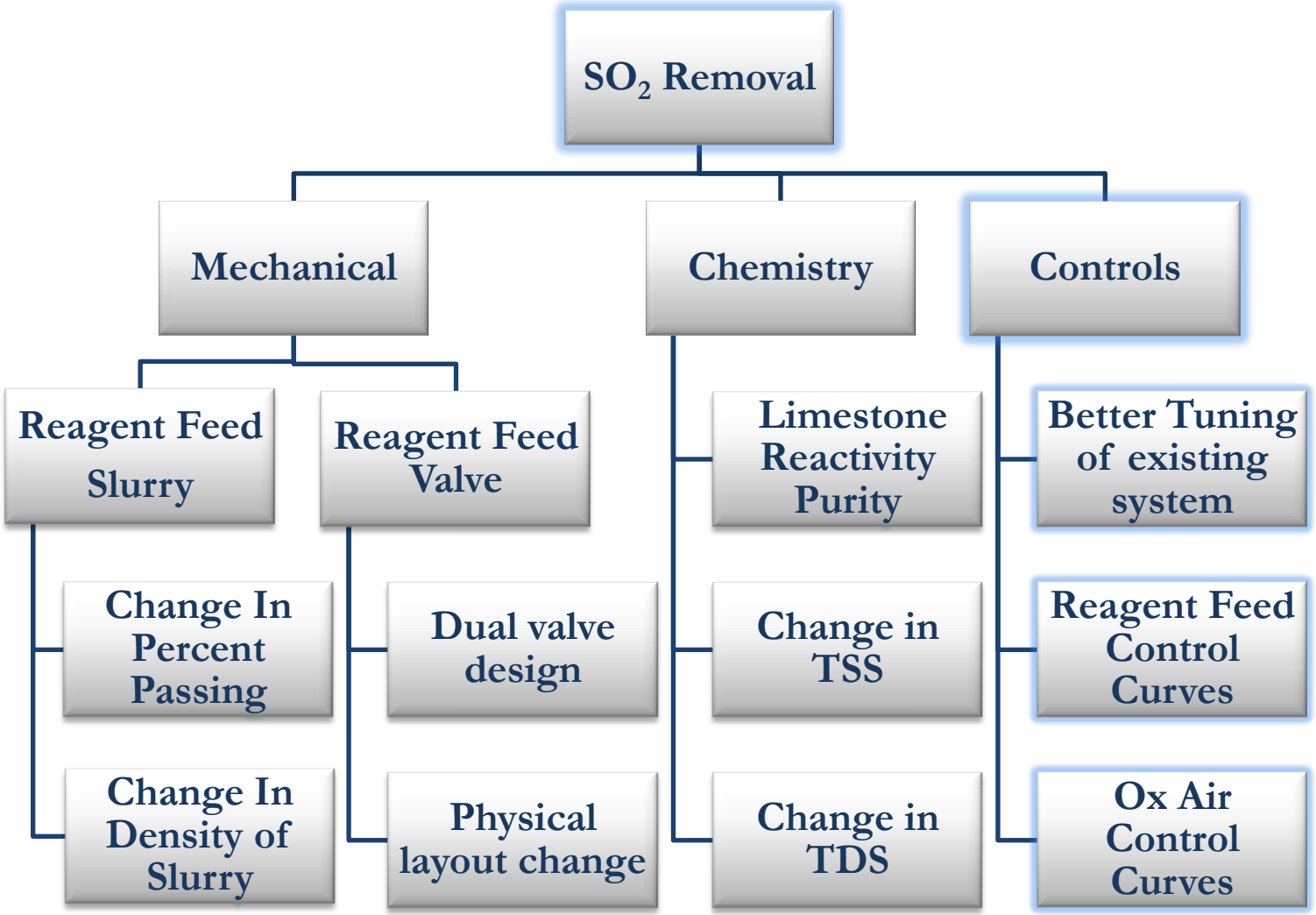
