

REINHOLD ENVIRONMENTAL Ltd.



**2014 APC Round Table
& Expo Presentation**

July 14-15, 2014, in Louisville, KY / Hosted by LG&E/KU

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Wet FGD Training Session

Part I

- Wet FGD Types**
- Wet FGD Fundamentals**
- Wet FGD Subsystems**
- Wet FGD Equipment**
- Wet FGD Materials**

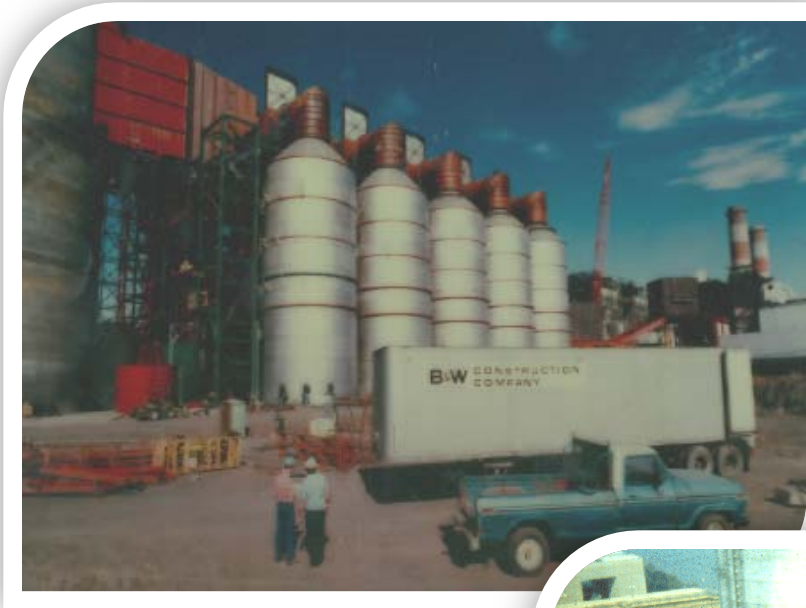
Wet FGD Types

- **Wet FGD Arrangement**
- **Absorber Tower Configuration**
- **Reagent and Chemistry**

Wet FGD Arrangement

<i>Yesterday</i>	<i>Today</i>
<ul style="list-style-type: none">• Multiple Towers per Boiler Unit• Flue Gas Quencher vs. Inlet Awning• External Reaction Tank	<ul style="list-style-type: none">• Single Absorber Tower per Boiler Unit• Inlet Awning• Integral Reaction Tank

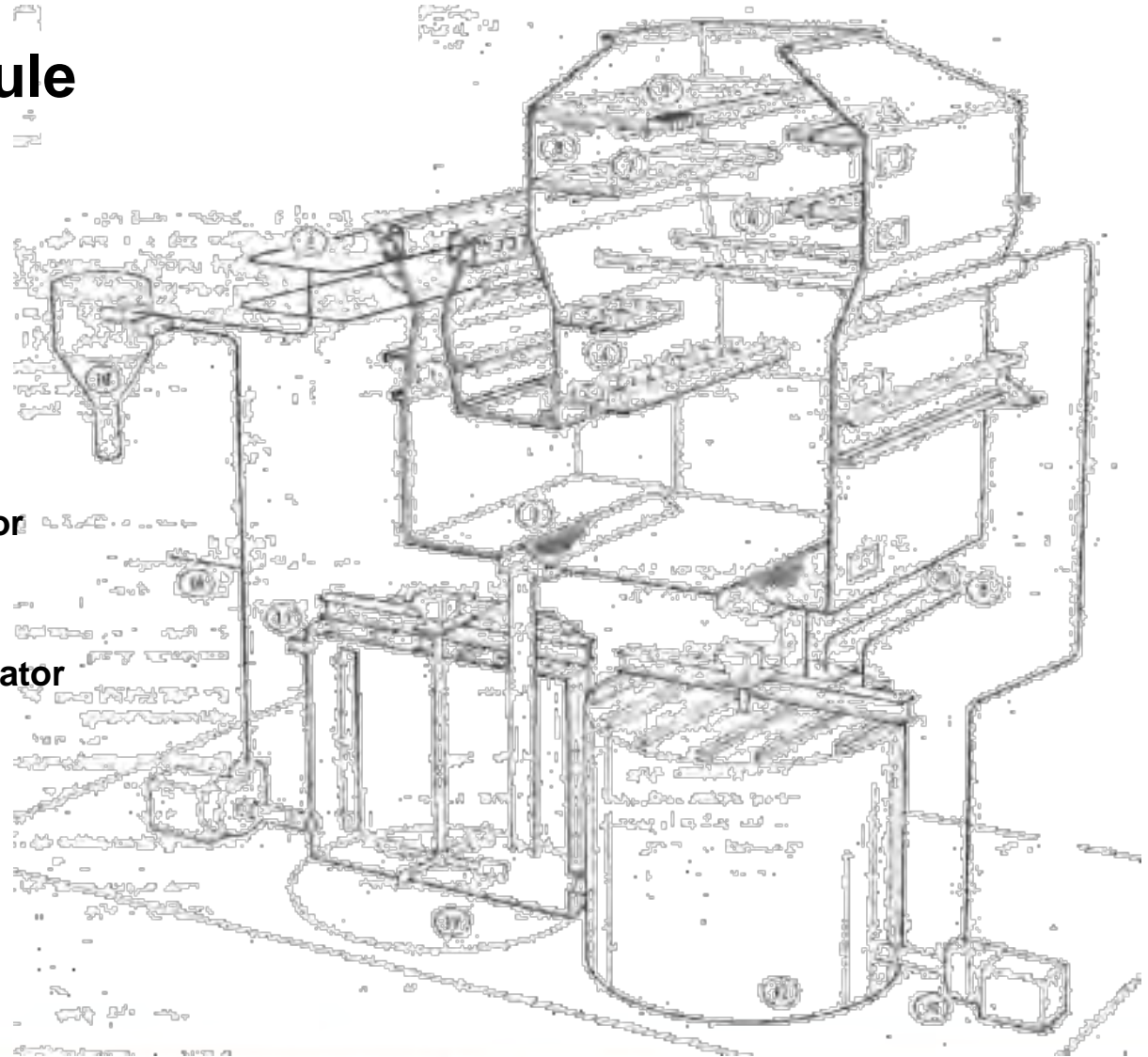
Multiple Absorber Towers per Boiler



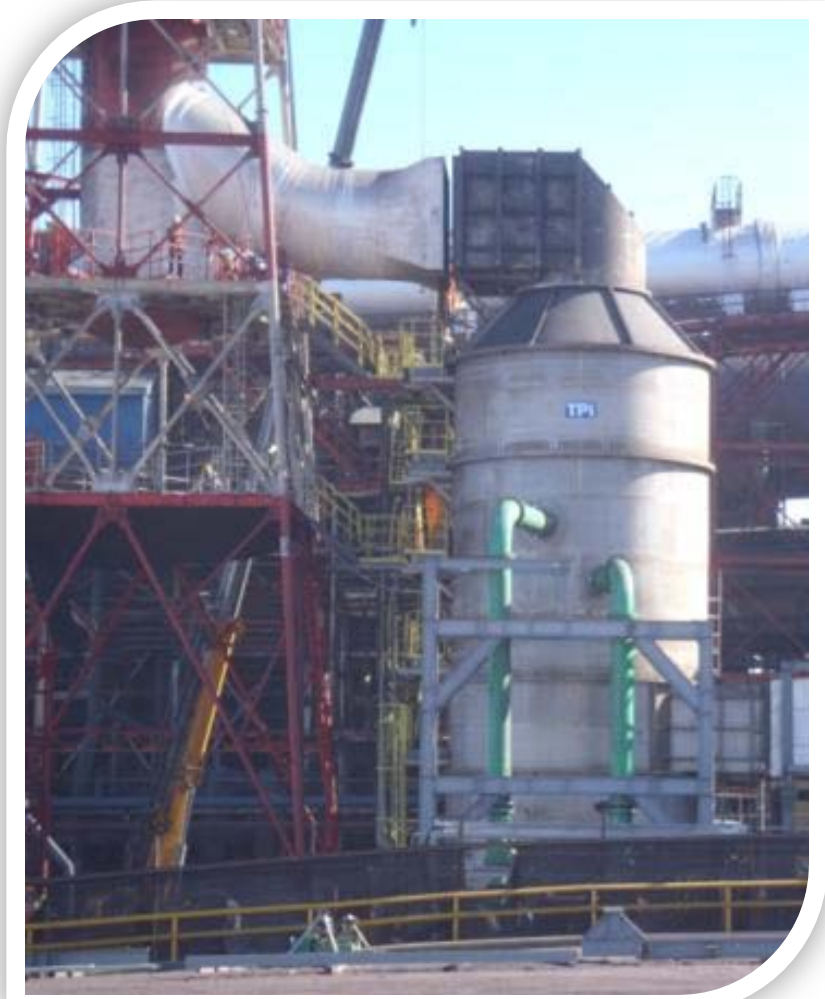
Absorber With Quencher & External Rxn Tank

SO₂ Scrubber Module

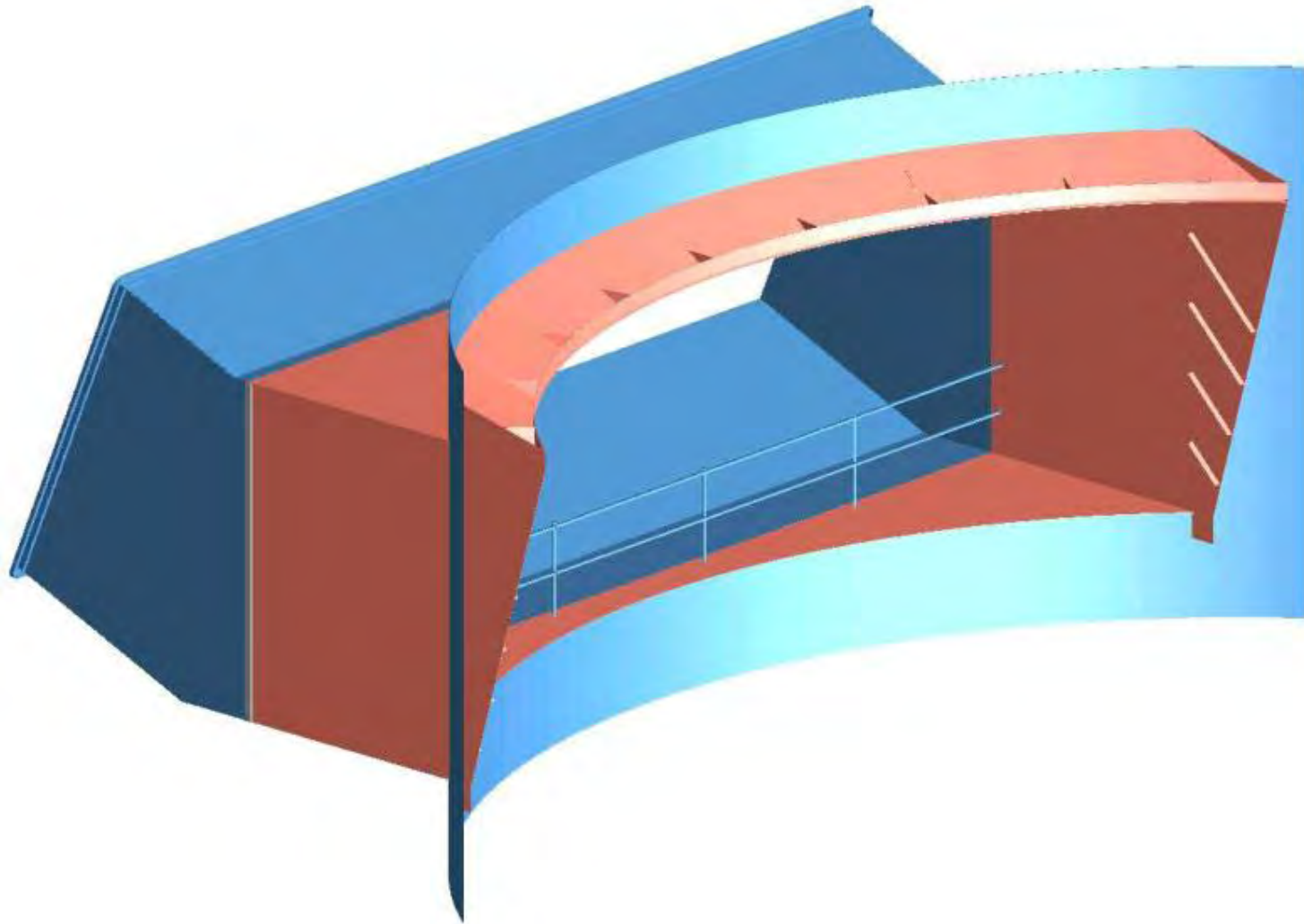
1. Quencher
2. Wall Wash
3. Sump
4. Concurrent Tray Absorber
5. Feed Slurry
6. Moisture Separator
Wash Nozzle
7. 1st Stage Moisture Separator
8. Moisture Separator
Wash Nozzles
9. Final Stage Moisture Separator
10. Hydro-clone
11. Recirculating Pump
12. Recirculation Tank
13. Overflow Air
14. Spent Slurry
15. Make-up



Single Absorber Tower per Boiler



Absorber Inlet Awning

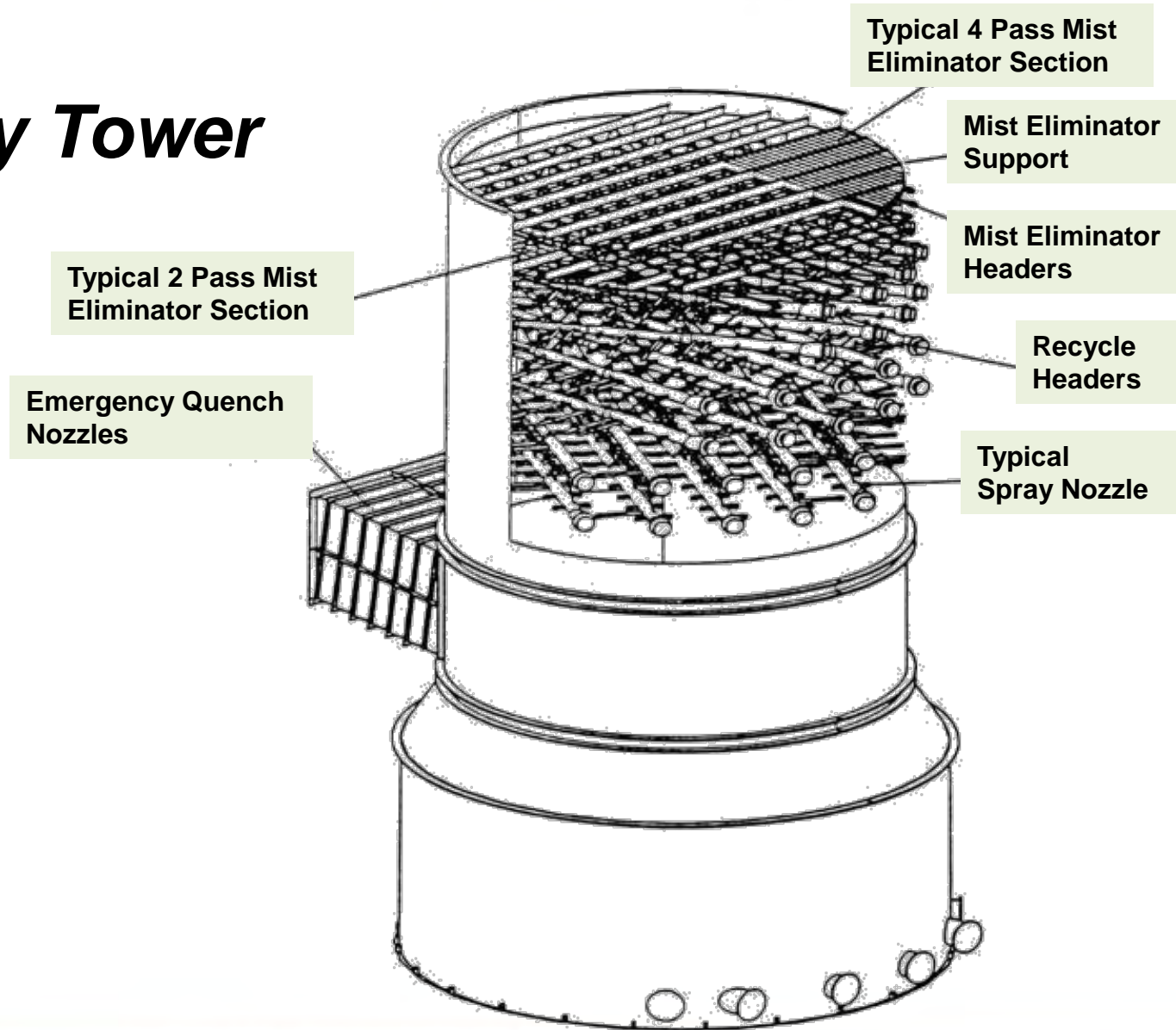


Wet FGD Types

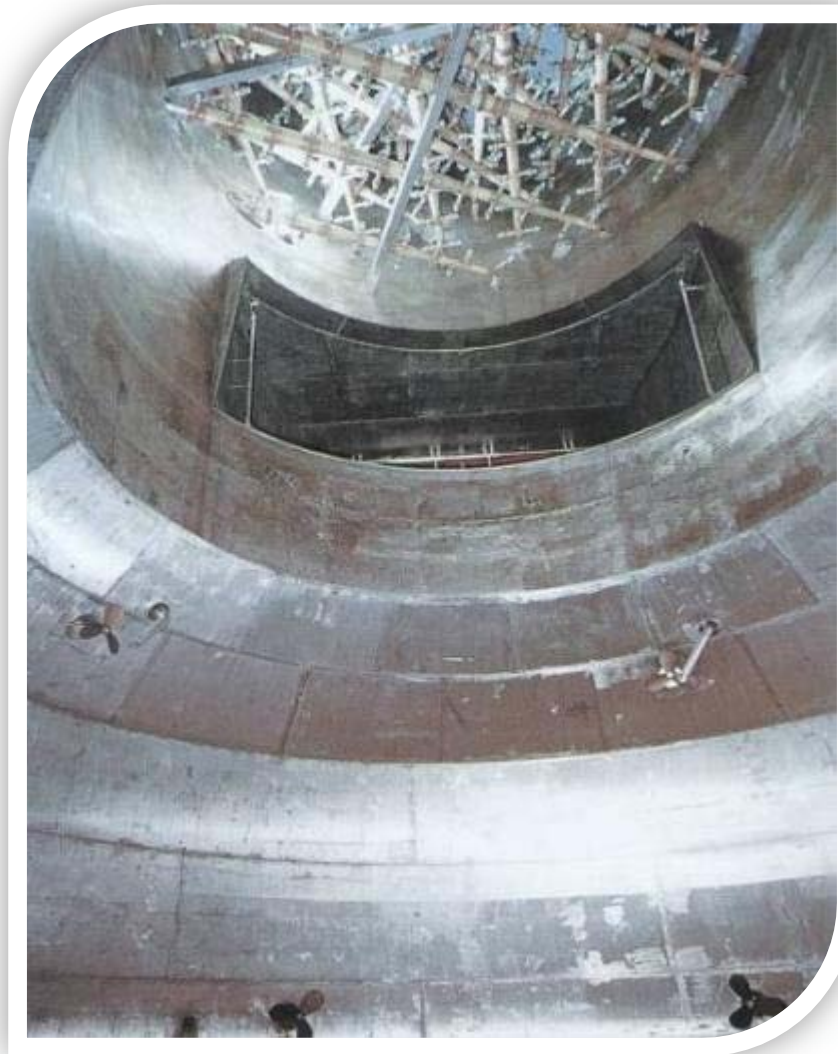
Absorber Tower Configurations

- **Open Spray Tower**
- **Spray Tower with Tray**
- **Double Contact Flow Scrubber**
- **Bubbling reactor**
- **Packed tower**

