Reinhold Environmental Ltd.

2009 NOx-Combustion Round Table & Expo Presentation

February 9 & 10, 2009, Cleveland, OH

babcock & wilcox power generation group

SO_3 and H_2SO_4 Formation & Control

SO_3 and H_2SO_4 Formation & Control

- Issues
- Sources
- Measurement
- SO_3 Control
    - Dry Sorbent
    - WESP

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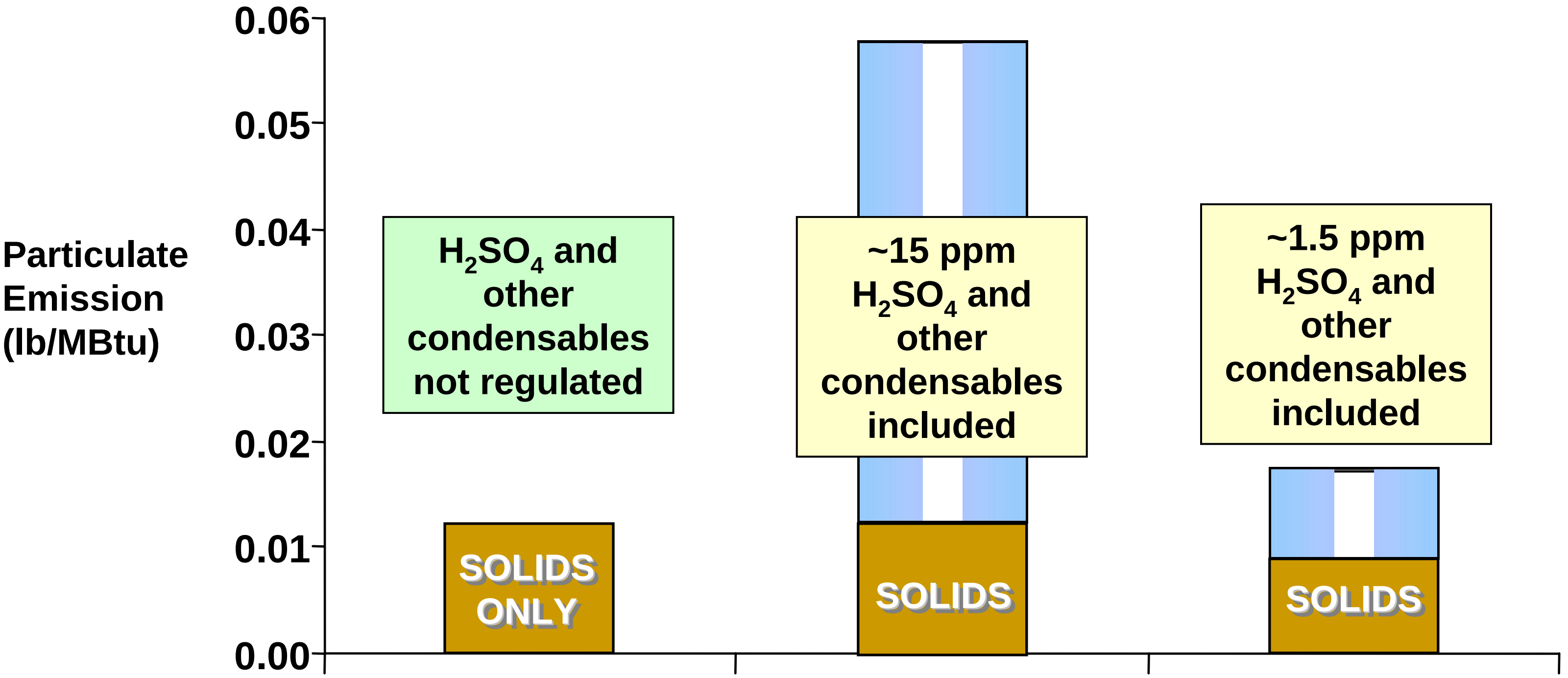
The Issues with SO_3

- Control of sulfuric acid mist may be required for permits as $PM_{2.5}$
- Corrosion of air heaters and flues
- Adsorbs on flyash and PAC readily which reduces Hg removal
- Stack Opacity
- Difficult to Measure

Particulate Permit Requirements Redefined for Power Plants (New Plants)



Pre - 2002

2002+
Total particulate permit requirement redefined

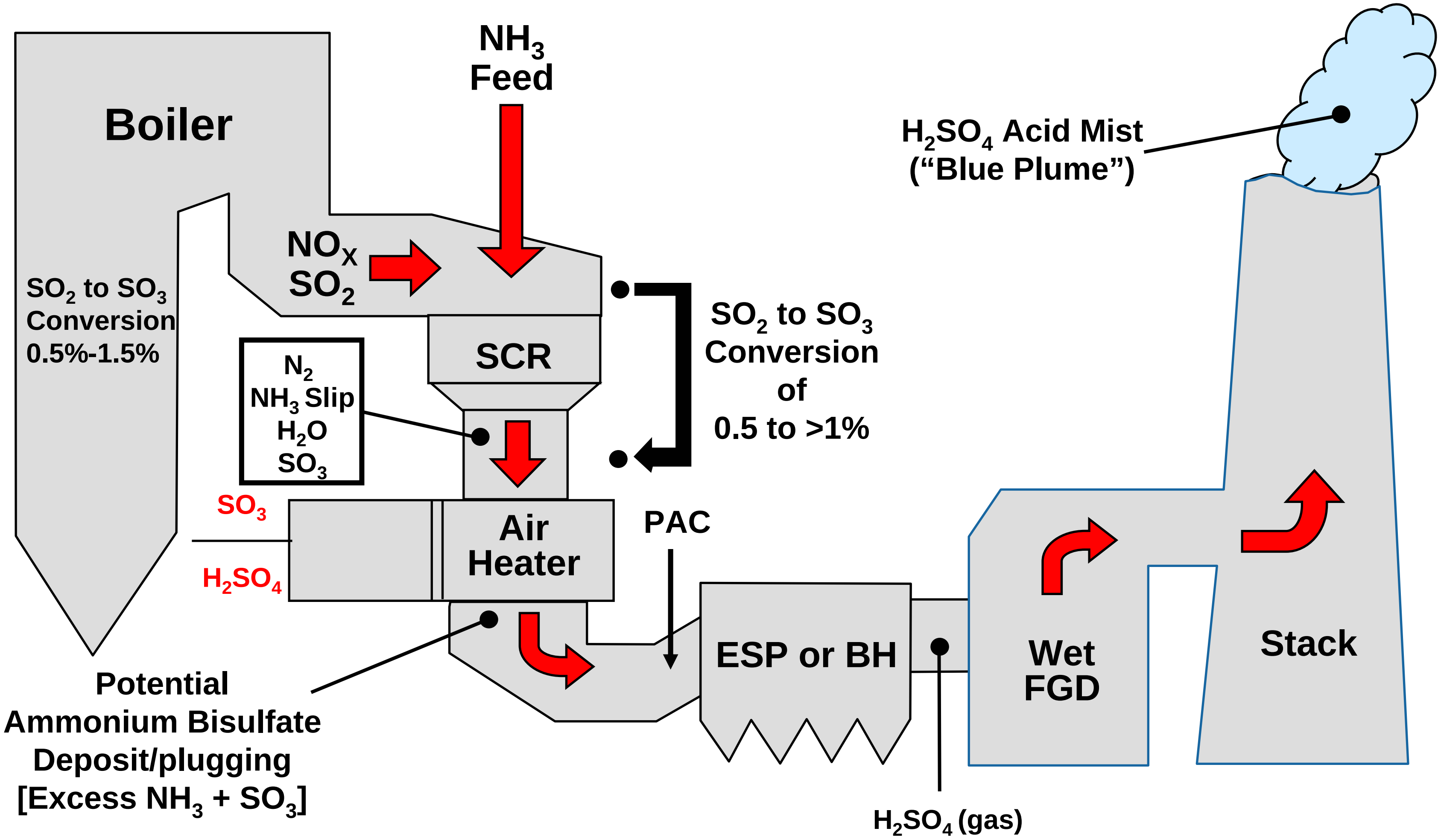
2004+
Permit levels for total particulate, including condensables, are significantly reduced

SO_3 and H_2SO_4 Formation & Control

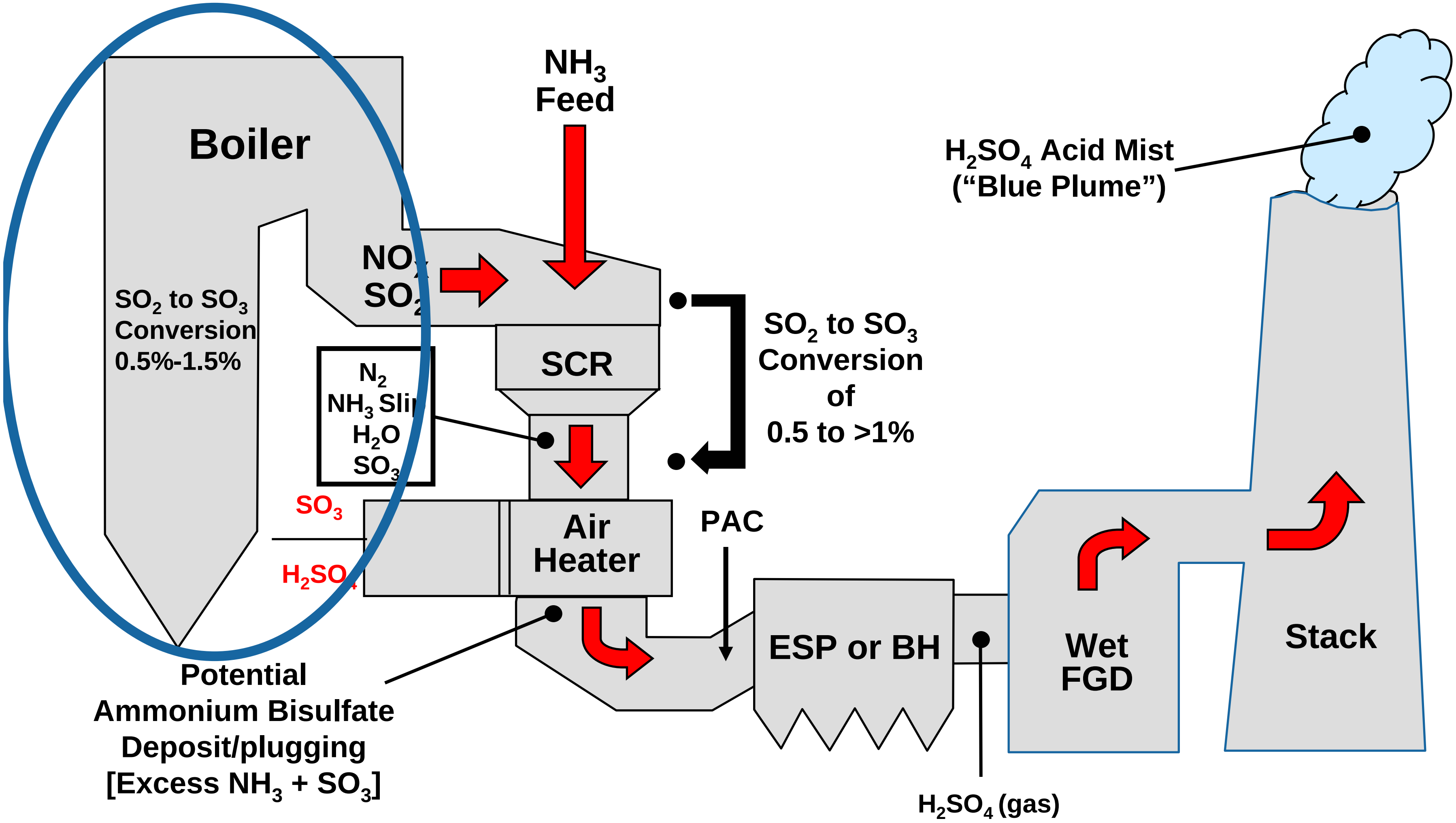
- Issues
- Sources
- Measurement
- SO_3 Control
    - Dry Sorbent
    - WESP

Industry-Wide Issue: Bituminous Coal

SO_2 to SO_3 Conversion



Boiler Conversion



SO_3 Formation in a Combustor

When a fuel containing sulfur is fired in a combustor, the sulfur in the fuel combines with oxygen and forms gaseous sulfur dioxide (SO_2)

Some SO_2 is further oxidized into sulfur trioxide (SO_3) through gas phase combustion reactions with catalytic compounds such as iron oxides or vanadium

$$SO_2 + FeO_x => SO_3 + FeO_{x-1}$$

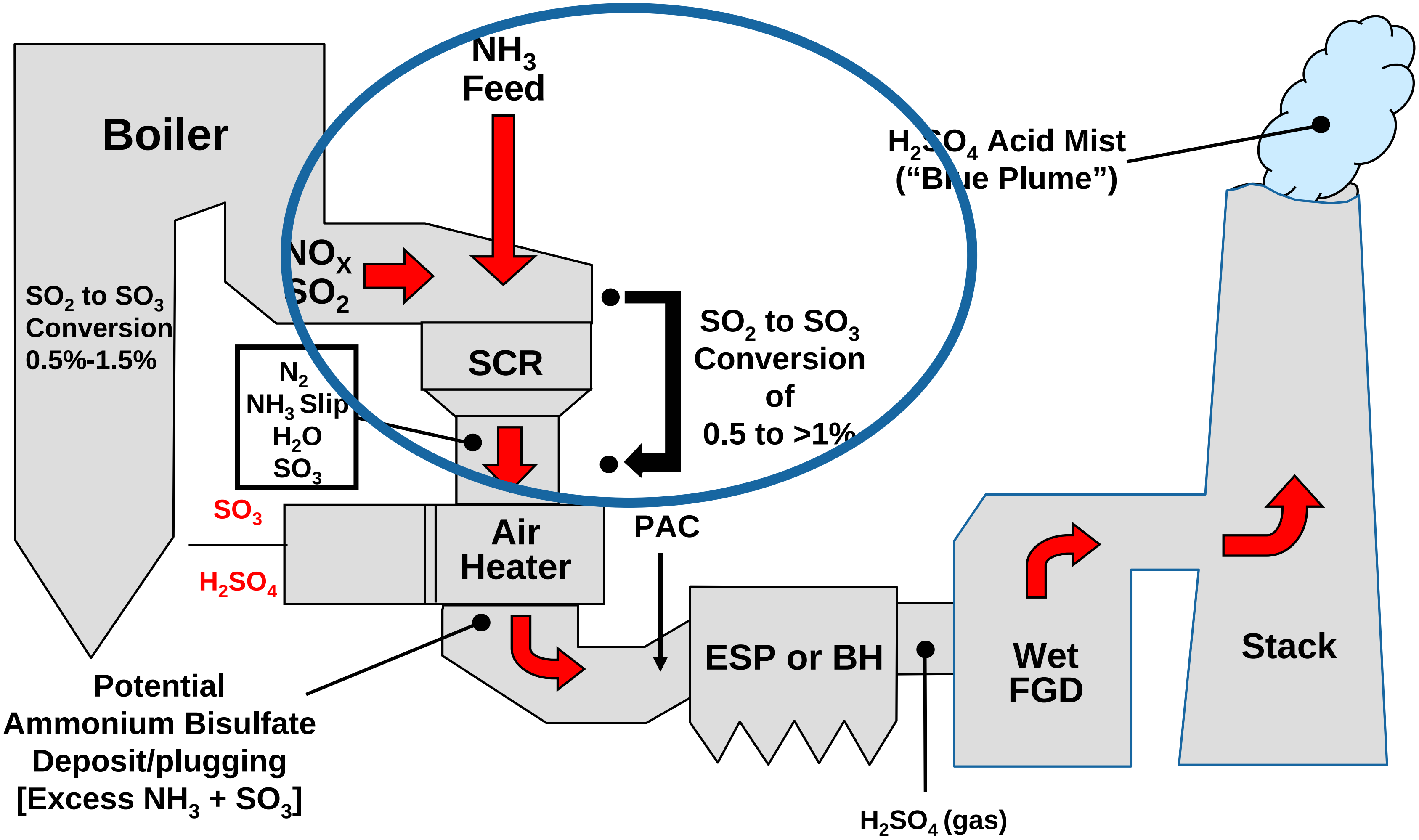
SO_3 Formation in a Combustor

- Oxidation reaction based on temperature, excess O_2, coal sulfur content, boiler load, area of tubes in boiler and amount of fouling on the tubes
  - can be oxidized on boiler surfaces
  - ash build up on tubes reduces oxidation
  - Fe in coal can increase conversion
  - vanadium in the fuel causes oxidation
  - ash composition – amount of alkali
  - Typically 0.5 – 1.5% conversion

SO_3 Formation in a Combustor

- Power River Basin (PRB) coal
  - <0.5% conversion due to high alkalinity in ash
- Petroleum Coke or Fuel Oil
  - Typically over 2% conversion due to high vanadium content

SCR Conversion



Boiler

SO_2 to SO_3
Conversion
0.5%-1.5%

NH_3
Feed

NO_X
SO_2

SCR

N_2
NH_3 Slip
H_2O
SO_3

SO_3

H_2SO_4

SO_2 to SO_3
Conversion
of
0.5 to >1%

Air
Heater

PAC

ESP or BH

Wet
FGD

Stack

H_2SO_4 Acid Mist
("Blue Plume")

H_2SO_4 (gas)