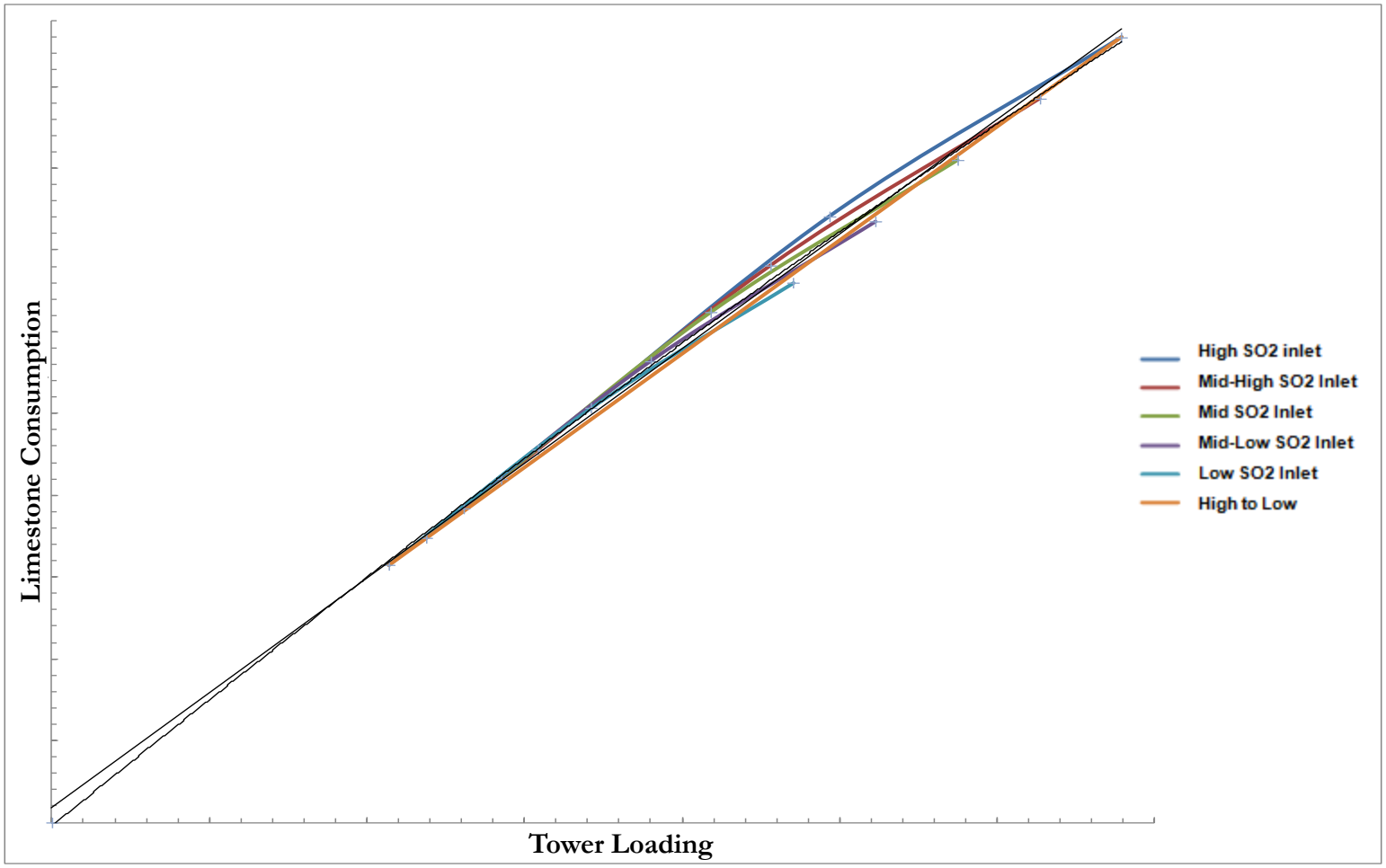