Typical Open Spray Tower

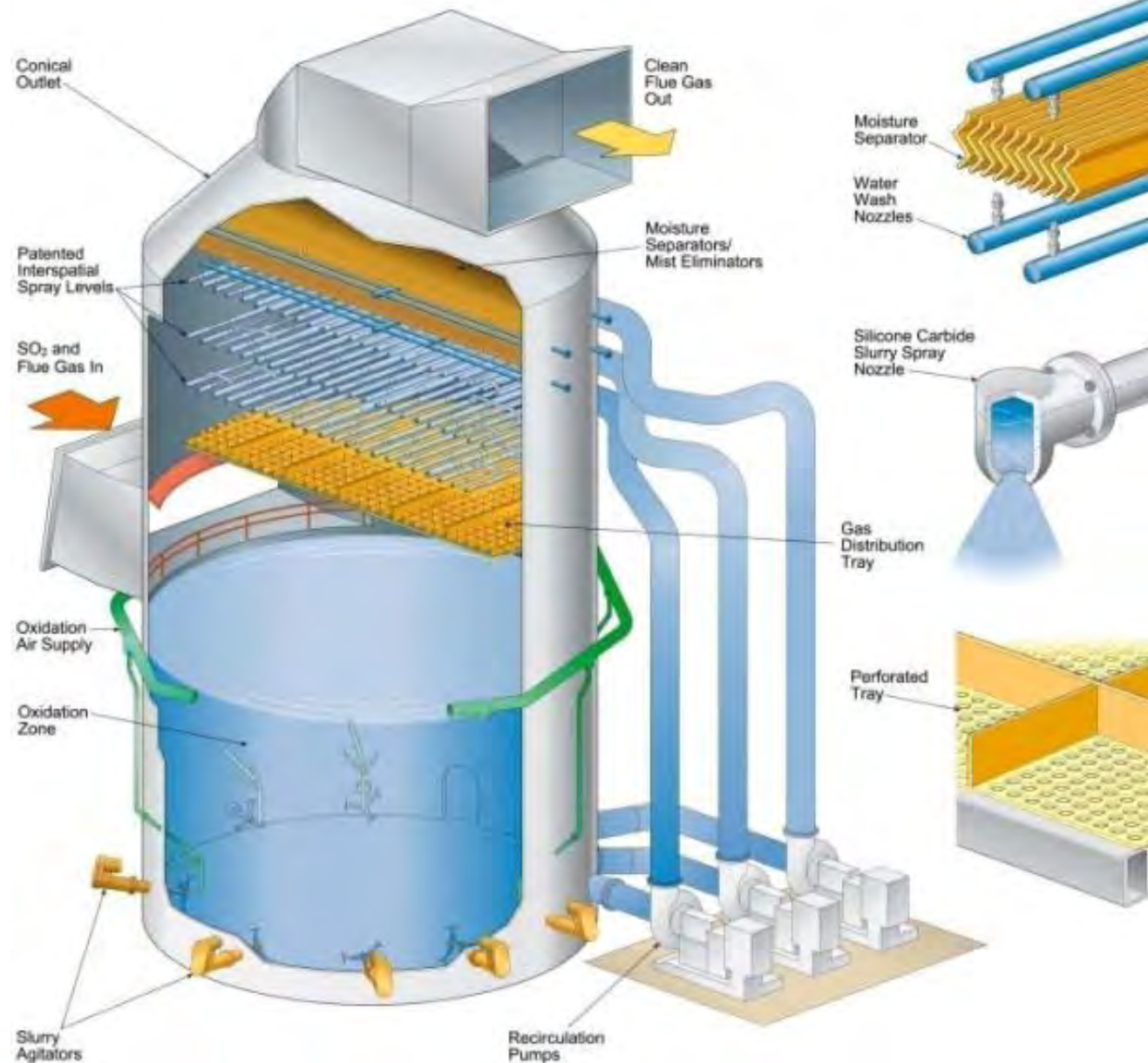


Open Spray Tower



*Source:
Babcock Power Inc.*

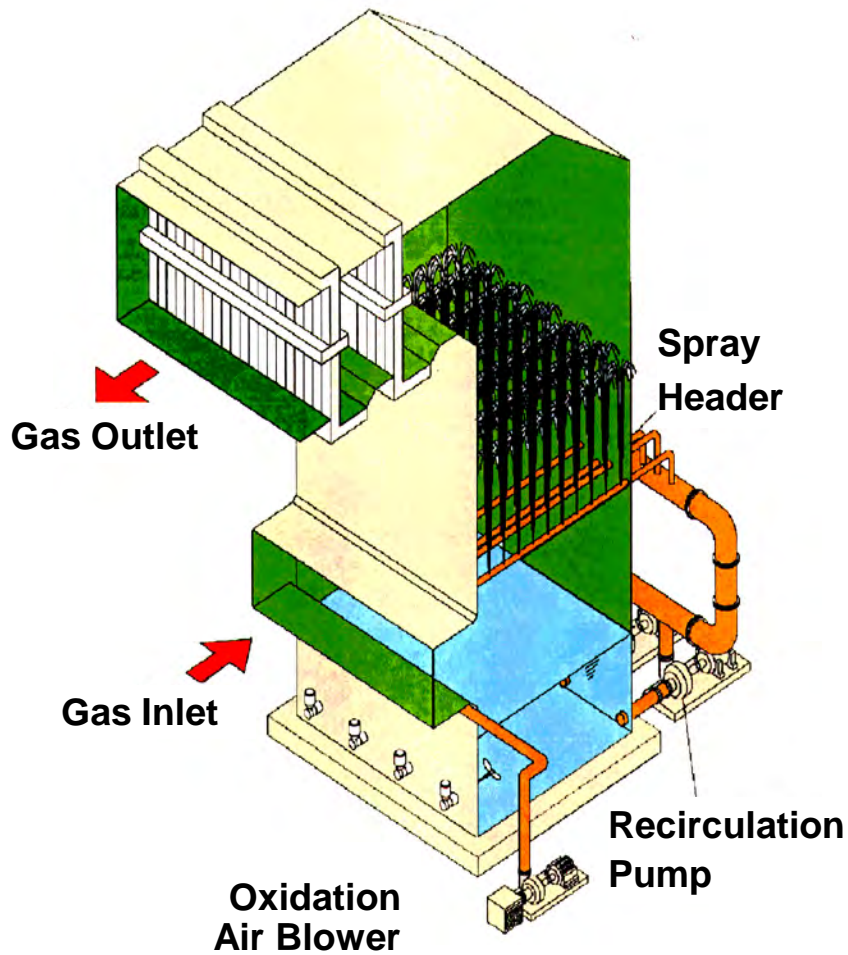
Spray Tower Absorber with Tray



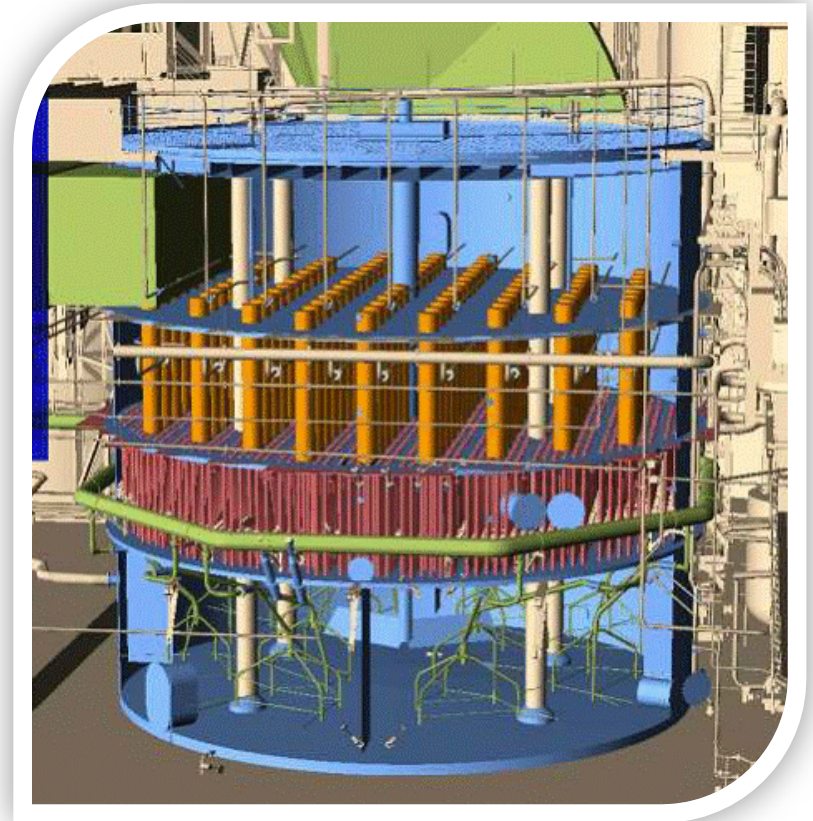
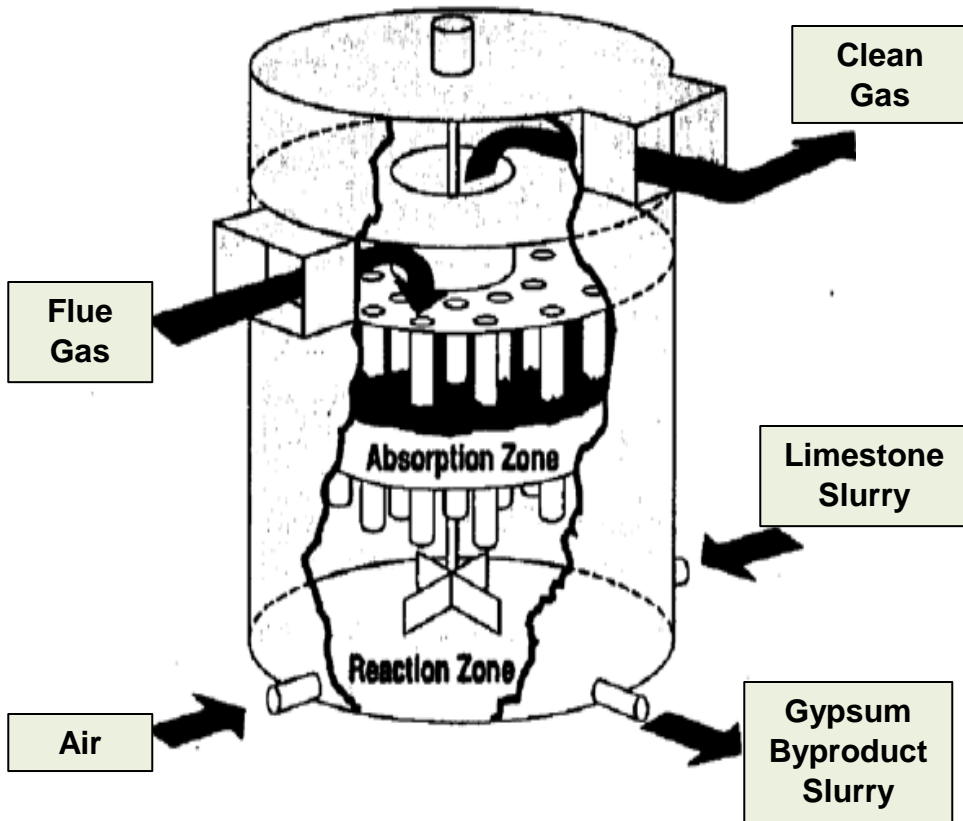
Absorber With Tray



Double Contact Flow Scrubber



Jet Bubbling Reactor



Wet FGD Reagent and Chemistry

Common Reagents

- **Limestone**
- **Lime**
- **Magnesium Enhanced Lime**
- **Caustic**
- **Soda Ash**

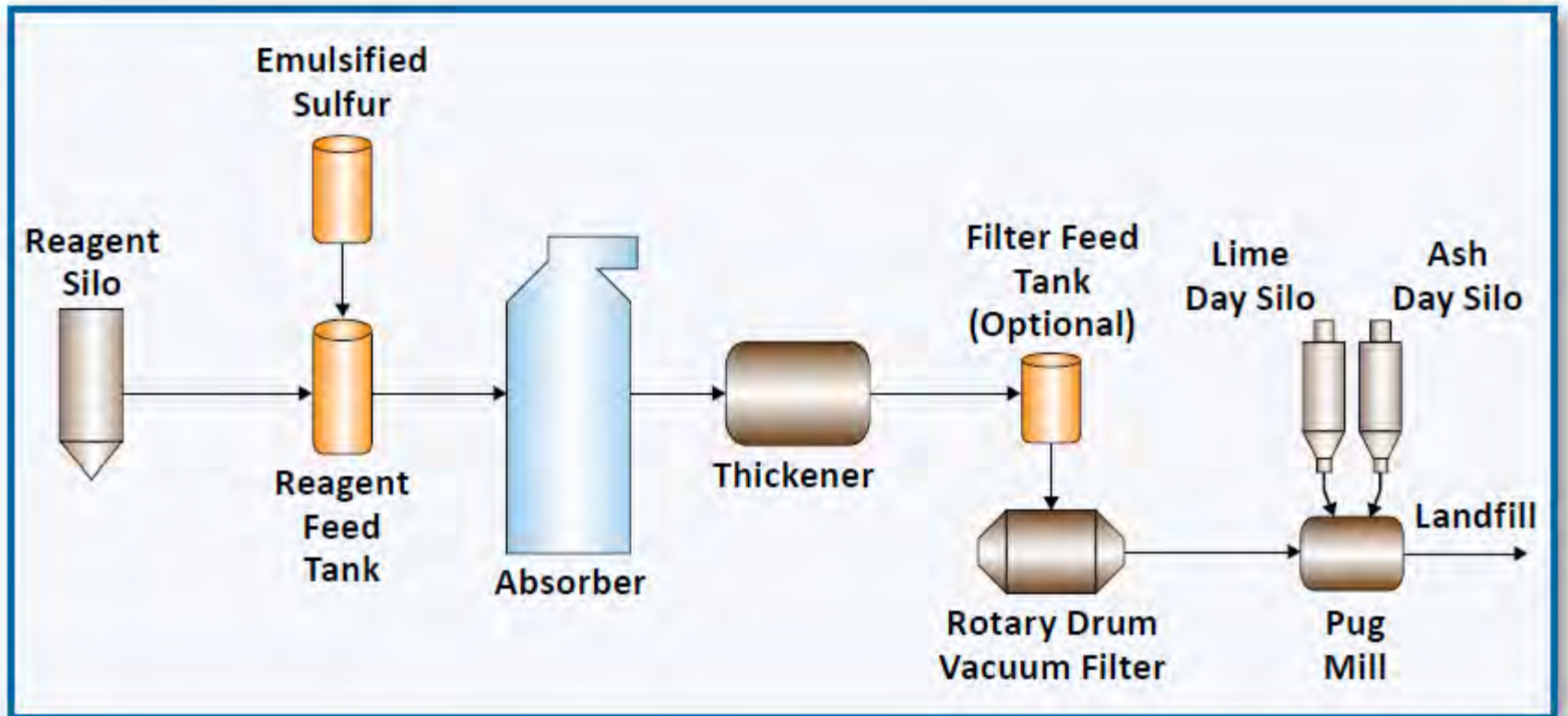
Oxidation

- **Inhibited Oxidation**
- **Natural Oxidation**
- **Forced Oxidation**

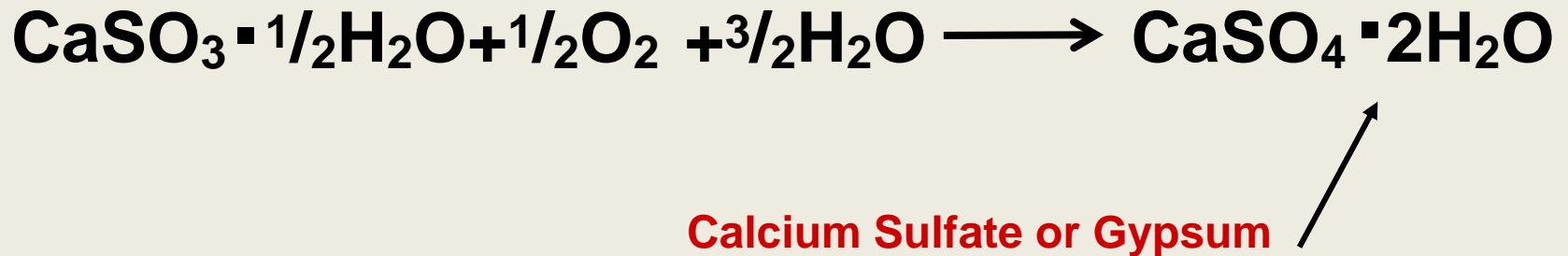
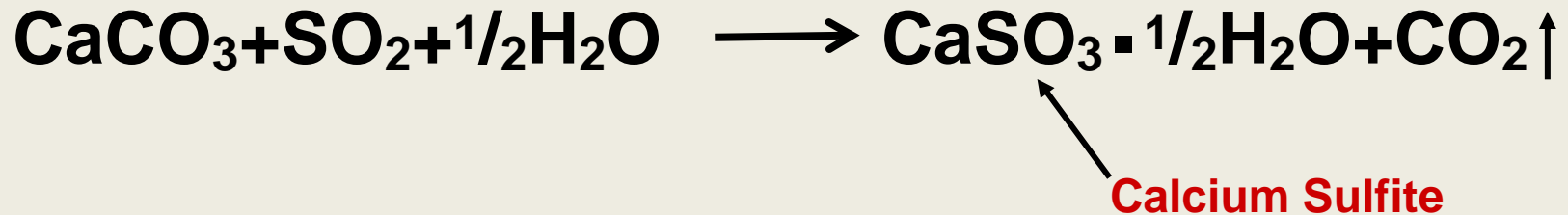
Wet FGD System Types

	<i>In-situ Forced Oxidation</i>	<i>Ex-situ Forced Oxidation</i>	<i>Natural Oxidation</i>	<i>Inhibited Oxidation</i>
<i>Limestone</i>	Yes	Yes	Yes	Yes
<i>Lime</i>	Yes	Yes	Yes	Yes
<i>Mg-Lime</i>	No	Yes	No	Yes
<i>Sodium</i>	No	No	Yes	No

Lime/Limestone Inhibited Oxidation Systems



Inhibited Oxidation



Limit to < 15% Complete

Magnesium Enhanced Lime Wet FGD Systems

Characteristics

**Can not be in-situ
forced oxidized**

- **Mg enhancement
eliminated by
oxidation**

**Can be ex-situ
forced oxidized**

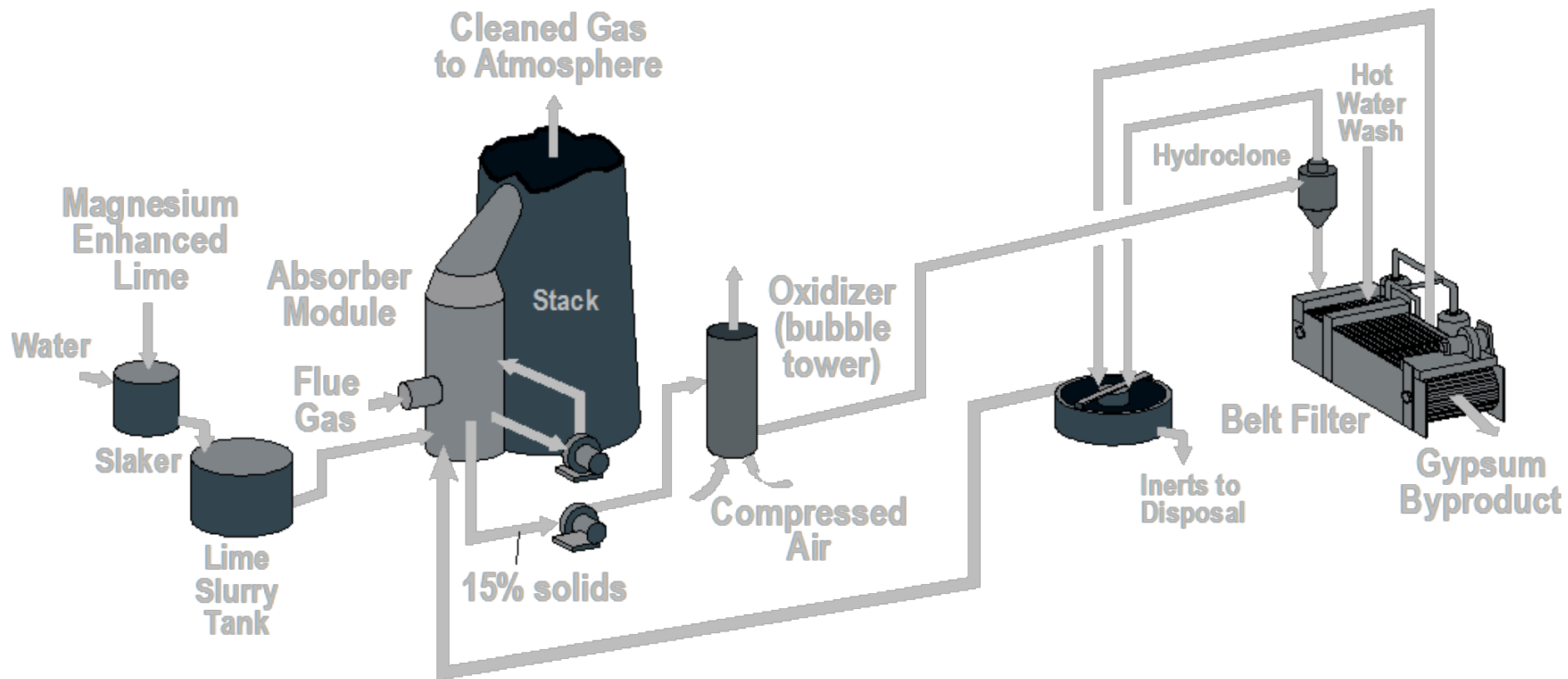
- **Sellable gypsum
byproduct**

**Can be inhibited
oxidation**

- **Disposable
byproduct that
requires stabilization**



Magnesium Enhanced Lime Wet FGD Systems



Overall Reaction in Lime based Wet FGD



Mg Enhancement Reaction



Sodium Wet FGD Systems

Typical Equipment

Liquid Reagent Receiving System

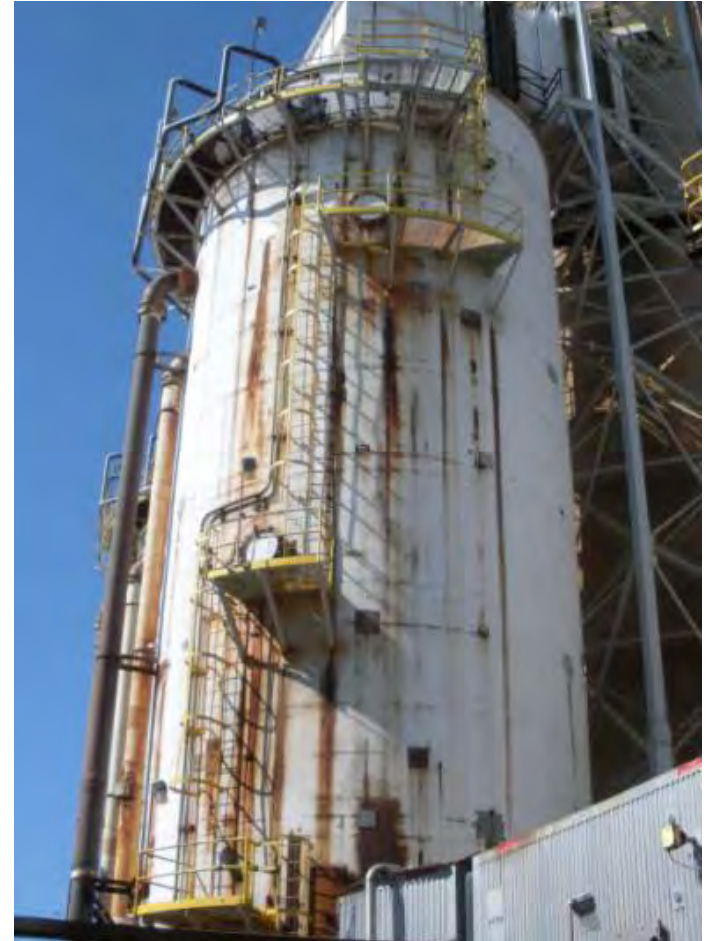
- Or dry soda ash / water mixing system

Wet FGD Absorber

- No forced oxidation system required
- No agitators required

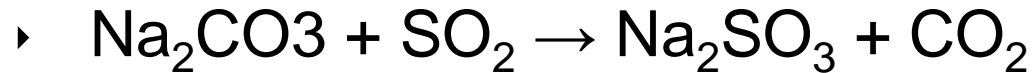
Waste liquor blowdown system

- No dewatering equipment



Reactions in Na based Wet FGD

Overall Reaction



Solution Chemistry

- ▶ $\text{Na}_2\text{CO}_3 = 2\text{Na}^{+1} + \text{CO}_3^{-2}$
- ▶ $\text{Na}_2\text{SO}_3 = 2\text{Na}^{+1} + \text{SO}_3^{-2}$
- ▶ $\text{Na}_2\text{SO}_4 = 2\text{Na}^{+1} + \text{SO}_4^{-2}$
- ▶ $\text{NaHSO}_3 = \text{Na}^{+1} + \text{HSO}_3^{-1}$

Limestone Forced Oxidized (LSFO) Systems

Characteristics of LSFO Systems

Lower cost reagent

- **Lower operational costs**

Less reactive reagent

- **Higher capital costs**

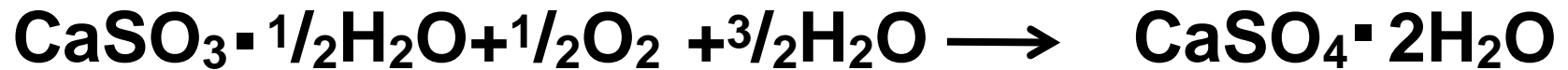
Produces gypsum

- **Sellable byproduct**

**Scrubbing media
is slurry with suspended solids**



Today: Forced Oxidation

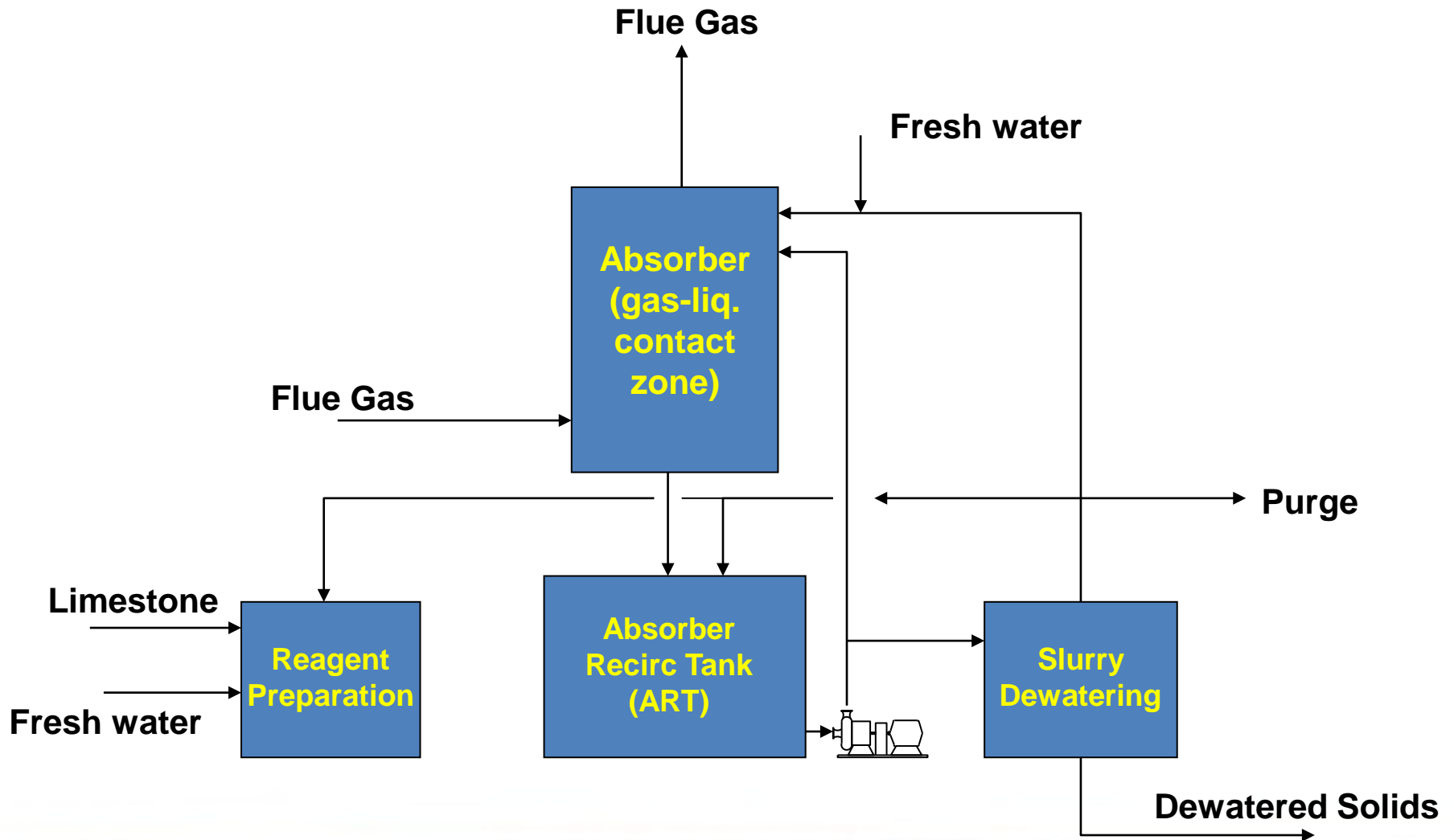


(Forced Oxidation Reaction)

Calcium Sulfate or Gypsum

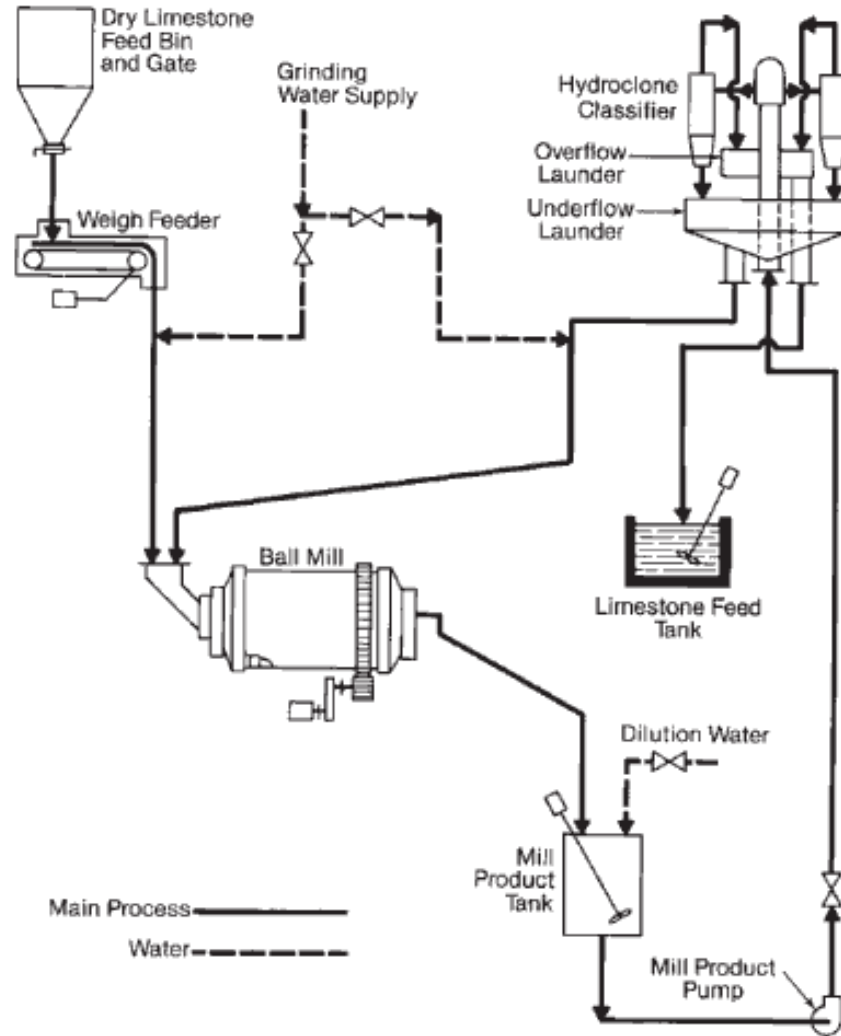
~100% Complete

Wet FGD Fundamentals



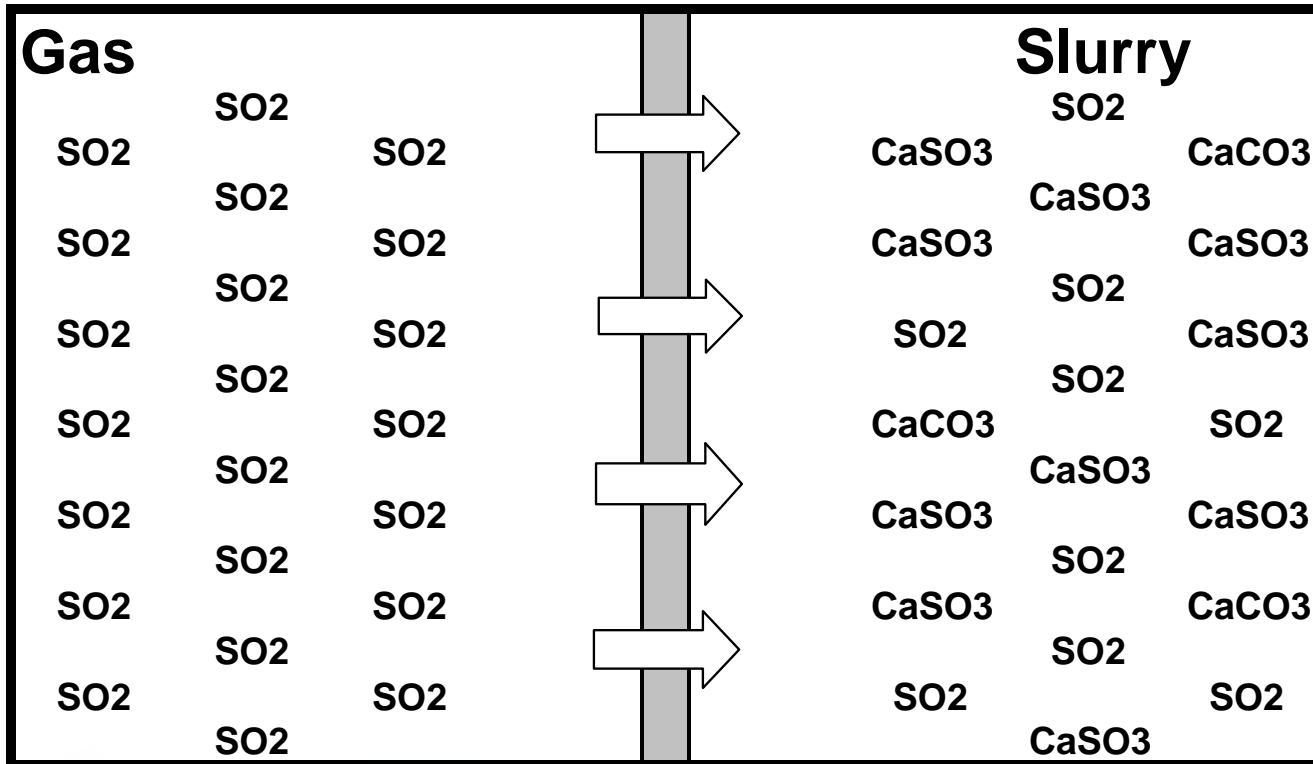
Wet FGD Process Overview

Prepare Reagent (limestone)