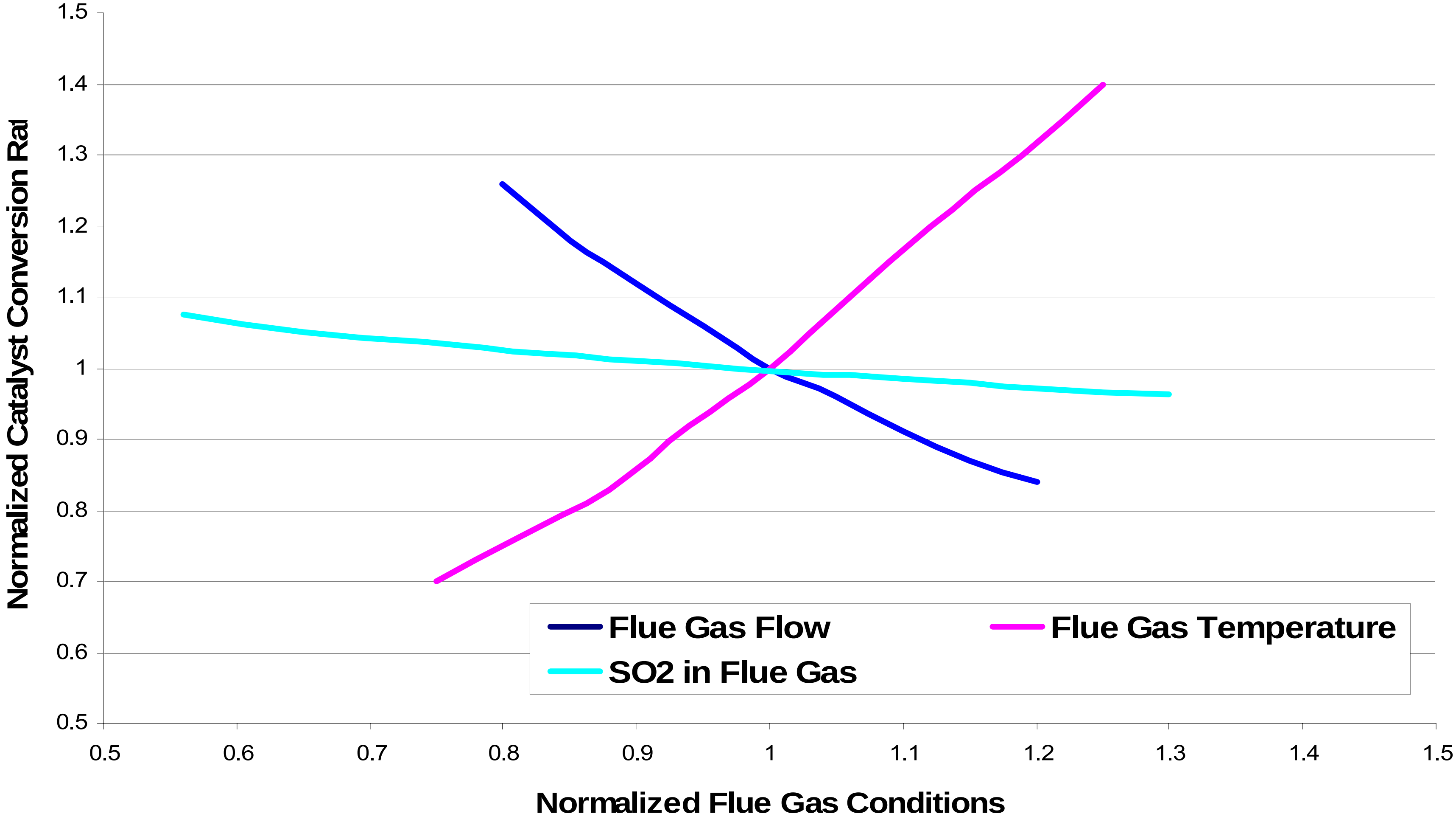
Potential
Ammonium Bisulfate
Deposit/plugging
[Excess NH_3 + SO_3]

SO_3 Formation in the SCR

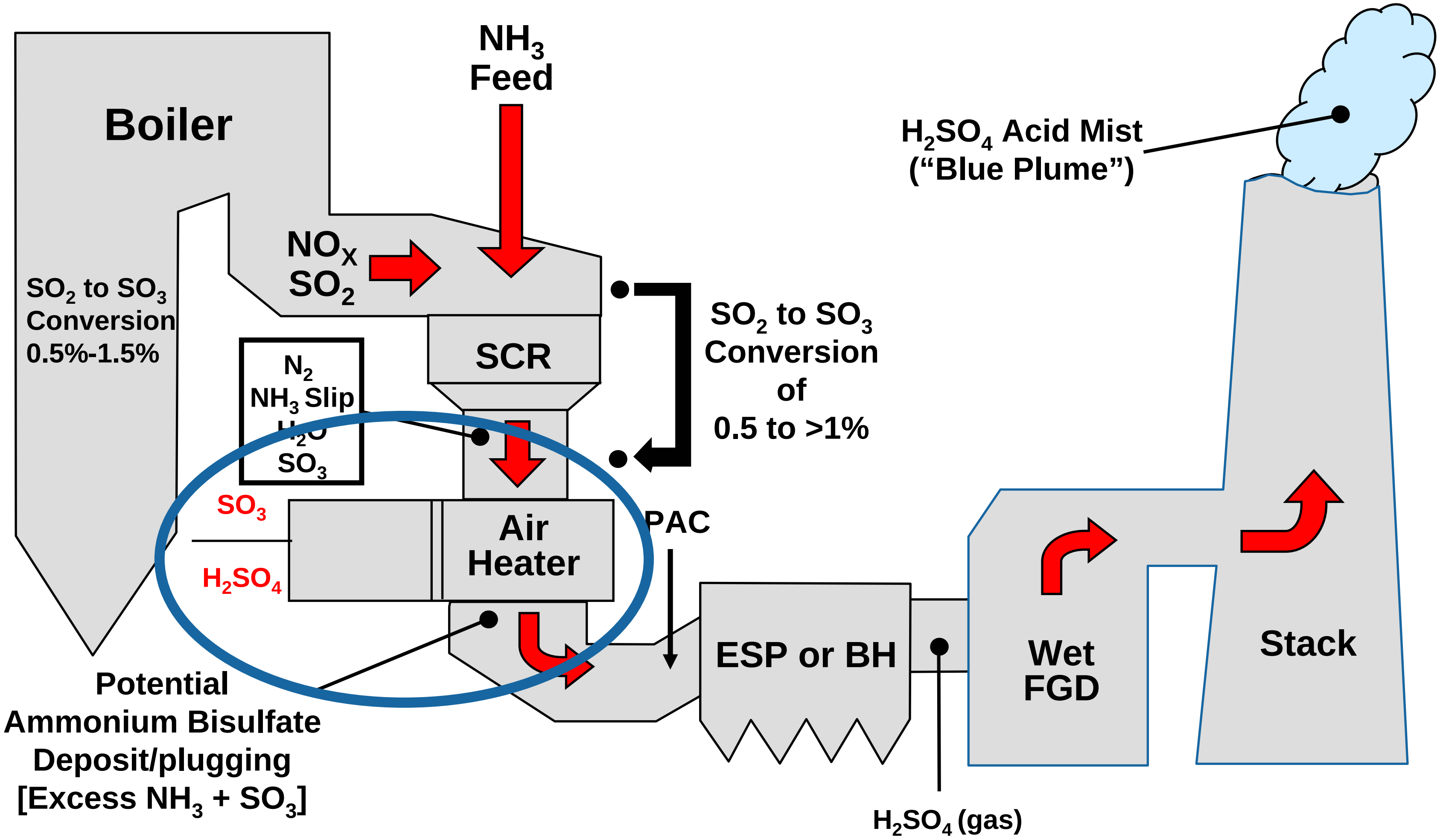
Some of the SO_2 is converted to SO_3 in the SCR

- SCR catalyst type affects conversion ratio – typical 0.5% to >1% percent conversion of SO_2 to SO_3 in the SCR
- Conversion rate affected by gas temperature, flow rate and SO2.
- Conversion rate increases without NH_3 injection

Flue Gas Effects on SO_2 Conversion



Air Heater Removal



Boiler

SO_2 to SO_3 Conversion 0.5%-1.5%

NH_3 Feed

NO_X
SO_2

SCR

N_2
NH_3 Slip
H_2O
SO_3

SO_2 to SO_3 Conversion of 0.5 to >1%

SO_3

H_2SO_4

Air Heater

PAC

ESP or BH

Wet FGD

Stack

H_2SO_4 Acid Mist (“Blue Plume”)

H_2SO_4 (gas)

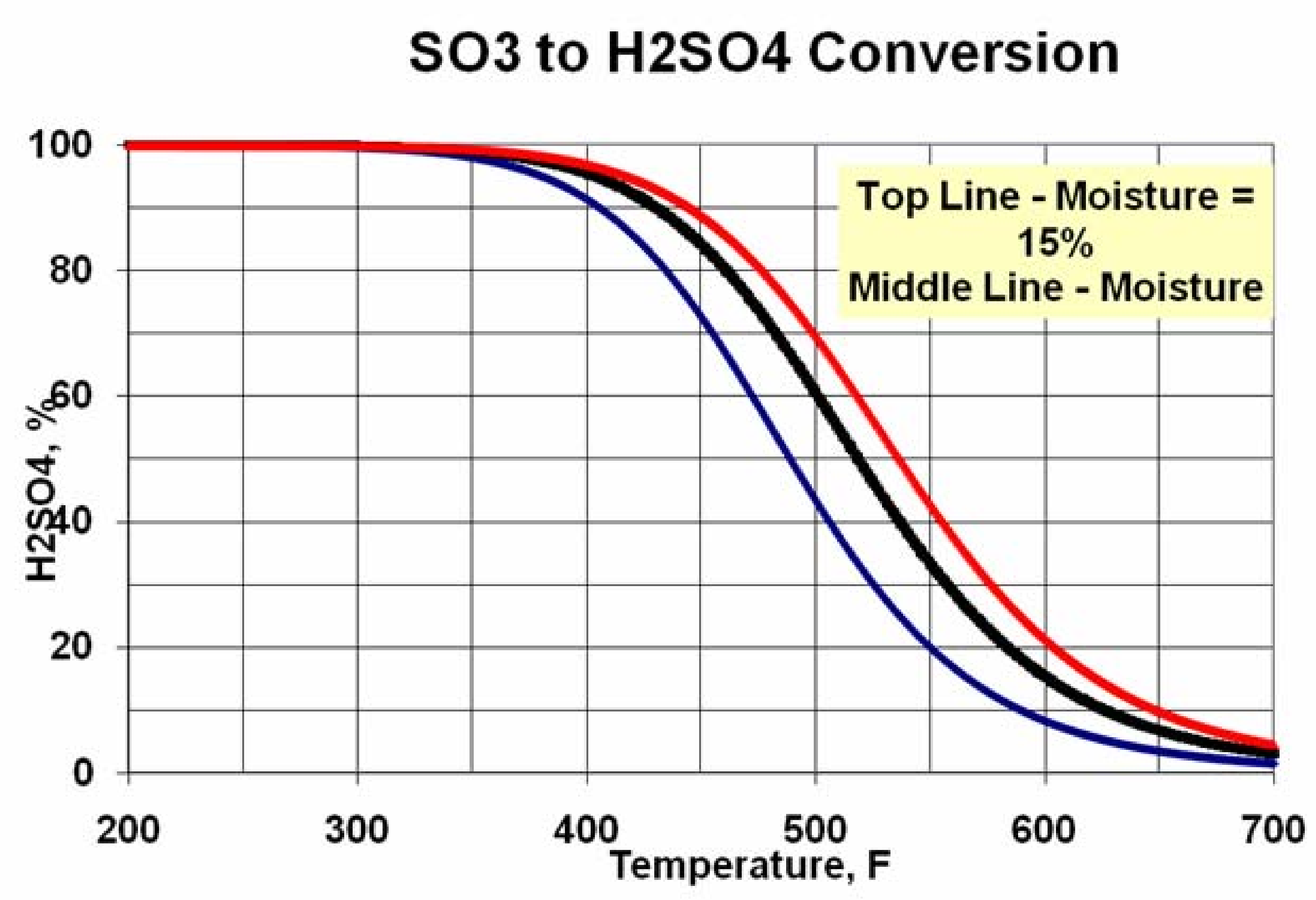
Potential Ammonium Bisulfate Deposit/plugging [Excess NH_3 + SO_3]

Formation of H_2SO_4

- SO_3 combines with H_2O to form H_2SO_4 vapor below approximately 1000F
  - SO_3 is hydroscopic
- Typically forms as flue gas passes through the air heater

$$SO_3 + H_2O \rightarrow H_2SO_4$$

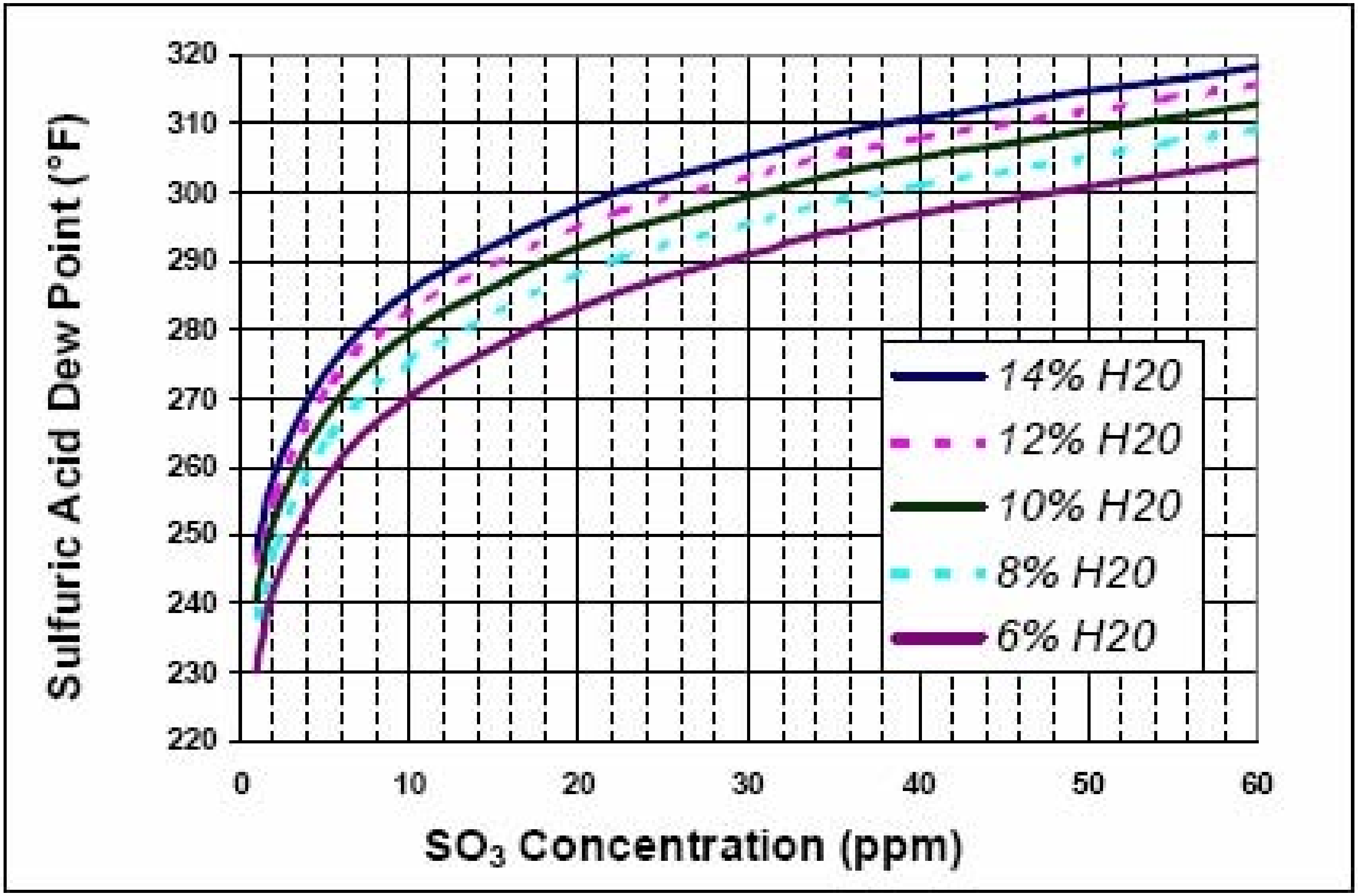
Formation of H_2SO_4



Formation of H_2SO_4

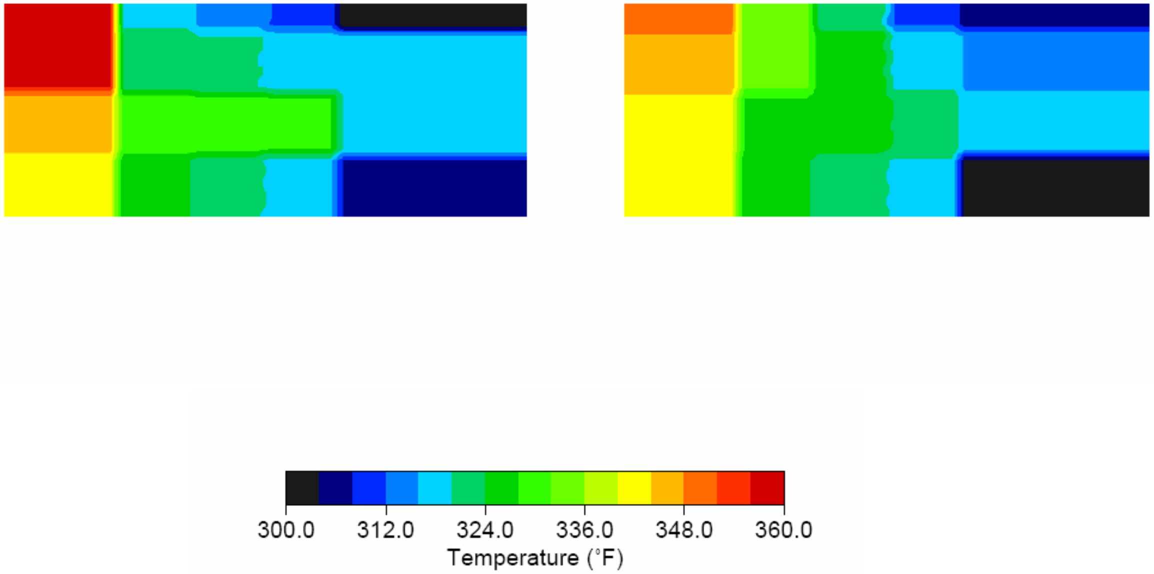
- ***Condensation to H_2SO_4 liquid occurs below the acid dew point temperature***
  - **Acid dew point temperature varies with H_2SO_4 (as SO_3) concentration, pressure and moisture content**
  - **As concentration increases, acid dew point temperature increases and vice versa**

