

Wet FGD Chemistry and Performance Factors

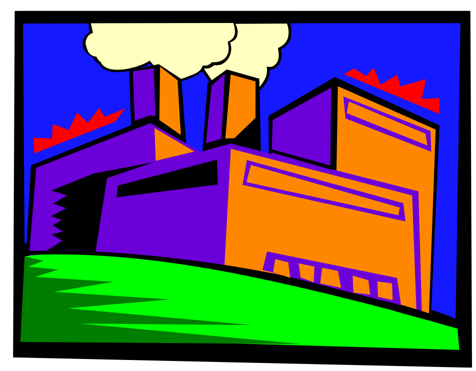
Gordon Maller – URS Corporation

Presented at:
2008 Power Gen Conference
December 1, 2008

URS

Presentation Outline

- FGD Chemistry Overview
- Effect of Key Process Variables on FGD Operation and Performance
- Chemical Process Problems – How To Identify and Correct



URS

What Are Chemical Reactions?

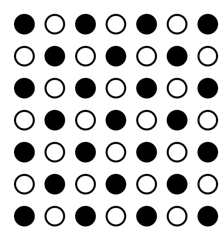
- **Two or more reactants (molecules) combining (reacting) to form different products**
- **Reactants and products can be gas, liquid or solid**
- **Examples:**
  - SO_2 (g) + H_2O H_2SO_3 (aq)
  - Ca^{++} + $SO_4^{=}$ + $2H_2O$ $CaSO_4$ *$2H_2O$
- **The rate of a reaction depends on:**
  - Nature and concentration of the reactants and products
  - Temperature

Types of Solutions

Gas-Liquid
(CO_2 and Water)

Solid-Liquid
(Coffee and Sugar)

Liquid-Liquid
(Gin and Tonic)

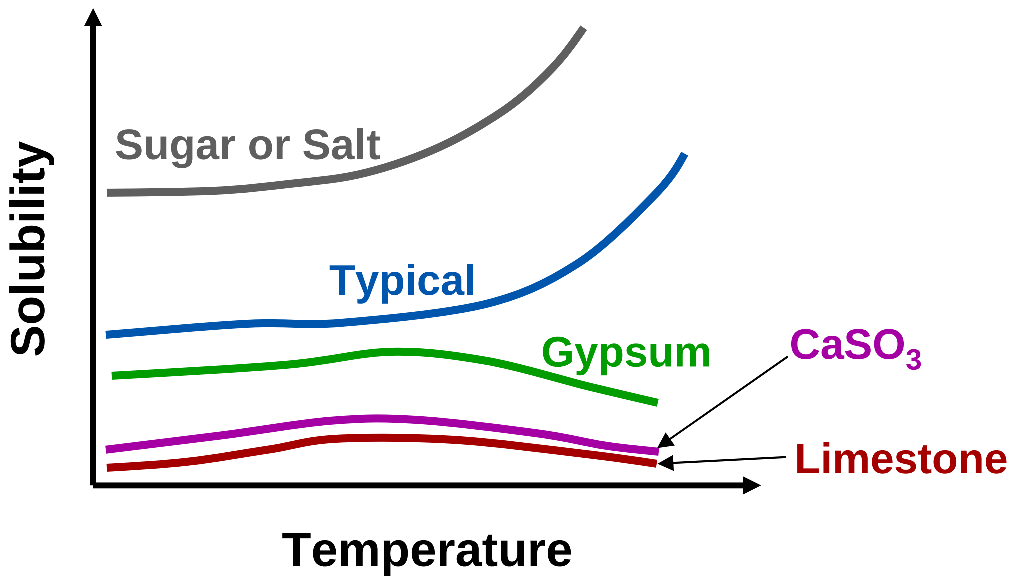


Solid Solution
(A crystal which contains a mixture of molecules from two different solids)

Solubility

Definition: **Amount of substance required to produce saturated solution. The substance is the solute. The liquid substance it is dissolving into is the solvent.**

Temperature Effects:



URS

Acids and Bases

Definition: **Acid = pH < 7** **Base = pH > 7**

Buffers

Definition: **Chemical species that can absorb a H^+ ion and moderate a pH change:**

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{++} + HCO_3^- + H^+ \rightleftharpoons Ca^{++} + H_2CO_3$$

Overall Chemistry of a Limestone Forced Oxidation FGD System

Sulfur Dioxide	+	Lime-stone	+	Oxygen	+	Water	$\longrightarrow$	Gypsum	+	Carbon Dioxide

$$SO_2 + CaCO_3 + O_2 + H_2O \longrightarrow CaSO_4 \cdot 2H_2O + CO_2$$

SO_2	$CaCO_3$	O_2	H_2O	$CaSO_4 \cdot 2H_2O$	CO_2
Gas	*Solid*	*Gas*	*Liquid*	*Solid*	*Gas*

Reactions involve gas, liquid, and solid phases

URS

Chemical Reaction Steps in FGD Process

- SO_2 absorption in absorber
- Neutralization of the absorber SO_2 to keep the SO_2 vapor pressure low so that more SO_2 can be absorbed
- Dissolution of the limestone or lime reagent to provide alkalinity for neutralization and calcium ion for precipitation
- Oxidation of absorbed SO_2 to form sulfate (SO_4)
- Precipitation of calcium and sulfate or sulfite to form byproduct

URS

Wet Limestone Forced Oxidized Process Chemistry

SO_2 Absorption:

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Limestone Dissolution:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{++} + HCO_3^- + OH^-$$

Oxidation:

$$HSO_3 + O_2 \rightleftharpoons H^+ + SO_4^=$$

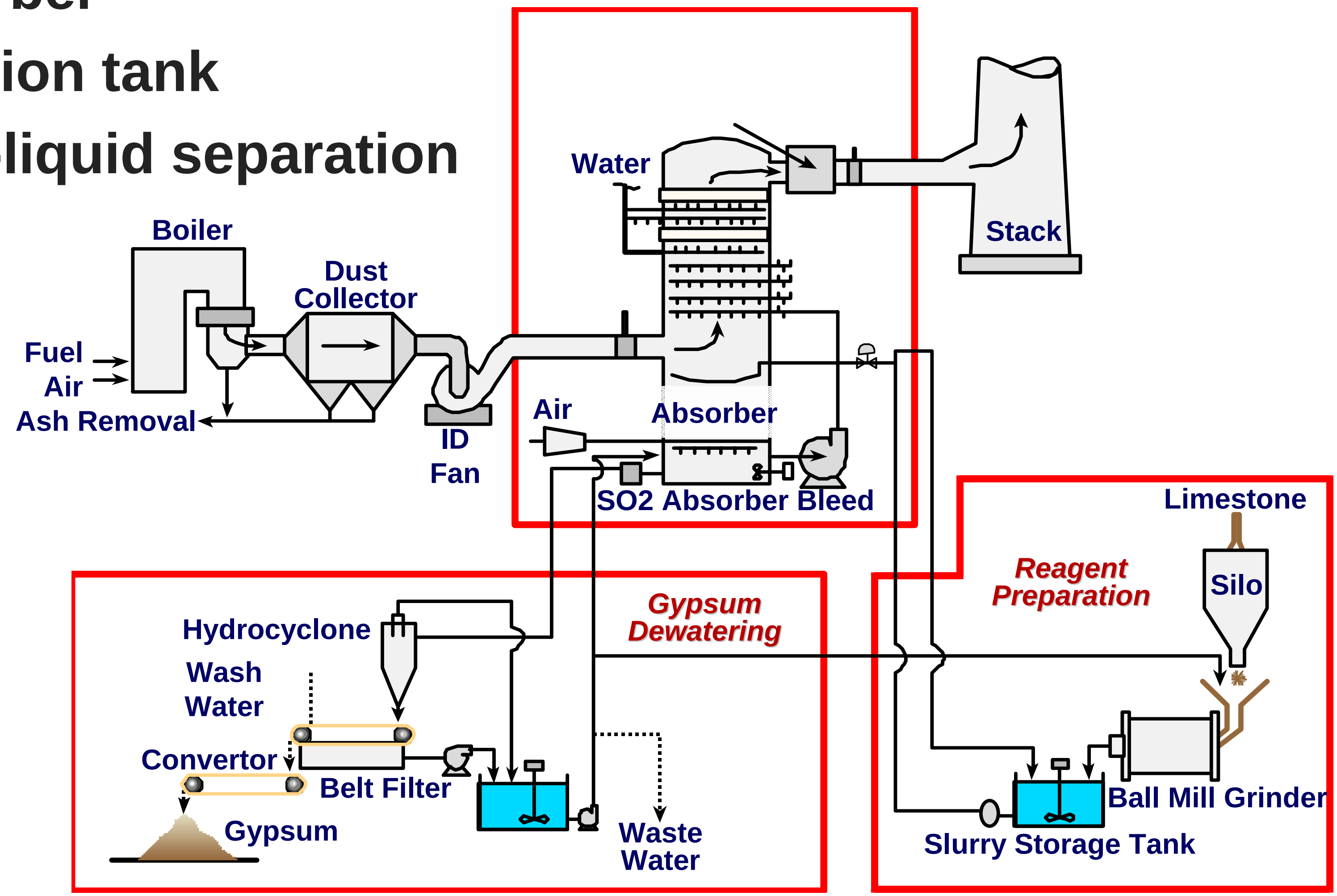
Precipitation:

$$Ca^{++} + SO_4^= + 2H_2O \rightleftharpoons CaSO_4 * 2H_2O$$

URS

Mass Transfer and Reaction Steps Occur at Several Places in FGD System

- Absorber
- Reaction tank
- Solid-liquid separation

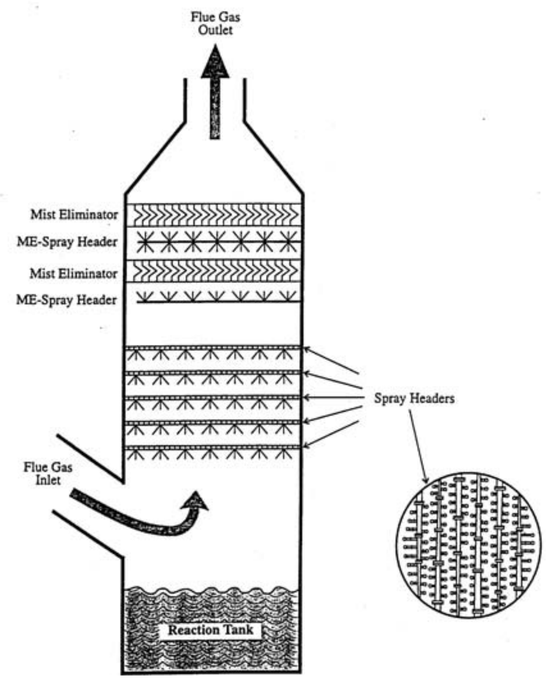


URS

Mass Transfer and Reaction Steps Occur at Several Places in FGD System (cont.)

Absorber

- **SO_2 absorption**
- **Reagent dissolution**
- **CO_2 evolution or absorption**
- **Sulfite oxidation**
- **Solids precipitation**
- **HCl and HF absorption**

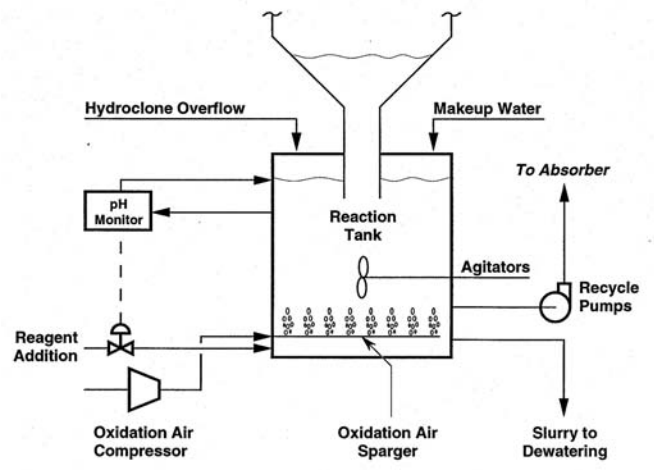


URS

Mass Transfer and Reaction Steps Occur at Several Places in FGD System (cont.)

Reaction Tank

- **Limestone dissolution**
- **Scrubber solids precipitation**
- **Sulfite oxidation**



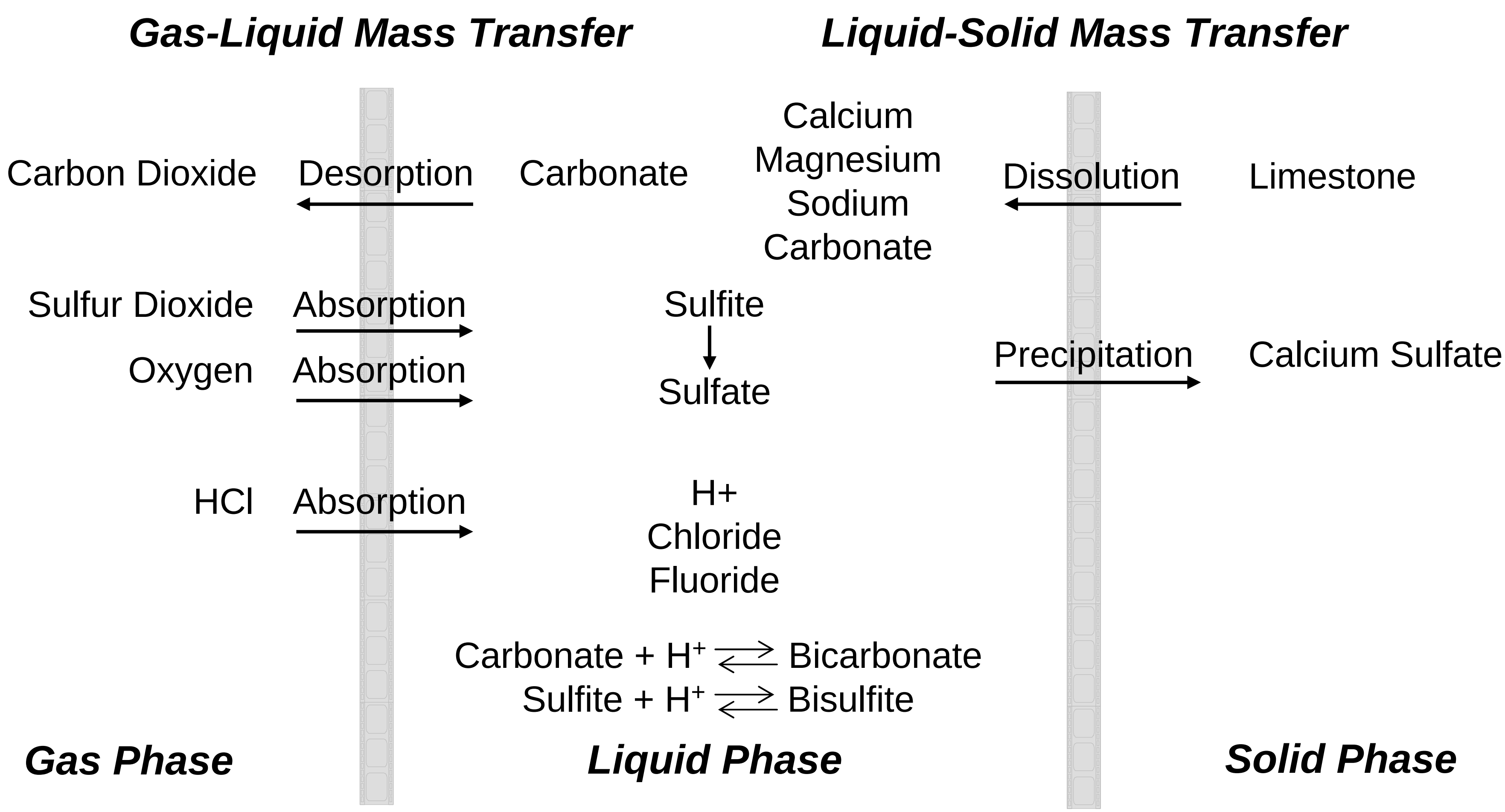
URS

Mass Transfer and Reaction Steps Occur at Several Places in FGD System (cont.)