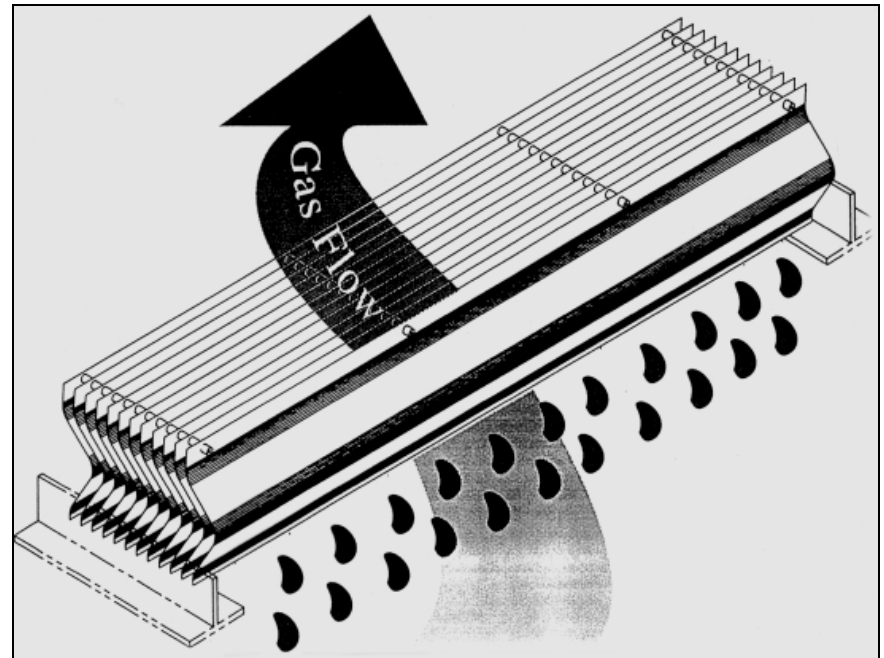
Wet FGD Process Overview

- Prepare reagent (limestone)
- Absorb SO₂
- React SO₂ with reagent



Wet FGD Process Overview

- **Prepare reagent (limestone)**
- **Absorb SO₂**
- **React SO₂ with reagent**
- **Remove entrained slurry from flue gas**



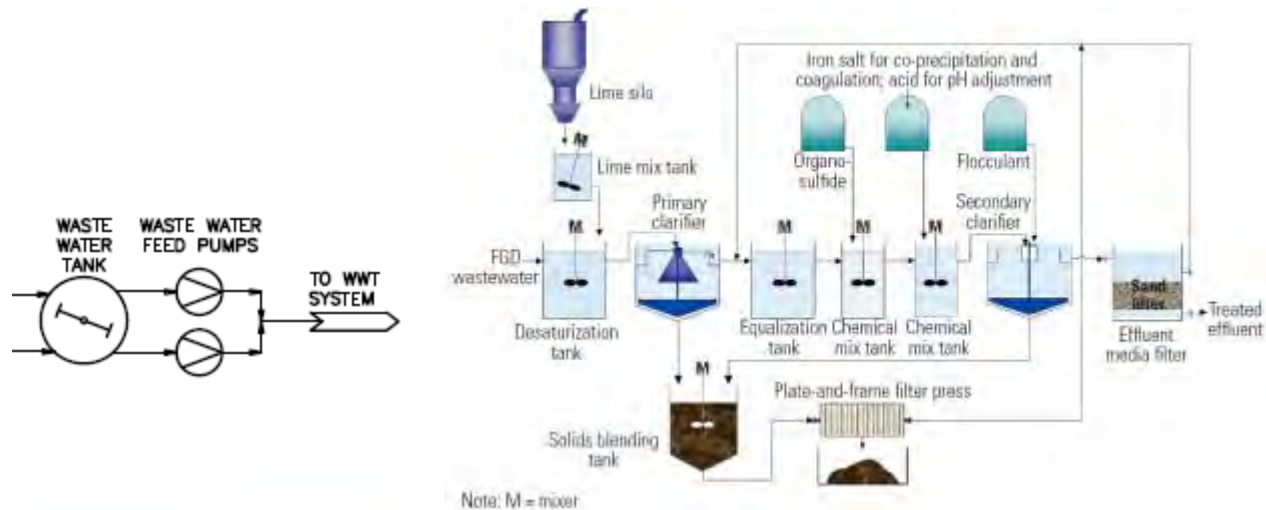
Wet FGD Process Overview

- **Prepare reagent (limestone)**
- **Absorb SO₂**
- **React SO₂ with reagent**
- **Remove entrained slurry from flue gas**
- **Oxidize slurry in reaction tank(s)**



Wet FGD Process Overview

- Prepare reagent (limestone)
- Absorb SO_2
- React SO_2 with reagent
- Remove entrained slurry from flue gas
- Oxidize slurry in reaction tank(s)
- Use a purge stream to eliminate fines and chlorides



Wet FGD Process Overview

- **Prepare reagent (limestone)**
- **Absorb SO₂**
- **React SO₂ with reagent**
- **Remove entrained slurry from flue gas**
- **Oxidize slurry in reaction tank(s)**
- **Use a purge stream to eliminate fines and chlorides**
- **Separate solid product (gypsum) from slurry (dewater)**




Wet FGD Process Overview

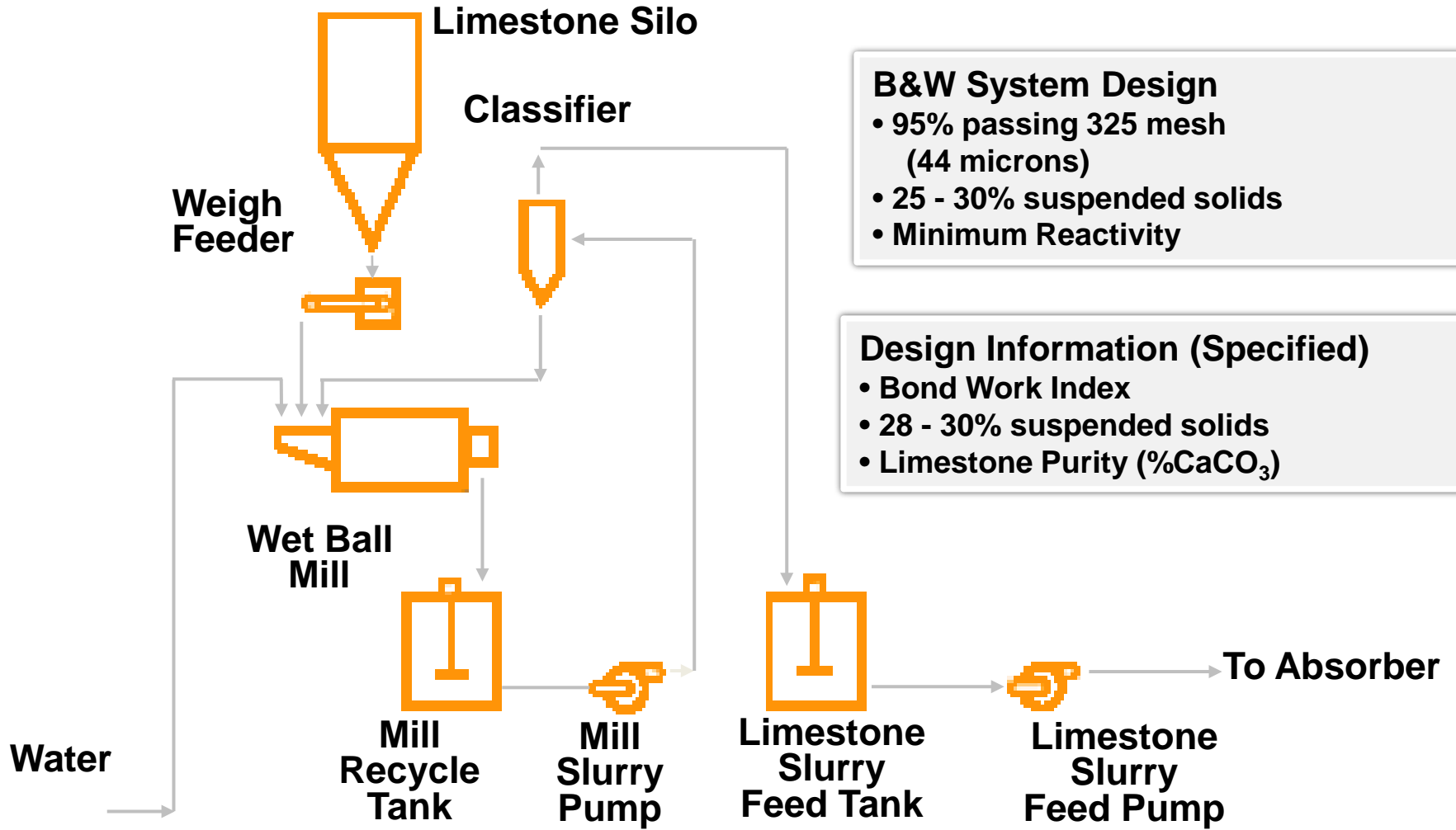
- **Prepare reagent (limestone)**
- **Absorb SO₂**
- **React SO₂ with reagent**
- **Remove entrained slurry from flue gas**
- **Oxidize slurry in reaction tank(s)**
- **Use a purge stream to eliminate fines and chlorides**
- **Separate solid product (gypsum) from slurry (dewater)**
- **Use recycled water to minimize the amount of fresh water needed in the system**

Wet FGD Sub-Systems

Design Basis of Sub-Systems

- 
- Limestone Preparation
 - Absorber System
 - Byproduct Dewatering System

Limestone Preparation System



Limestone Preparation Area Equipment

Ball Mill

- **Grinds limestone**
- **Grinding is achieved by tumbling action of steel balls (think of a rock tumbler) in the Mill Drum**
- **Approximately 70% solids slurry in mill**
- **Includes local panel for local control**
- **Noisy (well in excess of 85 dBA)**
- **Additional equipment systems part of ball mill system**
 - **Bearing lube oil system**
 - **Air clutch**
 - **Gear spray system**
 - **Drive motor**
 - **Inching motor**



Horizontal Ball Mills

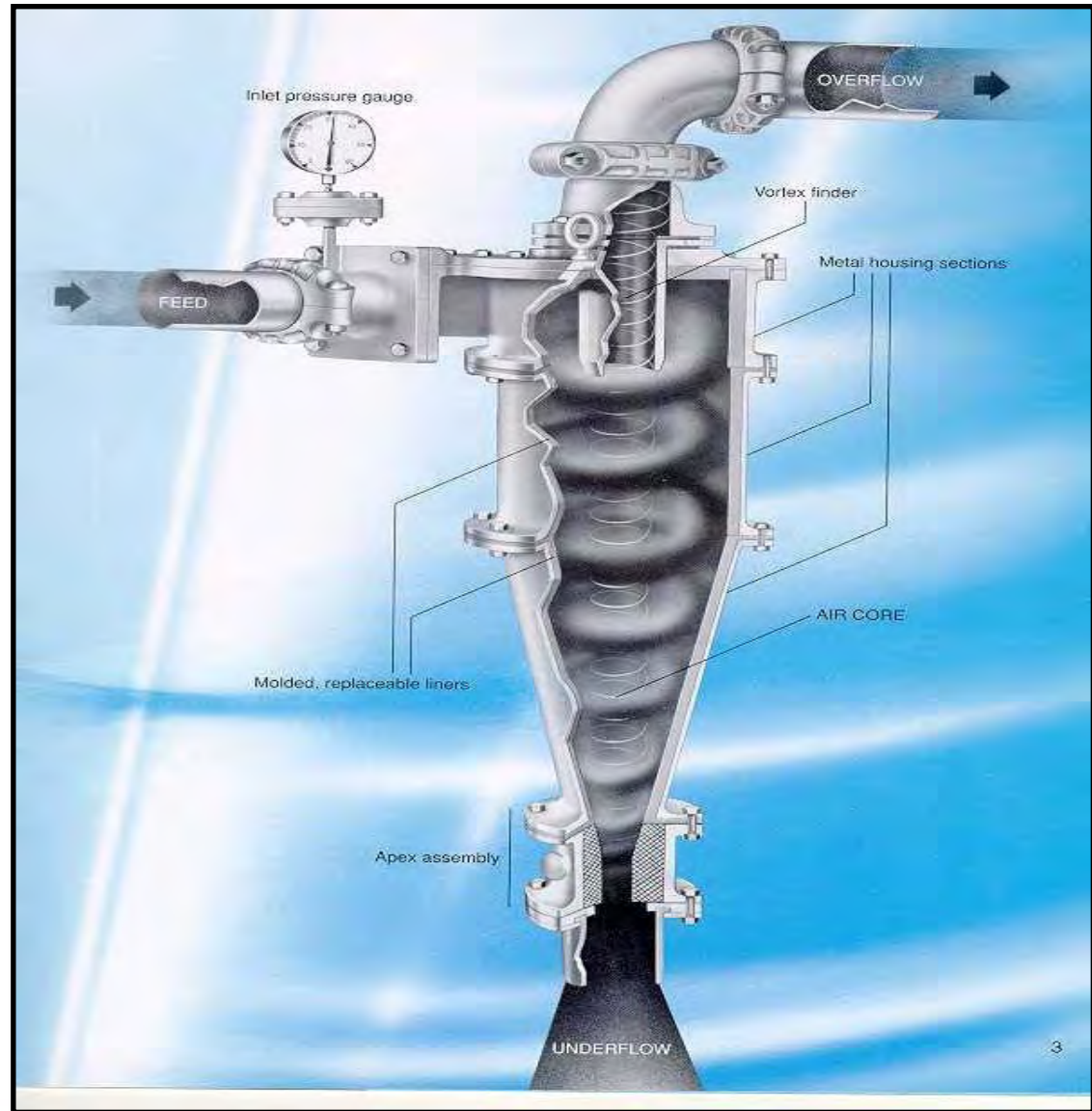


Limestone Preparation Area Equipment (cont'd)

Ball Mill Classifier

- **Classifies limestone slurry particles by size**
- **50-55 wt% solids feed enters feed chamber where a manifold system distributes slurry to individual cyclones that make up assembly**
- **As slurry enters cyclone, tangential swirl flow pattern results from geometry of cyclone. Swirl produces centrifugal force and causes solids separation, with larger, heavier particles exiting out of bottom of cyclone (underflow), and smaller, lighter particles leaving out of top of cyclone (overflow)**
- **Overflow, approximately 28 wt% solids, contains properly sized particles (325 mesh, 45 micron, 0.0017") and is sent to limestone slurry feed tanks for use in absorbers. Underflow, approximately 70 wt% solids, consists of oversized particles and is returned to ball mill for further grinding**

Classifier / Hydroclone





Limestone Preparation Area Equipment (cont'd)

Limestone Slurry Storage Tank

- **Provides storage of fresh limestone slurry**
- **Becoming common to provide two tanks that are cross-tied (this is due to high availability requirements)**
- **Trash box is provided on tank inlet to prevent tramp material from entering tank via classifier launders**
- **Tanks typically receive limestone prep area drainage via limestone prep area sump pumps**
- **Slurry concentration is 28 wt% solids**

Limestone Slurry Storage Tank



Limestone Slurry Feed Loop

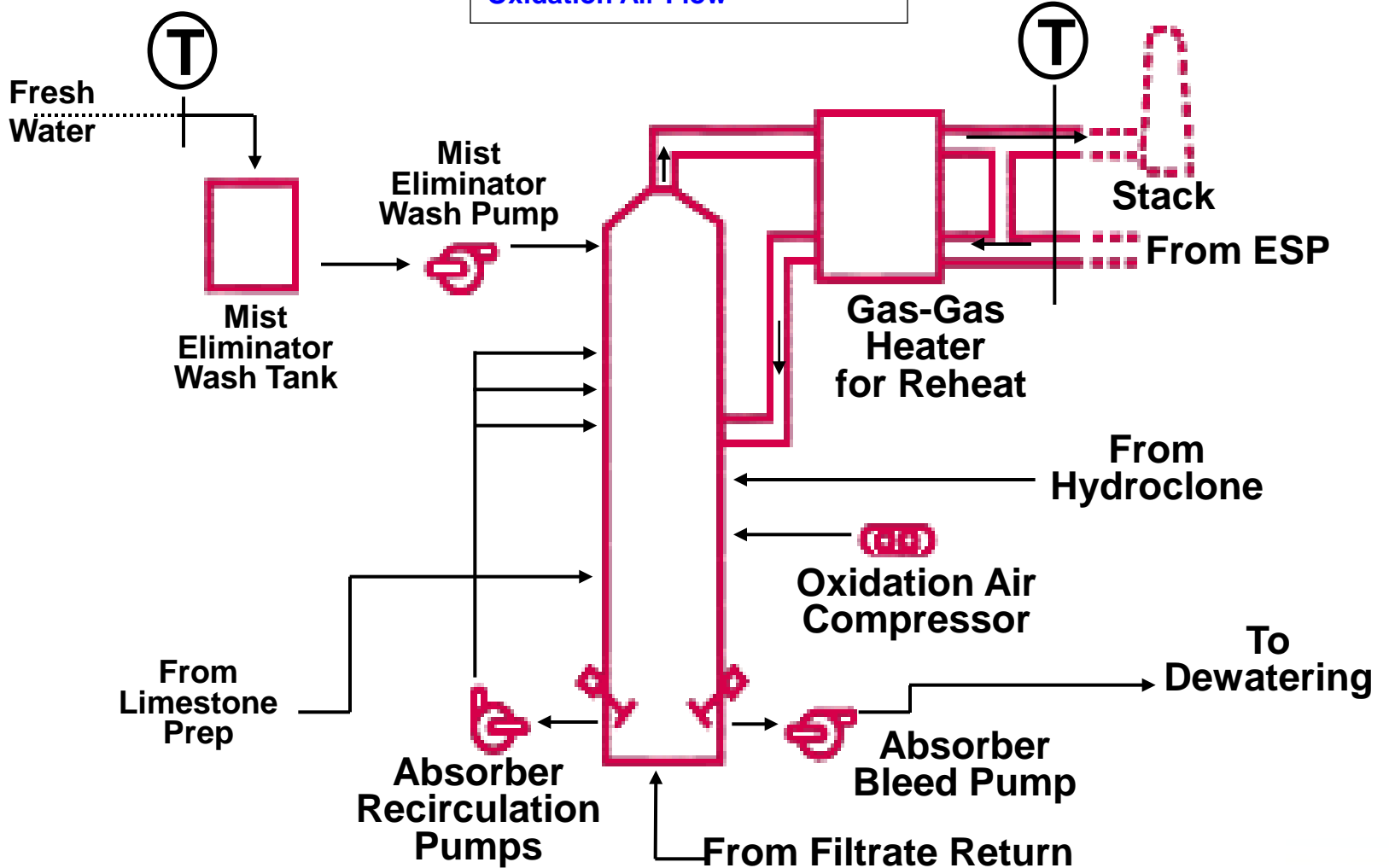
- **Limestone slurry feed pump and feed loop provide limestone slurry feed from limestone slurry feed tanks to absorbers**
- **A loop is utilized to maintain proper slurry flow velocity during times of variable slurry demand**



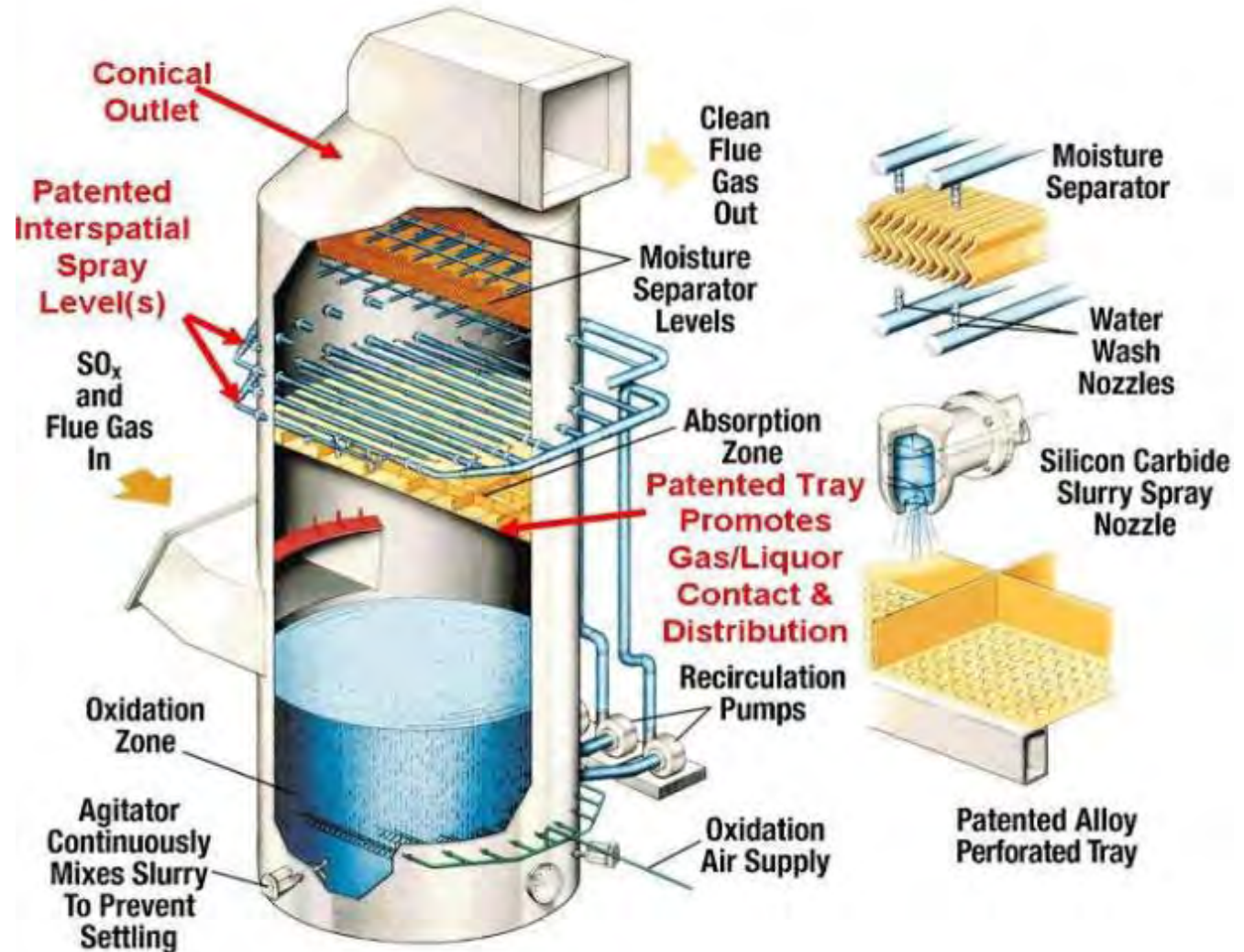
Absorber System

B&W System Design
 20 % suspended solids
 Slurry pH: 5.0 – 6.0
 Absorber Design Liquid Level
 Oxidation Air Flow

Specified Design Information
 Oxidation Air Stoich
 Design Chloride Concentration



Absorber Area Components



Absorber Area Equipment (cont'd)

Absorber Agitators

- **Side entry agitators are used**
- **Absorber agitators perform two roles**
 - **Keep absorber solids in suspension**
 - **Inject oxidation air via a lance and disperse it**
- **Quantity of agitators incorporates an “N-1” philosophy, meaning that loss of one agitator (air capable or not) will not impact performance**
- **An alternative for injecting oxidation air is through a grid of sparge pipes located at bottom of absorber tank. However, preferred method today is with lances in front of mixer**

Absorber Agitators



Absorber Area Equipment (cont'd)

Oxidation Air Compressor

- Provide oxidation air used in absorbers
- Compressor discharges are typically run into a common header. Each absorber is fed by means of a dedicated feed branching off of discharge header and is complete with flow control valving and instrumentation
- Oxidation air is humidified before it is injected into absorber. Cooling and saturating the air helps to eliminate potential for a wet/dry interface