Why Tuning/Controls?

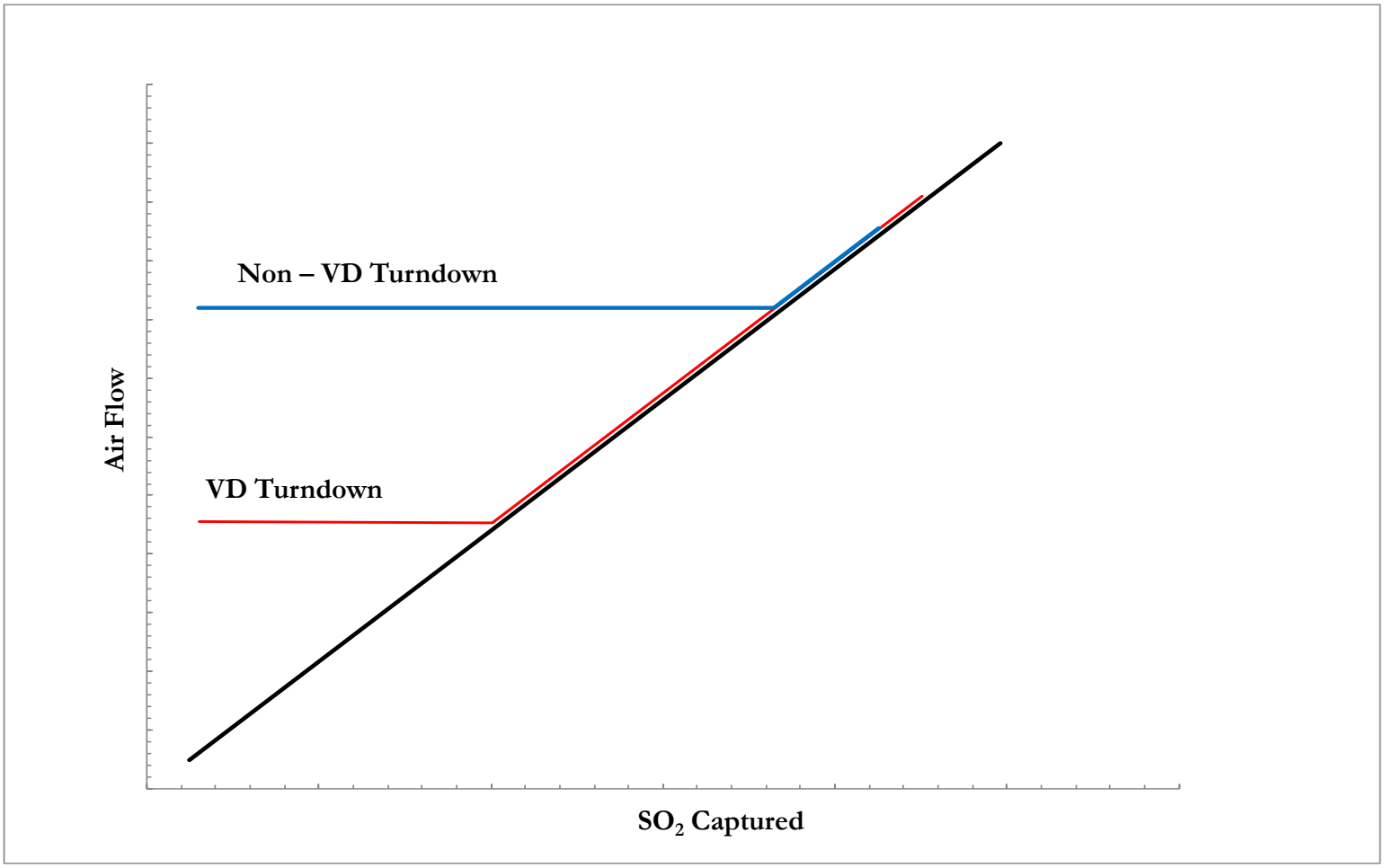
- **Tuning of AQCS chain for tailored bleed stream composition and loading eliminates or decreases the need for costly additives**
- **Decreased operating cost**
- **Improved response to load swings**
- **Improves wastewater treatment unit operation performance, ensuring compliance**