Solids-Liquid Separation

- **Solids concentration**
  - Gravity settling (e.g., thickener)
  - Hydroclones
  - Filtering
  - Centrifuging

Overview of Mass Transfer and Reaction Steps by Phase



URS

Acid-Base Equilibrium Reactions

pK 1.81 | pK 6.91

$$SO_{2(g)} + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^=$$

Sulfurous Acid | Bisulfite | Sulfite

pK 6.37 | pK 10.25

$$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^=$$

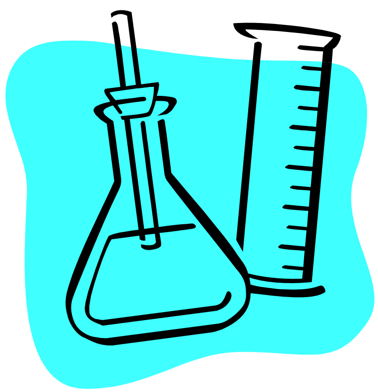
Carbonic Acid | Bicarbonate | Carbonate

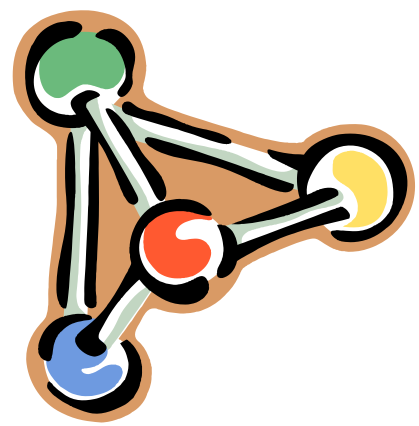
→ **Increasing pH**

← **Decreasing pH**

Liquid-Phase Alkalinity

- Concentration of liquid species that are alkaline with respect to SO_2 absorption
- Main source of alkalinity for inhibited-oxidation FGD process





Liquid-Phase Alkalinity (cont.)

Examples:

Absorption

$$SO_2 \text{ (Gas)} + H_2O \rightleftharpoons H^+ + HSO_3^-$$

Neutralization

$$SO_3^{=} + H^+ \rightleftharpoons HSO_3^-$$

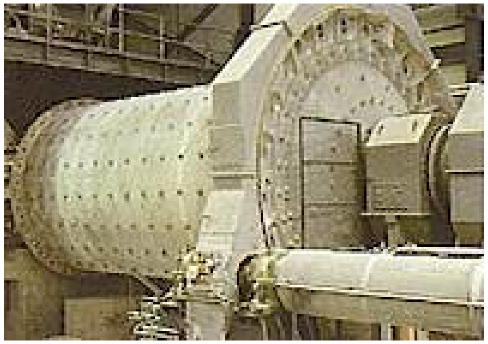
$$CO_3^{=} \text{ (Aqueous)} + H^+ \rightleftharpoons HCO_3^-$$

Overall

$$CO_3^{=} \text{ (Aqueous)} + SO_2 \text{ (Gas)} + H_2O \rightleftharpoons HSO_3^- + HCO_3^-$$

Solid-Phase Alkalinity

- Dissolution of limestone in absorber replenishes alkalinity and allows scrubbing to continue
- Main source of alkalinity for forced-oxidation FGD process



Solid-Phase Alkalinity

Examples:

Absorption $SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$

Gas

Dissolution $CaCO_3 \overset{H_2O}{\rightleftharpoons} Ca^{++} + CO_3^=$

Solid

Neutralization $CO_3^= + H^+ \rightleftharpoons HCO_3^-$

Aqueous

Overall $CaCO_3^= + SO_2 + H_2O \rightleftharpoons Ca^{++} + HSO_3^- + HCO_3^-$

Solid *Gas*

URS

Sulfite Oxidation Reactions
(Free Radical Chain Reactions)

$SO_3^{=}$ + Fe^{+++} $\longrightarrow$ SO_3^{*} + Fe^{++}

where SO_3^{*} is a free radical

$SO_3^{*\cdot}$ + $^{1}/_{2}O_2$ $\longrightarrow$ $SO_4^{=}$

Ca^{++} + $SO_4^{=}$ + $2H_2O$ $\longrightarrow$ $CaSO_4 \cdot 2H_2O$ (gypsum)

URS

Sulfite Oxidation

Depends On:

- **Ratio of O_2:SO_2**
- **Solution chemistry**
  - pH
  - [$SO_3^{=}$]
  - Trace metals
- **Temperature**

Solid-Liquid Equilibrium

- Determines if limestone will dissolve
- Determines if gypsum will precipitate
- Dissolution refers to formation of ions in solution from a solid
- Precipitation refers to formation of solids from ions in solution

What is Present in the Liquid Phase?

Ions:

Ca^{++}, Na^{+}, Mg^{++}, $SO_4^{=}$, Cl^{-}, etc.

Ion Pairs:

$CaCO_3$, $CaHCO_3^{+}$, $MgHSO_3^{-}$, $MgSO_3$, $CaSO_4$, etc.

All liquid phase reactions are at equilibrium:

$$Ca^{++} + CO_3^{=} \rightleftharpoons CaCO_3$$

$$Ca^{++} + HCO_3^{-} \rightleftharpoons CaHCO_3^{+}$$

URS

Relative Saturation

Q: Will limestone dissolve?

$$R.S. = \frac{[Ca^{++}] \cdot [CO_3^{=}]}{K_{sp}}$$

$[Ca^{++}]$ = Ca^{++} Activity (Conc.)

$[CO_3^{=}]$ = $CO_3^{=}$ Activity (Conc.)

K_{sp} = $CaCO_3$ Solubility product constant

A: Yes – when R.S. is < 1 (subsaturated)

No – when R.S. is > 1 (supersaturated)

URS

Q: Will Gypsum ($CaSO_4 \cdot 2H_2O$) Precipitate?

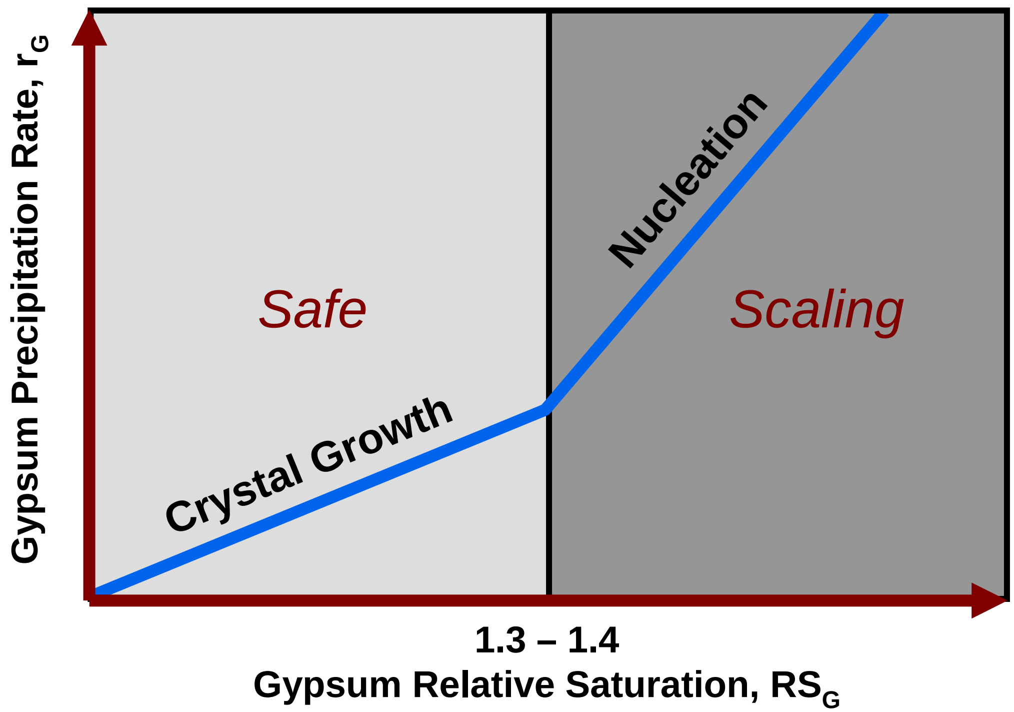
$$R.S. = \frac{[Ca^{++}] \cdot [SO_4^{=}] \cdot [H_2O]^2}{K_{sp}}$$