Oxidation Air Compressor



Agitator with Oxidation Lance



Oxidation Air – Slurry in Reaction Tank

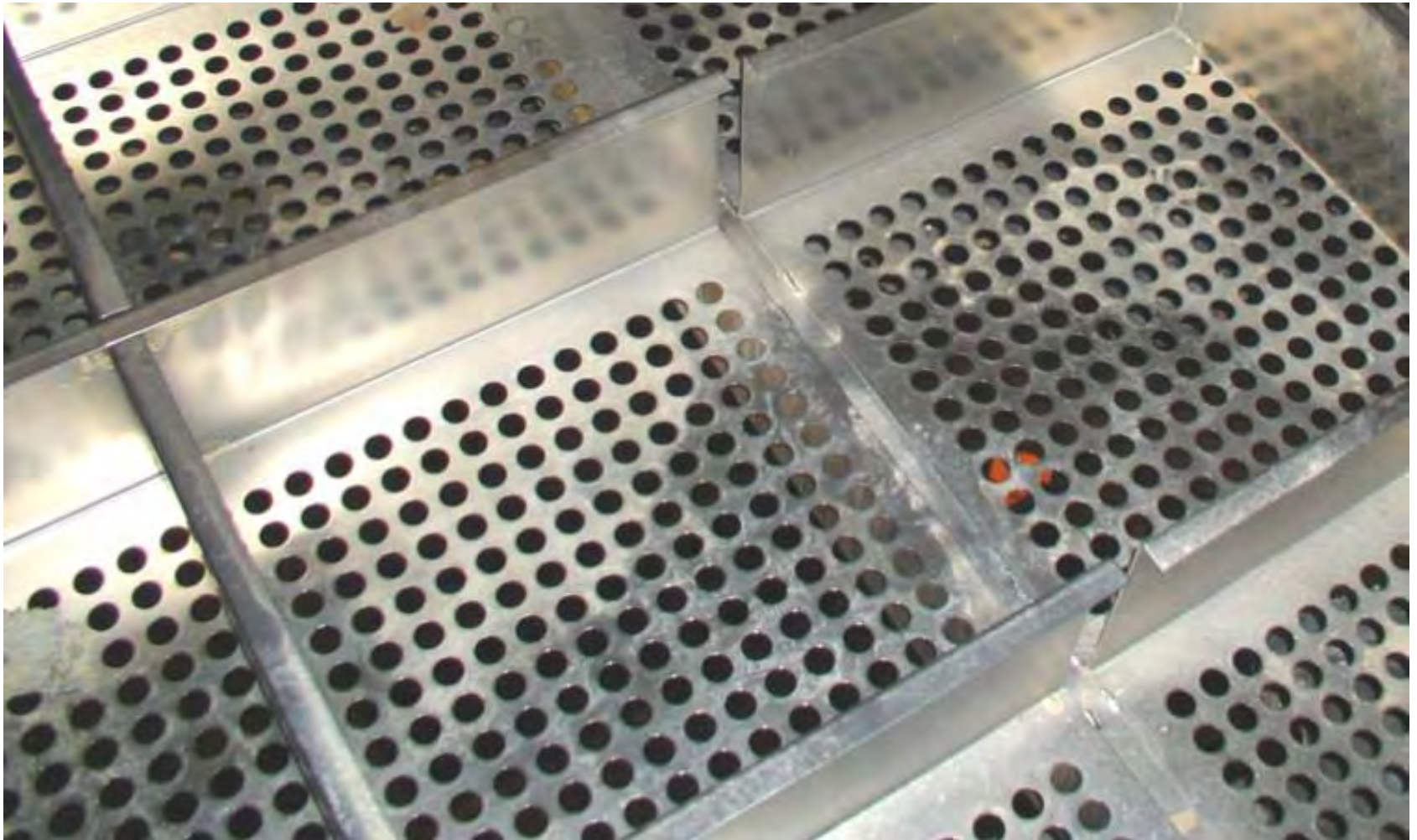


Absorber Area Absorber Components (cont'd)

Absorber Tray(s)

- **Absorber tray(s) are flooded with slurry to provide resistance to flue gas. Promotes proper gas distribution and efficient SO₂ removal**
- **Trays are constructed of alloy and are sectioned into compartments by baffles to insure adequate slurry retention within all the tray sections**
- **Patented**
- **Easy retrofit into existing Absorbers to upgrade performance**

Absorber Tray



Absorber Area Equipment

Absorber Recirculation Pumps and Piping

- **Absorber recirculation pumps and their associated piping are used to circulate reactive slurry from absorber reaction tank to spray headers**
- **Each pump dedicated to a spray header**
- **Typical materials for absorber recirculation suction and discharge piping is fiberglass reinforced plastic (FRP) with an abrasion-resistant lining**
- **Automated valve is located in pump suction piping. A non-automated valve or a rubber bladder is provided on discharge piping to be used during pump maintenance and inspection to prevent flue gas from venting out through piping**

Absorber Recirculation Pumps

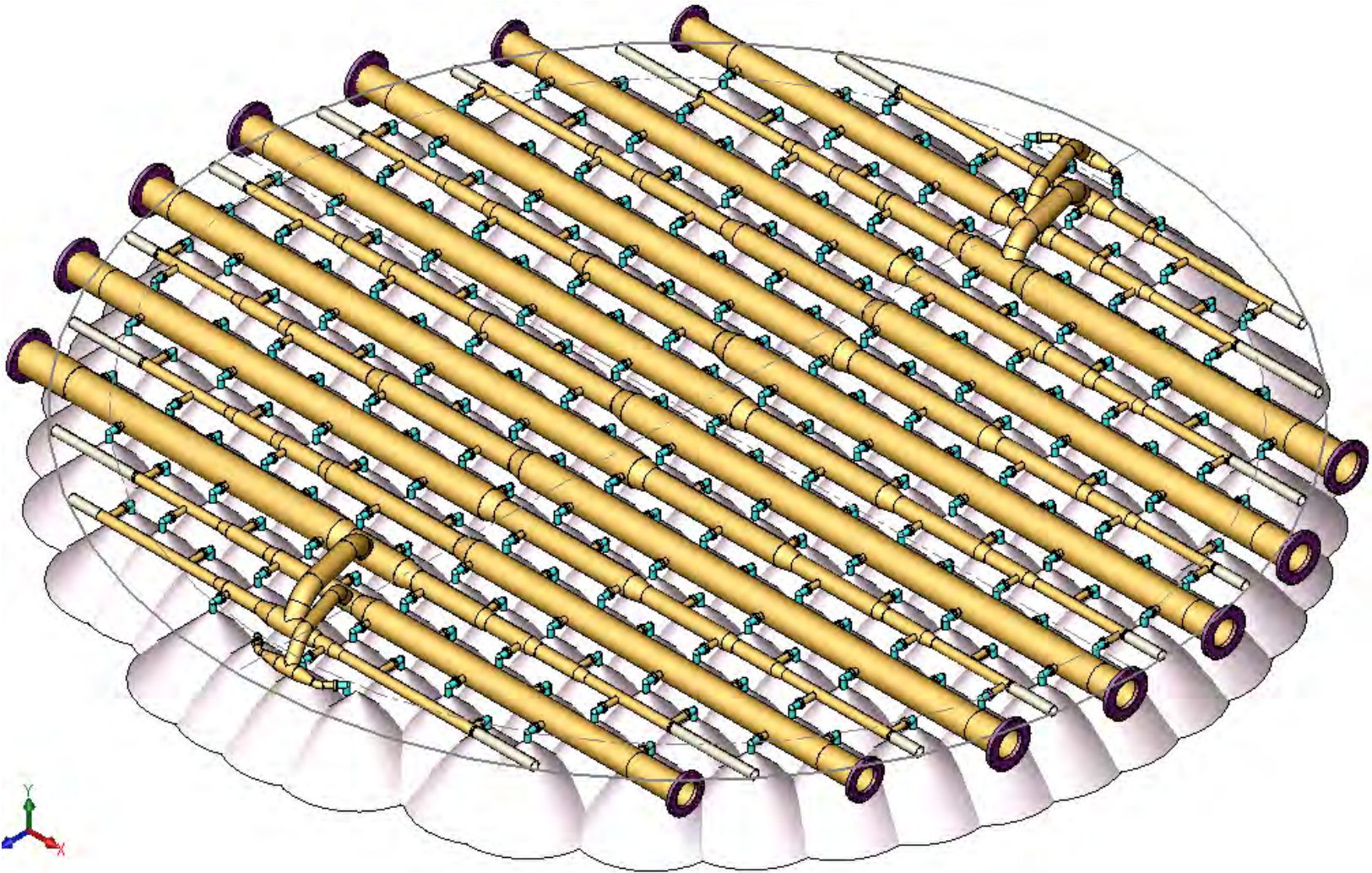


Absorber Area Absorber Components (cont'd)

Spray Headers and Nozzles

- **Used to spray recycle slurry into flue gas**
- **Spray headers are normally of interspatial design. This design saves absorber height as two spray headers are put at the same elevation (patented design)**
- **Typical material of construction for headers is FRP although some projects are using alloy**
- **Typical material of construction for nozzles is silicone carbide**

Spray Headers & Nozzles Full Coverage



Spray Headers

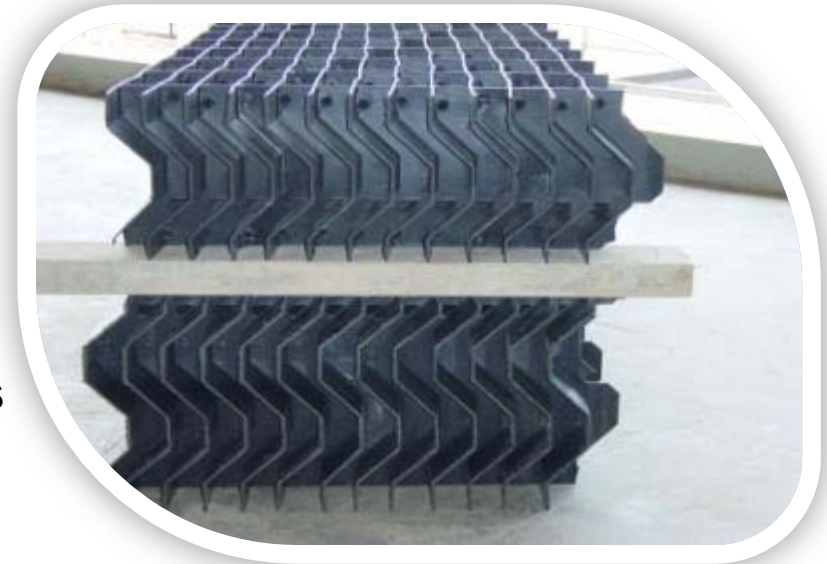


Spray Nozzle

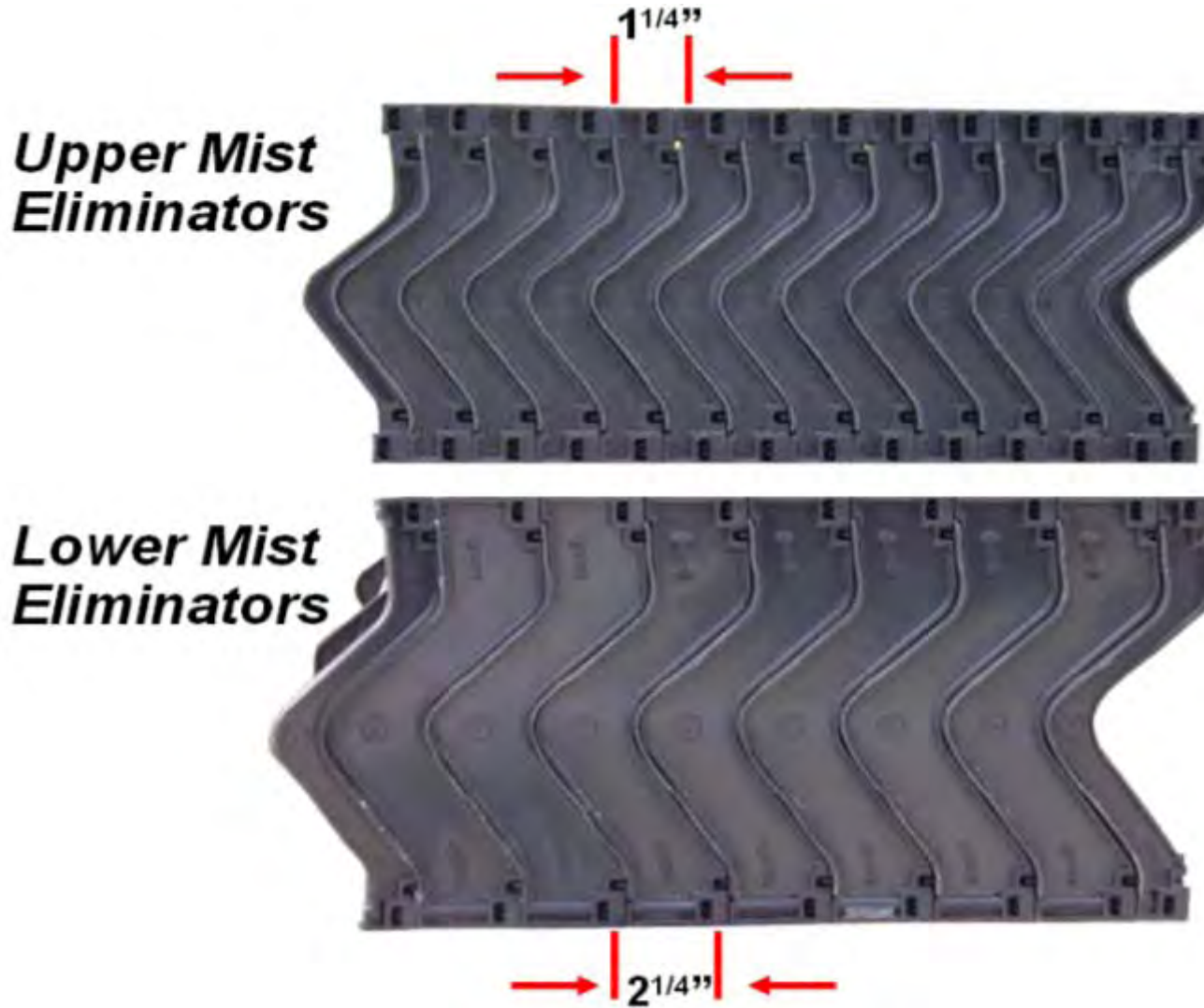


Mist Eliminators

- **Momentum separation device that separates liquid droplets from gas as it passes through tortuous path of mist eliminator chevrons**
- **Two stages of chevrons**
 1. **First stage captures large slurry droplets**
 2. **Second stage captures finer droplets including wash water droplets**
- **Require washing to prevent solids from building up on blades**
- **Array of wash headers and wash nozzles are provided**



Mist Eliminators



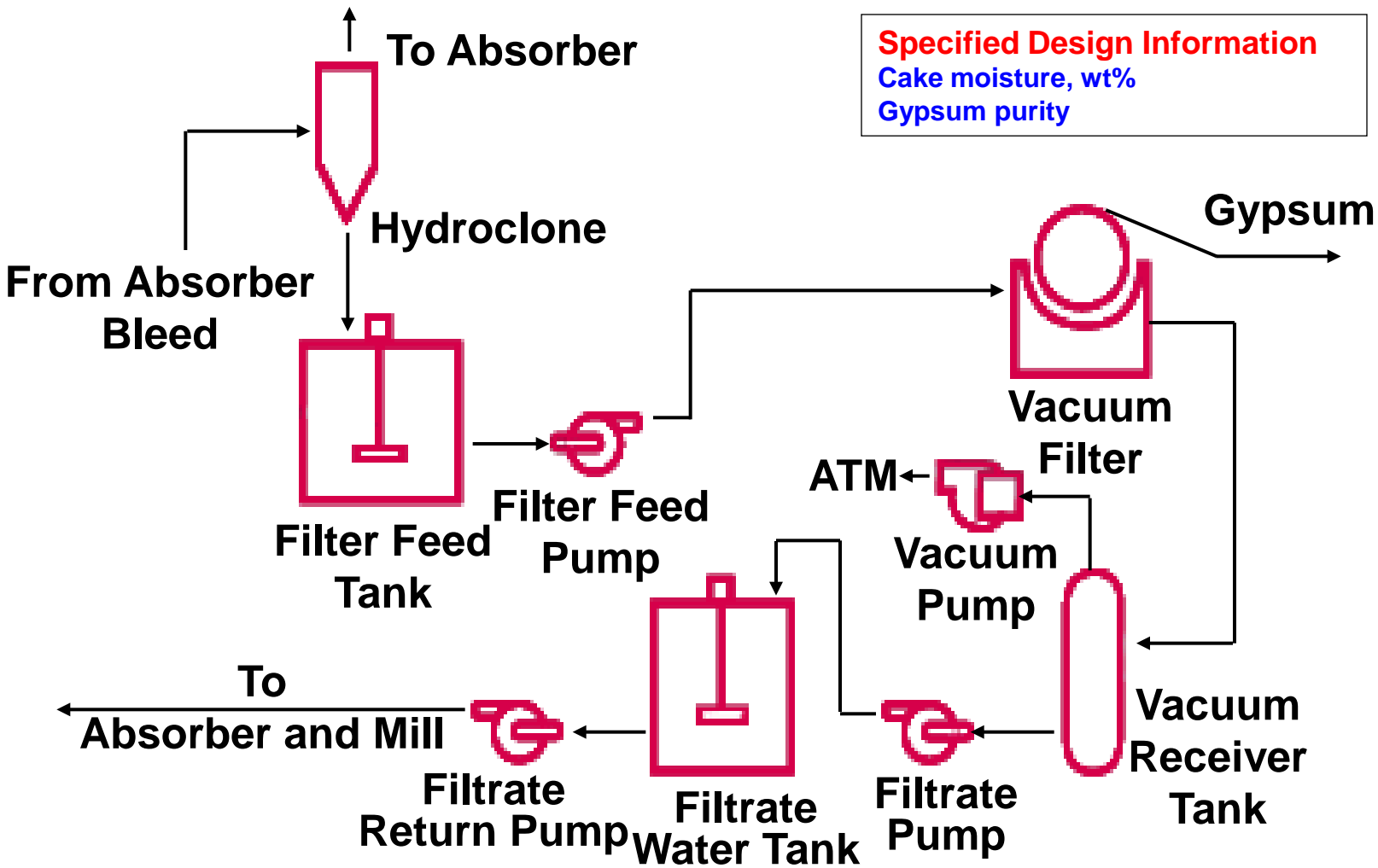
Mist Eliminator Wash In Service



Dewatering System

B&W System Design
50 - 60% filter feed solids
20% solids hydroclone feed
Filter Capacity

Specified Design Information
Cake moisture, wt%
Gypsum purity



Primary Dewatering Area Purpose

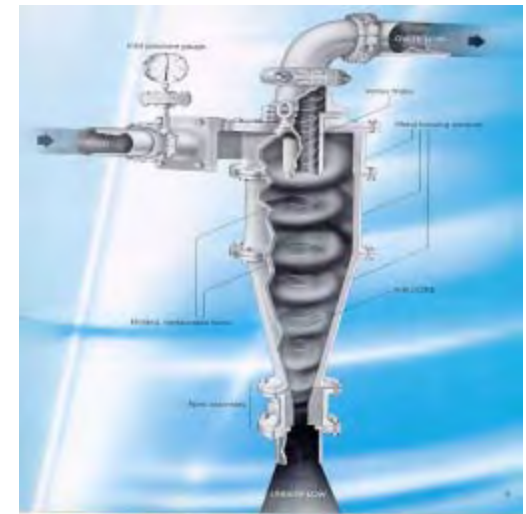
Purpose of Primary Dewatering System is Two Fold

- **Concentrate solids from absorber bleed stream**
This provides a better quality feed for secondary dewatering system as compared to just feeding with absorber bleed
- **Provides purge stream from system**
This is used to eliminate chlorides and fines
Note: A purge stream is not required for every project

Primary Dewatering

Hydroclones – Current State-of-the-Art

- **Small footprint - cost effective**
- **Multi-stage functionality for fines control and improved reagent utilization**
- **Typically sized for a specific “cut size” with 95% of particles > 35 micron**



Primary Dewatering Area Equipment

Primary Hydroclones

- **Classify absorber slurry particles by size; function in same manner as ball mill classifier**
- **18-22 wt% solids feed enters feed chamber where a manifold system distributes slurry to individual cyclones that make up assembly**
- **As slurry enters cyclone, a tangential swirl flow pattern results from geometry of cyclone. Swirl produces centrifugal force and causes solids separation, with larger, heavier particles exiting out of bottom of cyclone (underflow), and smaller, lighter particles leaving out of top of cyclone (overflow)**
- **Underflow, approximately 45 wt% solids, contains large gypsum particles and is sent to vacuum filters for further dewatering. Overflow, ~5 wt% solids, consists of small particles (small gypsum crystals and impurities) and is returned to absorber to allow gypsum particles to grow in size**

Primary Hydroclone



Primary Dewatering Area Equipment (cont'd)

Purge System

- ▶ **Secondary Hydroclone Overflow**
 - **Portion of primary hydroclone overflow is fed to a secondary hydroclone for further dewatering of purge stream**
 - **System requires additional equipment**
 - **Advantages**
 - **Wt% solids in purge stream is greatly reduced**
 - **“Good” solids are classified out of purge stream and are returned to absorber so they can grow. Purge stream is now just the “bad” stuff (the inerts)**



Secondary Dewatering



Vacuum Filtration ***– Current State-of-the-Art***

Horizontal Belt Filter

- Facilitates gypsum wash for by-product quality control
- Accessibility for maintenance
- Better turndown/More Flexibility

Rotary Drum Filter

- Small footprint - cost effective
- Wash operation more complex
- Filter Feed Tank Required

Secondary Dewatering Area Equipment

Vacuum Filter

- **Dewaters gypsum slurry to form a fairly dry cake (85-90% solids)**
- **Two types of vacuum filters: Rotary Drums and Horizontal Belts**
 - **Drums are less expensive and have a smaller footprint than belt filers, but belts offer higher dewatering rates and are more forgiving in terms of allowable feed conditions**
- **Additional equipment systems part of vacuum filter system**
 - **Vacuum pump**
 - **Filtrate receiver**
 - **Filtrate pump**
 - **Cake wash system**

Horizontal Belt Vacuum Filter



Rotary Drum Vacuum Filter



Thickener



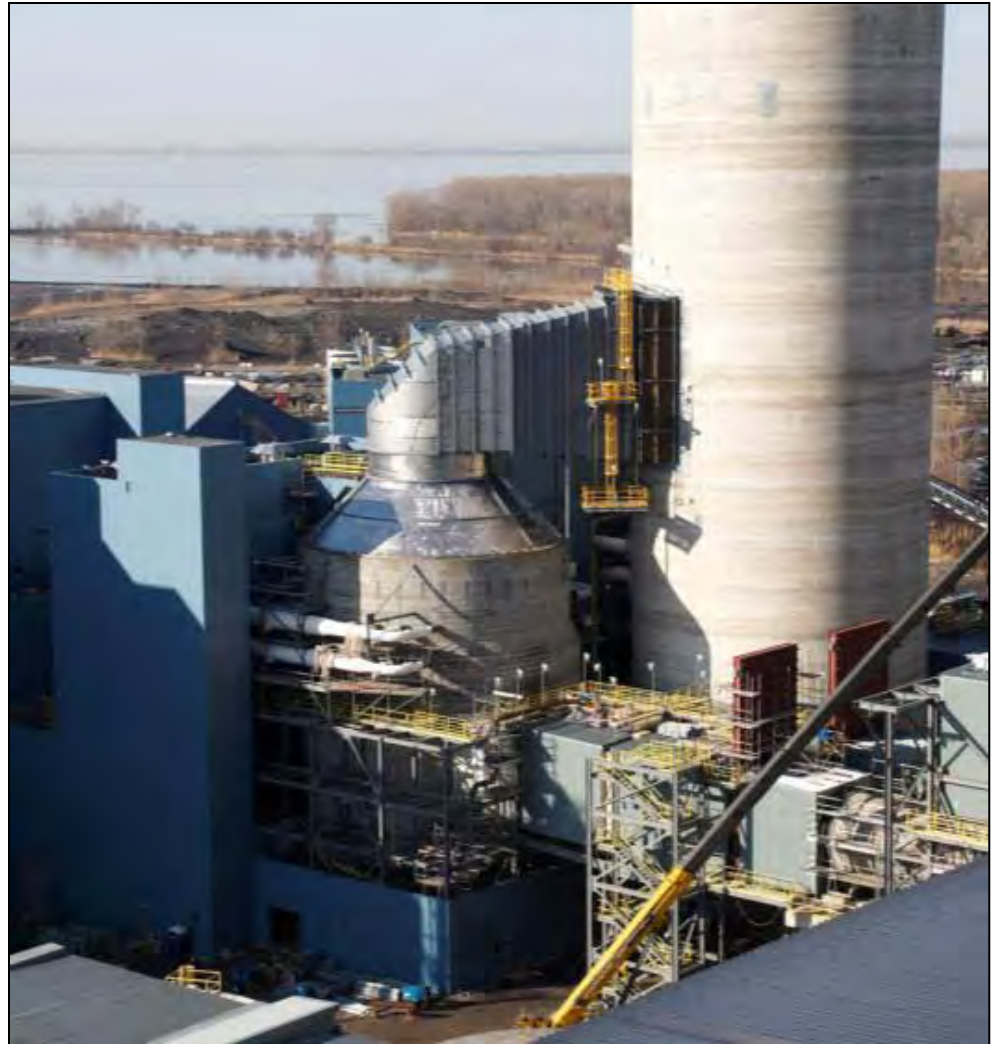
Absorber Tower Materials

- **Alloy Tower**
 - Austenitic Stainless Steel
 - Duplex Stainless
- **Lined Carbon Steel**
 - Rubber lined
 - Flake-filled Resin Coated
 - Acid Resistant Tile
- **Lined Concrete**
 - Acid Resistant Tile