Reagent Feed System
New Control Curve for SO_2 removal



Oxidation Air System

Oxidation Air
Example Oxidation Air Flow Control Curve



Oxidation Air

Calculated Air Flow

- Stoichiometry ratios based upon a contract
- Sized for full load based upon design sulfur coal and full load boiler operation
    - Some compressors have an integrated variable diffuser vane allowing for a lower turndown of 45% of full load capacity
- During low sulfur coal operations oxidation air required is decreased

ORP Control using Oxidation Air

- B&W is working on developing curves for Oxidation Air Flow versus tower load
- ORP control can be regulated by having excess sulfites in the system
- The turn-down of the compressor can be a trim function for high ORP conditions
- Currently no online measurements for sulfites in liquid phase
    - B&W working on developing correlations based on ORP

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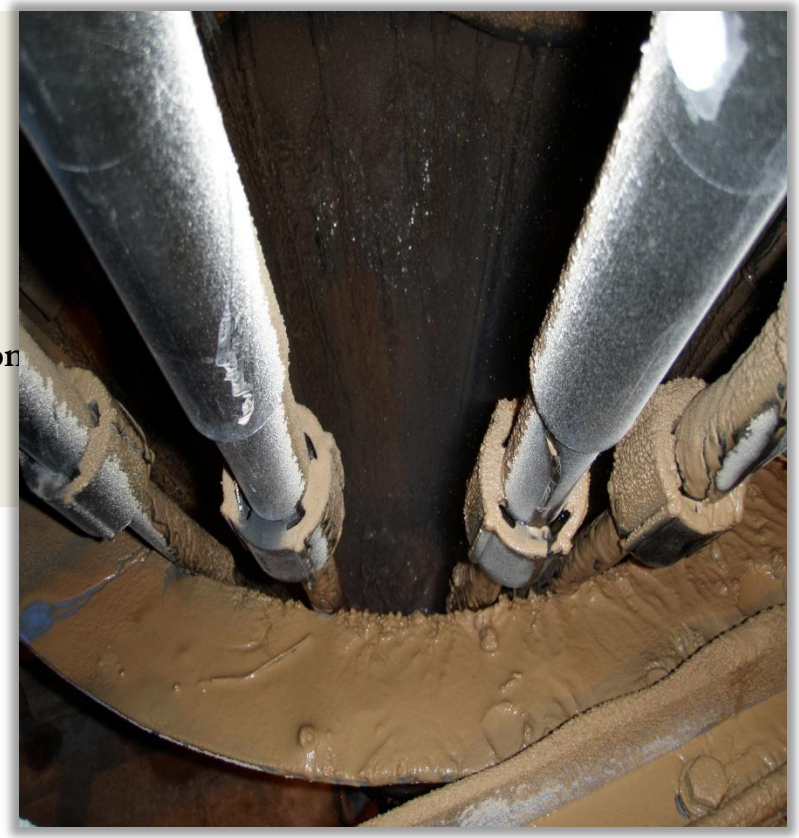
Chloride Purge Stream

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



Selenium

In a ORP environment < 300 mV

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

In a ORP environment > 300 mV

- Selenate, Se^{+6} will be dominate form
- Selenium will pass through wet-lands
- Problematic for bioreactors
- Dissolved phase
- Difficult to remove by chemical preciptation

Mercury

Within the bleed stream Mercury state is:

- **Particle Bound**
- **Dissolved Ionic Salt**
- **Precipitated**

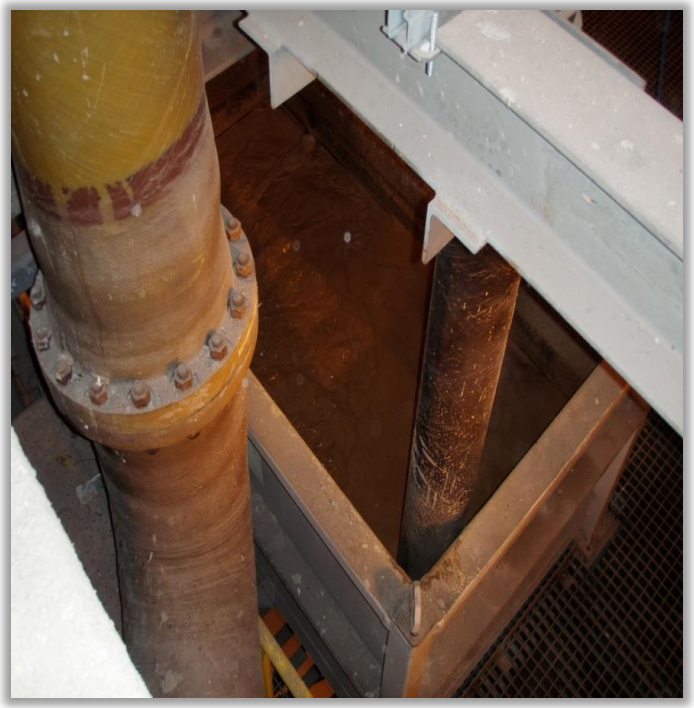
ORP levels ~500 mV dissolve $Hg^{2+,4+}$ increases

Emission of dissolved Mercury from the tanks

- **Stagnate water may lead to stratification of ORP levels**
- **Mixing of stratified layers may change bulk ORP**
- **Keep circulation of fluid in tanks**

Chloride Levels in the Slurry

- **May aid in the oxidation of the Mercury**



pH and Oxidizers

Bioreactor and oxidizer

- Strong oxidizer in the effluent stream
- Microbes can be killed

pH drop with high ORP

- High ORP levels can lead to hypochlorate formation
- This reaction causes a drop in pH
- Buffer capability of slurry removed from dewatering
- Equations

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

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Optimization – Water Balance

Control of TDS going to Waste Water Treatment

Decrease of TDS in Absorber

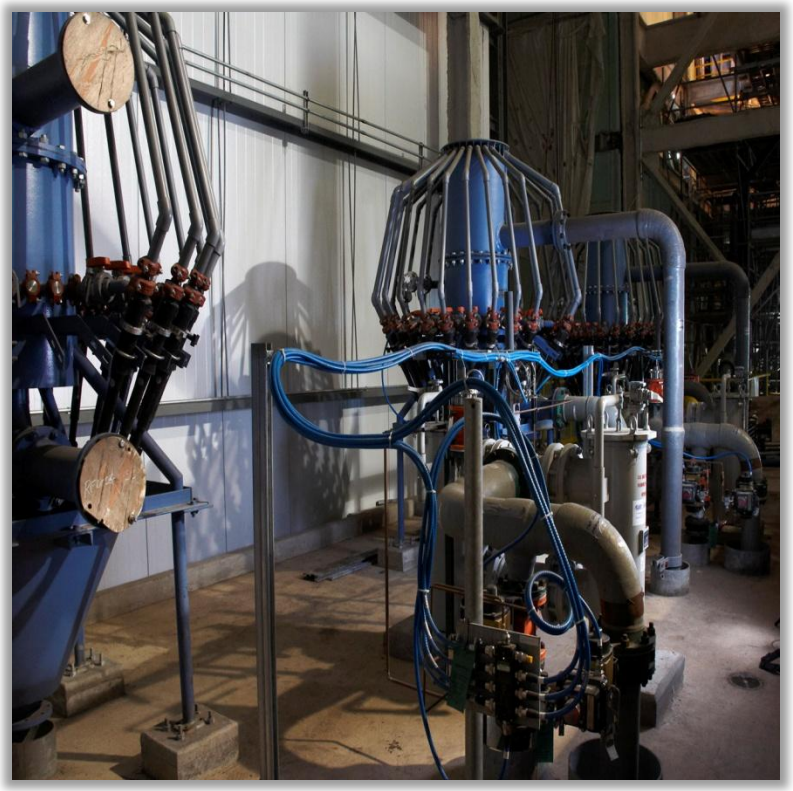
- Increase blow down rates
- Larger volume/lower concentration
- Increased Make-up Water