A: **Yes – when R.S. is > 1**

No – when R.S. is < 1

Two Types of Gypsum Precipitation

- **Nucleation (spontaneous)**
- **Crystal growth (controlled)**

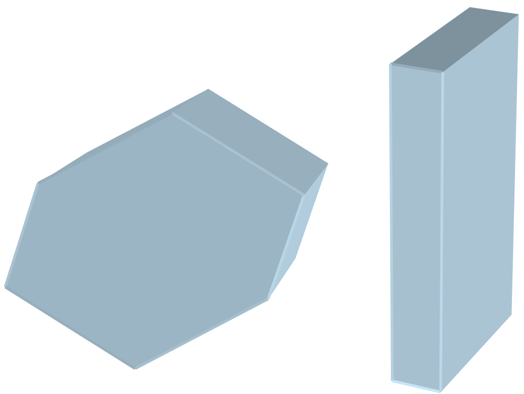


Factors that Determine Type of Gypsum Precipitation

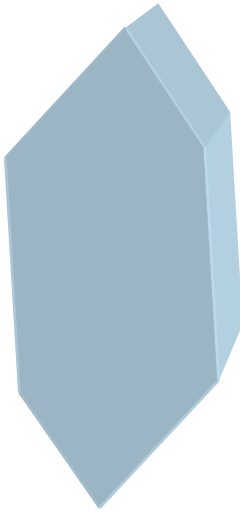
- Relative saturation of the solution
- The presence of sufficient amount of seed solids
- The rate at which the gypsum precipitates

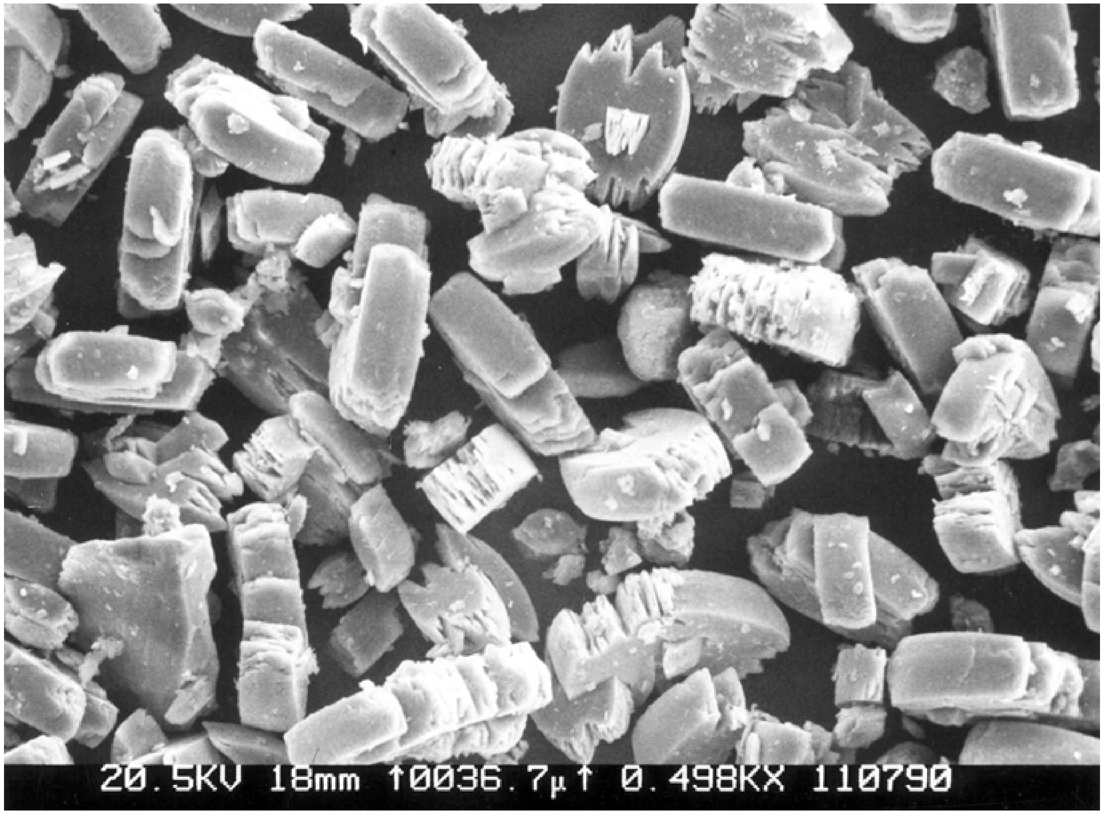
Crystal Size, Shape, and Habit

- **Affect dewatering and handling properties of solids**
- **Determined by:**
  - FGD process or design
  - Type of crystal (gypsum or calcium sulfite)
  - Contaminants in the crystal
  - Crystal habit modifiers
  - Residence Time



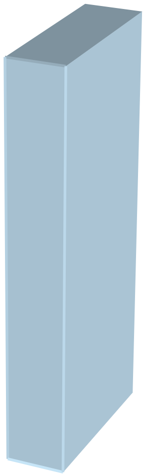
Gypsum Crystal: Triclinic System (No Axis of Symmetry)





URS

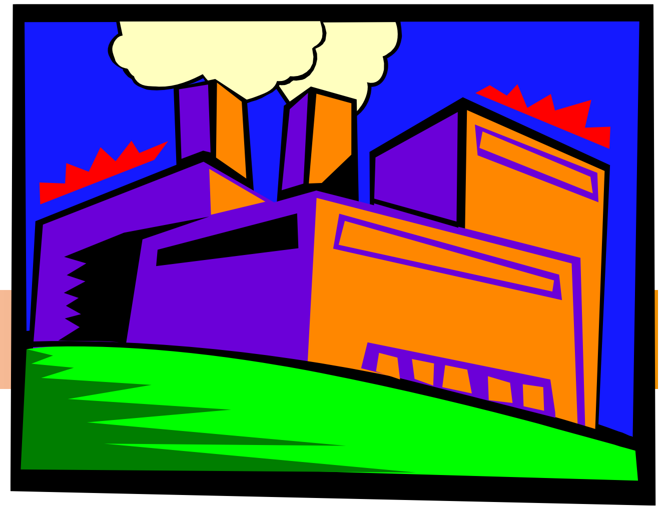
Calcium Sulfite Crystal: Orthorhombic System (Three, 2-Fold Axes of Symmetry)



FGD Gypsum Solids From Different Processes*

***(Same Magnification)**

Effect of Key Process Variables on FGD Operation and Performance



URS

Performance Variables That Require Control

- SO_2 removal efficiency
- Reagent utilization
- Scaling potential

SO_2 Removal Efficiency

Key Chemical Factors

- **pH or alkalinity**
- **Excess limestone in recycle slurry (key for forced oxidized process)**
- **Solution chemistry**
- **Inlet SO_2 loading (combination of concentration and load)**

SO_2 Removal Efficiency (cont.)