SO_3 Acid Dew Point Curve



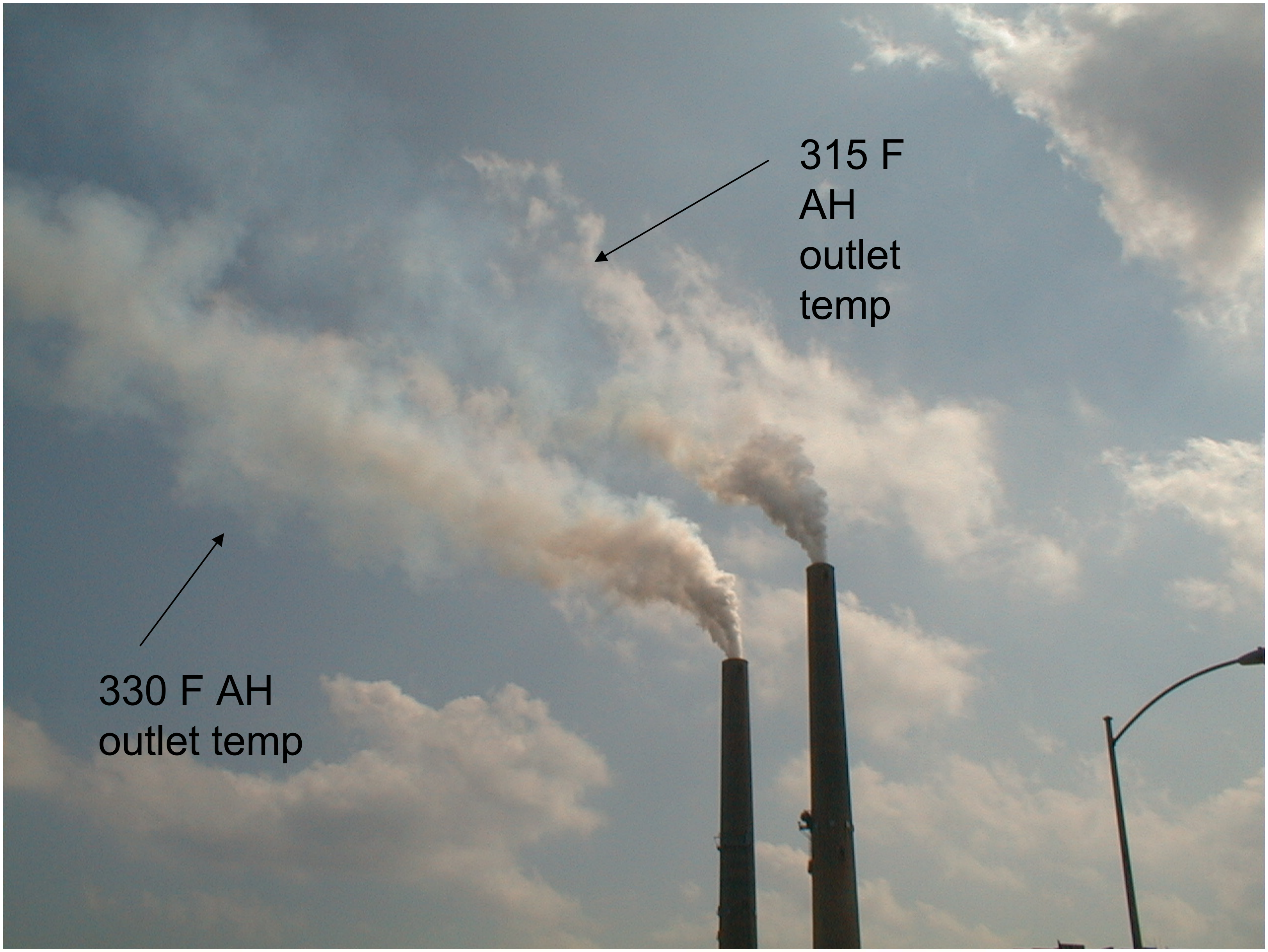
Formation of H_2SO_4

Air Heater Outlet Temperature Profile



SO_3 Removal in Air Heater

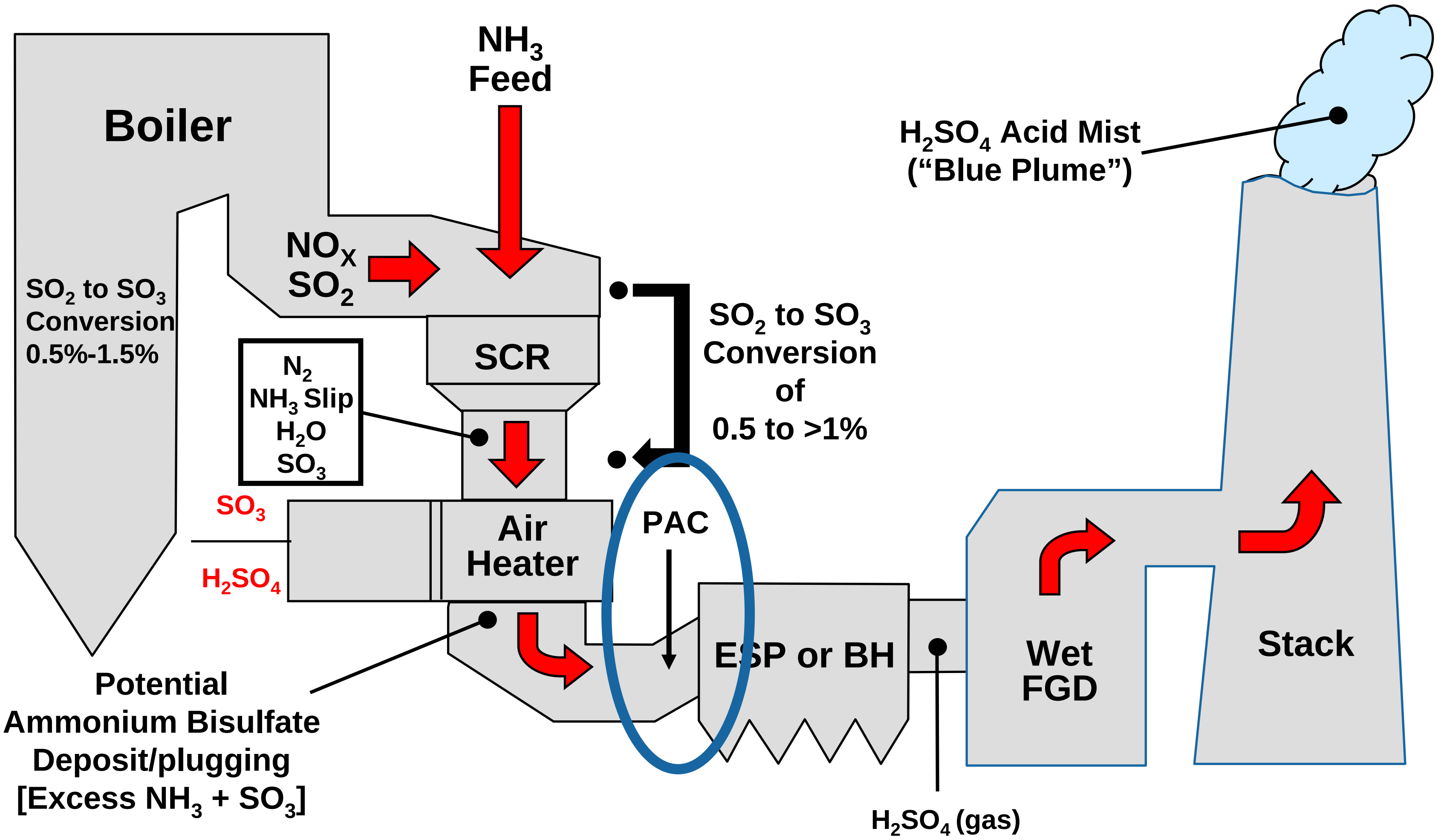
- Some of the acid (H_2SO_4) condenses and impinges on the colder surfaces of the air heater causing a portion to be caught in the air heater baskets and the ash
- The amount of SO_3 captured in the air heater depends on air heater design, cold end metal temperature, operating gas temperature and fuel and ash constituents
- Typically 20-30% of SO_3 entering the air heater is removed



315 F
AH
outlet
temp

330 F AH
outlet temp

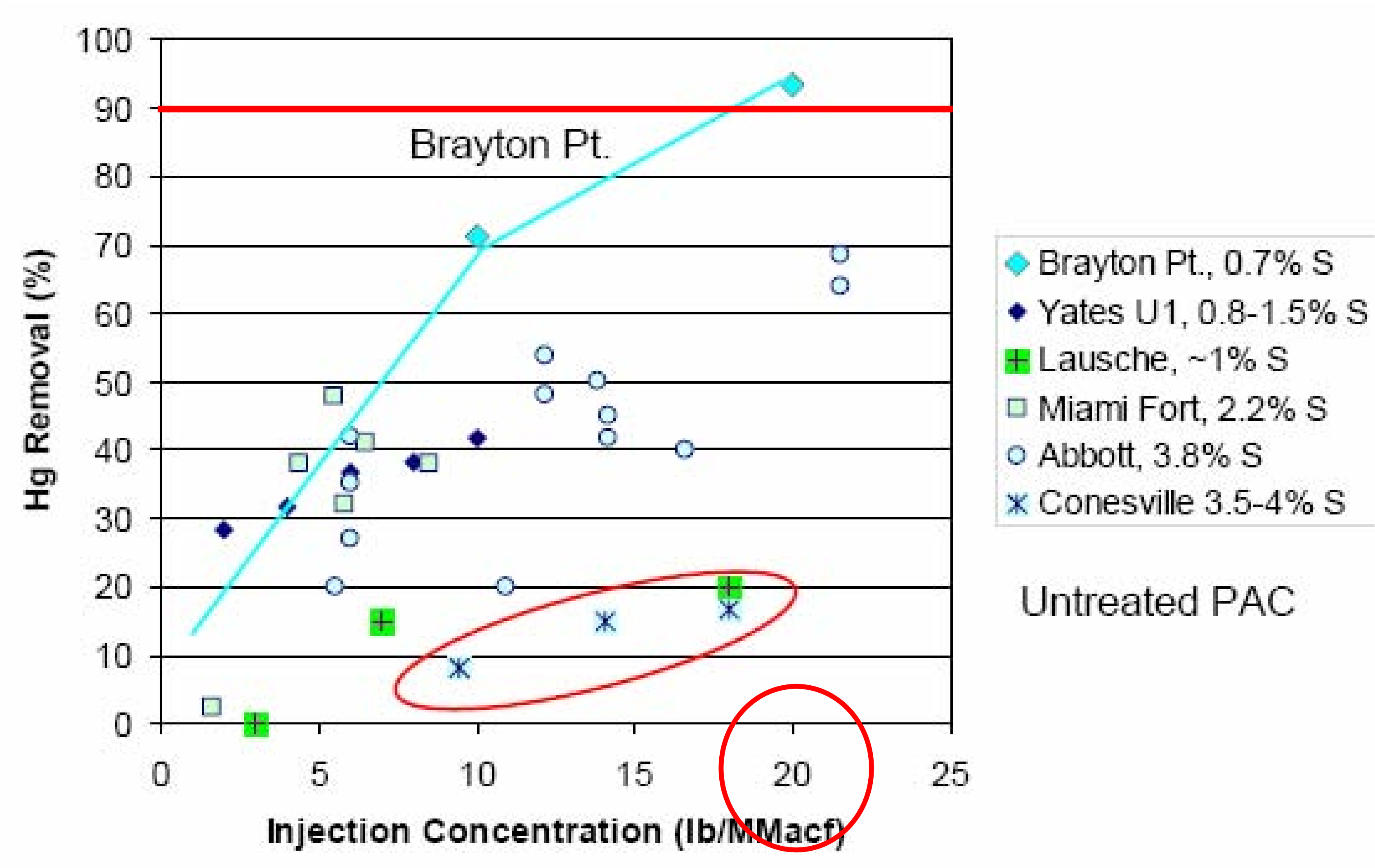
The Effect of SO_3 on Hg Control



The Effect of SO_3 on Hg Control

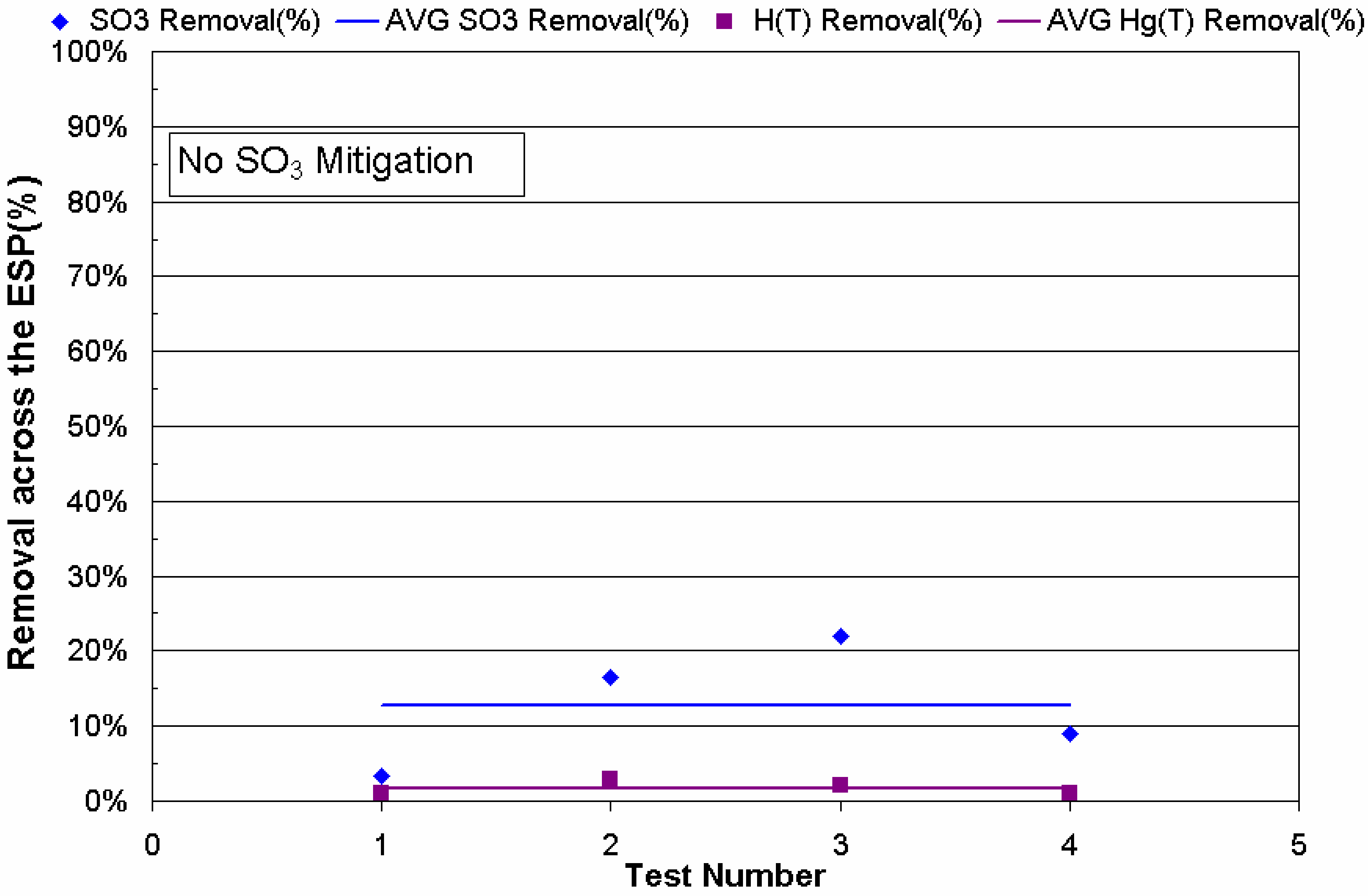
- SO_3 poisons unburned carbon by adsorbing on the surface
- SO_3 competes with mercury for the active sites on unburned carbon
- Concentrations of SO_3 greater than 10 ppmd reduce native mercury removal
- SO_3 also poisons powdered activated carbon for mercury control
- As the concentration of SO_3 increases, PAC consumption increases

Influence of SO_3 on Mercury Removal with Activated Carbon

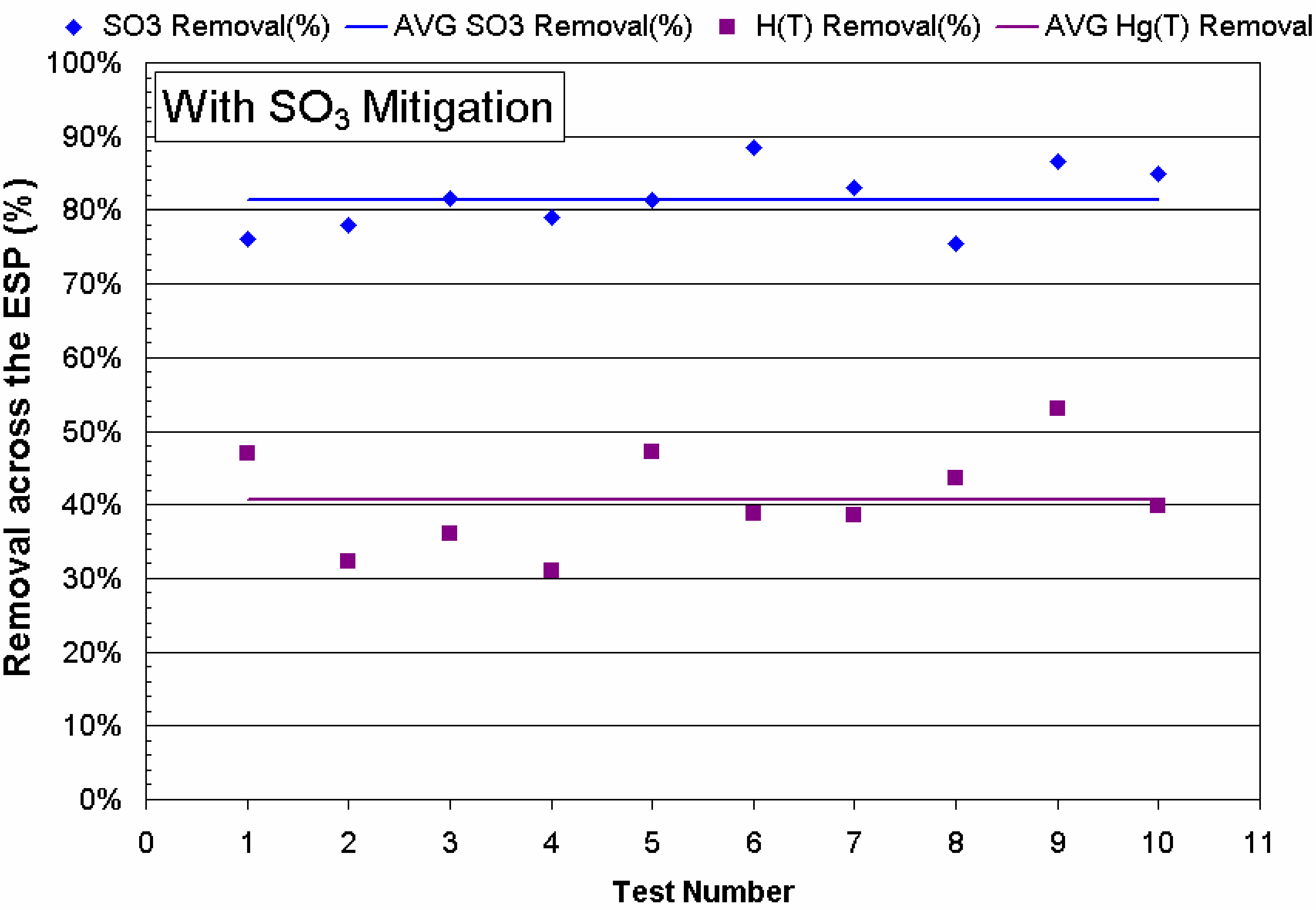


Untreated PAC

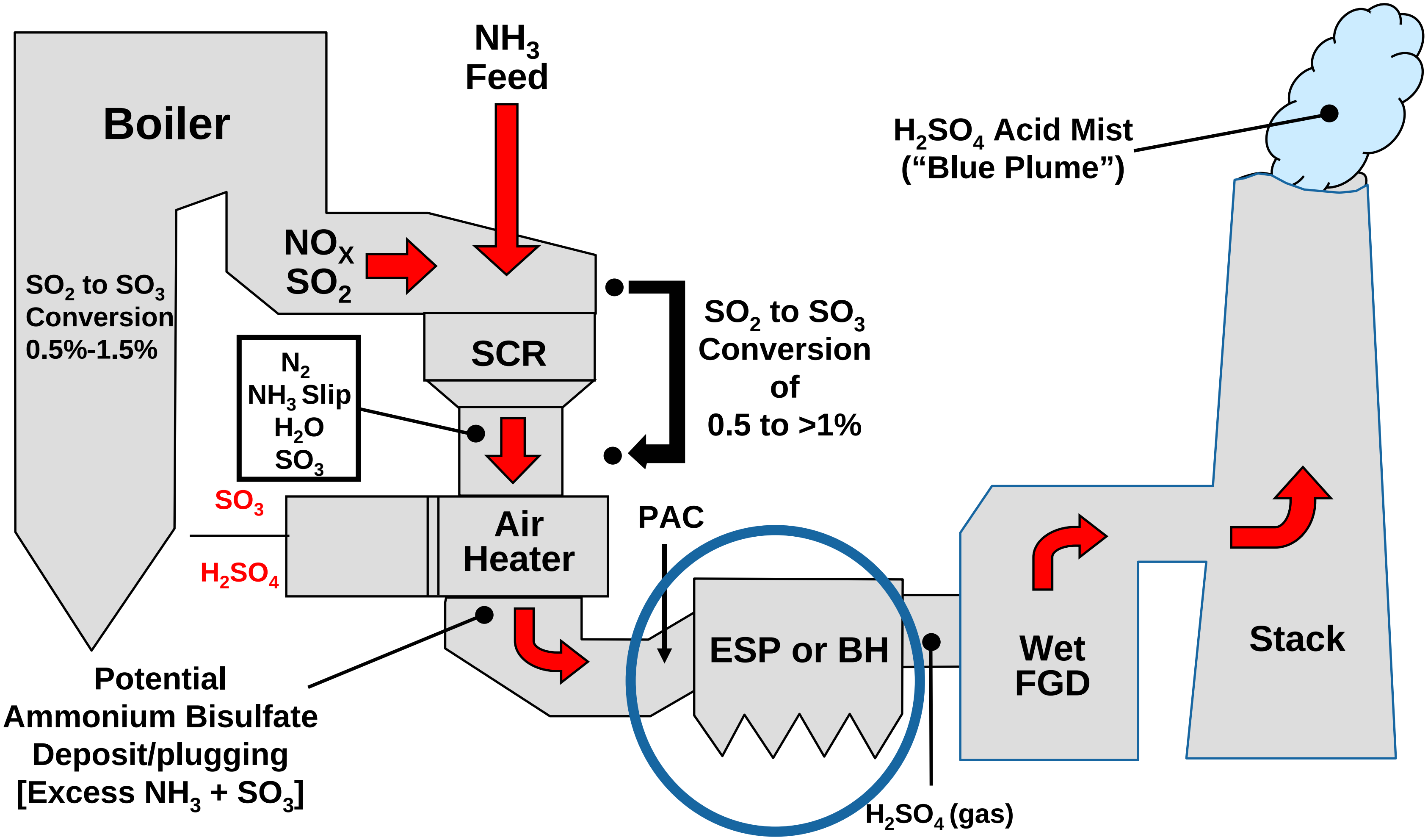
Hg Removal Across the ESP with no SO_3 Mitigation