Alloy Absorber Tower



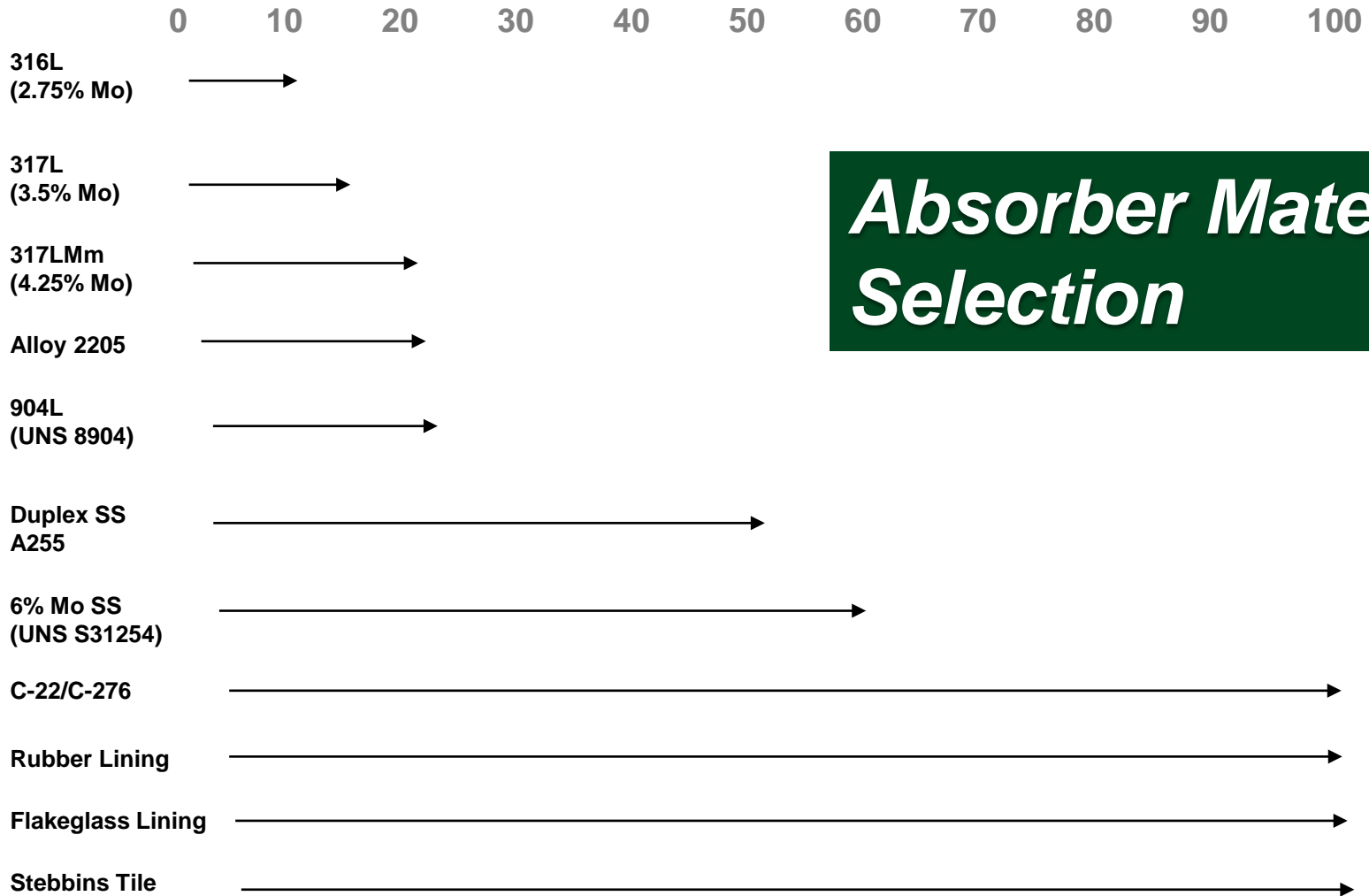
Stebbins Absorber Tower



Stebbins Tower Tiles



Chloride Ion Concentration, 1000's ppm



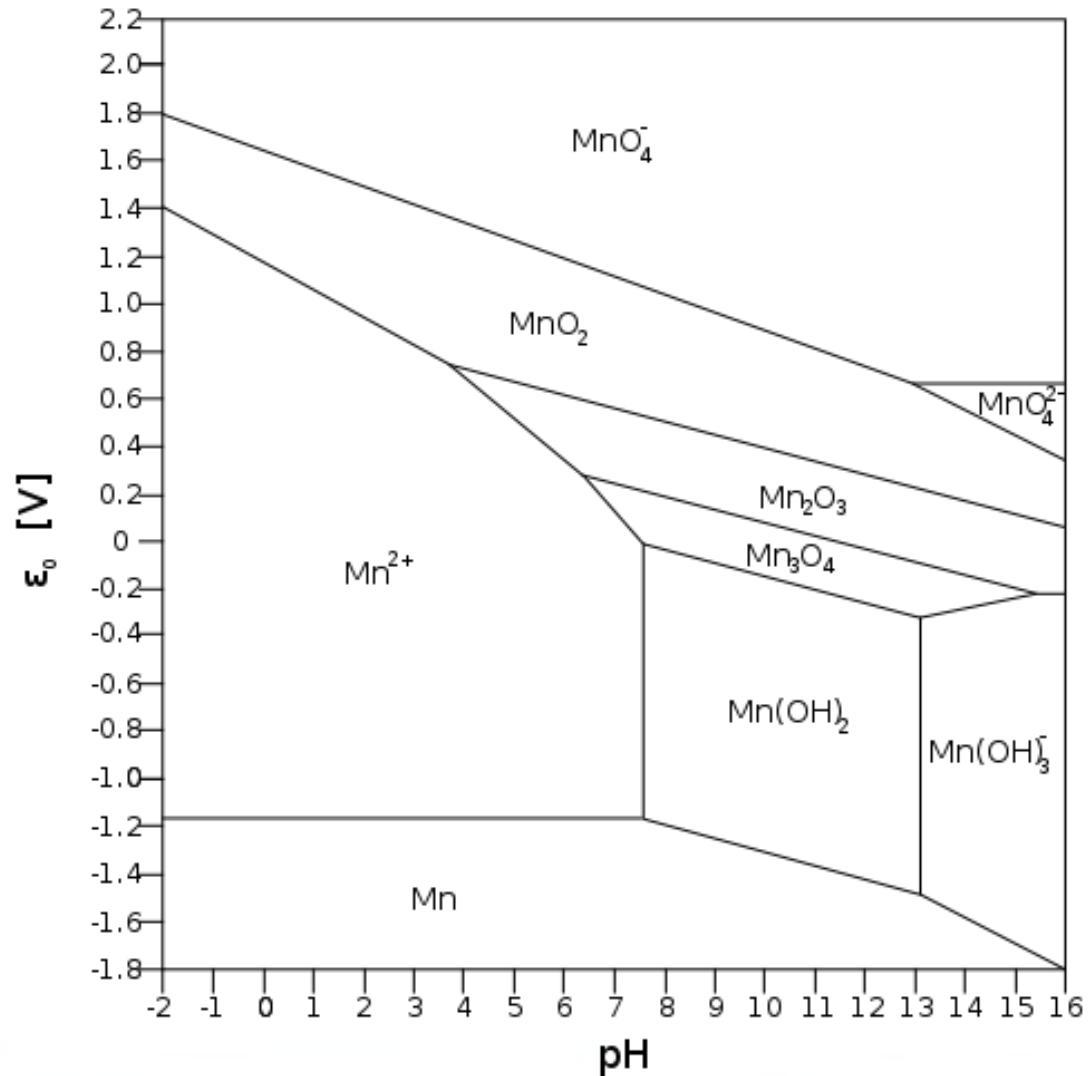
Absorber Material Selection

High ORP Aggressive Corrosion Mechanism

Observations

- Widespread deep corrosion observed on floor and walls
- Attack was only slightly worse along HAZ than at locations distant from the welds
- Alloy 625 weld metal was not attacked.
- Attack was not observed in areas where there was no deposit
- Attack severity decreased with elevation along the walls

ORP & Phase Partitioning of Chemical Species

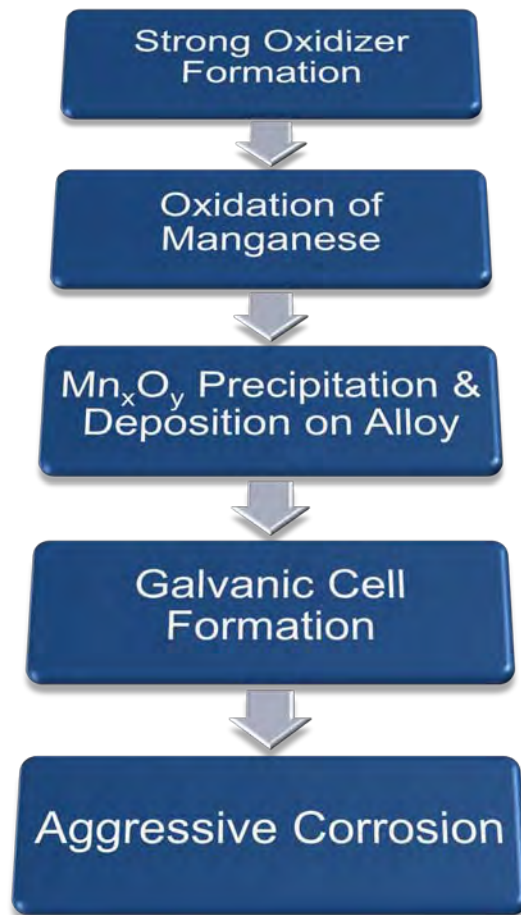


Wet FGD Alloy Corrosion

<i>Titration Results</i>	
Unit	Oxidizer (ppm)
Corrosion	1680
Corrosion	1592
Corrosion	1574
Corrosion	1571
No Mn _x O _y Scale	227
No Mn _x O _y Scale	169
No Mn _x O _y Scale	50
No Mn _x O _y Scale	29
No Mn _x O _y Scale	27
Uses Additive	19
No Mn _x O _y Scale	10
No Mn _x O _y Scale	<2

- Strong oxidizer is present it absorbers exhibiting Mn-catalyzed rapid corrosion
- Oxidizer raises slurry ORP
- Oxidizer reacts to precipitate out soluble manganese

Mechanism – Current Working Hypothesis for Units Exhibiting “Severe” Corrosion



MnO₂ deposits that physically contact metal surfaces, no matter how it occurs, serve as a galvanic cathode to promote corrosion of the metal.
~ Lutey

Aggressive ART Shell Corrosion



Aggressive Corrosion of ART Vertical Weld Seam



Thank You.



Questions



WFGD Chemistry & Performance Factors

*2014 Reinhold APC Conference
Louisville, KY – July 14-15, 2014*

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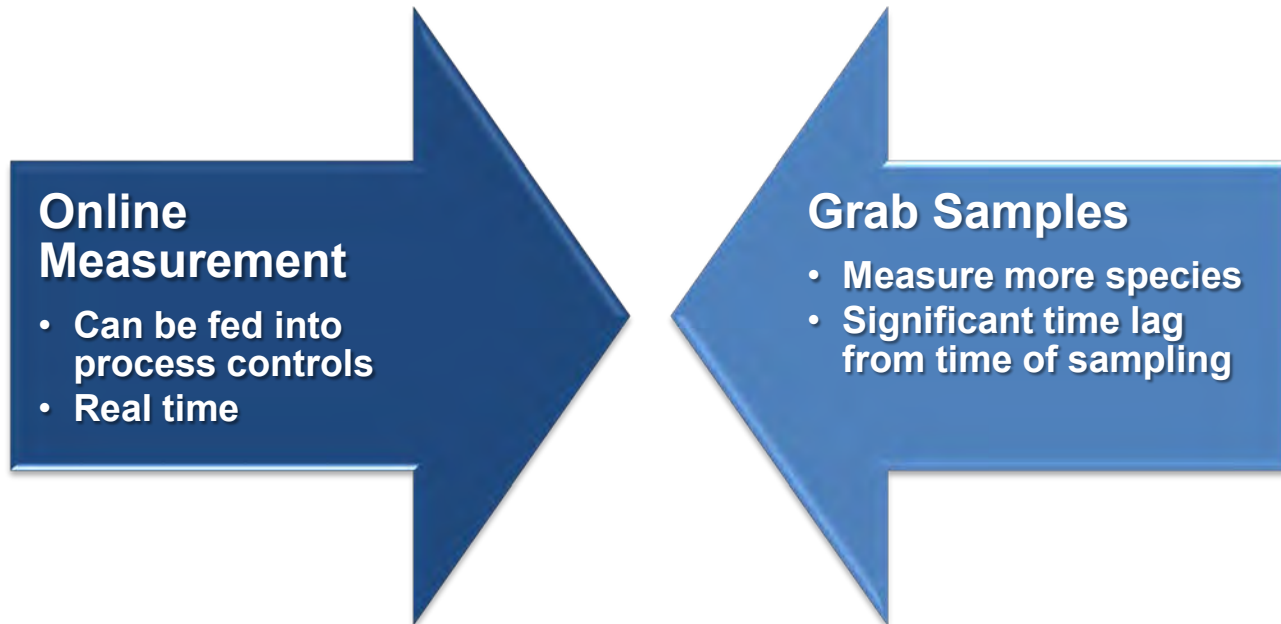
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Shannon R. Brown, AQCS Engineer

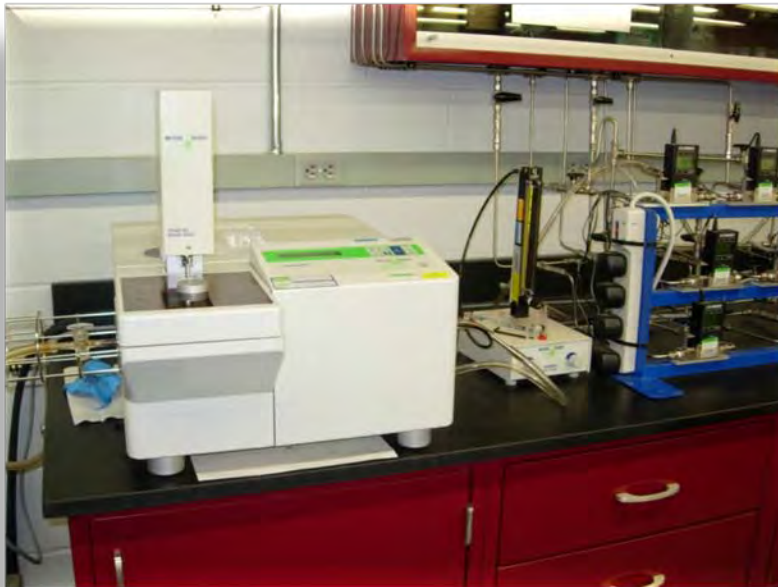
WFGD Chemistry: Characterization



Characterization

- **Online process measurement affords 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**

Notes about WFGD Characterization



- **Perform routine calibration and verification of online monitoring instrumentation**
- **Use proper sampling techniques for grab samples**
 - Glass sample containers needed for mercury analysis
 - Some analyses are time sensitive
- **Validate laboratories**
 - Due diligence in making sure results reported are accurate and repeatable
 - Certification

Reagent Feed System



Reagent Feed System

Why is Reagent Feed Control is Important

- › Control of excess carbonates and gypsum purity
- › Proper control of SO₂ removal and pH operating band
- › Smoother operation prevents batch feeding of reagent

Control Parameters for Optimization of Reagent Feed

- › Limestone Reactivity – B&W Design Standard
- › Limestone Grind – 95% passing 325 mesh typical
- › Limestone Slurry Density – 28% typical
- › Limestone Purity – control fines in dewatering and inerts entry into system

ORP Levels vs. Reagent Feed

- › Kinetic vs. Thermodynamic control of WFGD chemistry
- › High ORP levels can lower the system pH
- › pH control system will add limestone due to lower pH from ORP, not SO₂ demand

Limestone use in WFGD

- ▶ **Most common reagent for WFGD**
- ▶ **Provides the alkalinity which neutralizes the acid resulting from SO₂ absorption from the flue gas**
- ▶ **Ground and mixed with water to provide a slurry that is used as reagent in WFGD Absorber**
- ▶ **A solid gypsum product results from the WFGD Process**

What is Limestone?

Naturally Occurring Rock

▶ **Mineralogically**

- Calcite, substituted calcites
- Dolomite
- Inerts

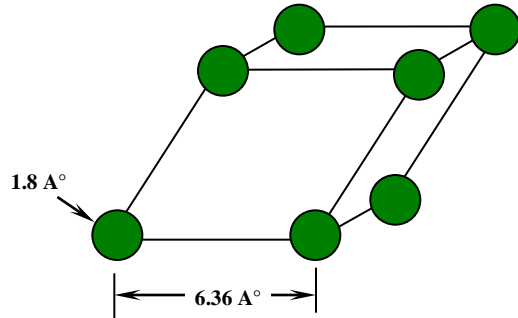
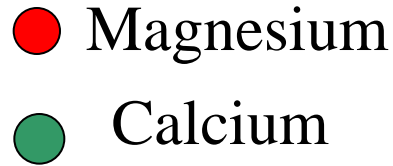
▶ **Chemically**

- CaCO_3
- $\text{CaCO}_3 \cdot \text{MgCO}_3$
- Inerts

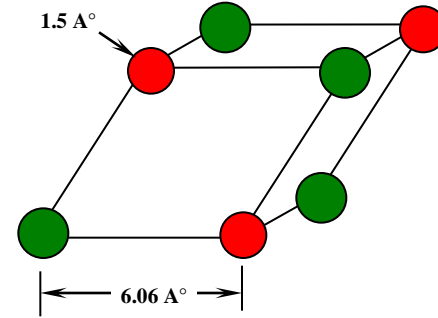
The alkalinity used to neutralize acid coming from SO_2 in flue gas



Crystal Structure of Calcite and Dolomite



Calcite



Dolomite

Reagent Use

- ▶ **SO₂ is absorbed into the recirculated slurry and forms sulfurous acid**
- ▶ **CaCO₃ dissolves to neutralize the acid and forms CaSO₄ and releases CO₂ as a gas**
- ▶ **Dissolved CaCO₃ reacts in the absorption zone first and the reaction is completed in the reaction tank**
- ▶ **The residence time of the reaction tank and the reactivity of the limestone determine the dissolved alkalinity (pH) in the tank and recirculated slurry**
- ▶ **The dissolved alkalinity sets how much SO₂ can be absorbed in the absorption zone**



Methods for Limestone Compositional Analysis

TGA

- Distinguishes mineralogical phases (Calcite, Dolomite)

XRF

- Elemental (CaO, MgO)
- Information on other elements

OTM, APG & TAPPI - Wet Chemical Test Methods

- Elemental (CaO, MgO, CO₂)
- Labor intensive

XRD – Identify crystal structures

- Differences in preferred orientation

ICP-MS

TGA

MgCO₃ fraction is not always 1:1 ratio with CaCO₃

- Calcitic limestone (<5%MgCO₃)
- Magnesian limestone (5-35% MgCO₃)
- Dolomitic limestone (>35% MgCO₃)

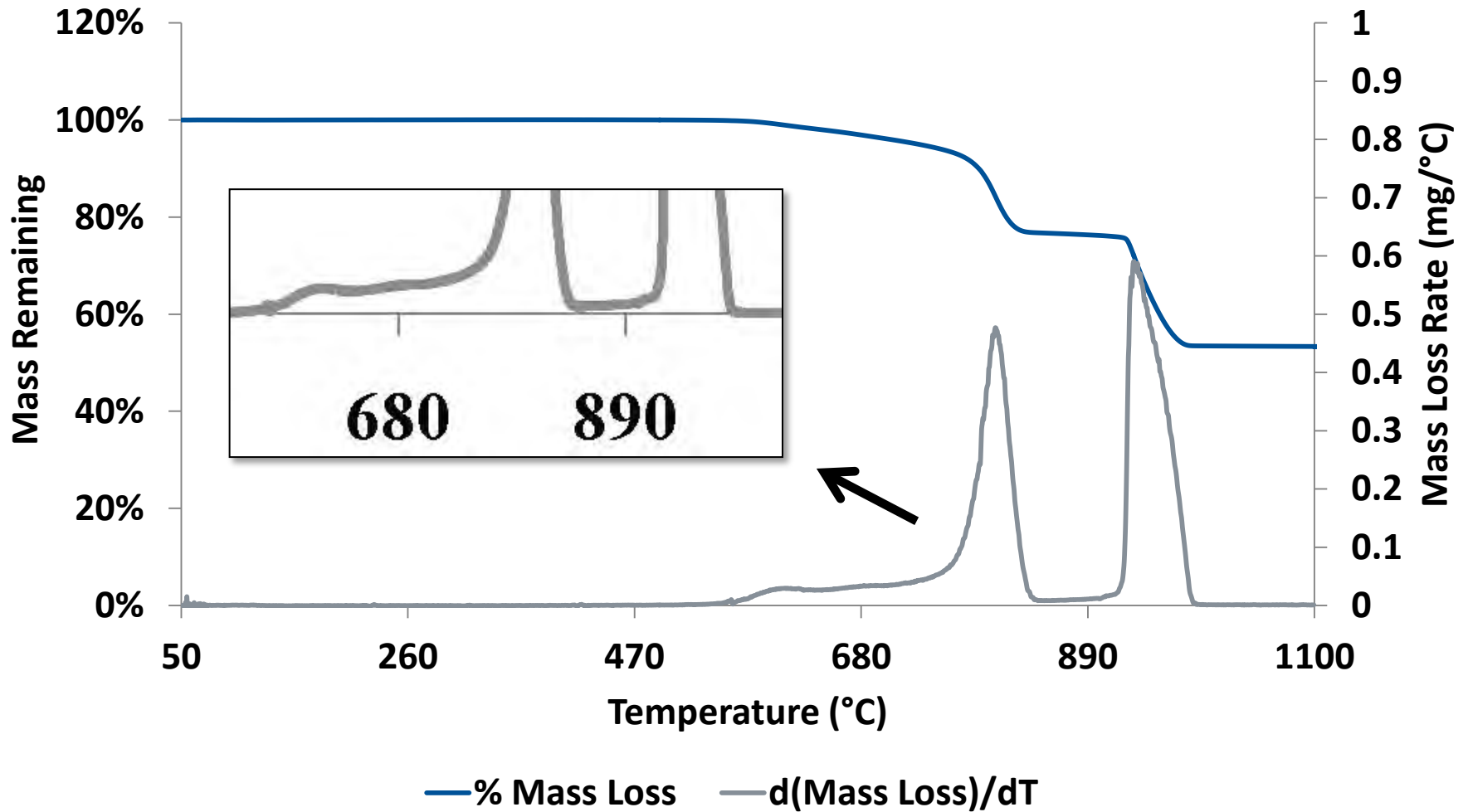
MgCO₃-CaCO₃ bonds are stronger

Some magnesian and dolomitic limestone will react

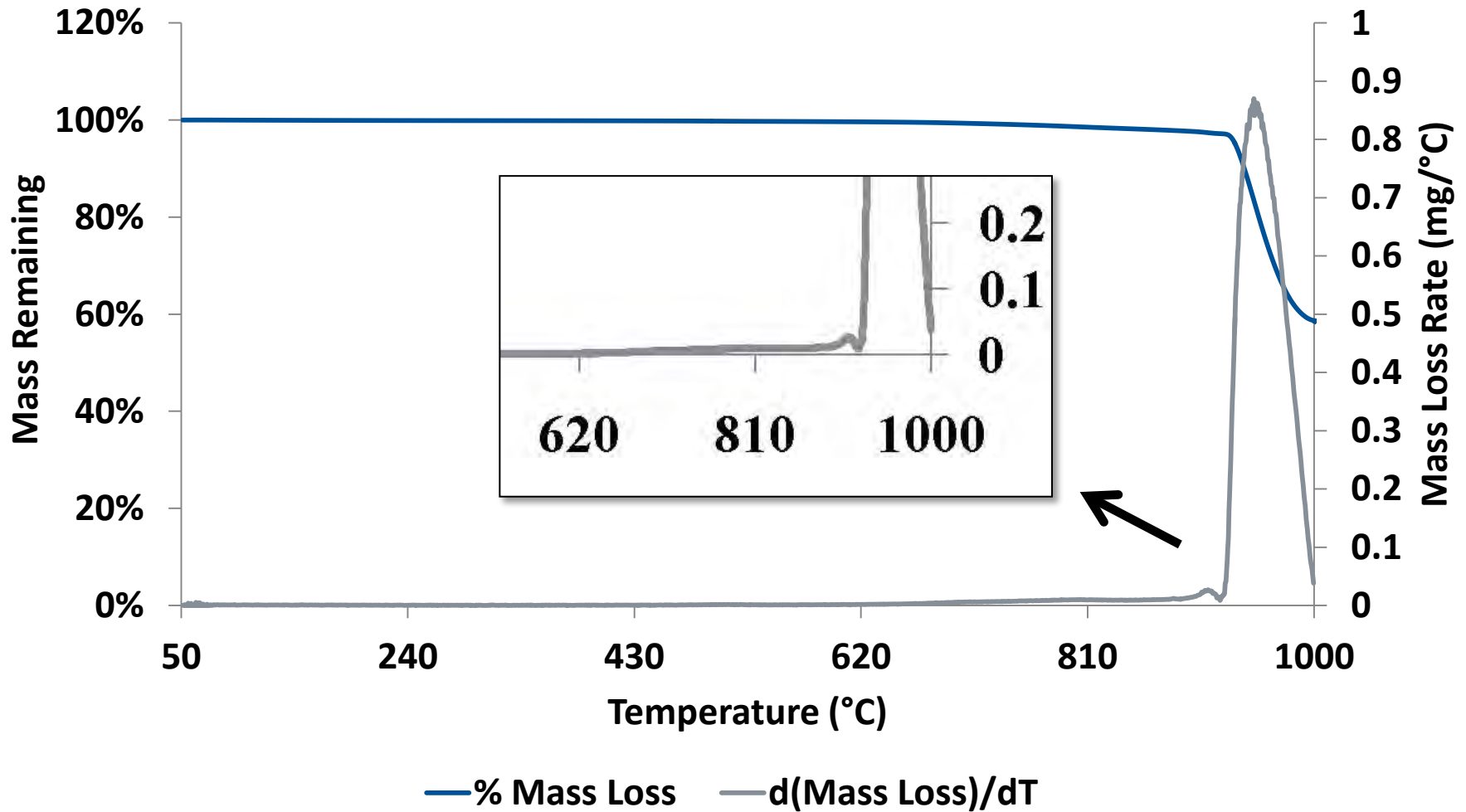
- MgCO₃-CaCO₃ interspacing in crystal lattice
- Exposure of more CaCO₃-CaCO₃ bonds