Key Mechanical Factors

- **Liquid-to-gas ratio (L/G)**
- **Mass transfer characteristics of absorber (e.g., trays, packing)**
- **Gas / liquid distribution**
- **Flue gas bypass (where applicable)**

Reagent Utilization

Key Factors

- pH
- Solution chemistry
- Solids residence time
- Surface area (grind size)
- Limestone reactivity

Causes of Scaling

Key Factors

- Oxidation (not usually a factor in forced oxidation process)
- Limestone utilization
- Slurry density
- Reaction tank volume
- ME wash design or operation
- ME wash water quality

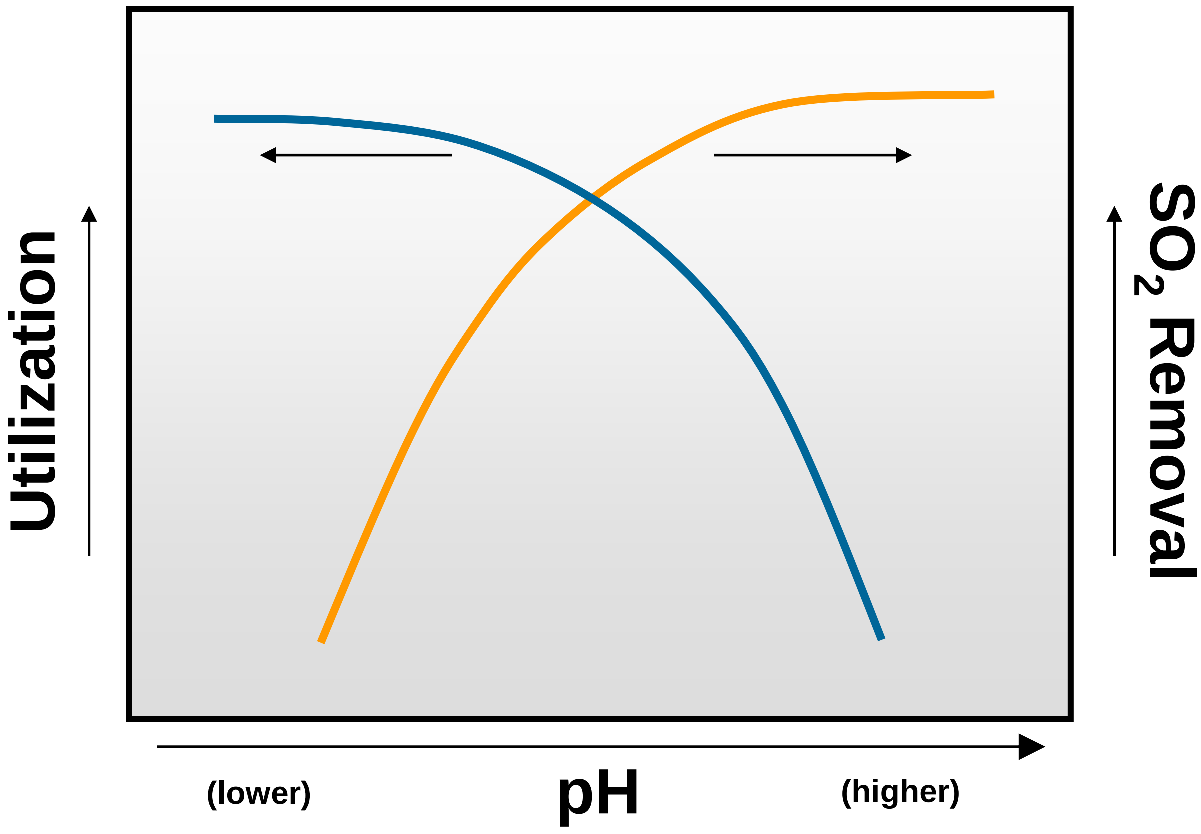
Factors That Affect FGD Performance and Reliability

Operators have direct, limited or no control of key parameters

- **Direct Control**
  - pH**
  - Slurry density**
  - L/G
- **Limited Control**
  - Limestone properties**
  - Solution chemistry**
  - Mechanical factors
  - Water management
- **No Control**
  - Boiler load cycles
  - Coal S variations
  - Inlet flue gas

***To be discussed*

pH / Utilization / SO_2 Removal Relationships



Slurry Density (Slurry Solids Concentration)

- **Minimum slurry density ensures adequate crystal surface area for precipitation. This is important to prevent scaling**
- **Maintaining a higher slurry density can improve limestone utilization**
- **Slurry density affects solids residence time which, in turn, affects limestone utilization and scaling potential**

URS

Explanation of Effect of Slurry Density on Limestone Utilization

- **Maintaining pH and SO_2 removal requires a specific limestone loading (g-limestone/L-slurry) level for the system.**
- **At low density (low concentration of solids in the slurry), a higher concentration of the solids will be limestone. Therefore limestone utilization will be lower.**

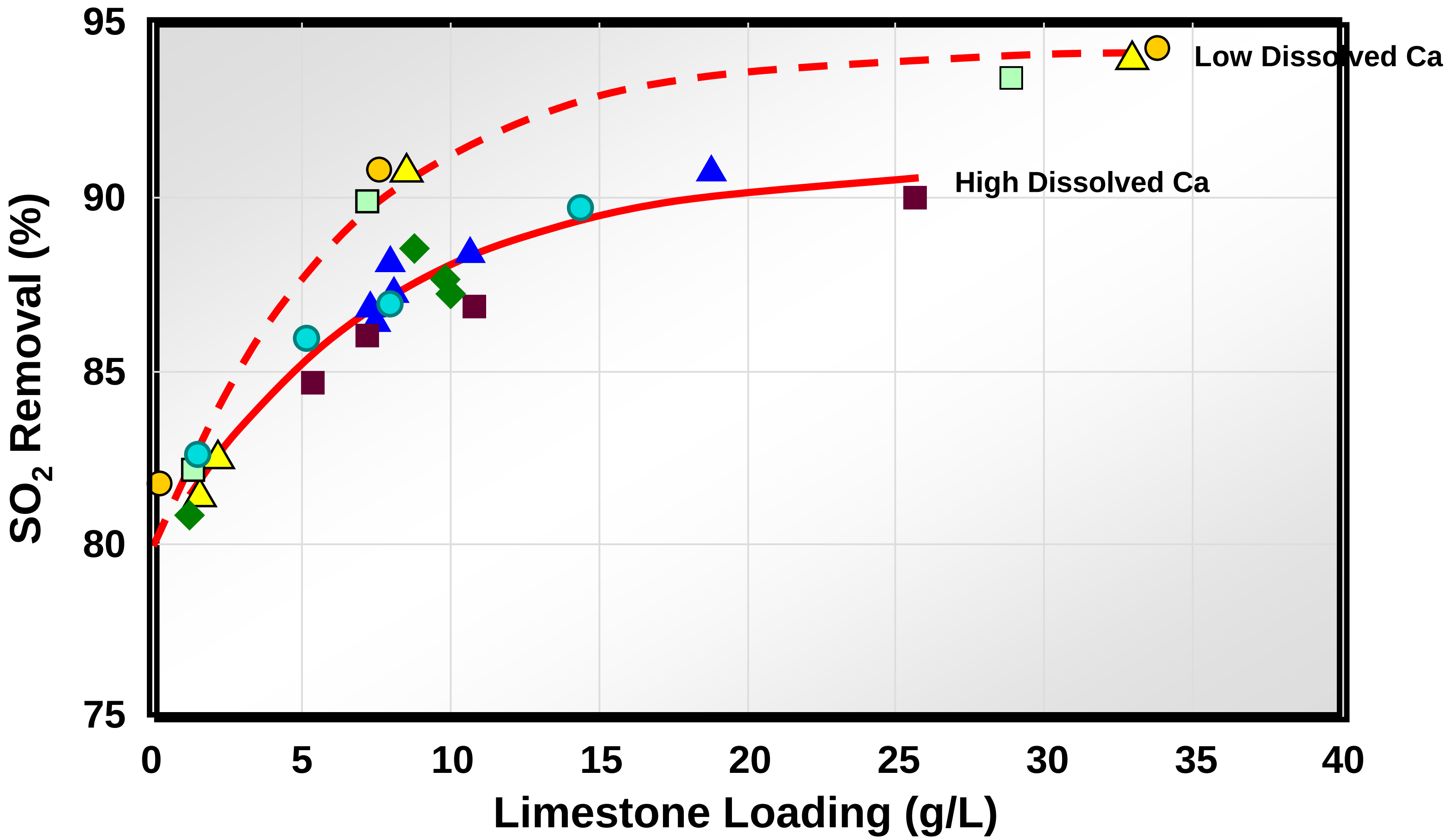
URS

Solution Chemistry

- **Dissolved Cl^- (Ca^{++}) Concentration**
  - Inhibits dissolution due to common ion effect
- **Forced oxidation vs. natural oxidation**
  - Stripping of CO_2 tends to enhance dissolution
- **Aluminum fluoride blinding**
- **Sulfite blinding**
  - Problem during periods of incomplete oxidation
- **All can affect the ease with which reagent dissolves and removal performance of scrubber**