Hg Removal Across the ESP with SO_3 Mitigation



Particulate Device Capture



Boiler

SO_2 to SO_3 Conversion 0.5%-1.5%

NH_3 Feed

NO_X
SO_2

SCR

N_2
NH_3 Slip
H_2O
SO_3

SO_3

H_2SO_4

Air Heater

SO_2 to SO_3 Conversion of 0.5 to >1%

PAC

ESP or BH

H_2SO_4 (gas)

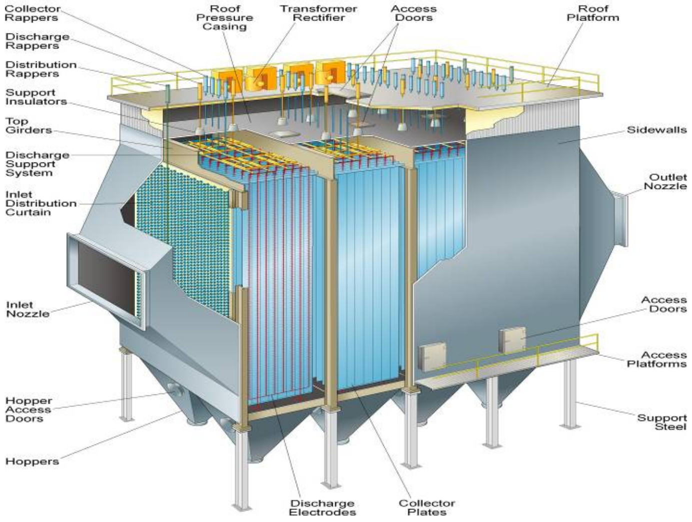
Wet FGD

Stack

H_2SO_4 Acid Mist ("Blue Plume")

Potential Ammonium Bisulfate Deposit/plugging [Excess NH_3 + SO_3]

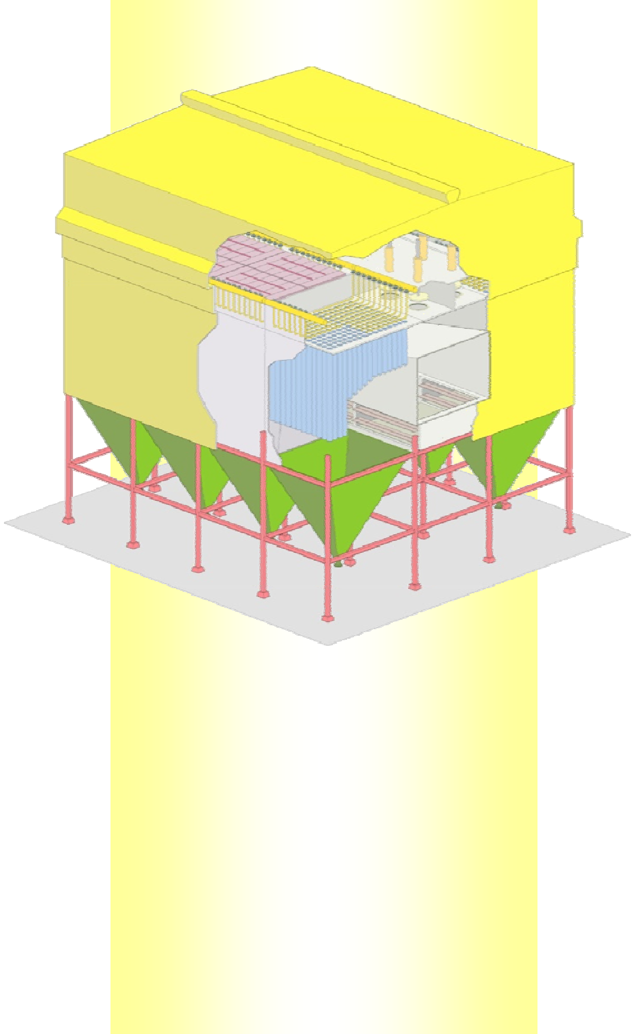
Capture of SO_3 in Dry ESP



The Dry ESP is the industry standard for particulate capture on units burning medium to high sulfur fuels and depends on some SO_3 for greatest performance

Condensed H_2SO_4 removal efficiency is dependent on type of ESP (hot or cold side), alkalinity in the ash, size of the H_2SO_4 aerosol particle size, flue gas temperature and overall particulate removal efficiency

Removal in Fabric Filter



As ash is removed in the fabric filter, a cake builds up on the bag

- Depending on the alkalinity of the ash, this cake can enhance removal as the H_2SO_4 passes thru the bags

Fabric filter is utilized after air heater or as the particulate collector in Dry FGD system

High SO_3 capture is achieved

Fabric Filter and Dry ESP Comparison

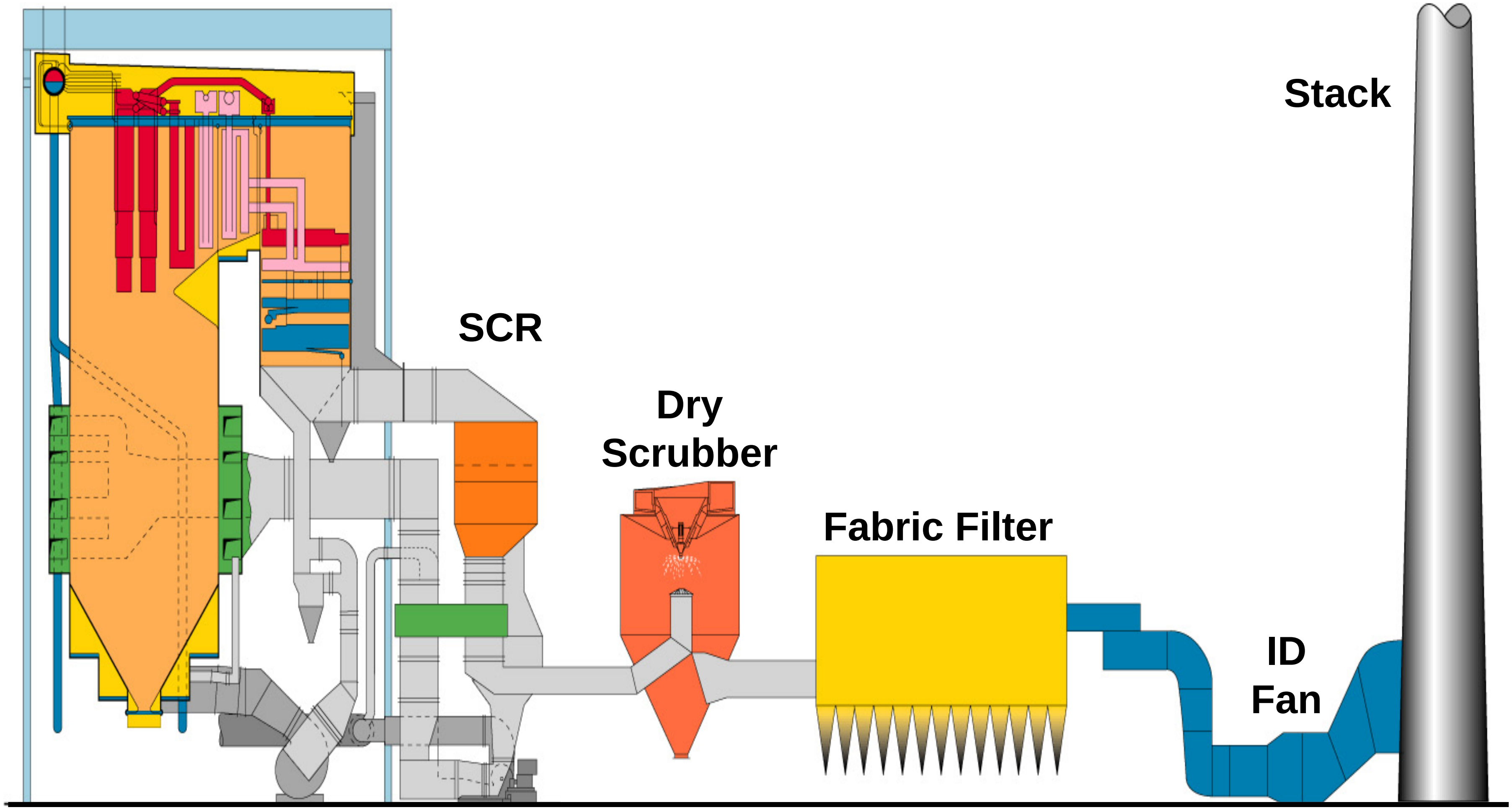
Data on low sulfur fuels indicates that a fabric filter is more effective at capturing H_2SO_4

ESP allows for lower inlet operating temperatures compared to fabric filter which equates to greater boiler efficiencies

Fabric filter operation is limited by:

- Fabric material of the bags
- Flue gas temperature
- Acid dew point

Typical Dry Scrubber & Fabric Filter

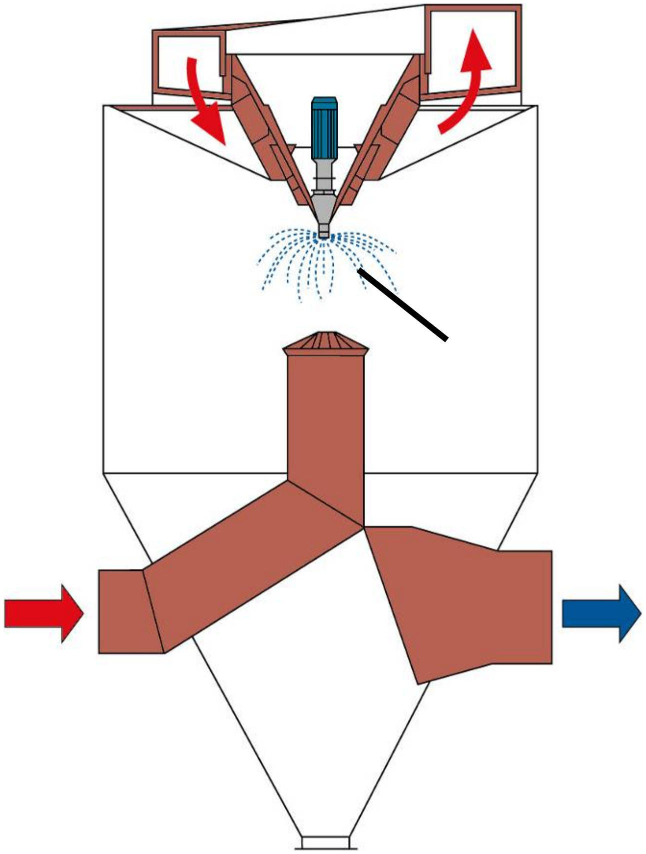


Dry FGD / Fabric Filter and SO_3

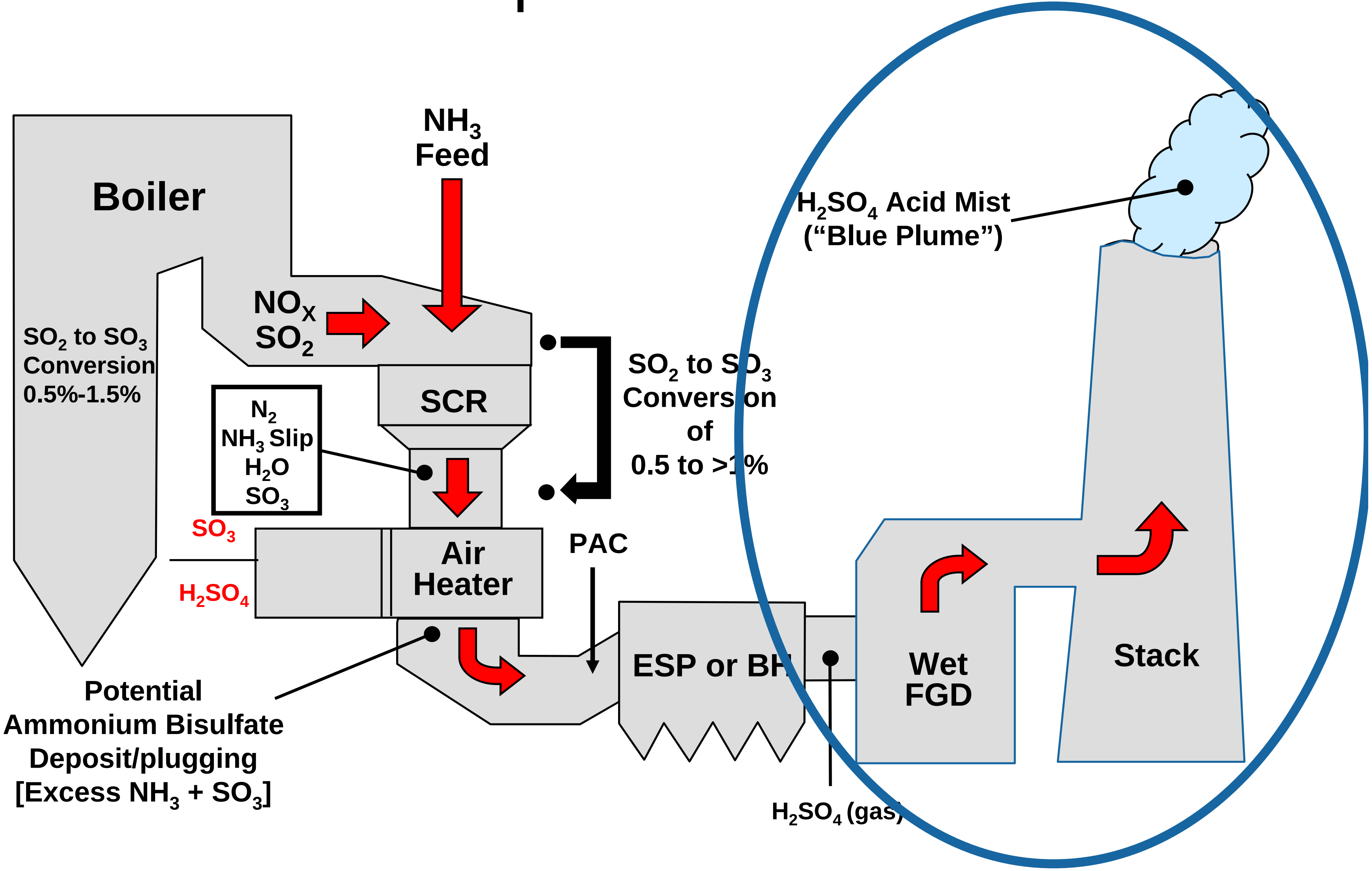
Lime slurry is injected allowing reduced temperature and lime reactions with SO_2 and SO_3 in favorable conditions and in filter cake

Effective system control of SO_2 and SO_3 for lower sulfur fuels including PRB coals

Measured H_2SO_4 emissions of <1 ppm



WFGD – Vapor to Mist Conversion



Mechanism for H_2SO_4 Removal in Wet FGDs

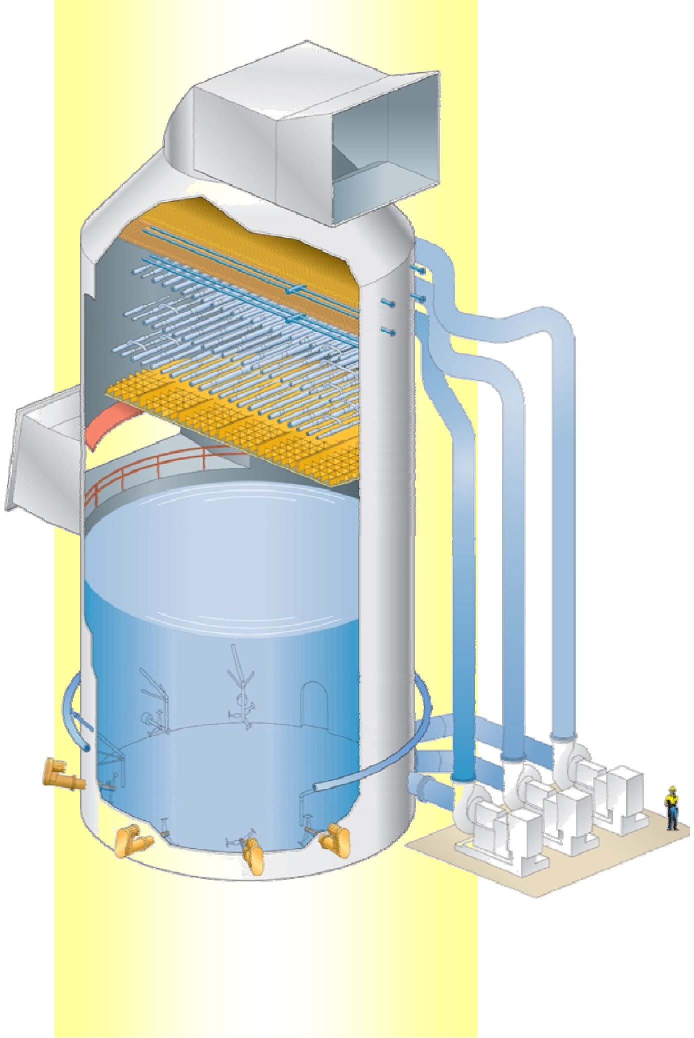
A Wet FGD system provides the ideal conditions for aerosol formation