MgCO₃ availability is being studied

TGA Data - Dolomite



TGA Data – Argillaceous Limestone

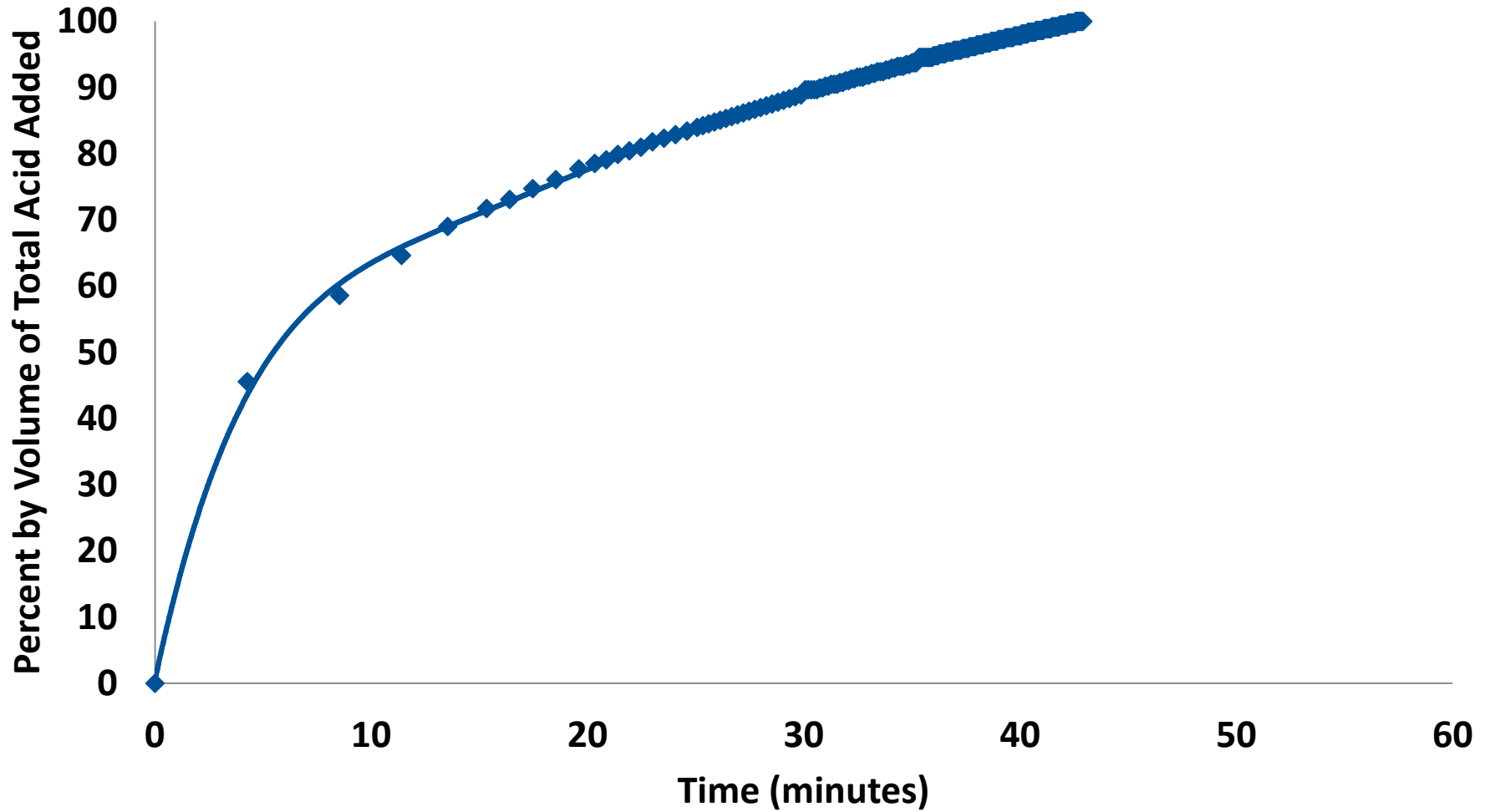


Limestone Reactivity Testing: State of the Industry

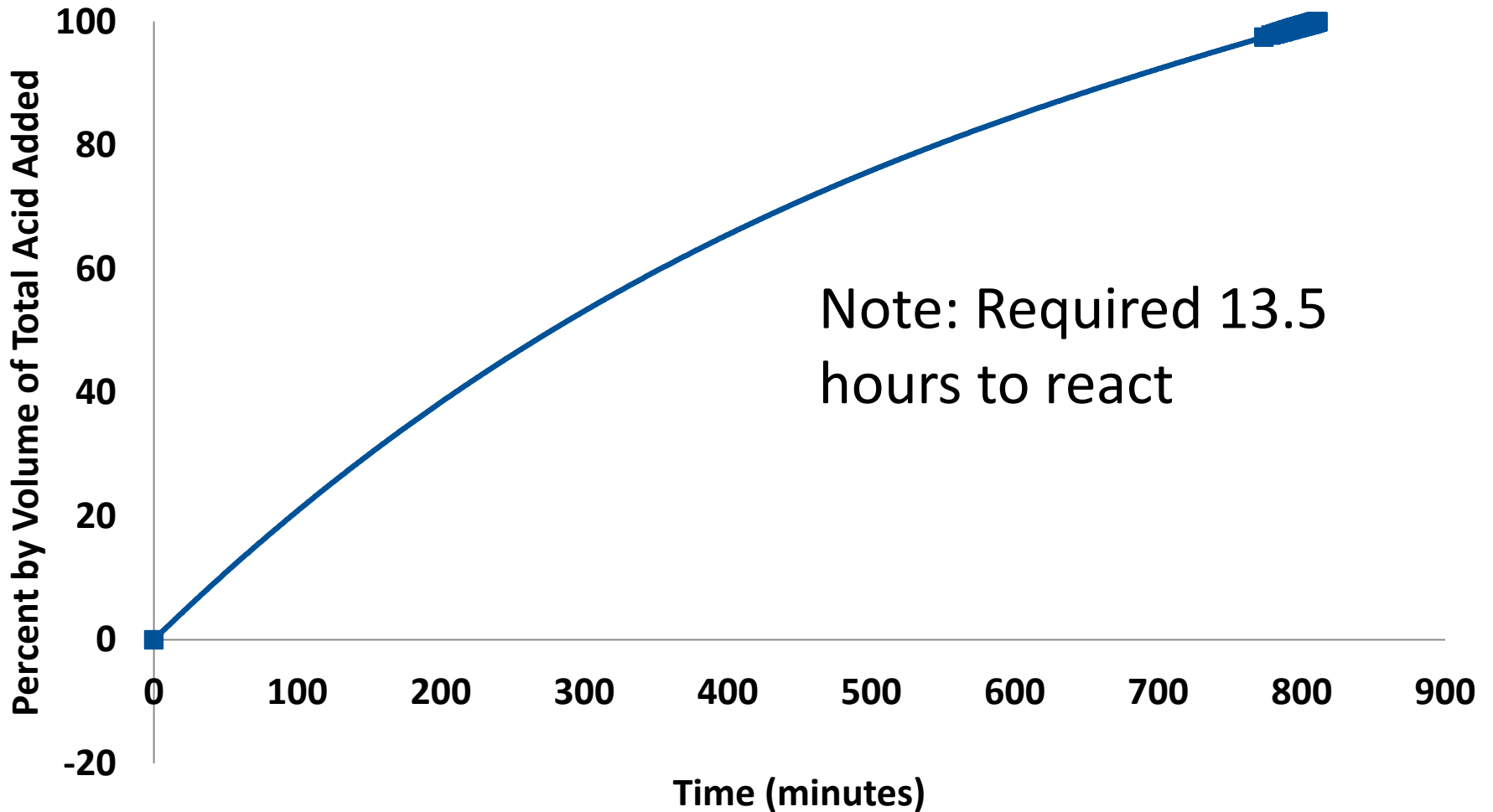
An Industry Standard Method for Determination of Limestone reactivity for Application to Limestone force-oxidized (LSFO) wet flue gas desulphurization (WFGD) does not presently exist

EPRI, OEMs, Utilities and Limestone Suppliers all have their own methods

Titration – WFGD Limestone



Titration – Dolomite



Reagent Usage

If your limestone stoichiometry has increased

- ▶ **Has your limestone quality decreased?**
- ▶ **Is your ball mill tuned?**
- ▶ **Is your limestone feed tuned for changes in tower load?**

$$\text{Stoichiometry} = 1 + \left(\frac{\text{Moles of } CO_3 - 2 * \text{Moles of } Mg}{\text{Moles of Sulfur}} \right)$$

LIMESTONE BLINDING

SULFITE BLINDING –

High pH at surface of limestone promotes reaction between dissolved calcium and bisulfite ions

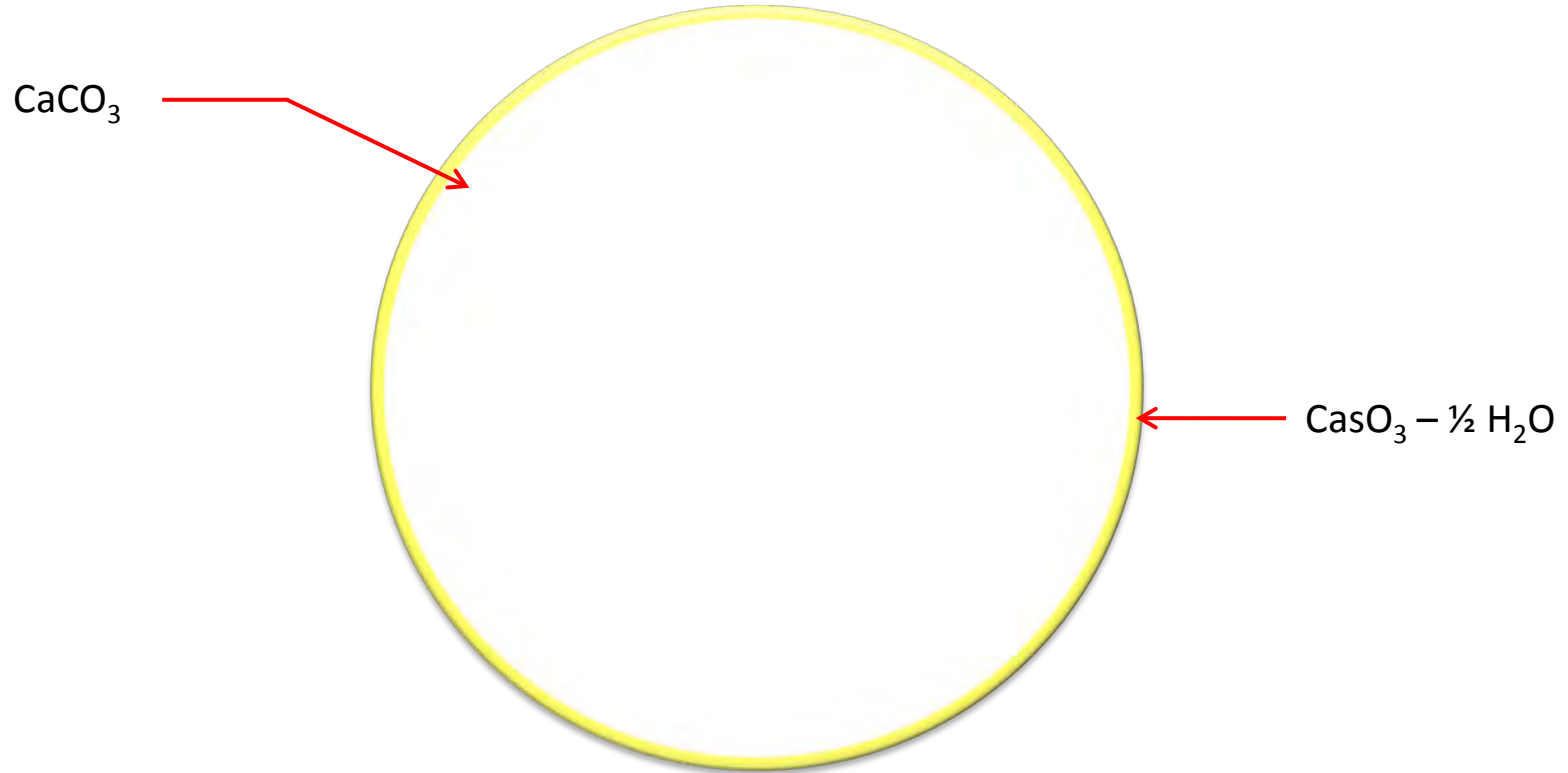


ALUMINUM FLUORIDE BLINDING –

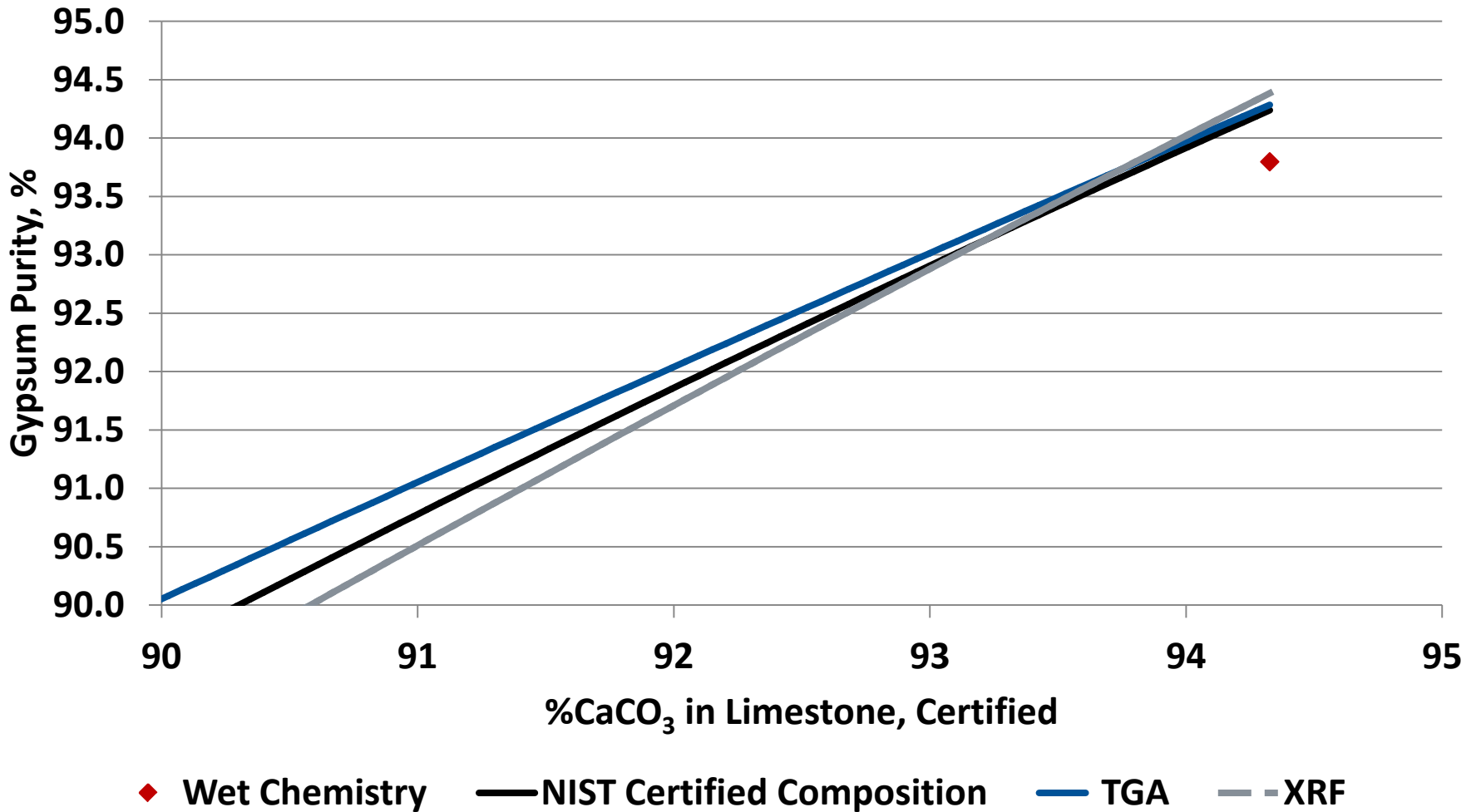
Aluminum is present as Al_2O_3 , $\text{Al}(\text{OH})_3$, and Fluoride as CaF_2

When in a certain ratio of concentrations, Soluble Aluminum and Fluoride forms a complex and coats limestone particles

LIMESTONE BLINDING



Sensitivity of Gypsum Purity

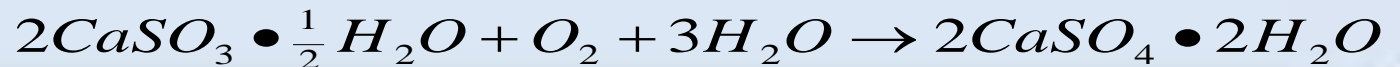
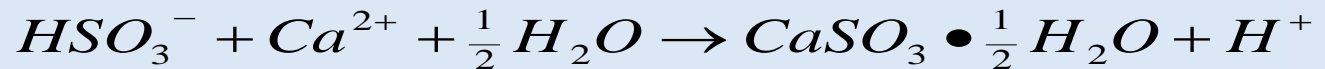
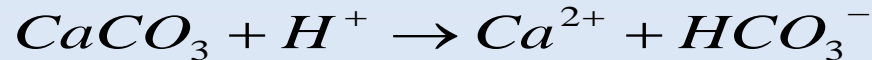
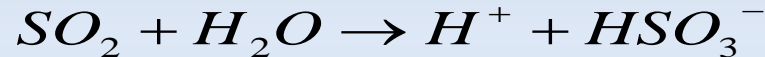


SO_2 to $CaSO_4$ Basic Equations

Basics of conversion

- › The conversion from $SO_2(g)$ to $HSO_3^-(aq)$ 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 dissociate. This allows for the
- › formation of the calcium sulfite, $CaSO_3$
- › Oxidation to $CaSO_4$ in ART

Equations:



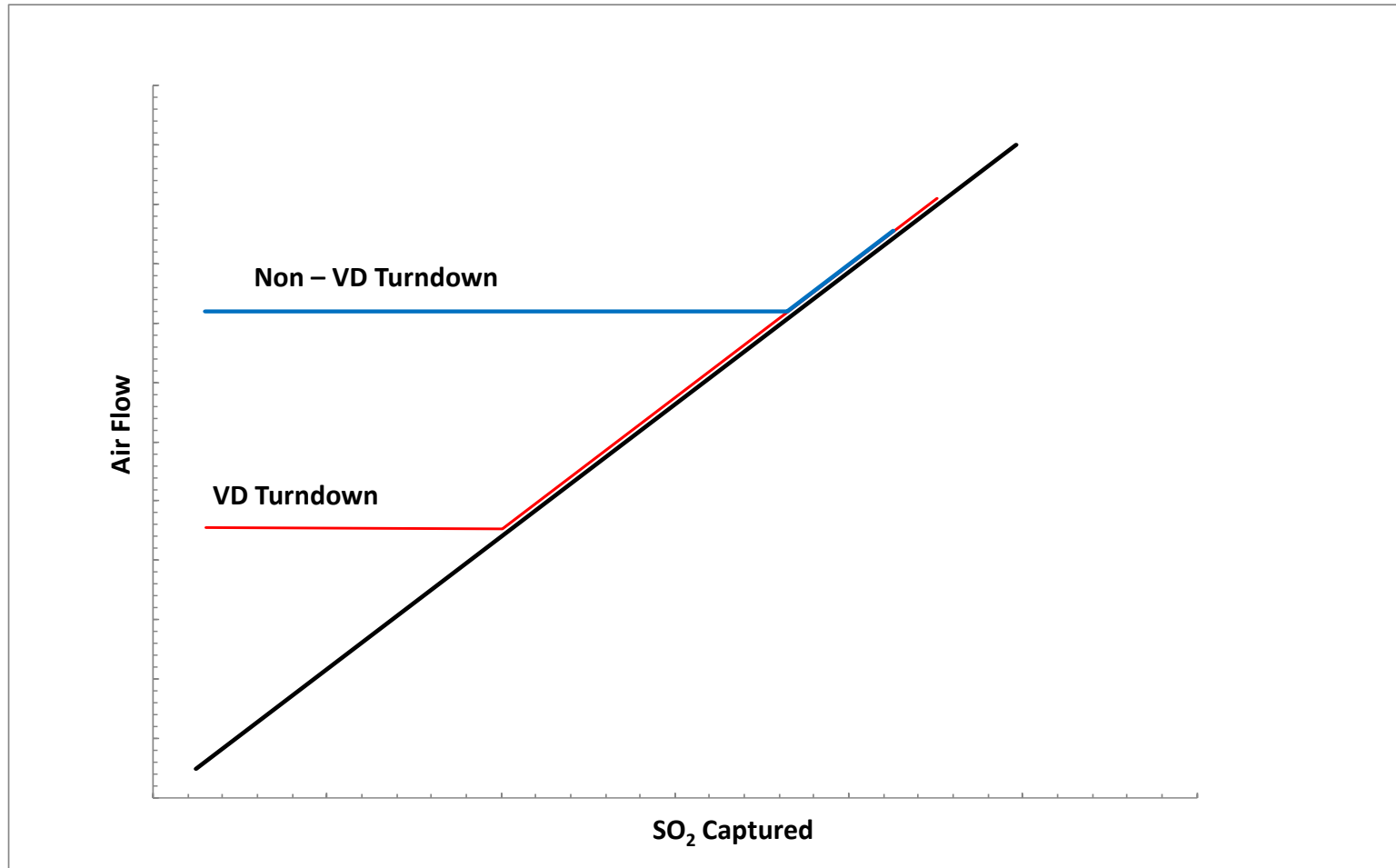
Oxidation Air

Calculated Stoichiometric Air Flow

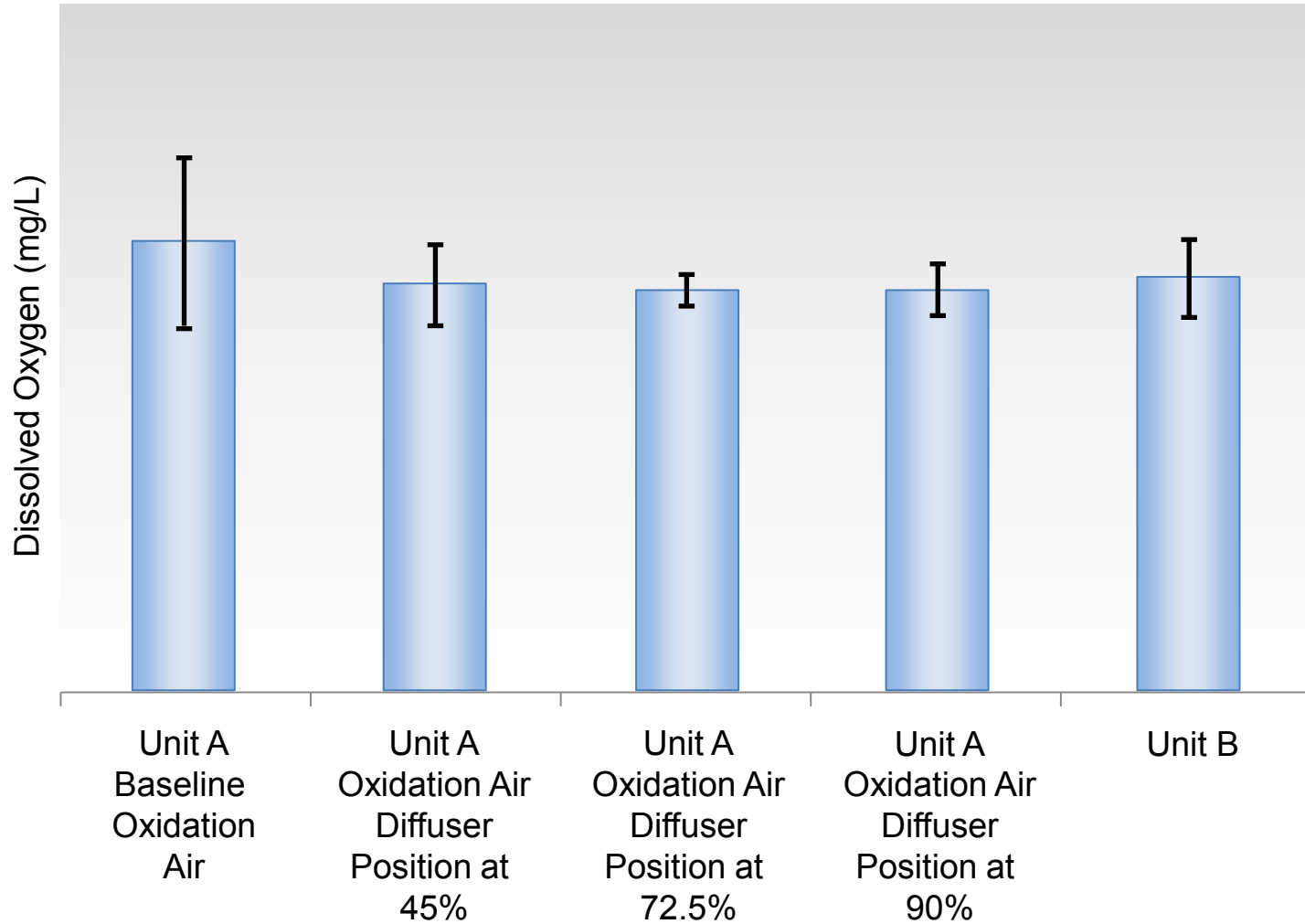
- ▶ Stoichiometric ratio based upon design standards
- ▶ Sized for full load based upon design sulfur coal and full load boiler operation
 - Some compressors have an integrated variable diffuser vane allowing for a lower turndown to 45% of full load capacity
- ▶ During low sulfur coal operations, oxidation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



Oxidation Air Example Oxidation Air Flow Control Curve



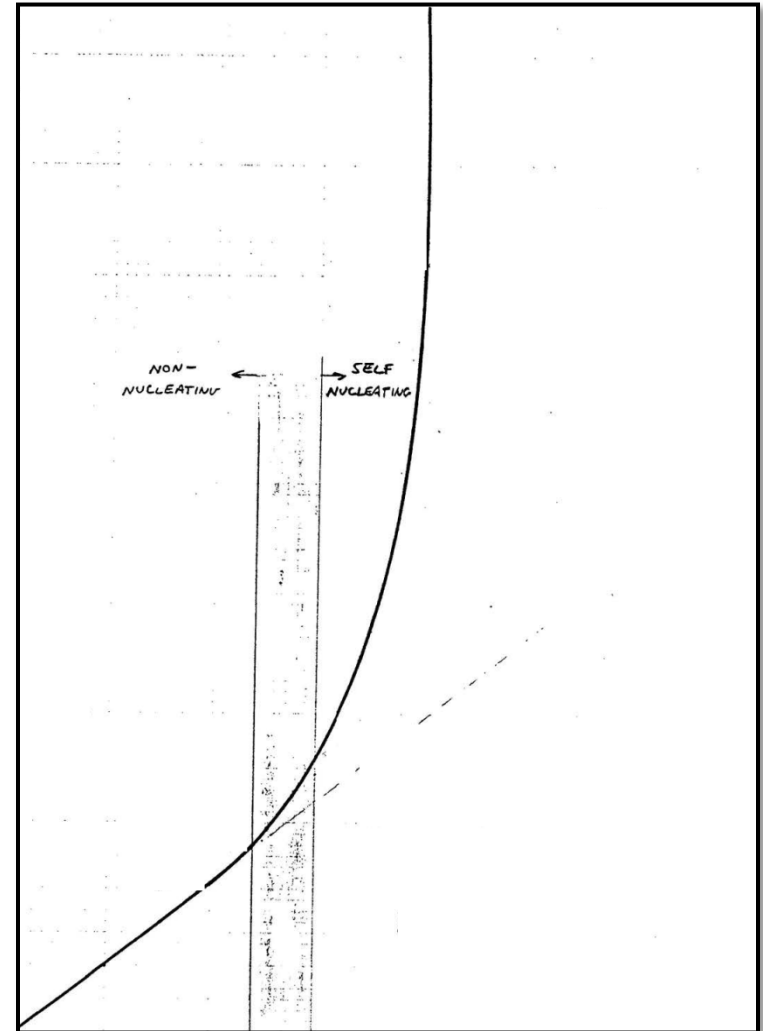
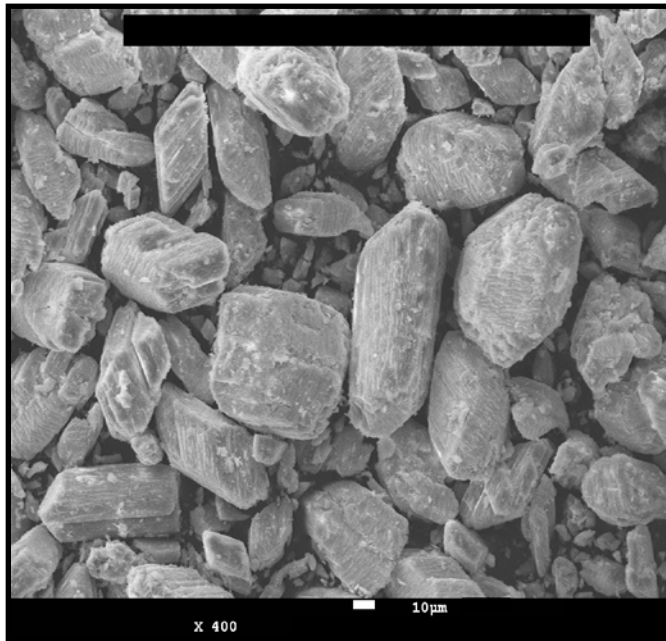
Oxidation Air Turndown – Parametric Test Results