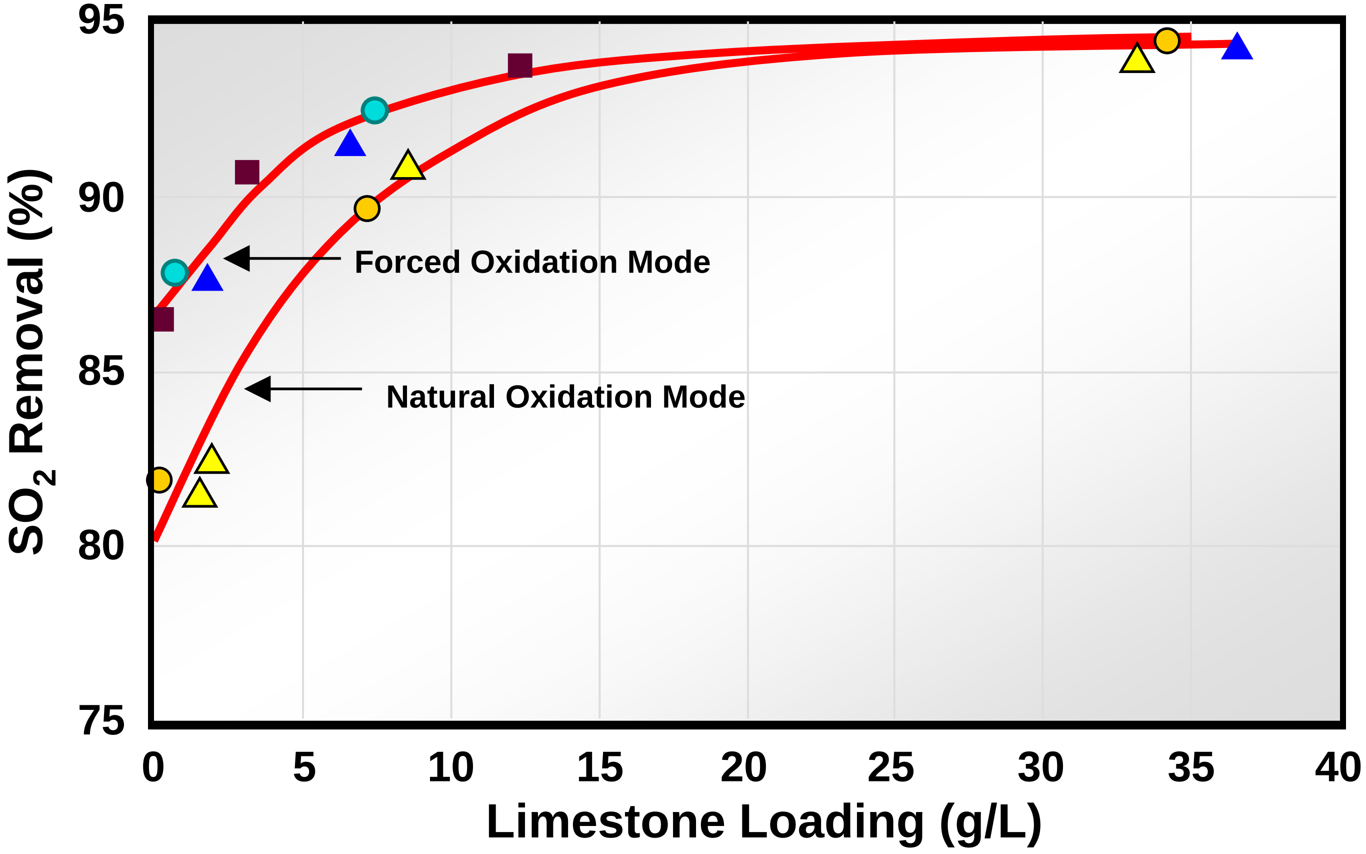
Effect of Dissolved Calcium Concentration

(Different Shaped Symbols Represent Different Limestone Tested)

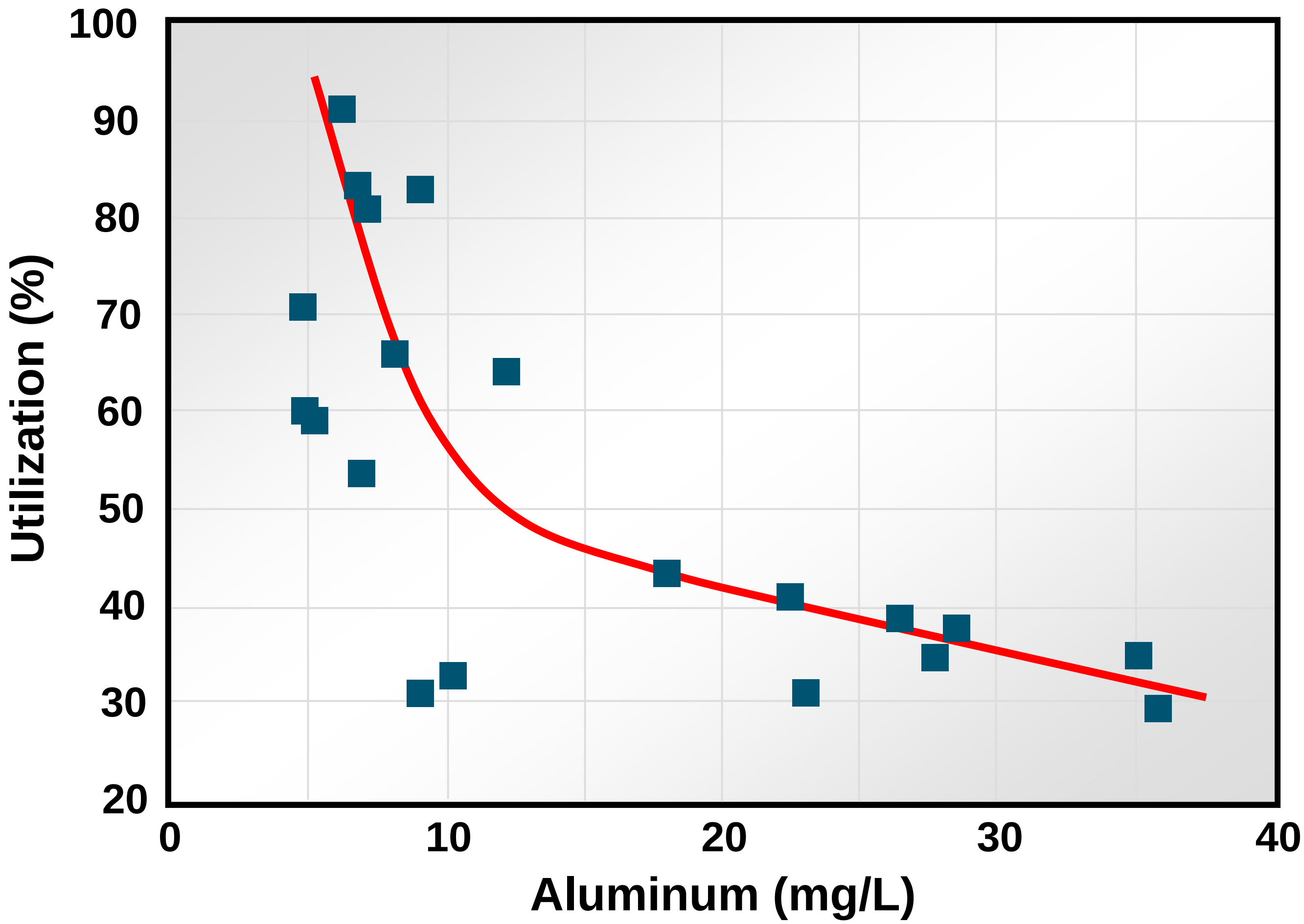


Effect of Oxidation Mode

(Different Shaped Symbols Represent Different Limestone Tested)