As the flue gas enters the scrubber quench zone, the H_2SO_4 vapor is quickly cooled below its dew point

- The rapid condensation that takes place in the scrubber results in ultra-fine (sub-micron) aerosols, 0.4 – 0.7 microns
- The size of the H_2SO_4 aerosol particle may be dependent on how fast it is condensed

Removal of the aerosol in the scrubber is dependent on particle size

- This explains the variability in acid mist removal in scrubbers in a given plant



H2SO4 acid mist formation in WFGD

Temperature = 70 F
25 to 30 ppm H_2SO_4 mist above ME's
Absorber flux = 0 gal/ft2

Temperature = 70 F
20 to 25 ppm H_2SO_4 mist above ME's
Absorber flux = 60 gal/ft2

H_2SO_4 and FGD

- **H2SO4 acid mist formation in WFGD (cont'd)**
  - **Even though a portion of H2SO4 is removed across a WFGD, it may not be enough to reduce opacity**
    - Downstream of WFGD, forms an aerosol that contributes to a visible, trailing "Blue Plume"
  - **Small amounts of H_2SO_4 (> 5 ppmv) can cause opacity issues at the stack**
  - **High stack opacities are typically associated with eastern bituminous fuels, due to:**
    - **Higher S coal**
    - **Low ash alkalinity**
  - **Less buoyancy with wet (cooler) plumes which can result in touchdown at certain ambient conditions (i.e. high ambient temperatures)**

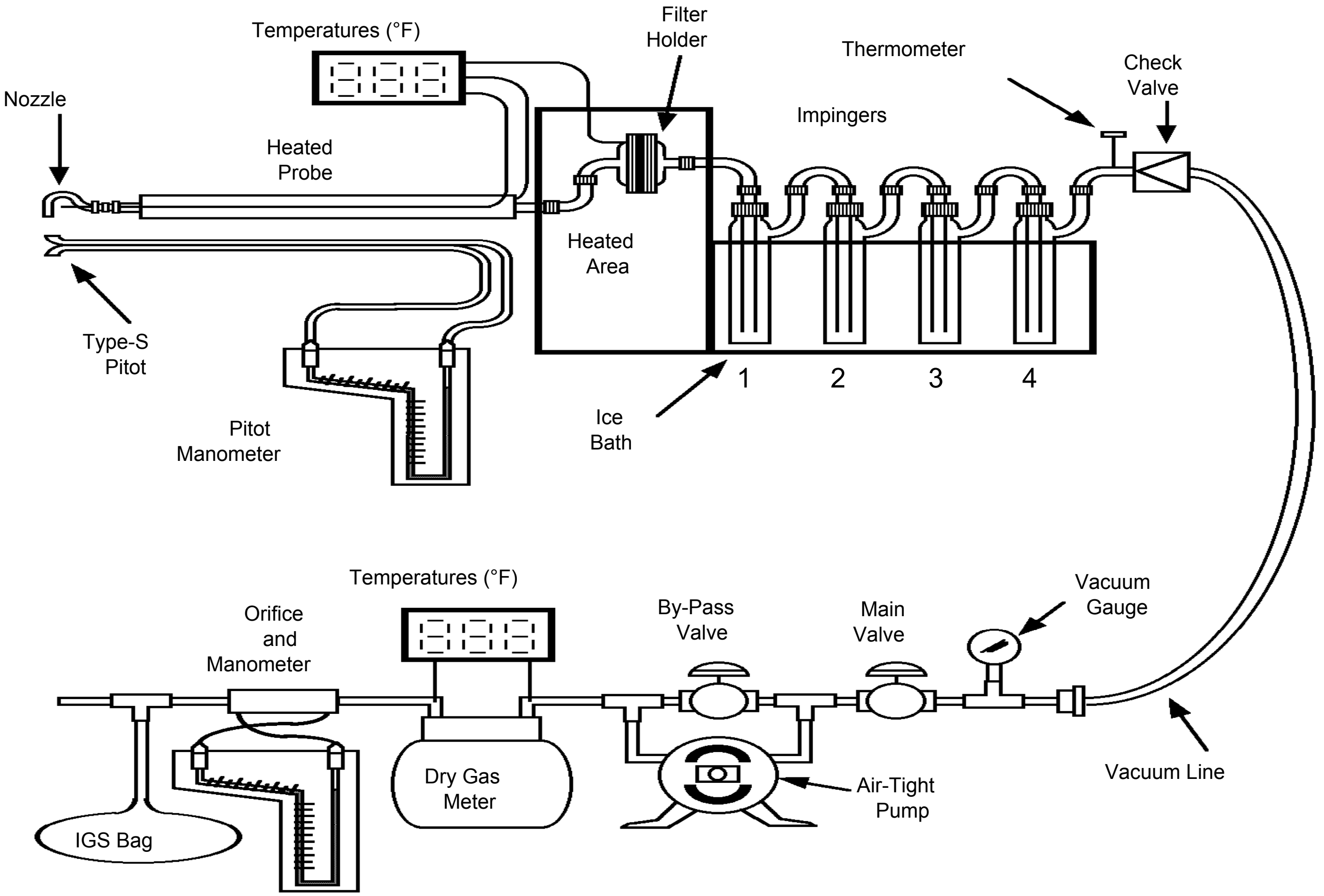
SO_3 and H_2SO_4 Formation & Control

- Issues
- Sources
- Measurement
- SO_3 Control
  - Dry Sorbent
  - WESP

SO_3 and H_2SO_4 measurement

- **Method 8**
- **Controlled Condensation**

EPA Method 5B + 8 Sampling System



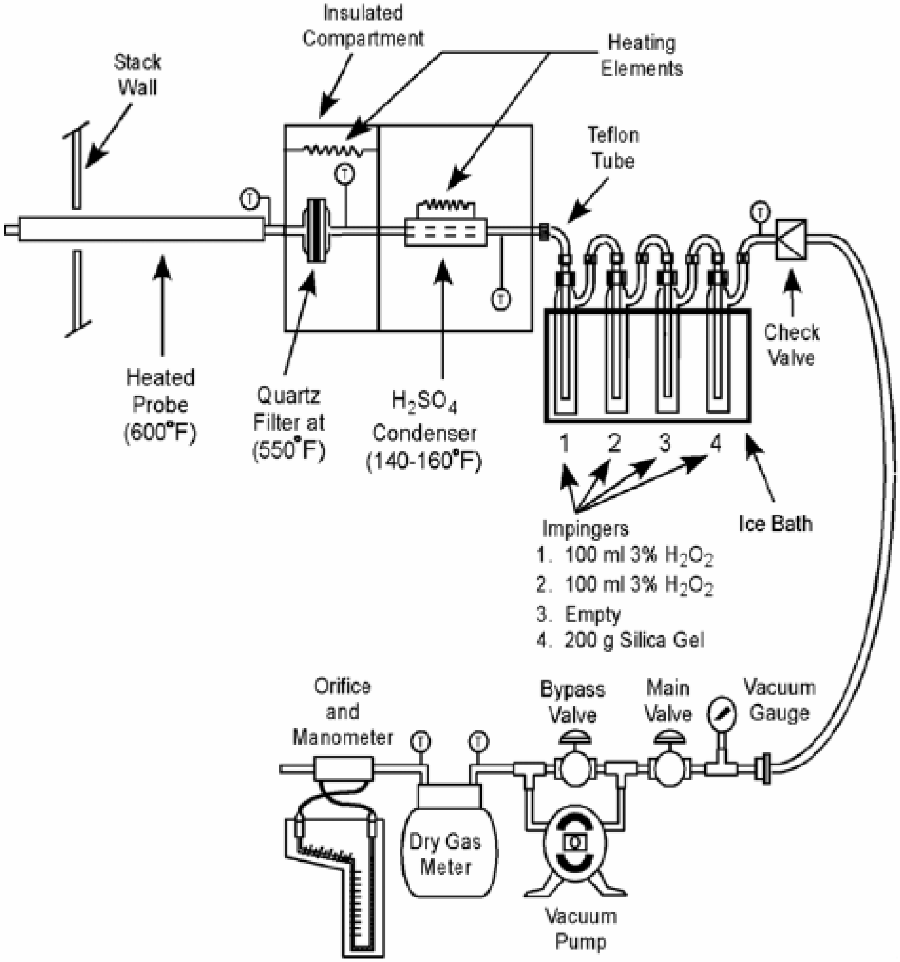
IMPINGER 1 = 80% ISOPROPANOL

IMPINGER 2 = 3% H_2O_2

EPA Method 8

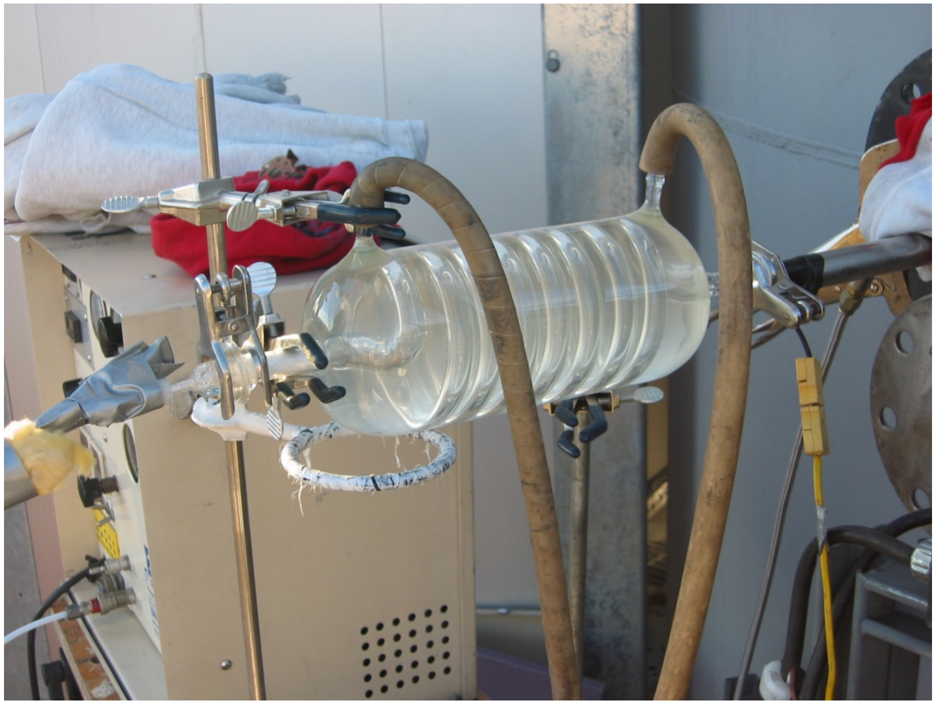
- Designed to measure [SO_3 + H_2SO_4], and SO2
- 80% Isopropanol filled impinger followed by a filter then by two impingers <u>with 3% peroxide</u>.
- [SO_3 + H_2SO_4] is collected in the isopropanol impinger and following filter
- SO_2 is collected in the peroxide impingers
- A particulate filter upstream of the impingers is not required per the method but is allowed, as per methods 5 or 5B, if filterable particulate is also measured.
- Method was developed and intended for sulfuric acid plants, not coal burning plants

SO_3 Measurement by Controlled Condensation System



“Controlled Condensation” for SO_3 vapor.

Method utilizes a glass condenser operated in a controlled temperature water bath (160F)



SO_3 and H_2SO_4 Formation & Control

- Issues
- Sources
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Injection Options:

- **Sorbent injection (ammonia, calcium, magnesium, or sodium compounds)**

Hardware Solution:

Wet ESP

SO_3 and H_2SO_4 Formation & Control

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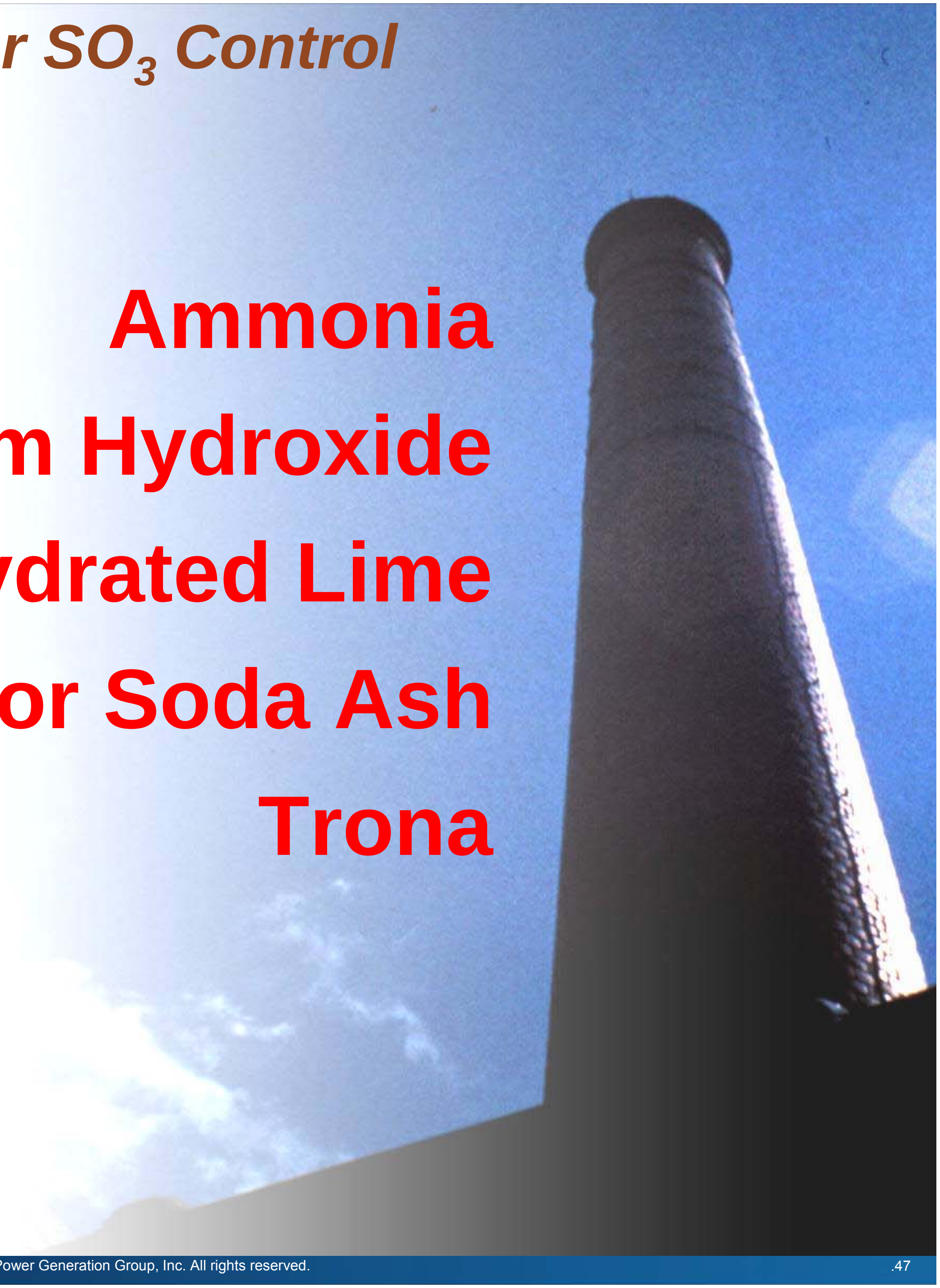
Popular Sorbents Used for SO_3 Control



Ammonia

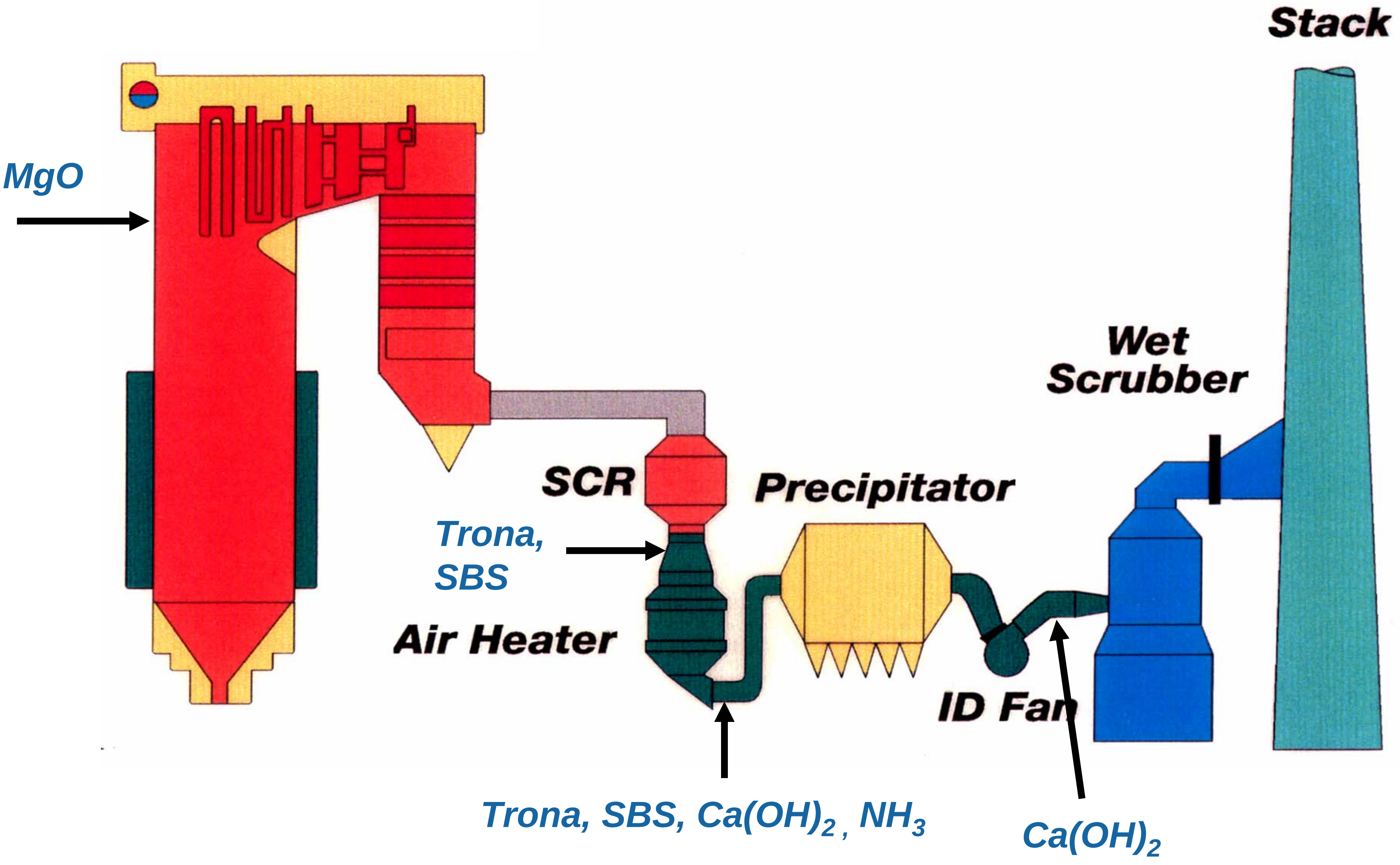
Magnesium Hydroxide

Hydrated Lime

Sodium Bisulfite or Soda Ash

Trona

Sorbent injection Locations (Typical)