Relative Saturation of Gypsum Crystals

Super-saturation

- Secondary nucleation (Non)
 - Min TSS value
- Primary nucleation (Self)
 - Max TSS value
- Ratio of Calcium to Sulfate concentrations



Gypsum Product Formation

If your gypsum purity decreased by over 1%

- **Does your system have more inerts**
 - **Fly ash, change in limestone, recycled inerts**
- **Is your limestone feed rate tuned to the load?**

If your gypsum average particle size has changed

- **Is their adequate oxidation?**
- **Does the system have significant fines buildup?**
- **Has the Ca/S ratio changed?**

Importance of Knowing RS

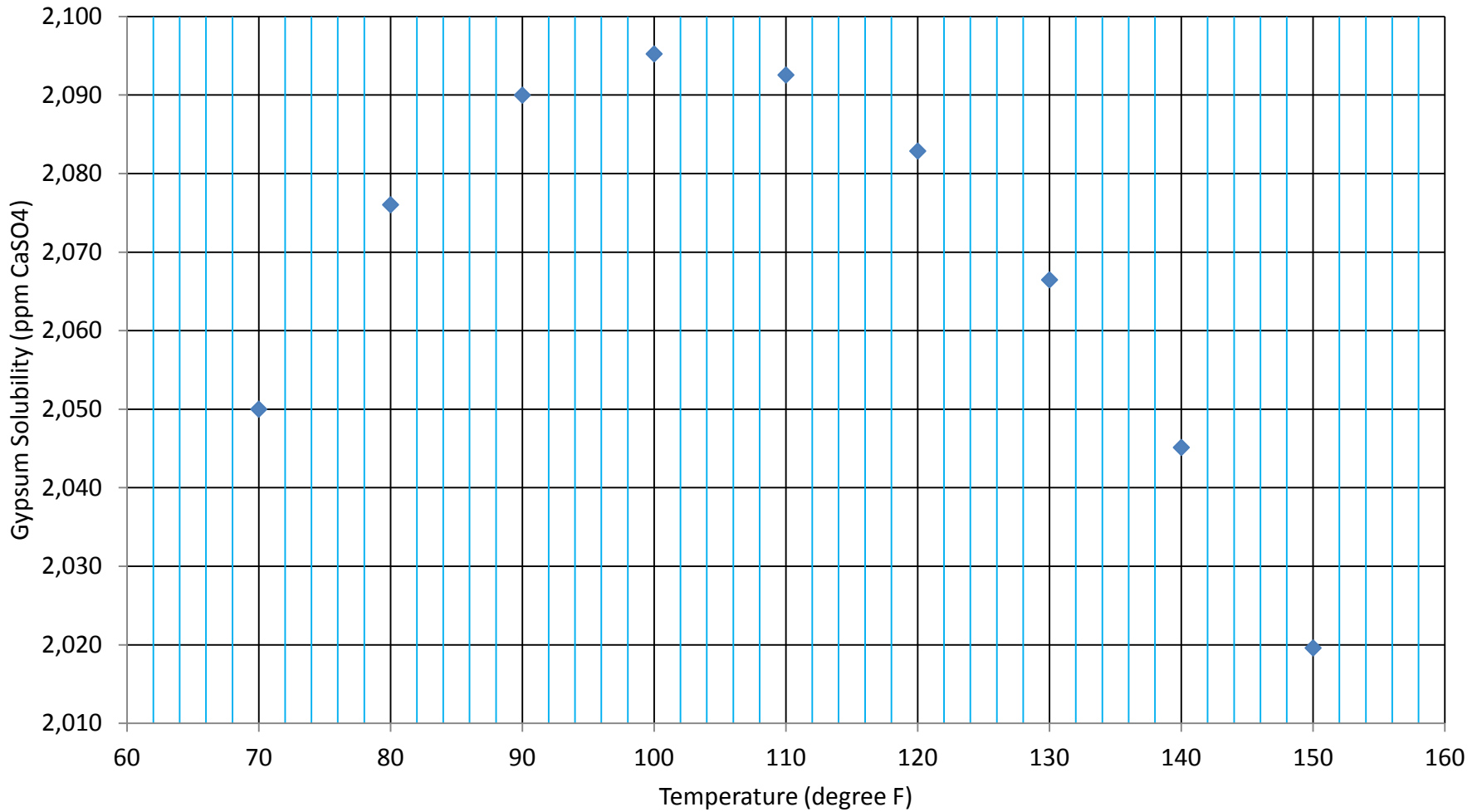
- **RS can be used to predict the gypsum crystal rate and severity of scaling and/or deposition**
- **Scaling/deposition**

Gypsum Supersaturation – ART Slurry Filtrate

- **Saturation (S) – Amount of gypsum that can dissolve in a given volume of water at a specified temperature (~ 2.1 g/L).**
- **Supersaturation (SS) – Amount of gypsum that can dissolve in a given volume of ART slurry filtrate at a specified temperature (~ 55° C), greater than saturation due to the operating conditions of the WFGD system.**
- **Relative Saturation (RS) – Relative measure of supersaturation (RS > 1) existing in the ART slurry filtrate;**

$$RS = SS/S \quad \text{and also, } RS = [Ca^{+2}] \cdot [SO_4^{2-}] \cdot [H_2O]^2 / K_{sp \text{ gypsum}}$$

Gypsum Solubility as a Function of Temperature



Gypsum Relative Saturation (RS) and ART Scaling

RS Affects the Rate of Gypsum Crystallization



Higher RS Increases the Rate of Crystallization



Faster Rate of Crystallization Increases Potential for Nucleation and Smaller Gypsum Crystals

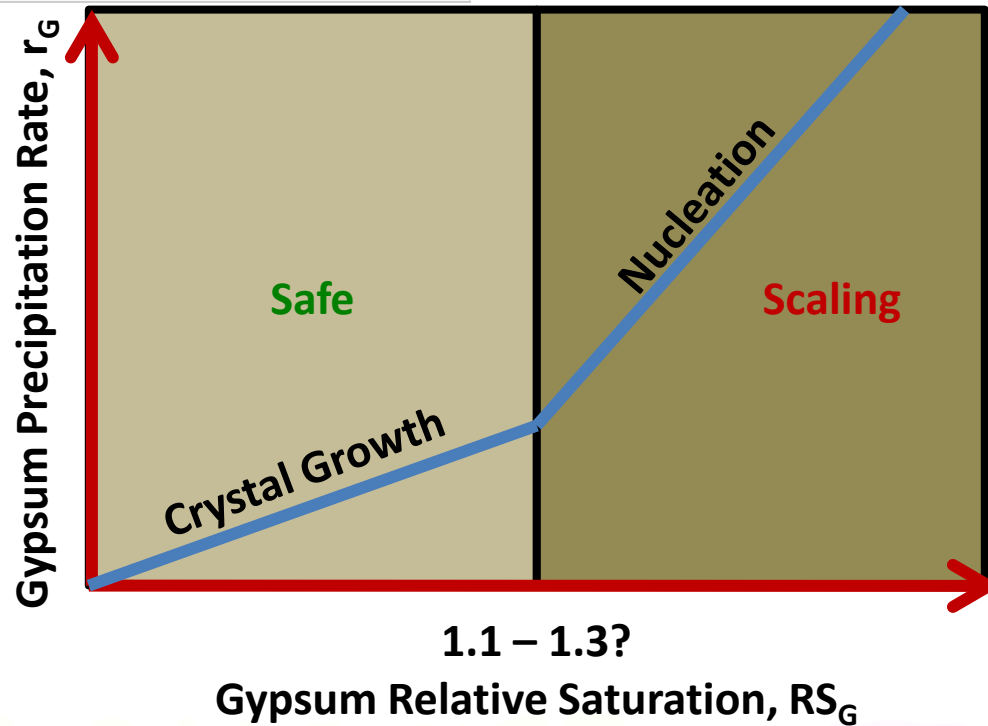


Nucleation Increases Potential for Scaling and/or Deposition

Two Types of Gypsum Precipitation

Control of Gypsum Crystal Growth

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



Deposit Analysis

- ▶ **Elemental analysis (XRF)**

- ▶ Provides information on the bulk composition of the sample

- ▶ **SEM/EDS**

- ▶ Can provide information on the morphology of the scale and elements present as a function of location

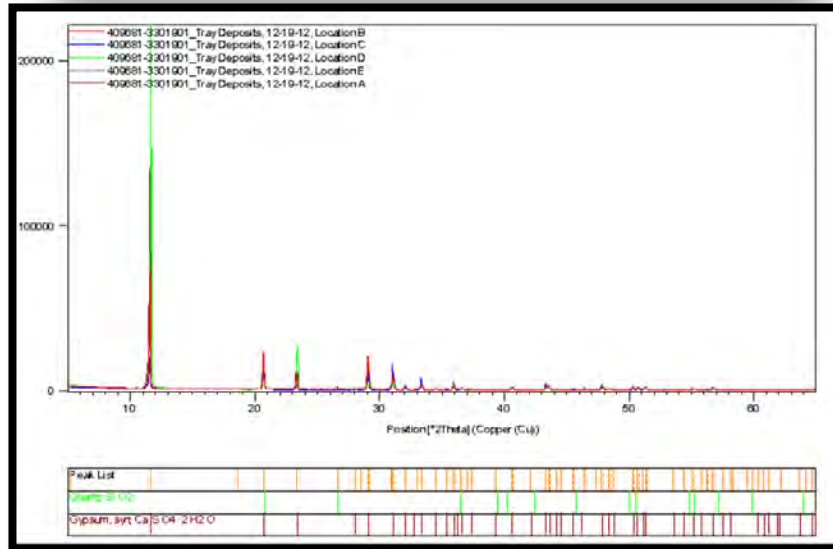
- ▶ **XRD**

- ▶ Used to identify crystal structure

Deposit Analysis



	Tray Deposits 12/19/2012	Deposit not adhered in eghtator
Client's Sample ID:	3301901	3301902
Material type:	Gypsum	Gypsum
CTL Sample ID:	3301901	3301902
Analyte	Weight %	Weight %
SiO ₂	5.10	1.02
Al ₂ O ₃	0.39	0.21
Fe ₂ O ₃	1.84	0.42
CaO	30.57	34.97
MgO	0.98	0.78
SO ₃	42.47	49.72
Na ₂ O	0.04	0.09
K ₂ O	0.14	0.09
TiO ₂	0.16	0.13
P ₂ O ₅	0.03	0.02
Mn ₂ O ₃	0.15	0.18
SiC	0.02	0.02
Cr ₂ O ₃	<0.01	<0.01
ZnO	0.02	<0.01
BaO	<0.01	<0.01
L.O.I. (950°C) ^a	21.06	12.63
Total	100.57	100.17
Calculated per ASTM C 471		
Gypsum % purity	91.34	51.93
SO ₃ combined as Gypsum	42.48	24.15
excess SO ₃	-0.01	25.57
% Anhydrite, CaSO ₄	-0.02	43.47
%CaO combined as Gypsum	29.75	19.91
%CaO combined as Anhydrite	-0.01	17.91
excess CaO	0.83	0.15
%CaCO ₃	1.12	0.27
% MgCO ₃	-2.05	-1.59
Thermogravimetric Analysis		
L.O.I. (ambient-45 °C)	0.24	0.36
L.O.I. (45-220 °C)	19.07	10.83
L.O.I. (220-550 °C)	1.25	0.90
L.O.I. (550-650 °C)	0.60	0.78



Deposit Analysis



Scale-Slurry
Interface

- ▶ Crystalline scale is predominantly gypsum
- ▶ Much higher fluoride concentration at scale-alloy interface than elsewhere in the scale
- ▶ Variable attack severity, morphology and locations

Scale-Alloy
Interface

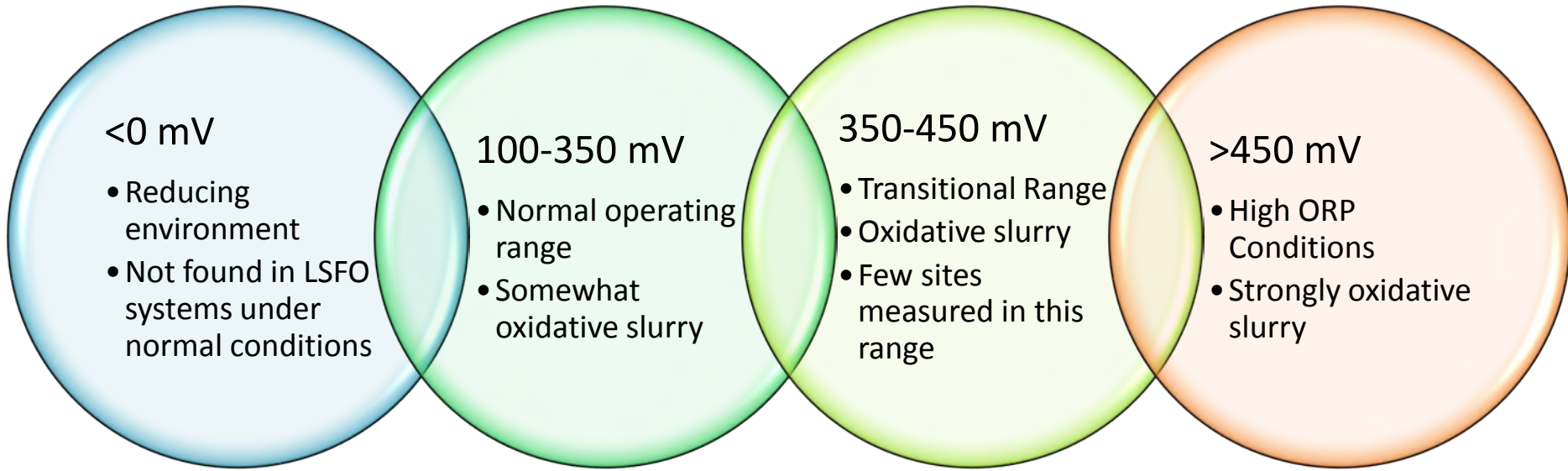
What is ORP?

- ▶ **Oxidation Reduction Potential (ORP)**
 - **A single voltage measurement against a reference electrode**
 - ▶ Measurement technique similar to pH
 - ▶ Can be monitored on-line
 - **Measures tendency for a solution to donate or accept electrons**
 - **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**
 - ▶ Indicator of Problem with Oxidation – Check Ox Air Compressors

Why is ORP important?

- ▶ **High ORP Excursions can Disable Bioreactors**
- ▶ **High ORP can Promote Corrosion via manganese oxide deposition**
- ▶ **Oxidation state often controls solubility & phase partitioning of many species, particularly dissolved metals – ORP can affect ease of treatment in Waste Treatment System**
- ▶ **ORP may affect Reagent Use in Wastewater Treatment**

LSFO WFGD ORP Ranges



For operating WFGD Units, ± 50 mV is common.

ORP and Chemistry in a WFGD

ORP Range	Selenium	Mercury	Manganese
≤300 mV	Selenite dominant	Associated with solids dominant	Dissolved ion
300-500 mV	Transitional	Transitional	Transitional
≥500 mV	Selenate dominant	Dissolved ion dominant	Oxide precipitate

WFGD Redox Chemistry

The species that loses electrons is oxidized.

The species that gains electrons is reduced.



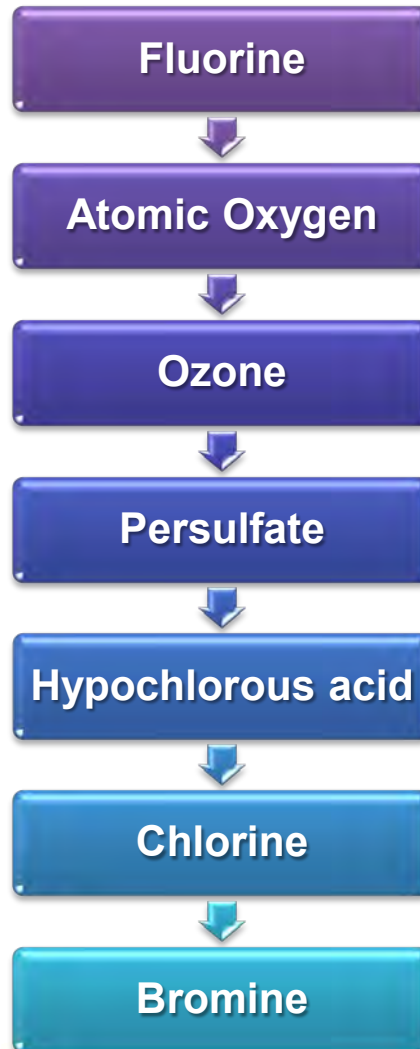
The species that takes electrons is an oxidizing agent (oxidizer).

The species that gives electrons is a reducing agent (reducer).

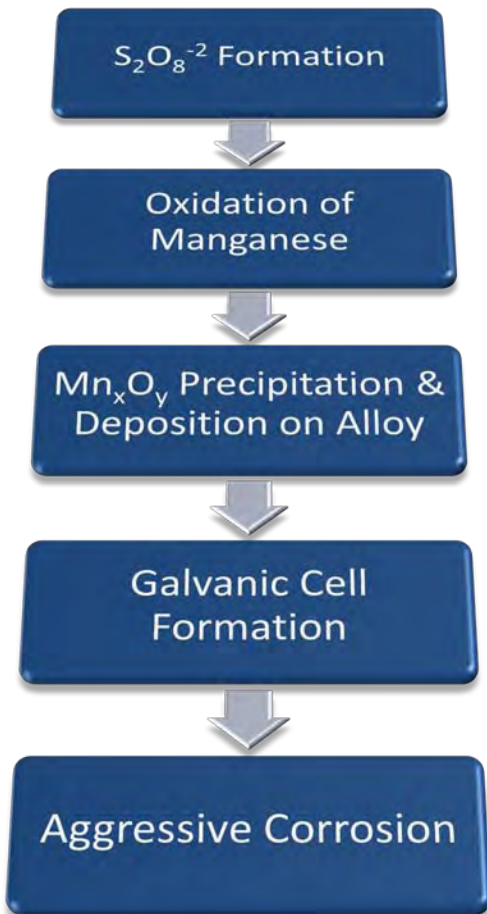
Redox Chemistry within the WFGD



Strength of Oxidizers



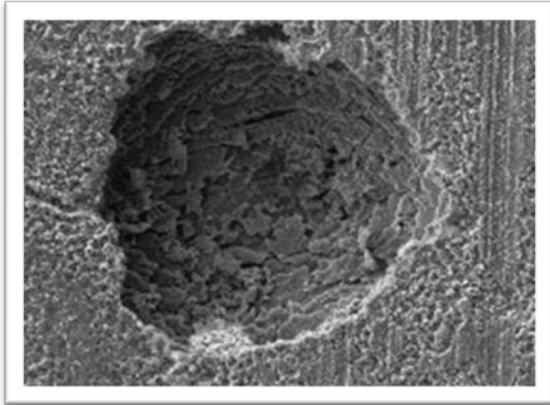
Mechanism – Current Working Hypothesis for Units Exhibiting “Severe” Corrosion



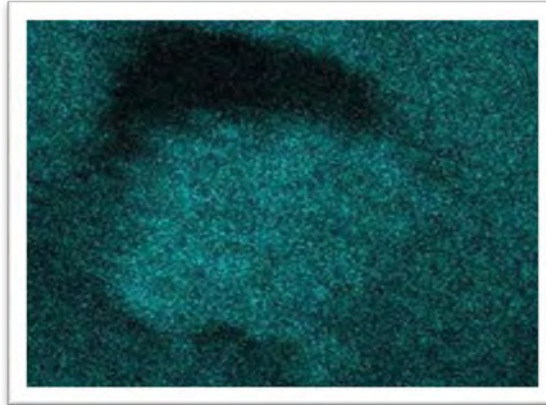
MnO₂ deposits that physically contact metal surfaces, no matter how it occurs, serve as a galvanic cathode to promote corrosion of the metal.

-Lutey

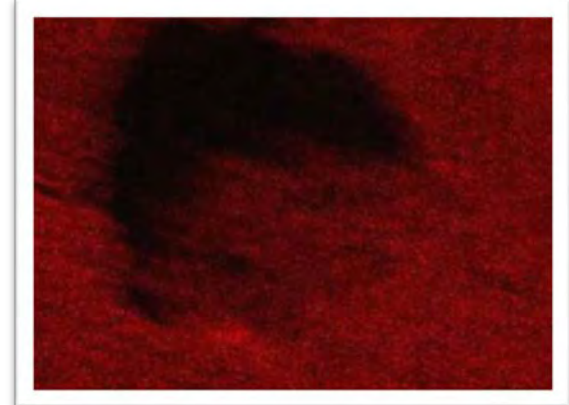
EDS Maps – Bench Scale Specimen - Pit in Weld Seam on Specimen Top



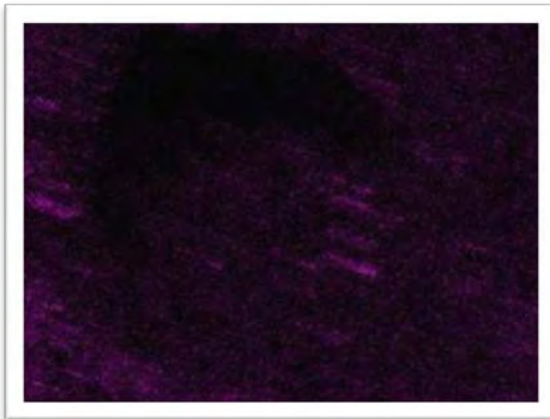
Pit @ 350X



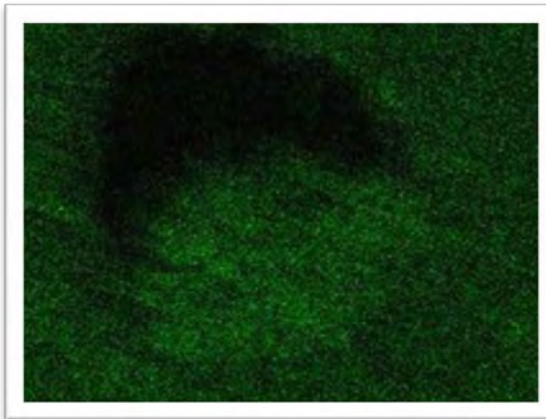
EDS Cr Map



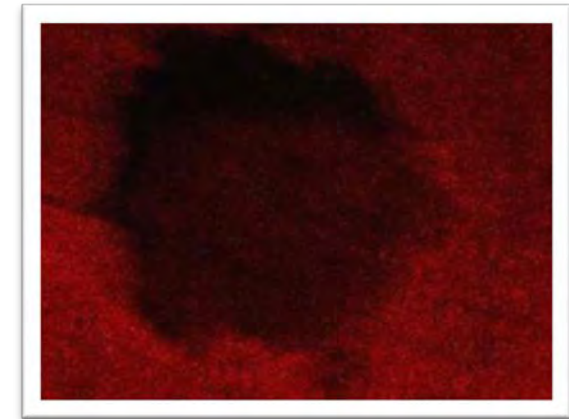
EDS O Map



EDS Ca Map



EDS F Map

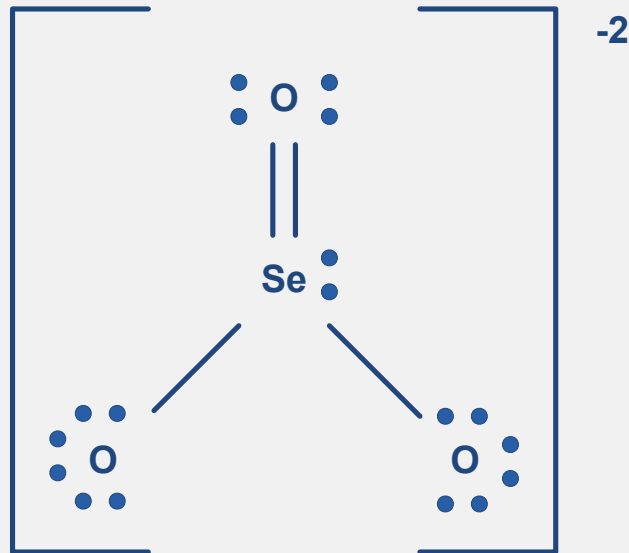


EDS Mn Map

- ▶ Most of the F not associated with Ca
- ▶ No Mn inside of the pit
- ▶ Mn that is present surrounds the pit