Effect of Soluble Aluminum on Limestone Utilization



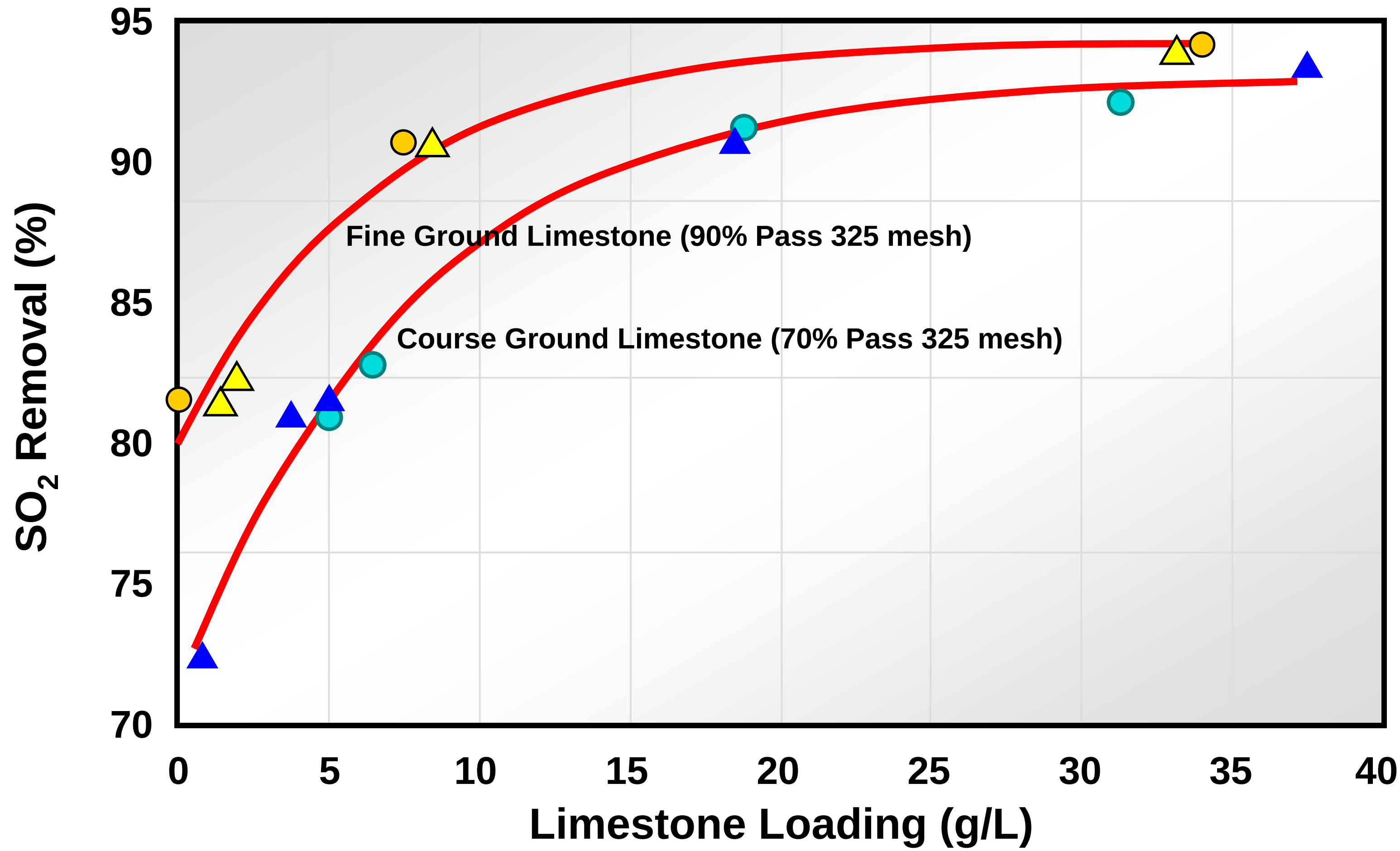
Limestone Properties Affecting Scrubber Performance

Properties will affect pH-Utilization-Removal relationship

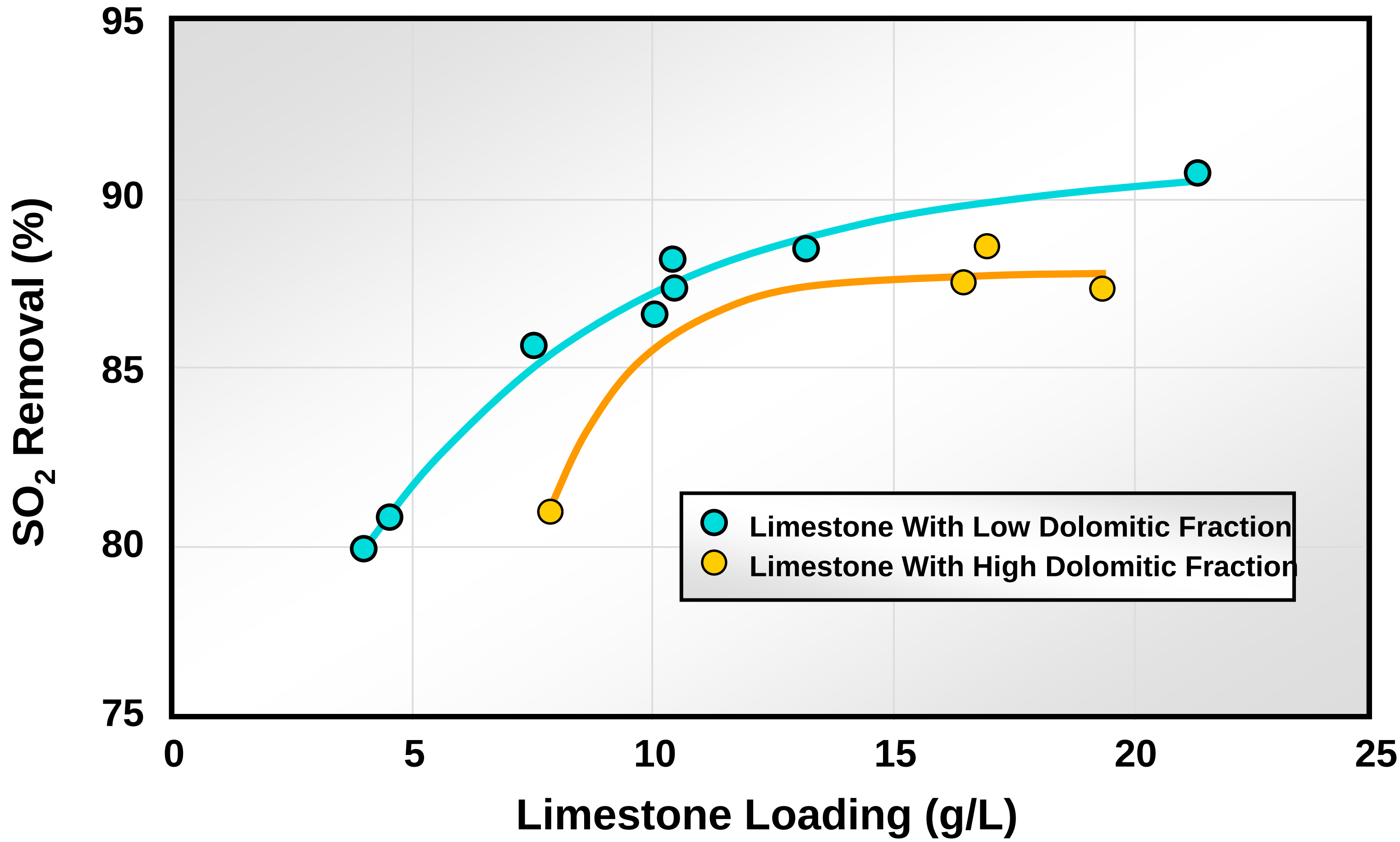
- **Grind**
- **Composition**
- **Reactivity (dolomitic fraction)**