MgO

Trona, SBS

Trona, SBS, $Ca(OH)_2$, NH_3

$Ca(OH)_2$

Ammonia

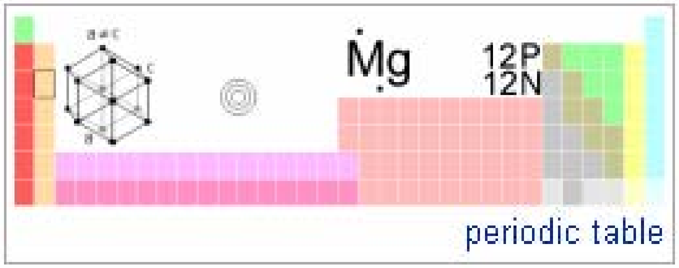
- Typically injected downstream of the air heater and upstream of the ESP to form ammonium bisulfate and/or ammonium sulfate
- Ammonia has minimal capital and O&M costs compared to other technologies – plants with an SCR system already have ammonia on site, which could be utilized for SO_3 mitigation
- Good for 20 ppm SO_3, Removal in the 80% range

Ammonia

- The use of ammonia for SO_3 mitigation can impact fly ash sales
  - Ammonia off-gassing from fly ash is a concern
  - Sites that stabilize scrubber sludge by mixing it with fly ash and lime could experience odor problems
  - Additional equipment may be required to burn off ammonia
- ABS formation may cause buildup in flues and cause ESP operational problems from ammonia salts
- There is also a risk of increased stack ammonia emissions

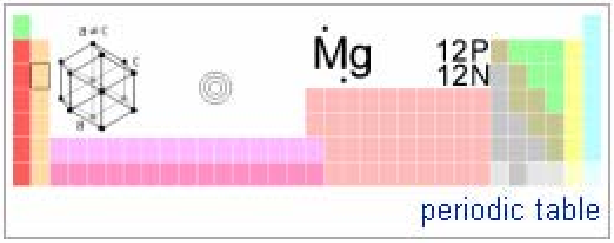
Magnesium Hydroxide

- Magnesium-based sorbents are primarily injected in the furnace
  - ✓$Mg(OH)_2$ is effective at capturing SO_3 formed during the combustion process in the furnace
  - ✓Not shown to be effective in controlling SO_3 formed from the catalyst
  - ✓Typically used in conjunction with mitigation technology
- This sorbent can also have a beneficial impact in reducing slag formation on furnace surfaces
- $Mg(OH)_2$ build-up on tubes may help to reduce SO_2 to SO_3 Oxidation in boiler.



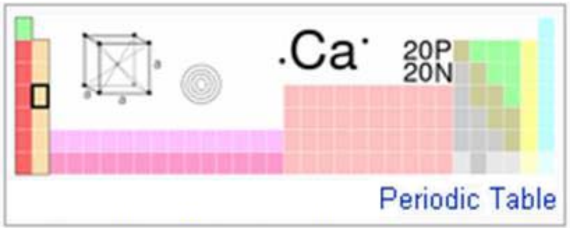
Magnesium Hydroxide

- Does not address conversion from SCR
- O&M factors include nozzle maintenance and the wear associated with pumping an abrasive slurry
- Capital costs must include the slurry preparation equipment needed, and if winter operation is required, heat tracing and insulation of slurry pipes
- Reagent Cost is very costly



Hydrated Lime

- Hydrated lime, $Ca(OH)_2$, has been successfully utilized as a means to mitigate SO_3
- Injected on a dry basis after the air heater and ahead of the particulate collector or in front of FGD
- The injection system is simple keeping capital costs to a minimum
- The sorbent is readily available.



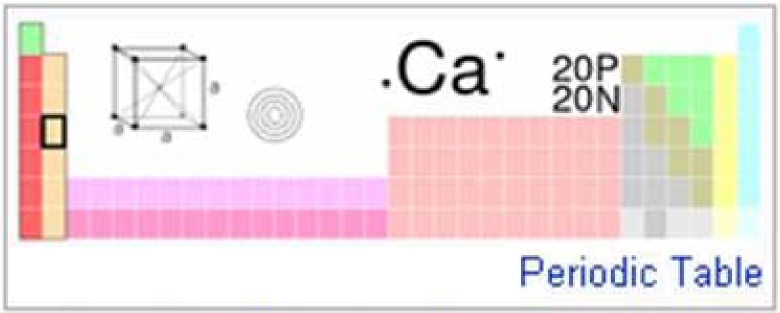
Hydrated Lime

Not all hydrated lime is the same. Surface areas and available Ca(OH)2 should be considered in any evaluation.

Works better with large ESP's

Does not impact ash sales

Lime tends to not be as reactive as sodium based sorbents. Thus may require a longer residence time than sodium sorbents to maintain similar SO3 reduction



Sodium Bisulfite (SBS) or Soda Ash

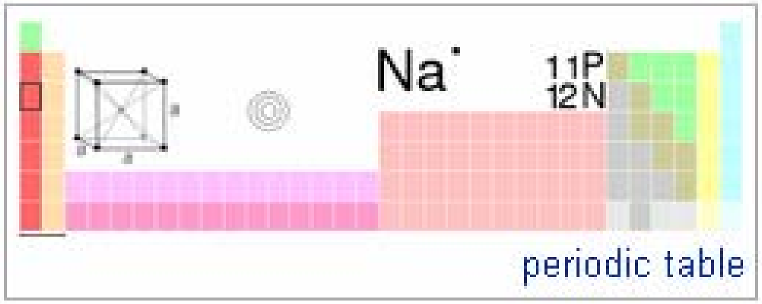
Sodium Bisulfite (SBS) or Soda Ash is very effective at removing SO_3

It is injected as a liquid

SBS can be purchased commercially or the by-product of a dual alkali FGD can be used

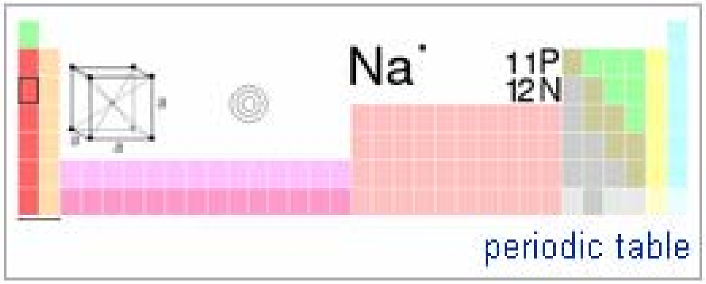
There are some reported maintenance issues:

- Nozzles
- Duct deposition
- Air heater fouling has occurred when injected prior to air heater



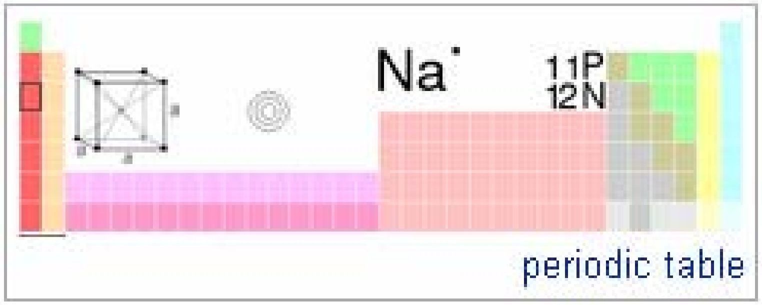
Sodium Bisulfite (SBS) or Soda Ash

- Compressed air is required for atomization
- Increased residence time is required to evaporate the moisture in slurry when compared to an all dry system
- Field tests have shown some improvement in ESP operation



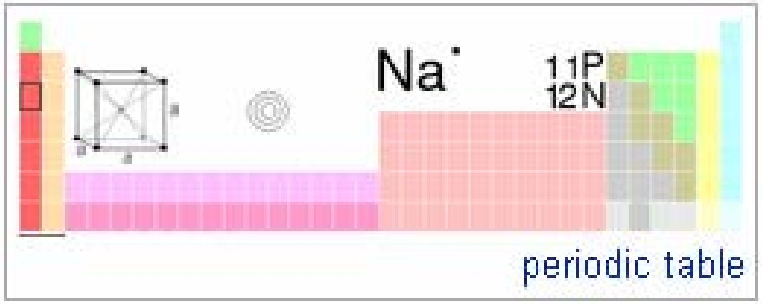
Trona

- Chemical formula is Na_2CO_3● $NaHCO_3$● 2H20
- Large mineral deposits found in Green River, Wyoming area
- Trona is used to manufacture Soda Ash
- Dry Trona is relatively benign and unreactive, minimizing plant safety concerns
- Like other sodium sorbents, Trona is very reactive and effective in removing SO_3



Trona

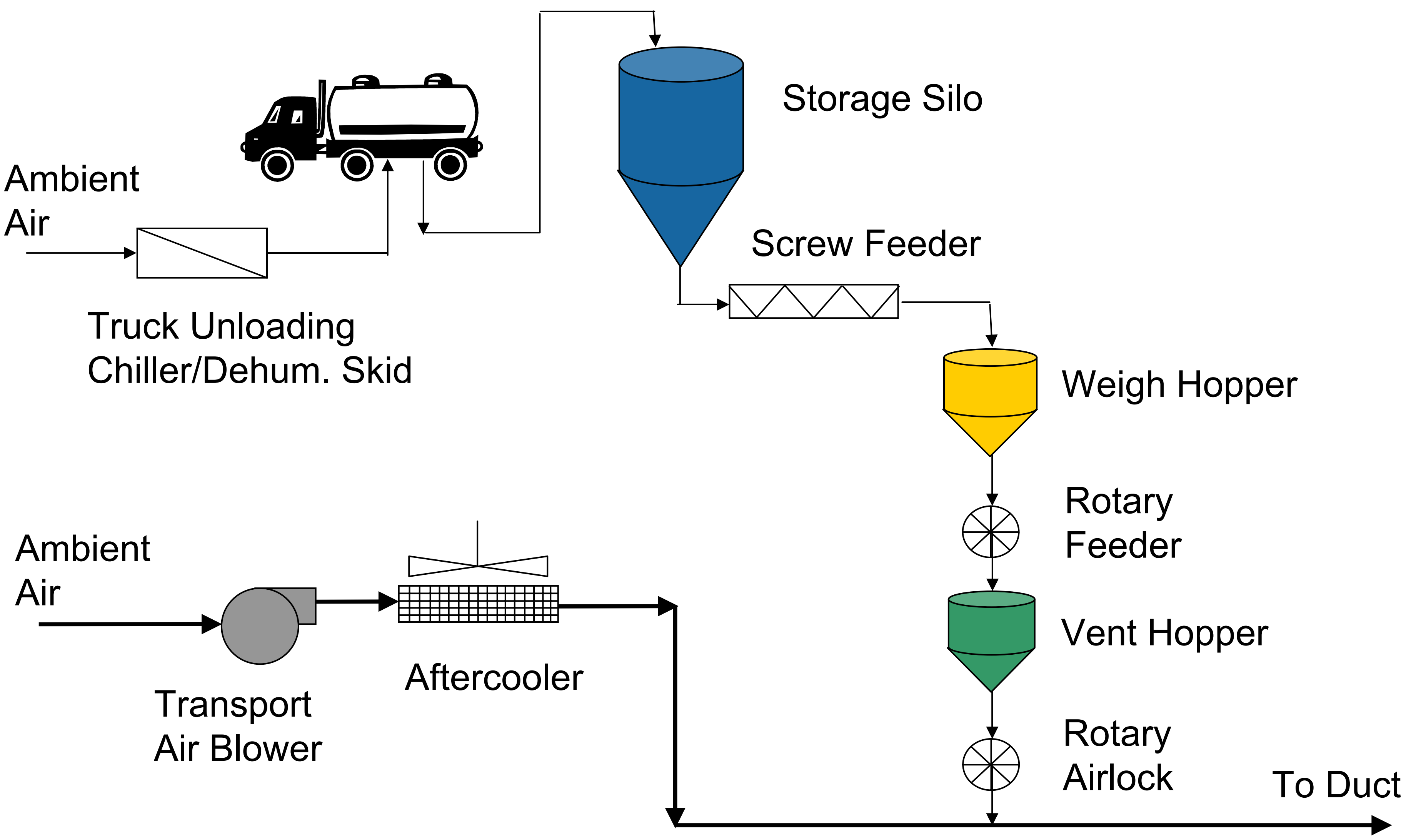
- Trona calcines in the flue causing a “popcorn” effect which increases the surface area and reactivity.
- Trona is injected in dry form which reduces the capital investment required to get it to the flue gas. Typically injected downstream of the Air Heater
- An additional benefit of injecting Trona is improved DESP performance by reducing the resistivity of the ash
- Flyash consideration



Dry Sorbent Injection - Key Design Parameters

- **Even flow distribution at injection location**
- **With temperature stratification leaving the air heater, it is important to match the sorbent injection with the acid gas stratification**
  - ✓ **Optimizes removal and minimizes sorbent usage**
  - ✓ **Higher temps correlate to higher acid concentrations**
- **CFD Modeling**
- **Residence time, >1 s**
- **Lance placement, complete coverage of sorbent injection**
- **Nozzle design, dispersion nozzle rather than open pipe**

Process Flow Diagram



Ambient Air

Truck Unloading Chiller/Dehum. Skid

Storage Silo

Screw Feeder

Weigh Hopper

Rotary Feeder

Vent Hopper

Rotary Airlock

Ambient Air

Transport Air Blower

Aftercooler

To Duct

SO_3 and H_2SO_4 Formation & Control

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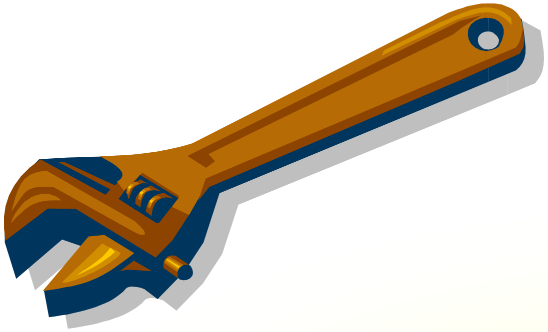
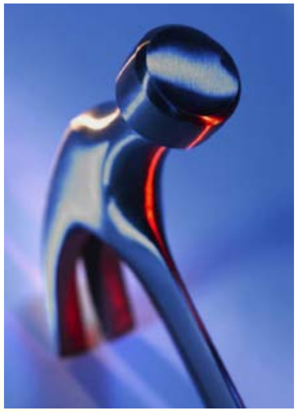
  - WESP

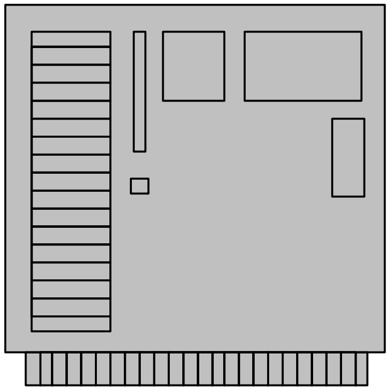




WESP

“Hardware Option”

The Ultimate Solution for SO3 and PM 2.5



Wet ESPs Are Not New!

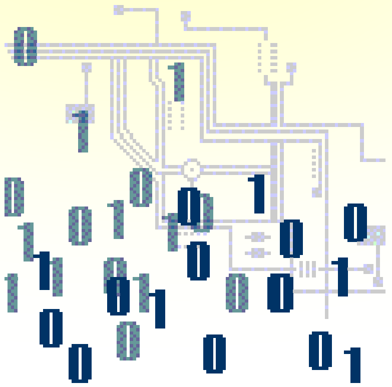
First commercial ESP was a wet unit put in service in 1907 in California for collection of acid mist

Wet ESPs have been used in the following industries/applications:

- Non-ferrous smelters
- Steel industry
- Spent acid plants
- Paper industry
- Incineration
- Power plants burning unique fuels

Thousands of industrial Wet ESPs have been installed since 1907

Wet ESP Theory



WESP Theory

- The basic theory of a wet ESP is the same as a Dry ESP
  - a WESP requires a water spray system rather than a system of plate & DE rappers

- Because acid mist is removed from a WESP in the form of a solution, hoppers are typically replaced with a drainage system.