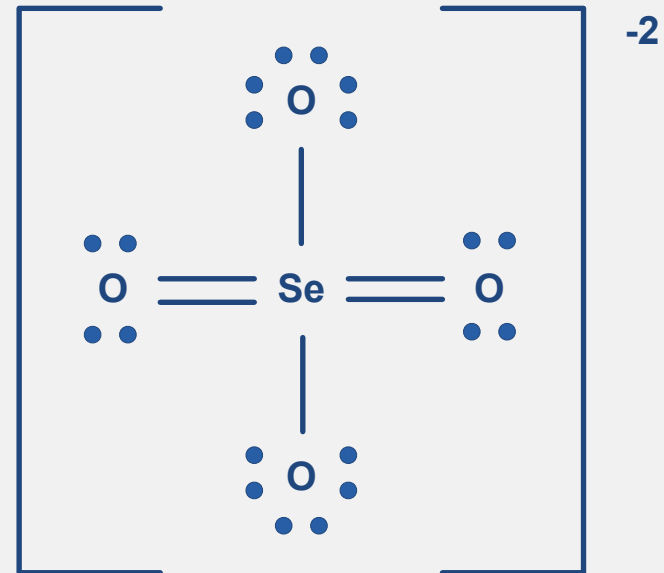
Selenium Chemistry

Selenite



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

Selenate



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

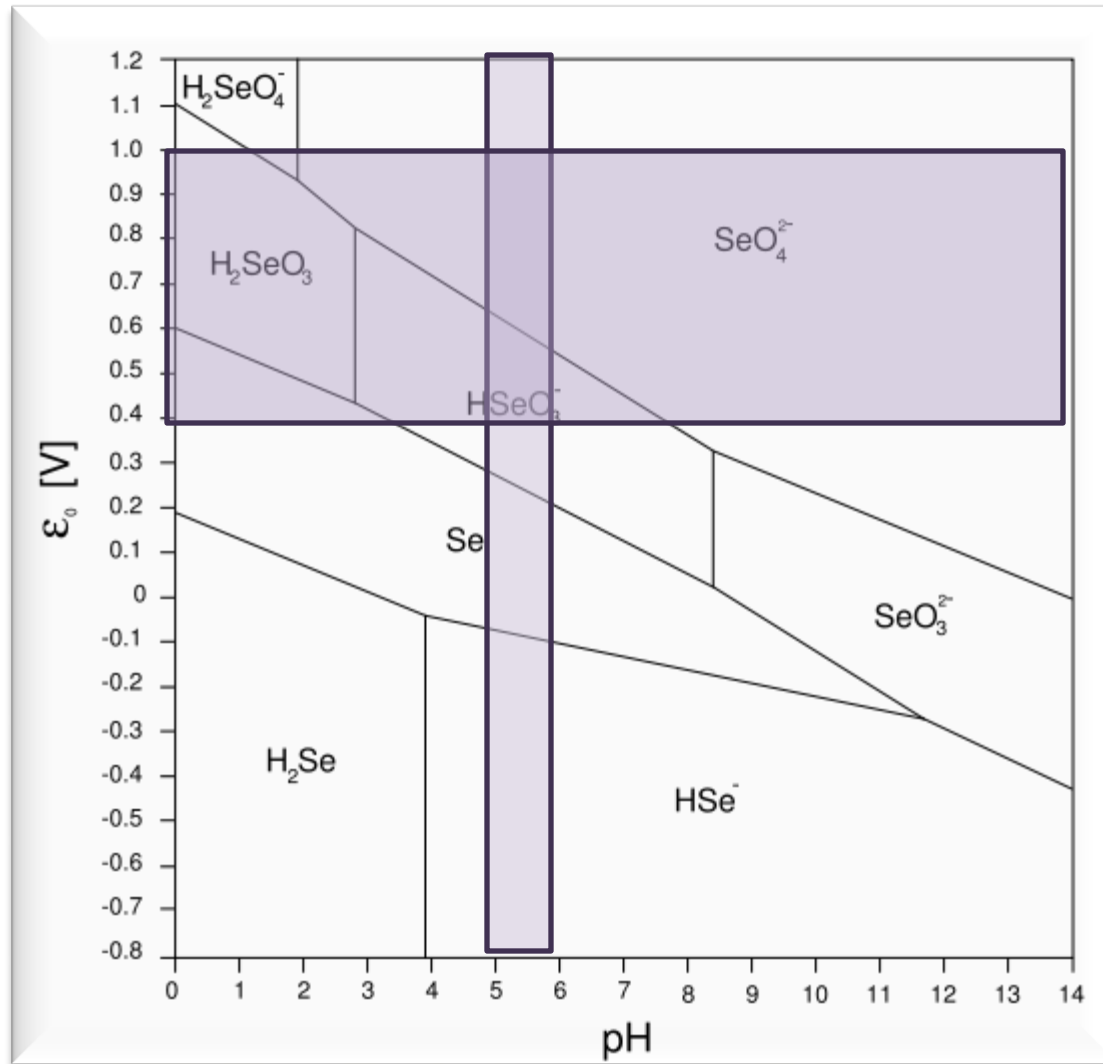
Selenium

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

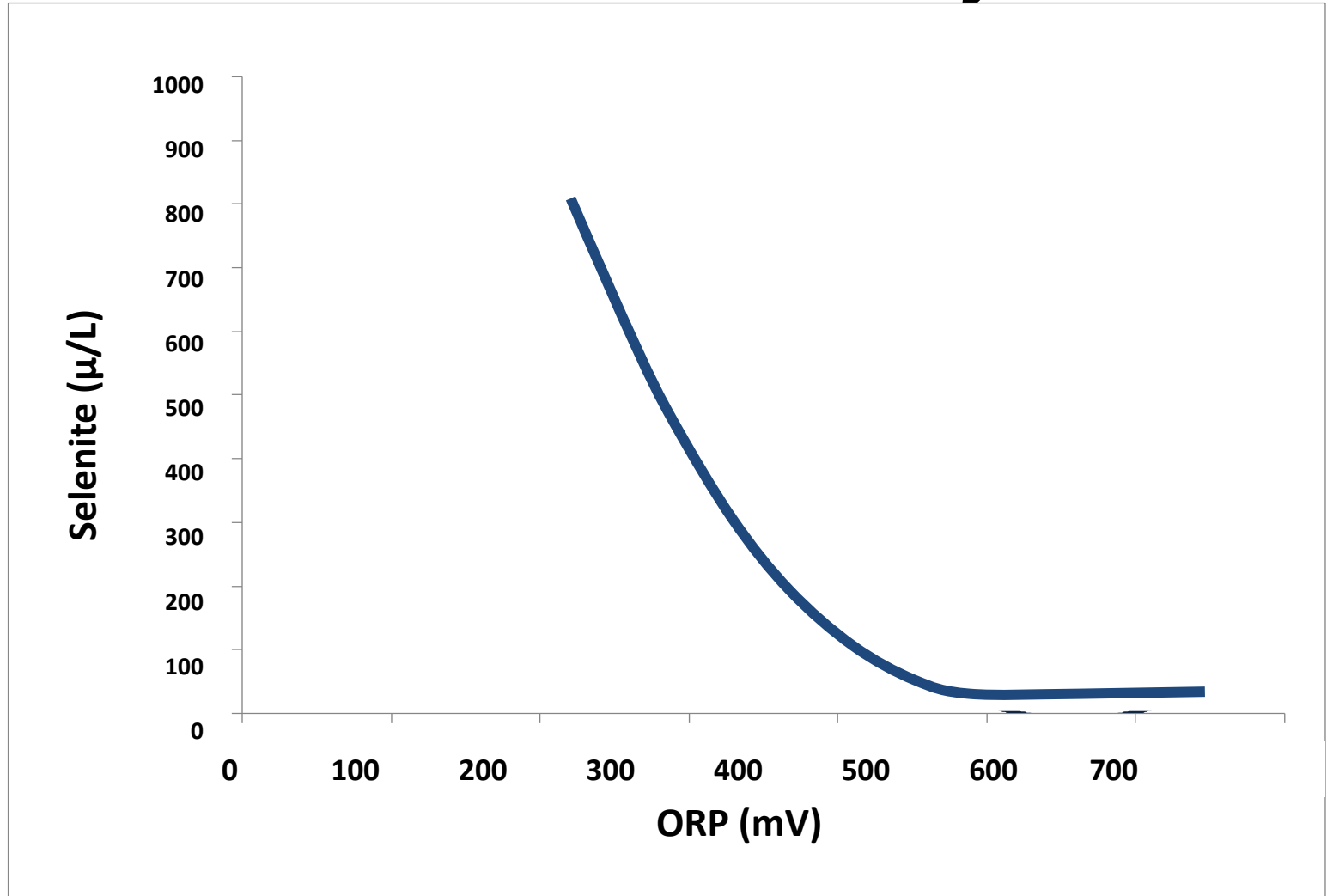
Selenate formation is problematic

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

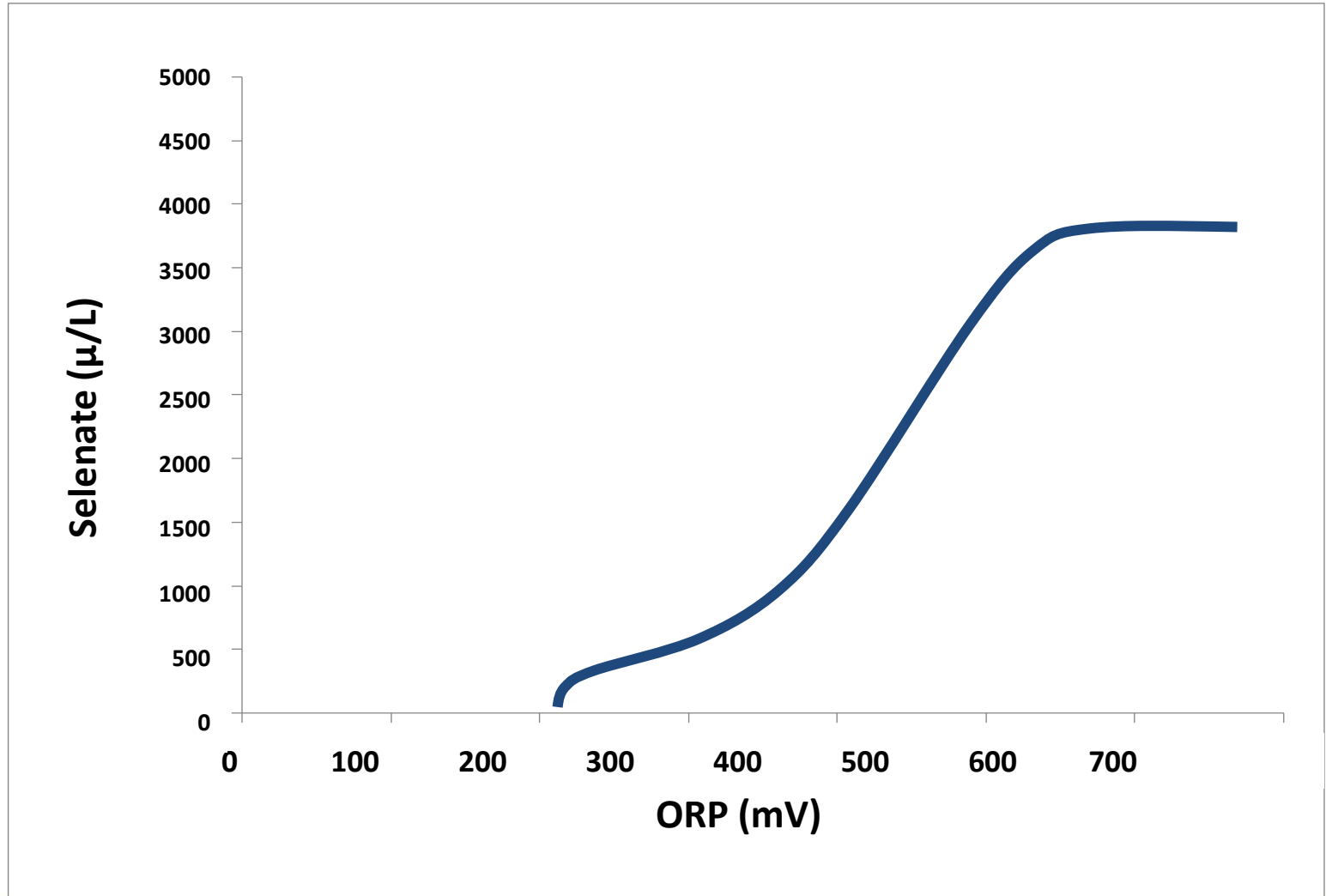
Phase Partitioning– Selenium



Selenite vs. ORP in WFGD ART Slurry



Selenate vs. ORP in WFGD ART Slurry



Selenium

In a ORP environment < 300 mV

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

In a ORP environment > 300 mV

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

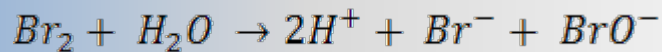
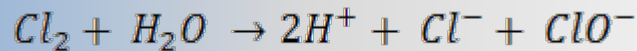
High ORP & pH Drop

- **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



High ORP
levels



Hypochlorite
formation &
lower pH

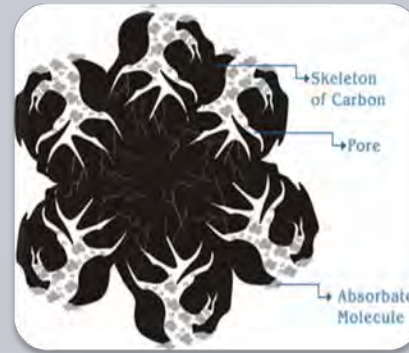
Forms of Mercury



- Elemental Mercury
- Vapor
- Sparingly Soluble



- Oxidized Mercury
- Readily Soluble Ion
- $HgCl_2$, $HgBr_2$



- Particle Bound Mercury
- Mercury is Adsorbed to the Particle



- Mercury Sulfide
- **Subset of Hg^{+2}**
- Insoluble Compound
- Stable compound

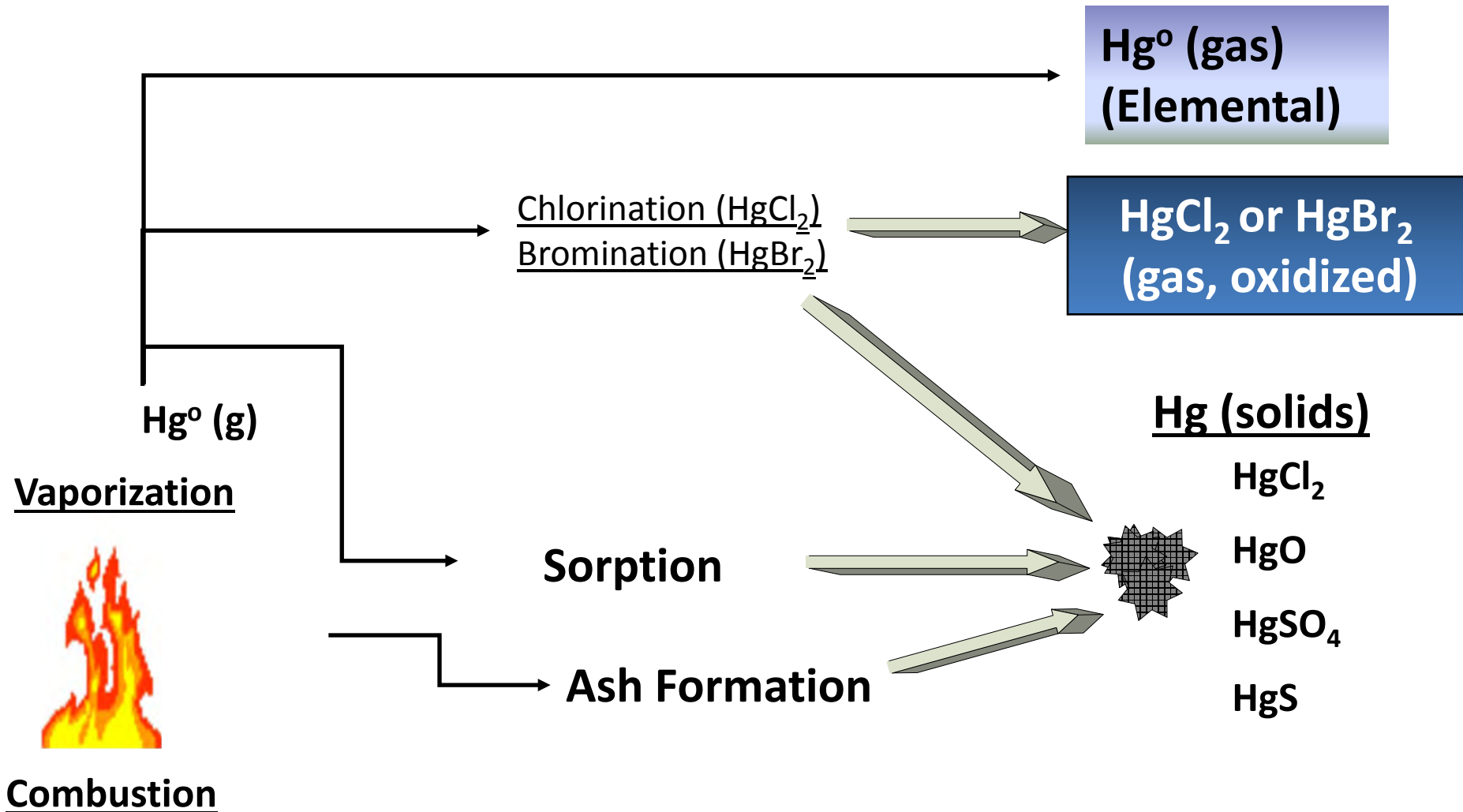
Hg⁰ image : <http://www.newmoa.org/prevention/mercury/projects/legacy/religious.cfm>, Accessed: 17 Sept 2013

Hg⁺² image : <http://www.enn.com/pollution/article/43796> Accessed 17 September 2013

PAC image: Jankura, Bryan. "Wygen 1 2006 Mercury Control Project: Background, Equipment and Test Results." 5 April 2007.

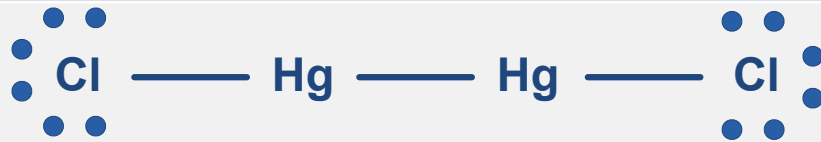
HgS image: http://www.dartmouth.edu/~rpsmith/Heavy_Metals.html Accessed 18 September 2013

Fate of Hg in Coal Combustion



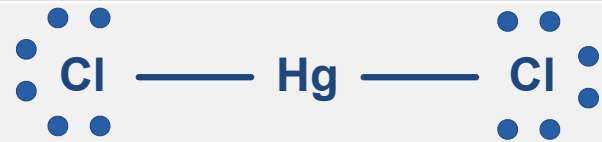
WFGD Mercury Chemistry

First Ionization



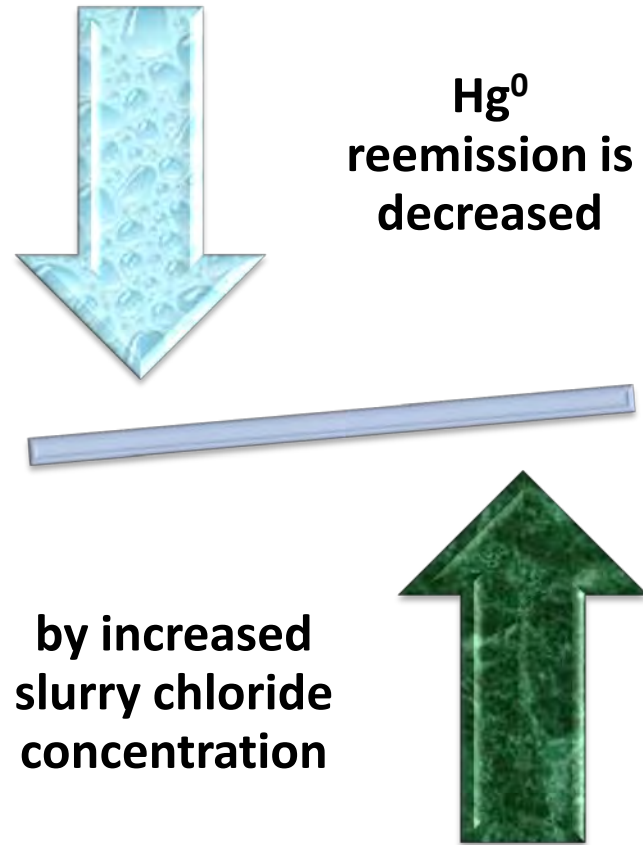
- HgCl, Hg₂Cl₂
- Mercury in +1 oxidation state
- Less Stable

Second Ionization



- HgCl₂
- Mercury in +2 oxidation state
- More Stable

WFGD Chemistry: Halide Concentration

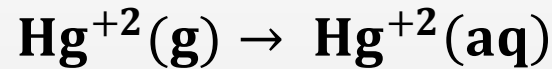


- **Mercury is more stable in solutions with higher Cl⁻ concentration**
 - Reported in literature
 - Supported by field trials
 - Mercury is more stable in the +2 oxidation state
- **Impact of increased bromide concentration is uncertain**

WFGD Redox Reactions

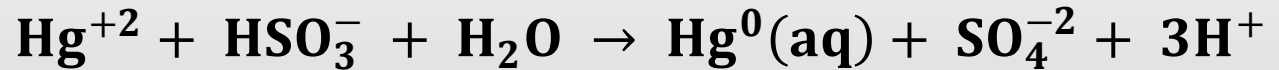
Oxidized Mercury Absorption:

**Oxidized Mercury is
Very Soluble**

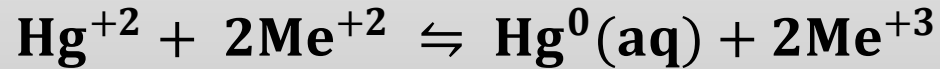


Mercury Reduction:

**S is Oxidized
Hg is Reduced**

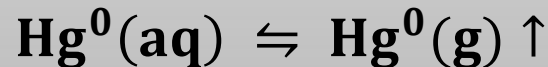


**Metal is Oxidized
Hg is Reduced**



Emission of Elemental Mercury:

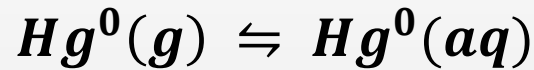
**Elemental Mercury Above
Saturation will Leave the
Slurry**



WFGD Redox Reactions

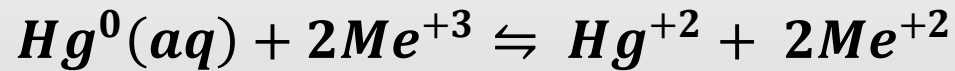
Elemental Mercury Absorption:

Elemental Mercury is
Sparingly Soluble



Mercury Oxidation:

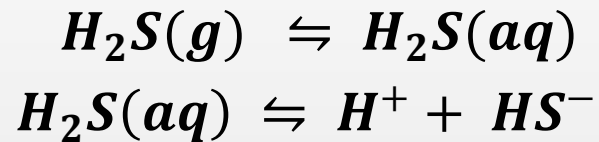
Hg is Oxidized
Metal is Reduced



Sulfide (NaHS) Reactions

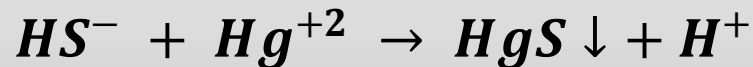
NaHS Dissociation:

NaHS forms H₂S upon
contact with acid



Mercury Sulfide Precipitation:

Mercury Remains in the
+2 state
Insoluble precipitate
formed



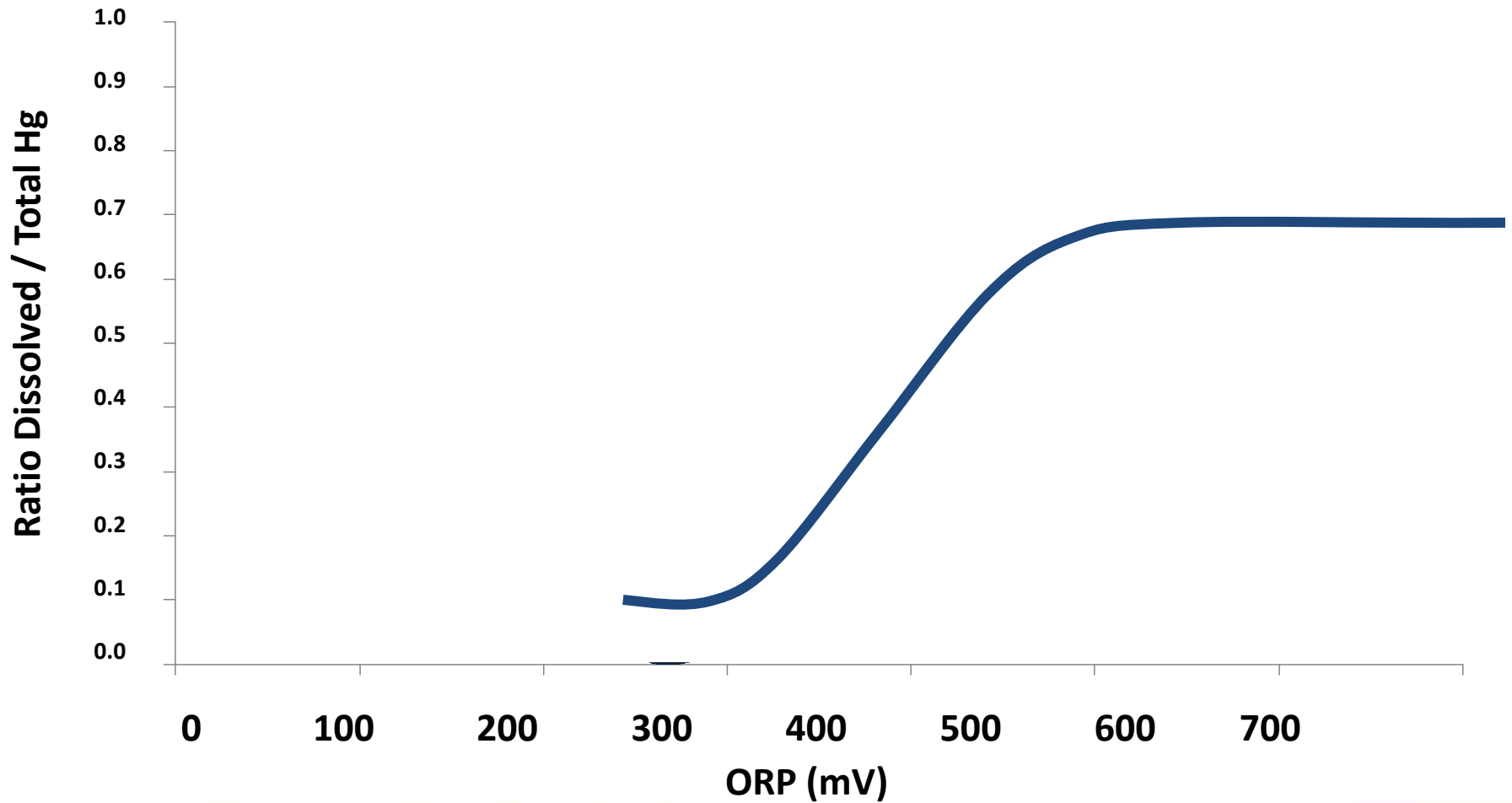
How is ORP important for Mercury?

- **Mercury is a trace metal within the absorber slurry**
- **Therefore, mercury content and speciation will not appreciably impact WFGD absorber slurry chemistry and ORP level.**
- **Slurry ORP will impact mercury speciation, and the ability of mercury to remain within solution.**

Dissolved Mercury vs. ORP in WFGD ART Slurry

- **The ORP of the solution shifts the mercury speciation from the solid to the dissolved phase.**
 - At low ORP, Hg is associated with the slurry solids.
 - When ORP shifts to strongly oxidative conditions, Hg shifts to the dissolved phase within the slurry.

Dissolved Mercury vs. ORP in WFGD ART Slurry



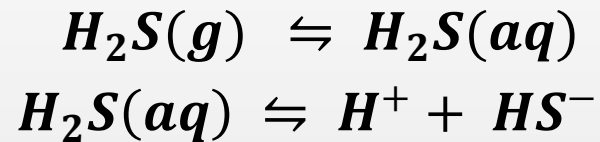
Absorption Plus (NaHS) Chemistry

- ▶ Added to absorber slurry
 - Evolves H₂S gas on low pH
 - Creates an insoluble product (HgS) with mercury
- ▶ HgS (cinnabar) is very stable.
 - The reaction is considered irreversible under WFGD conditions.
- ▶ HgS will exit the system as a solid
 - with the gypsum
 - with the wastewater stream

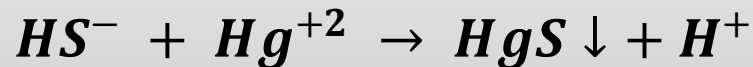


Known Sulfide (NaHS) Reactions

NaHS Dissociation:



Mercury Sulfide Precipitation:



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



WFGD Chemistry & Performance Factors

*2014 Reinhold APC Conference
Louisville, KY – July 14-15, 2014*

THANK YOU. QUESTIONS?

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