Effect of Limestone Grind

(Different Shaped Symbols Represent Different Limestone Tested)



Effect of Limestone Dolomitic Fraction



Chemical Process Problems – How To Identify and Correct

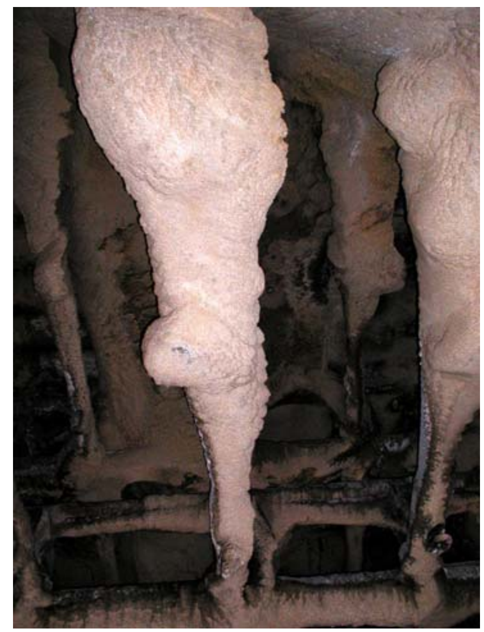
Problem Areas To Be Discussed

- Scaling and solids buildup
- Mist eliminator pluggage
- Limestone blinding
- Poor SO_2 removal
- Poor reagent utilization
- Poor gypsum byproduct quality

Scaling and Solids Buildup

Common areas for scaling:

- Scrubber inlet
- Absorber internal walls and support structure
- Absorber spray headers
- Inside spray piping
- Trays
- Reaction tank walls



URS

Causes of Scaling and Solids Buildup

- **Chemical (high gypsum relative saturation)**
  - Oxidation
  - Insufficient seed solids
  - Solid residence time that is too short
  - Poor wash water quality
- **Wet-dry interface and recirculation of slurry**
- **Poor reagent utilization**

Causes of Scaling in FGD Systems

***High Gypsum Relative Saturation*:**

- **Scaling can occur in all areas of absorber and on mist eliminator (ME) as result of solids nucleation due to high relative saturation**
- **High relative saturation usually result of insufficient seed material or high precipitation rates**
- **Scaling in ME may result from poor quality wash water (water saturated or nearly saturated with gypsum)**

Causes of Scaling in FGD Systems

Wet/dry Interface:

- **Occurs in area of absorber where hot flue gas is quenched**
- **Scaling results from fluctuations in gas flow and gas distribution. Causes areas along duct walls or other internal structures to vary from wet to dry**
- **If slurry is carried back into this area, it may dry and accumulate as a hard scale composed of calcium sulfate, and/or fly ash**

URS

Causes of Scaling in FGD Systems

Wet/dry Interface:

- **Scaling as result of a wet/dry interface is eliminated by:**
  - Modifying the physical design of the absorber inlet to eliminate the flow disturbance
  - Controlling the location of the wet/dry interface by modifying the way flue gas is quenched

Scaling and Solids Buildup

Steps to Correct:

- **Control process chemistry within design limits**
- **Ensure that inlet flue gas is quickly and completely quenched**
- **Modify absorber inlet design to eliminate flow disturbances and gas recirculation**
- **Maintain reagent utilization within design range**

Mist Eliminator Pluggage

- **Chemical causes**
  - –Poor reagent utilization
  - –Poor quality wash water
- **Mechanical causes**
  - –Poor design of wash system
  - –Broken or plugged wash system
  - –High gas velocity
  - –Non-uniform gas flow and liquid loading distribution

Mist Eliminator Pluggage

- **Indication**
  - Increase in pressure drop
  - Visual observation during inspection
- **ME pluggage can:**
  - Result in increased gas velocity through ME and liquid carryover into outlet duct and stack
  - Cause stack rainout and particulate emissions
  - Damage ME due to weight of solids

URS

Considerations For ME Wash System

- ME faces to wash
- Wash coverage (150 to 200%)
- Wash intensity and pressure (1.5 gpm/sq ft, 30 to 45 psi)
- Wash duration and frequency
- Recommended wash nozzles

Inhibited Dissolution of Limestone

- Limestone must dissolve in scrubber to provide alkalinity
- Certain dissolved chemical species can significantly slow or stop the dissolution of limestone
- Inhibition - Slowing of dissolution
- Blinding - Significant slowing or stopping of dissolution
- High concentrations of dissolved chloride and magnesium will inhibit dissolution
- The mechanism for this inhibition is called "common-ion" effect

Limestone Blinding

- In forced oxidation process, limestone blinding can result from high concentrations of dissolved sulfite or aluminum-fluoride complex
- Either sulfite or aluminum-fluoride complex will react on surface of limestone particle to block dissolving site
- Aluminum-fluoride blinding often initiated by high concentration of inlet fly ash
- Sulfite blinding initiated by incomplete oxidation

URS

Poor SO_2 Removal as Result of Chemical Problem

Cause	***Analytical Indication***	***Corrective Action***
Insufficient Limestone In Scrubber	Low carbonate measured in scrubber solids	Increase pH set-point
Malfunctioning pH Monitor	Poor agreement during pH calibration check	Make repairs to pH monitor system
Sulfite Blinding	Poor reagent utilization along with elevated levels of soluble sulfite	Verify operation of oxidation air system. Correct as required
Aluminum Fluoride Blinding	Poor reagent utilization along with elevated levels of aluminum and fluoride	Improve particulate removal upstream of scrubber
Poor Limestone Quality or Off-Spec Grind Size	Sieve analysis, composition analysis	Modify grind circuit and/or obtain better limestone

URS

Poor SO_2 Removal as Result of Mechanical Problem

Cause	*Indication*	*Corrective Action*
Plugged Spray Header(s) or Spray Nozzle(s)	Low recycle flow As indicated by flow meter or motor amps	Clean during outage
Broken Spray Header	Indication from flow meter or motor amps. Observed during inspection	Repair during outage
Loss of Recycle Pump Capacity	Low recycle flow as indicated by flow meter or motor amps	Repair during outage

URS

Poor Reagent Utilization

Cause	*Analytical Indication*	*Corrective Action*
Malfunctioning pH Monitor	Poor agreement during pH calibration check	Make repairs to pH monitor system
Sulfite Blinding	Poor reagent utilization along with elevated levels of soluble sulfite	Verify operation of oxidation air system. Correct as required
Aluminum Fluoride Blinding	Poor reagent utilization along with elevated levels of aluminum and fluoride	Improve particulate removal upstream of scrubber
Poor Limestone Quality or Off-Spec Grind Size	Sieve analysis, composition analysis	Modify grind circuit and/or obtain better limestone

URS

Poor Gypsum Byproduct Quality

- **High acid insoluble (inerts) fraction**
  - Verify operation of particulate control device upstream of scrubber
  - Optimize operation of process hydroclones to maximize concentration of inerts in overflow
  - Increase liquid purge rate
- **Poor reagent utilization**
- **Low sulfite oxidation**
  - Verify operation of oxidation air system

Poor Gypsum Byproduct Quality (cont.)

- **High moisture**
  - Verify operation of primary and secondary dewatering system
  - Purge fines from process
  - Check filter cloth for blinding. Clean or replace as required
  - Increase temperature of filtercake wash water
  - Verify system chemistry
    - High level of limestone
    - High level of acid insolubles
    - Presence of crystal modifier


Questions?