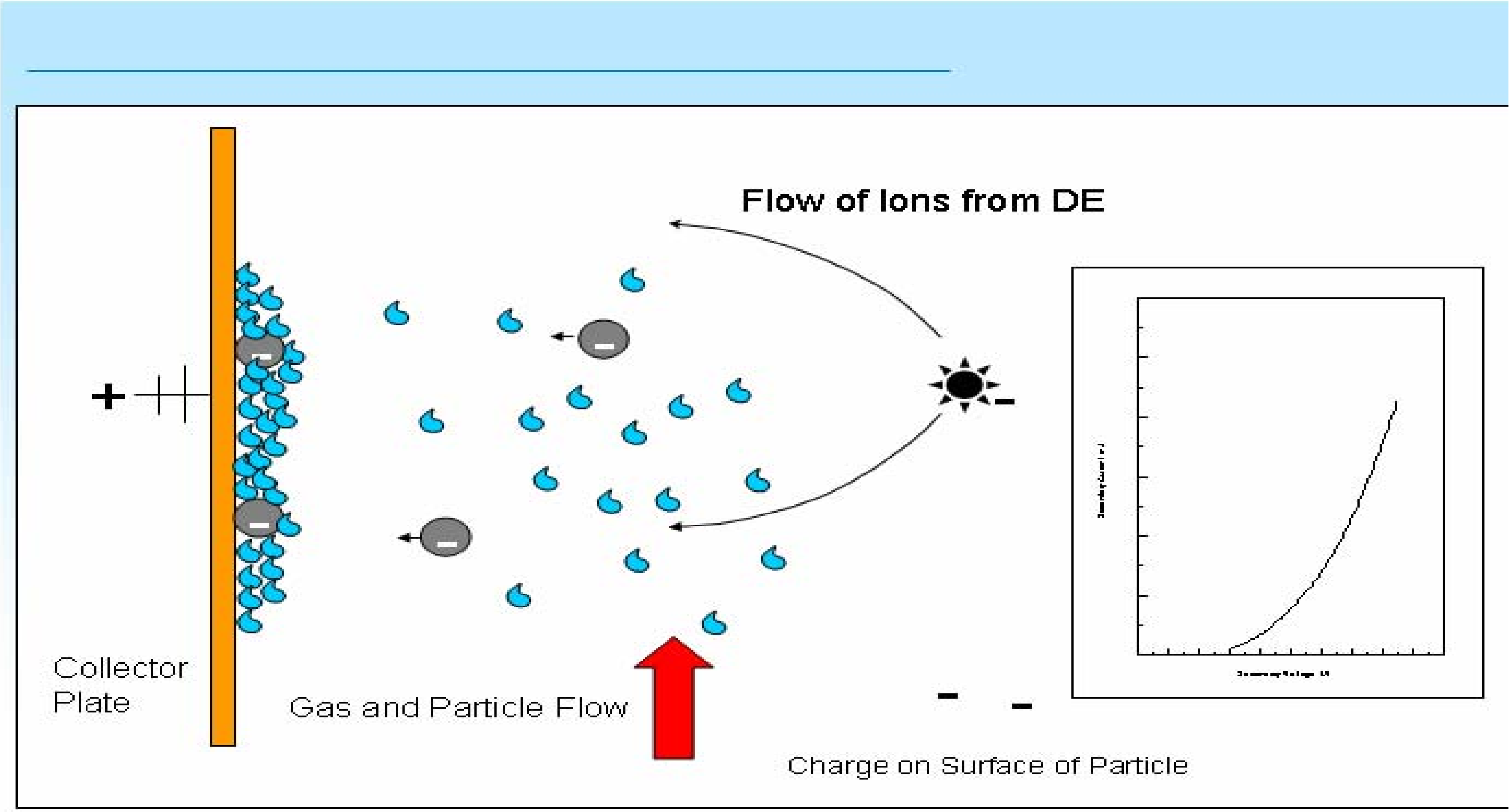
- WESP’s have several advantages over a Dry ESP
  - Can handle condensed particulate from scrubber
  - Compatible with scrubbers
  - Eliminate entrainment of captured particles

- Wet ESP’s are not limited by the particle resistivity, since the humidity in WESP lowers the resisitivity of normally highly resistive particles.

Wet ESPs vs. Dry ESPs

	Dry ESP	Wet ESP
Gas Temperature	250 - 850F range	Saturation temperature (typically 130F in Wet FGD)
Gas Humidity	< 10% typical	100%
Power Density	Variable with coal sulfur content and ash chemistry	Significantly higher than Dry ESP
Resistivity	Critical design factor	Not a design factor
Gas Velocity	5 fps ±	10 fps ±
Treatment Time	10 seconds ± typical	1- 5 seconds ± typical
Re-entrainment	Important factor	Not a factor
Corrosion	Mild steel (typical)	Specialty metals and/or plastics

WESP Theory


Flow of Ions from DE
+
-
Collector
Plate
Gas and Particle Flow
- -
Charge on Surface of Particle

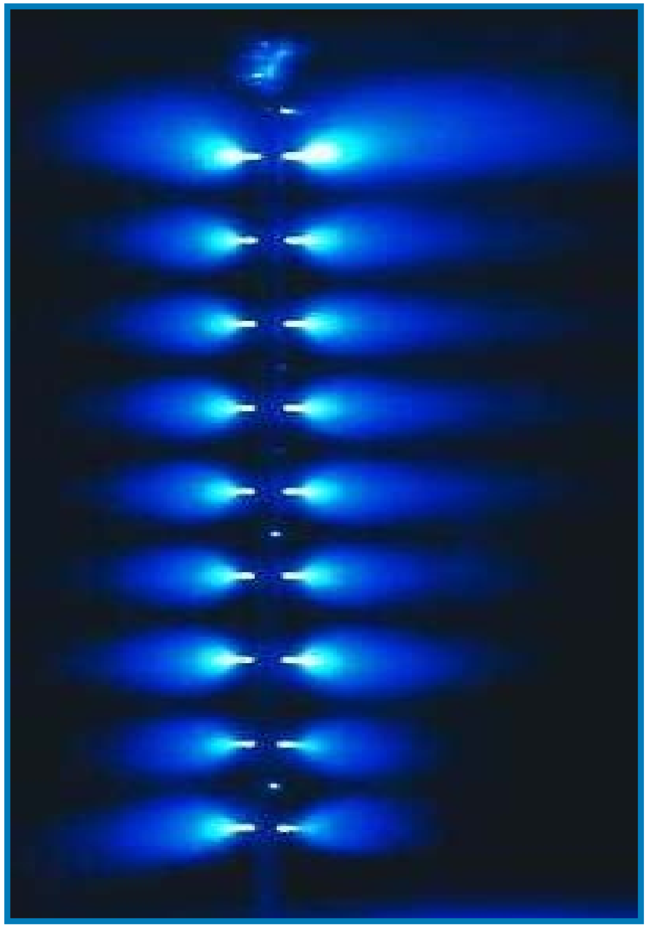
WESP Theory

In simple terms:

- A flow of electrons is emitted from the discharge electrode to create an electric field (Corona)
- The electrons (negative charge) flow through the discharge electrode to the collecting plate which is positively charged
- When a particle or mist passes though the electric field it becomes negatively charged.
- Being negatively charged, the particle or mist then migrates to the collecting plate and is captured on the plate.

Corona

The Corona is the electrically active region of the gas stream formed by the electric field



Deutsch-Andersen Equation

$$E=1-e^{-(Aw/V)}$$

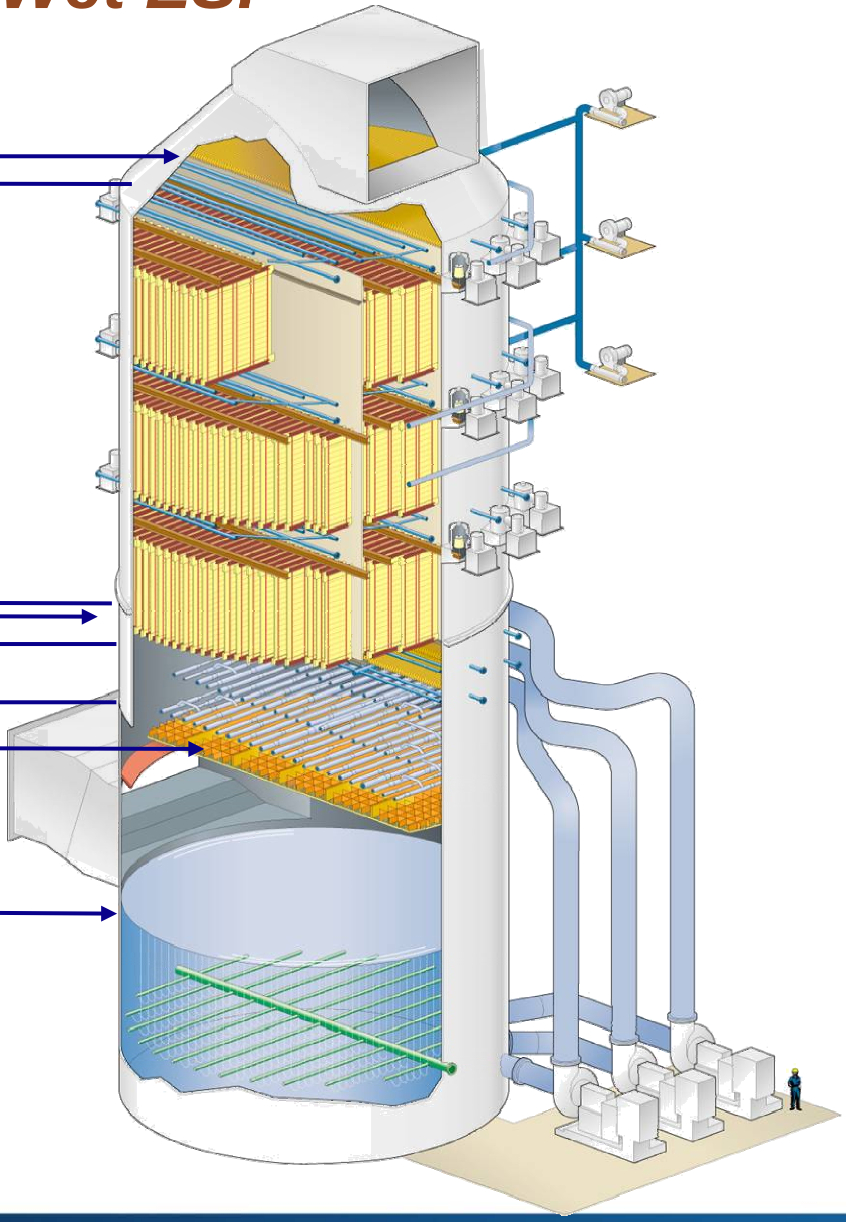
E = Collection Efficiency
V = Flue Gas Volume – ACFM
A = Total Collection Area - ft^2
w = Average Migration Velocity - ft/sec

Types of Utility Wet ESPs for Future New & Retrofit Installations

Close-Coupled (Integrated) Wet ESP

Wet FGD with Stand-Alone Wet ESP

Integrated Wet FGD / Wet ESP



Mist Eliminator

Wet ESP

FGD Mist Eliminator

Absorber Sprays

Tray

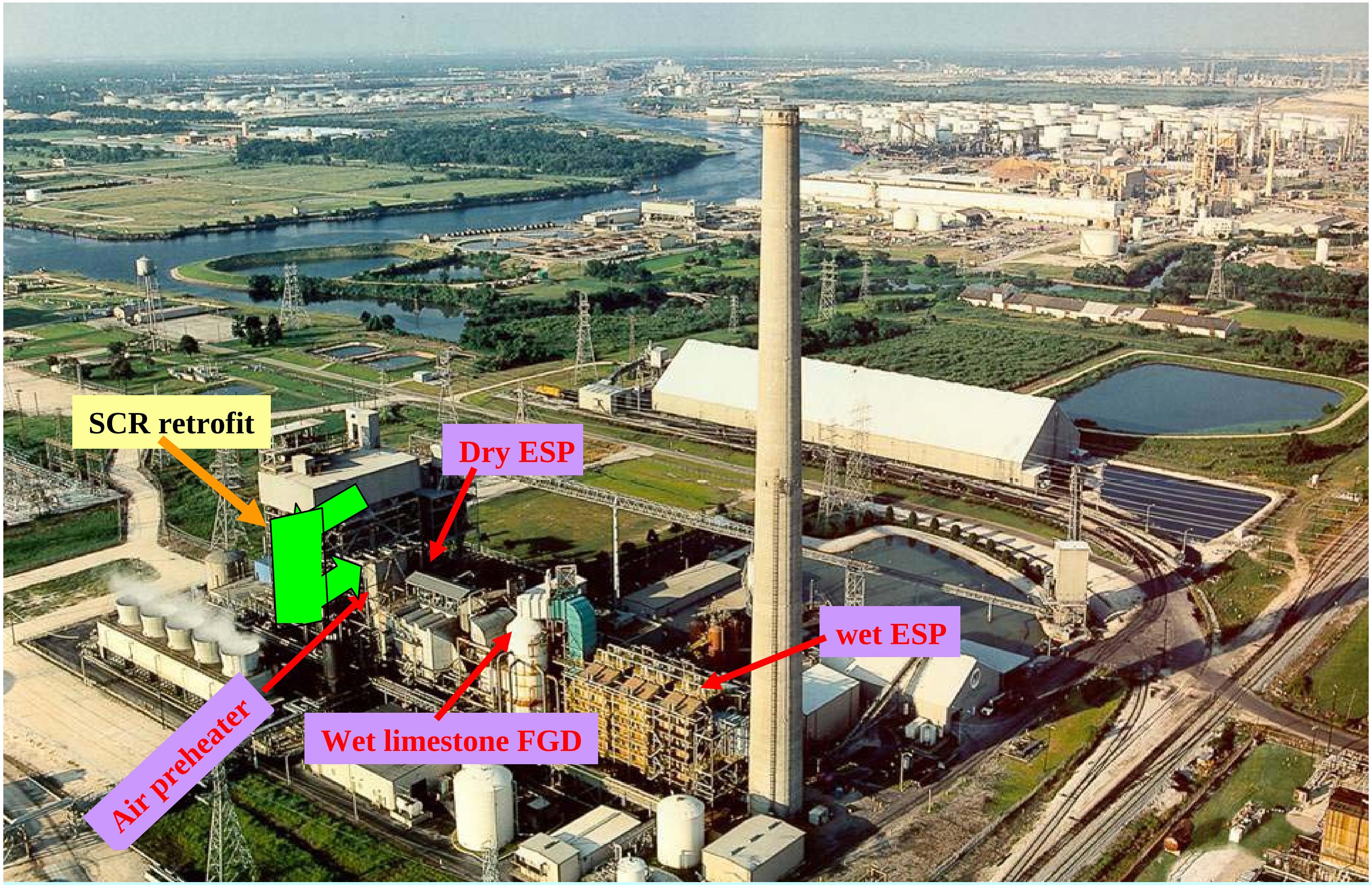
Normal Liquid Level

Types of Utility Wet ESPs for Future New & Retrofit Installations

Close-Coupled (Integrated) Wet ESP

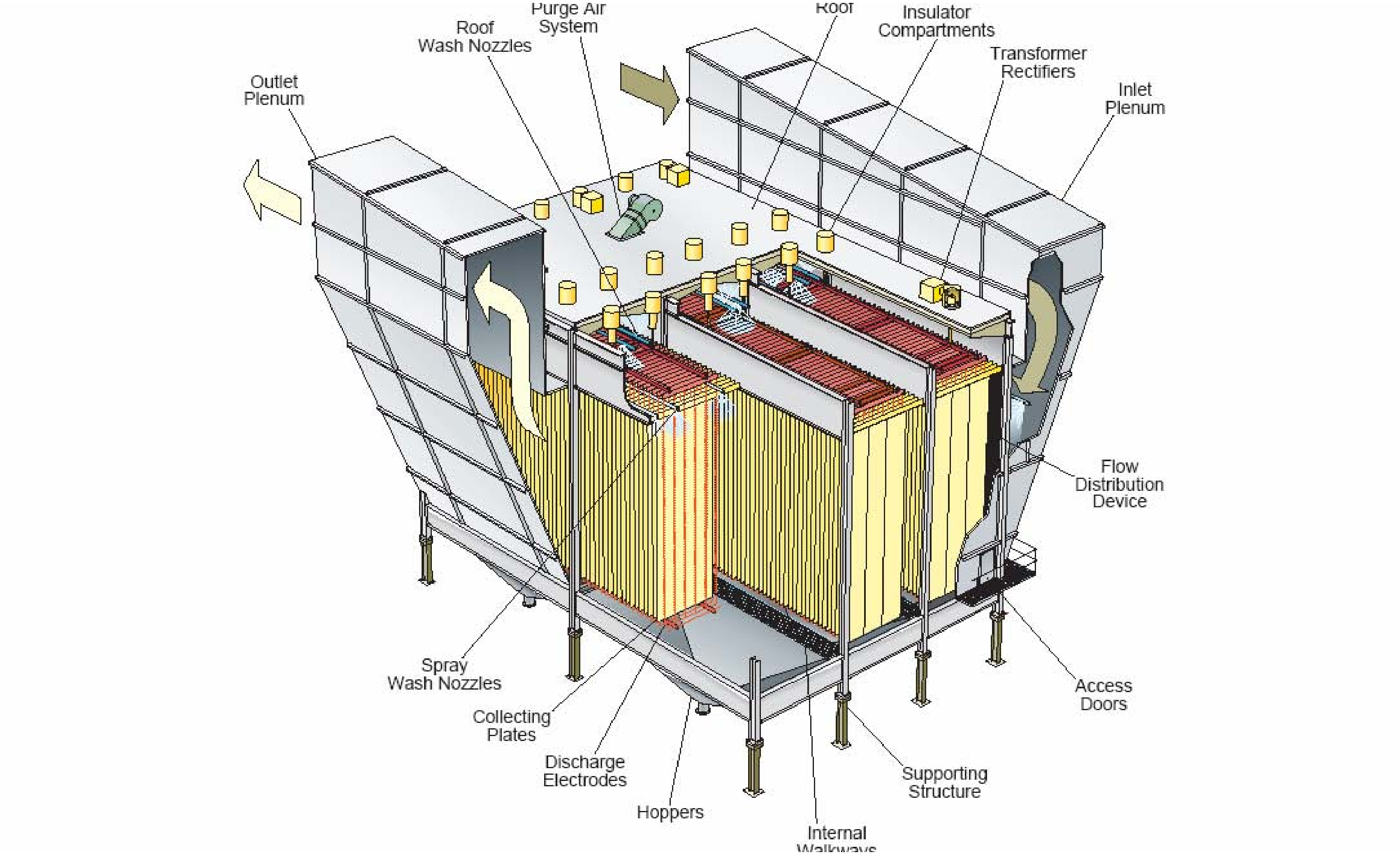
Wet FGD with Stand-Alone Wet ESP

AES Deepwater Cogeneration Plant – Plate Vertical

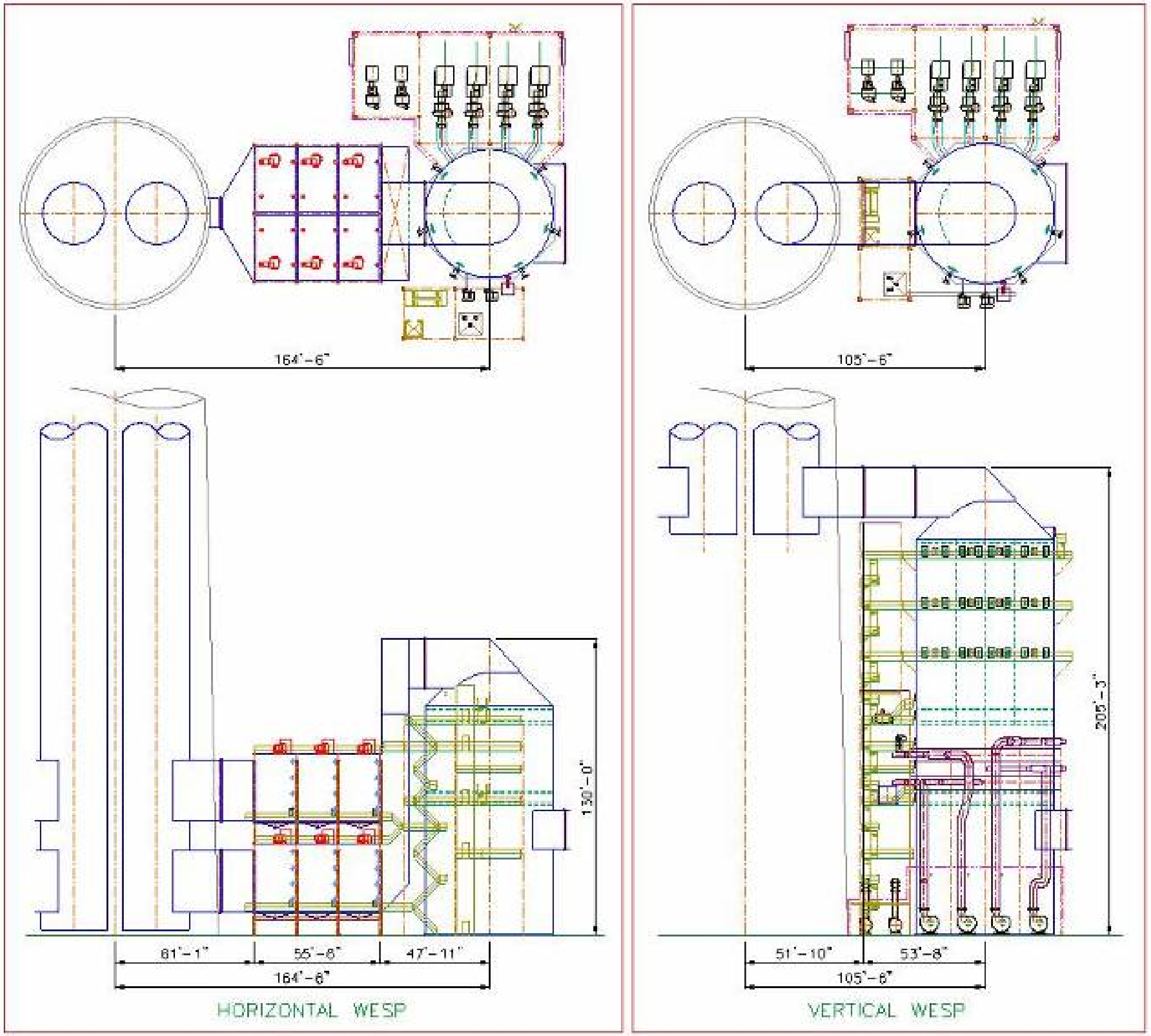


AES Deepwater – 160 MW gross, 100% petroleum coke pulverized boiler.