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



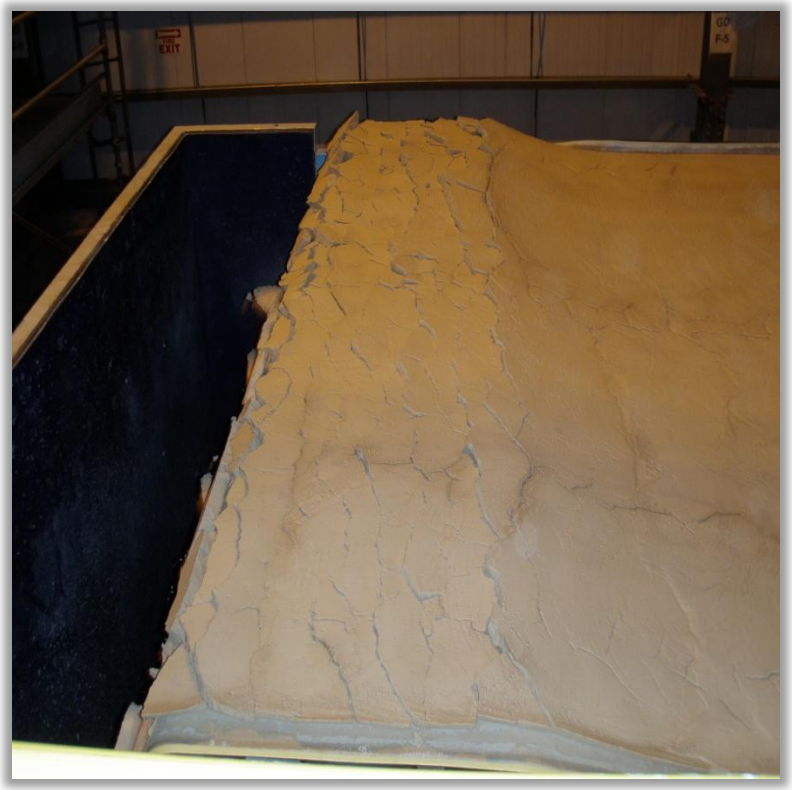
Optimization – Dewatering

Hydroclone Tuning

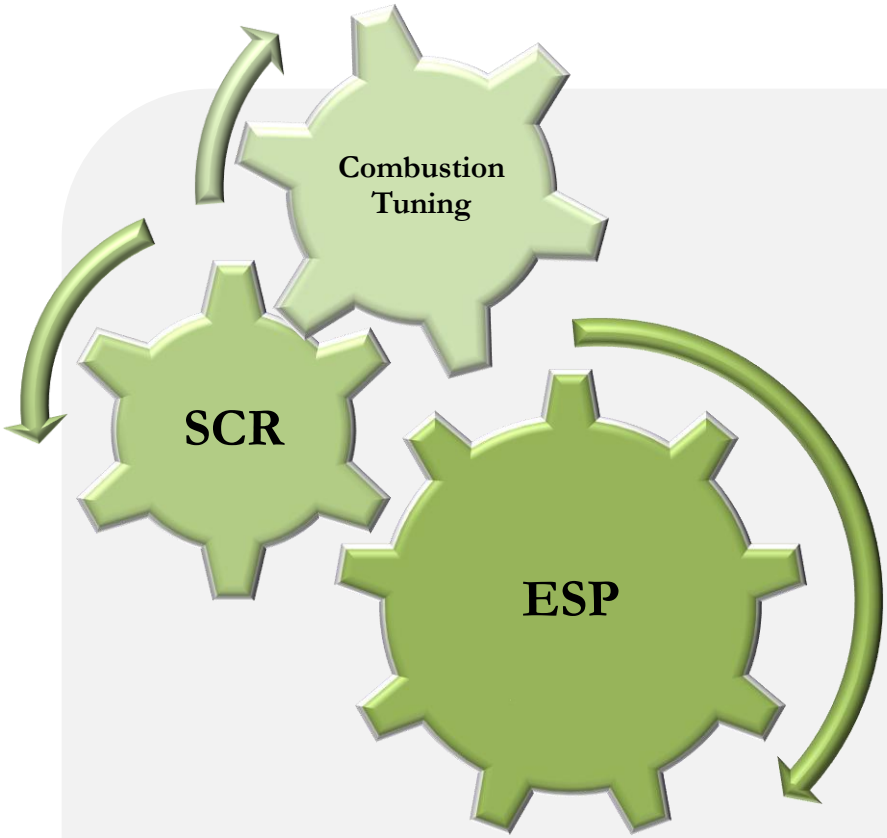
- Improved split between gypsum and wastewater
- Removal of excess water from gypsum slurry
- Improved operation of filter system

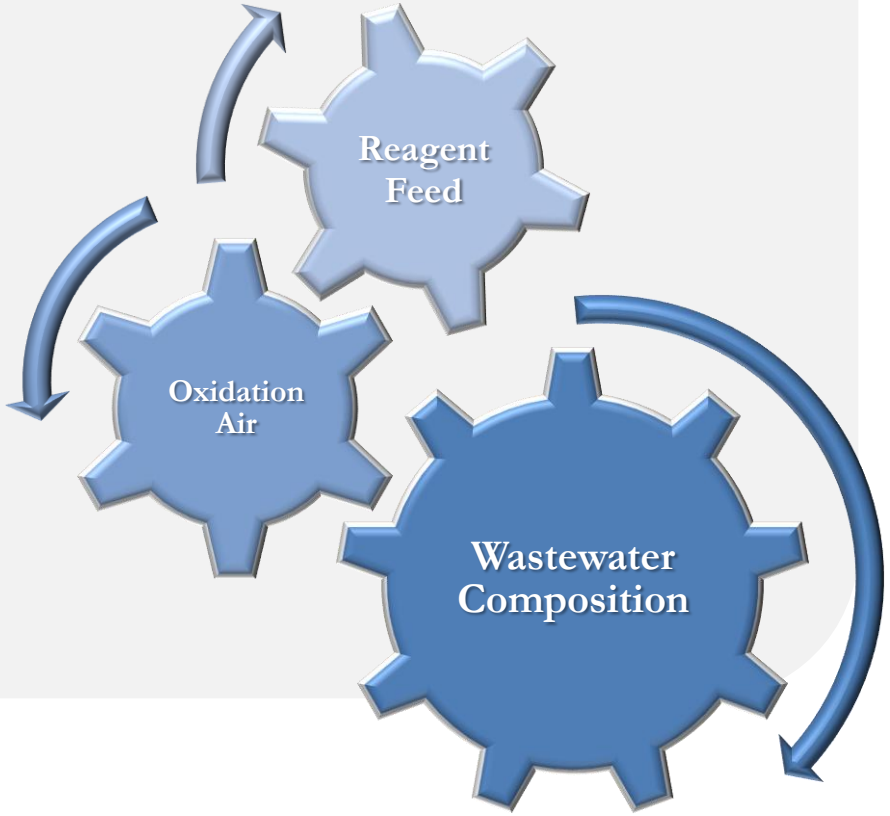
Operational Strategy for tank management

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



Effluent Optimization





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

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**
- ✓ **By tuning the Bleed Stream, performance of WWT unit operations is consistent or enhanced**
- ✓ **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**

Questions