B&W Horizontal WESP Isometric



Horizontal (Standalone) vs Integral Wet ESP



Main Electrical Parts of an ESP

- Collecting Electrode (CE)
  - Tube (Wet) or Plate (Dry or Wet)
  - Anode (Grounded, Positive)
- Discharge Electrode (DE)
  - Wire, Spiked Pipe, etc.
  - Cathode (Negative, High Voltage)
- Power Supply (Transformer-Rectifier, or T-R)
  - 80 to 100 Kilovolts
  - 100 to 3000 Milliamps
  - Rectified AC

Wet ESP Washing Methodology

1. Intermittent
   - Thorough washing with fresh water and section by section
   - Spent water serves as necessary FGD makeup (i.e. no net system increase)
2. Continuous Irrigation
   - Typically used with non-conductive collecting electrode material
   - Requires extra water or recycle system
   - Requires maintenance
3. Continuous Spray/Fogging
   - Requires extra water or recycle system
   - Dependent on proper design/maintenance
   - Offers use of more cost effective lower grade alloys

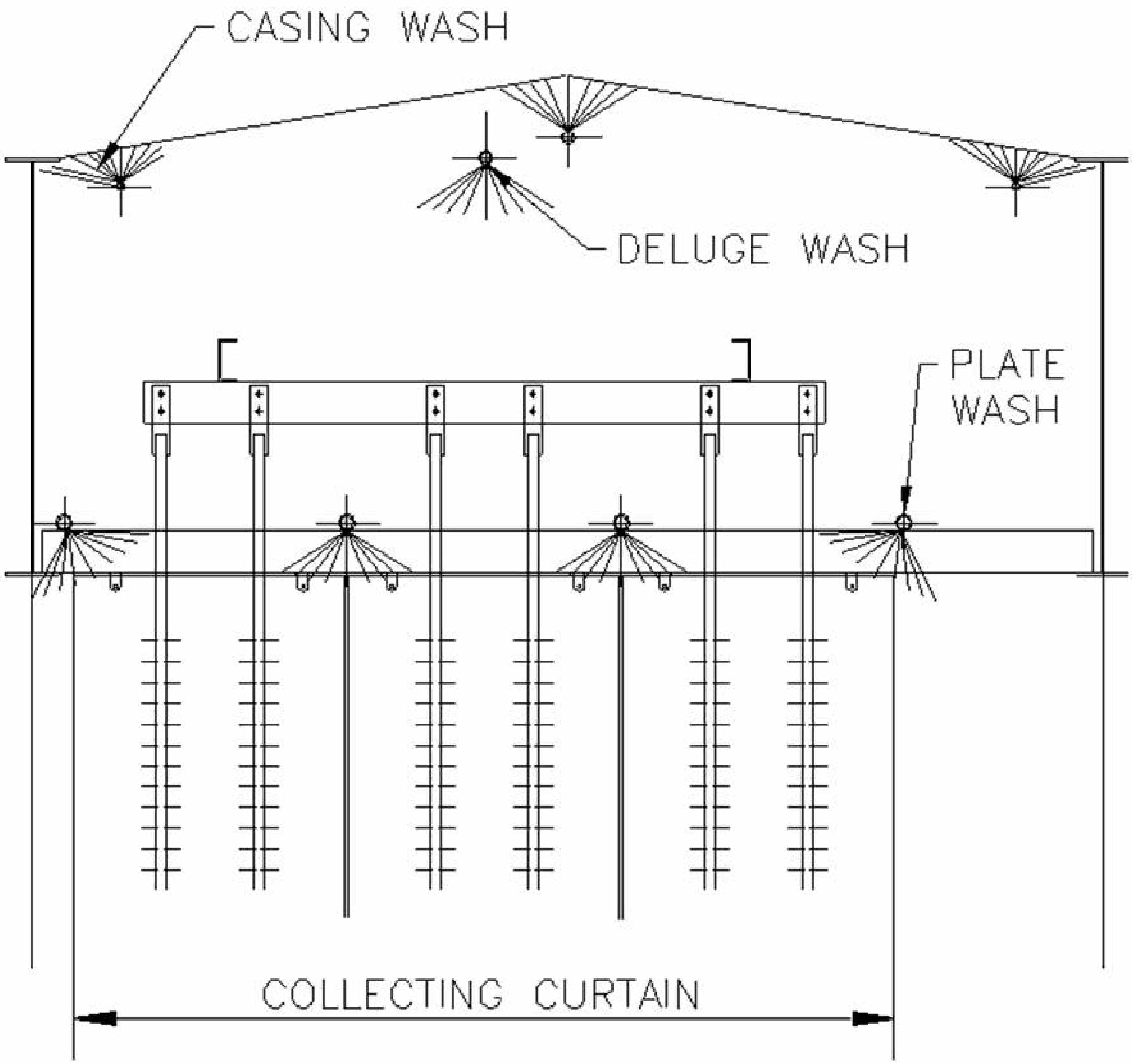
Wet ESP Wash Systems

Continuous Wash System (internal wash system)

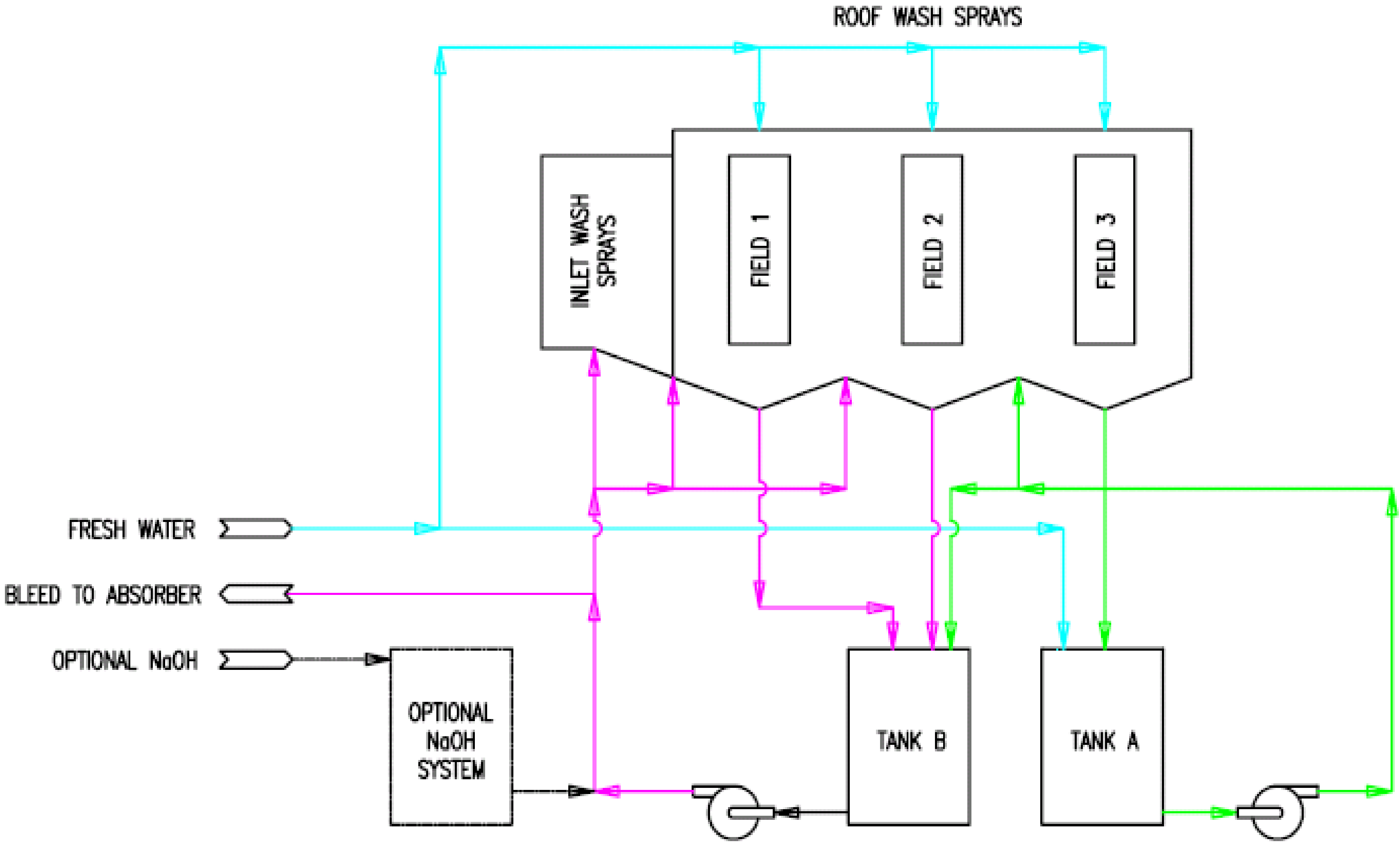
- Plate wash sprays
- Inlet casing wetting sprays
- Roof wetting sprays

- Deluge system

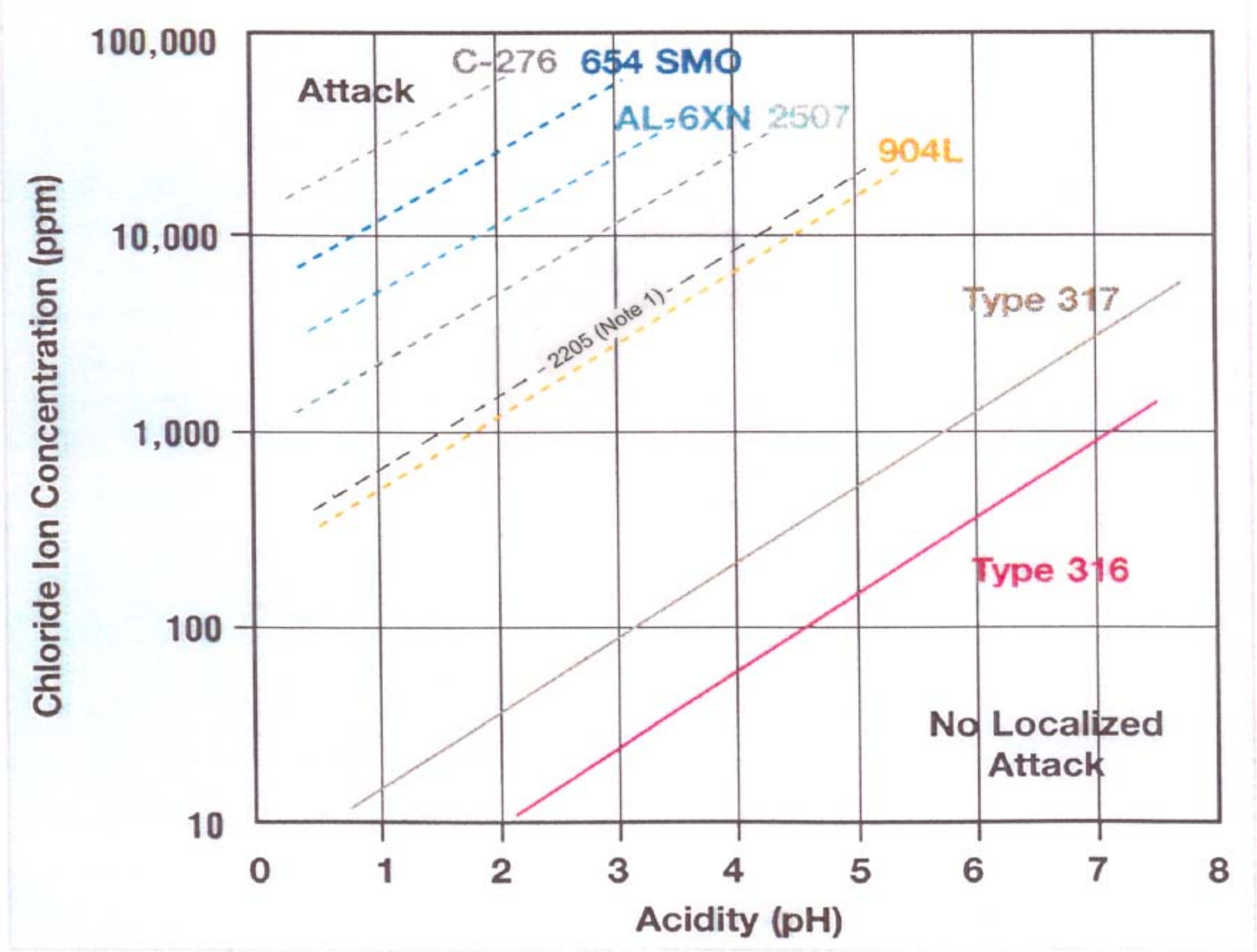
Wet ESP Washing



Wet ESP Continuous Wash System



Approximate Service Limits for Stainless Steels and Nickel-Base Alloys in Flue Gas Condensates and Acid Brines at Moderate Temperatures (140 – 176 F)



Note 1: This service limits plot for Alloy 2205 was super-imposed on this Figure by Babcock & Wilcox

Wet ESP for SO_3 Mitigation

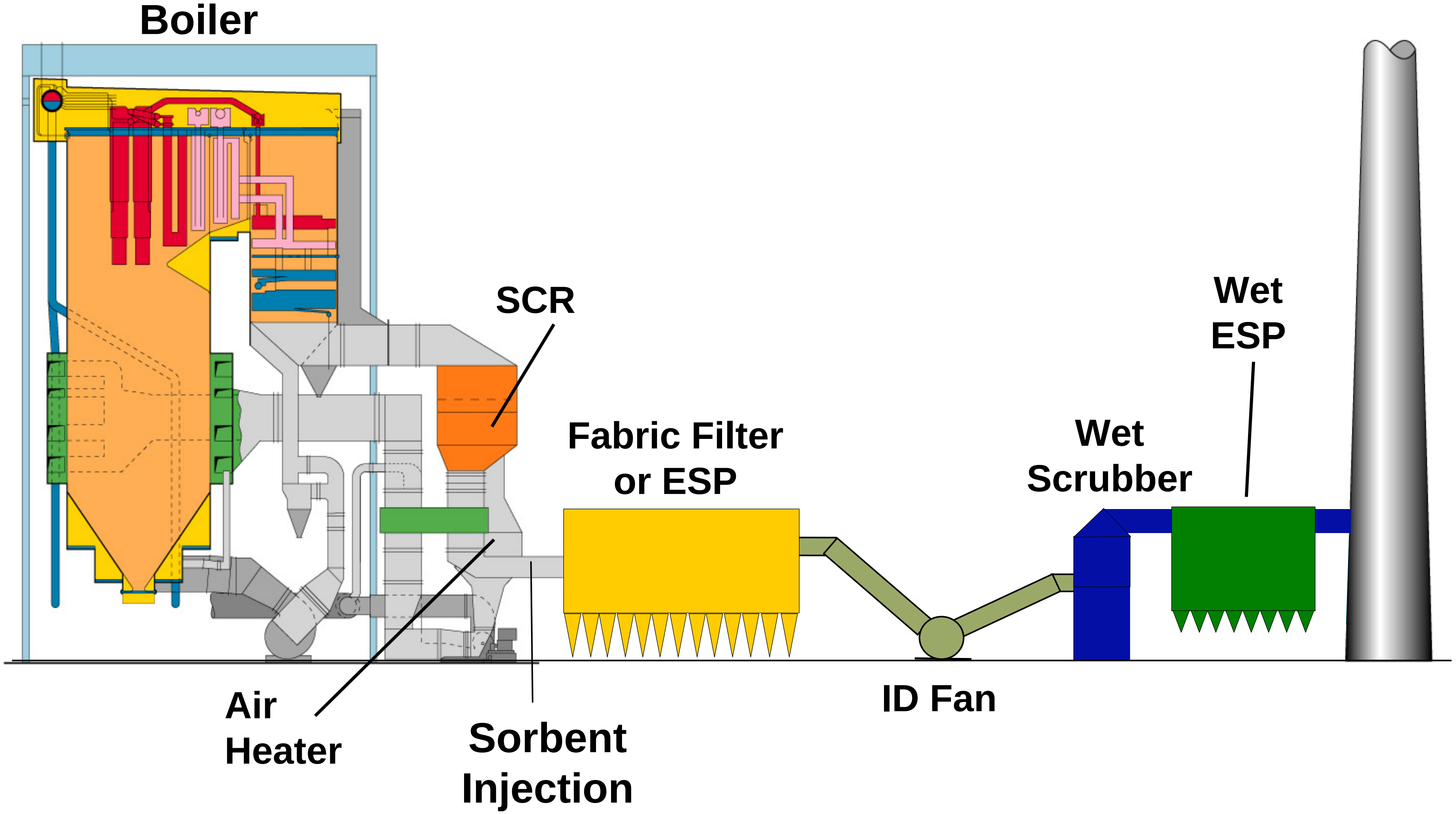
Advantages

- Exceptionally good device for collection of fine particulate (acids, condensed matter, fine solids).
- Not only collects acid but scrubber carryover and ash
- O&M cost low
- Potential capture of hazardous pollutants

Disadvantages

- Capital cost high
- More real estate required

Lowest SO_3 Emission Arrangement for Higher Sulfur Fuel



Conclusions

- There are many sorbents that are effective in mitigating SO_3
- A Wet ESP may be required by permit for new plants
- When designing a SO_3 mitigation system, a system approach based on plant specific conditions will reduce the overall cost of mitigation equipment and sorbent usage

B&W

power generation group

THANK YOU!