Reinhold Environmental Ltd.

2010 NOx-Combustion Round Table & Expo Presentation

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Measurement of Condensable Species in Flue Gas Streams

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Introduction

- Condensables:
  - From an environmental perspective: stack emissions that condense in the flue gas stream exiting the stack or downstream of the stack – includes aerosols (sulfuric acid) and VOCs
  - Plant operations/engineering perspective: a substance that condenses in the flue gas stream anywhere in the unit, some of which are directly or indirectly related to NO_x reduction systems – includes sulfuric acid, ammonium salts, arsenic, and soot

Presentation Outline

The following aspects of condensable materials will be discussed:

- Where do condensable materials originate?
- Why you want to measure concentrations of condensables?
- How do you measure flue gas condensables?
- Measurement techniques discussed are “manual methods” – can be used for engineering data collection, performance guarantee tests, etc.
- Some continuous analyzers available – not included in this discussion

Origins of Condensables

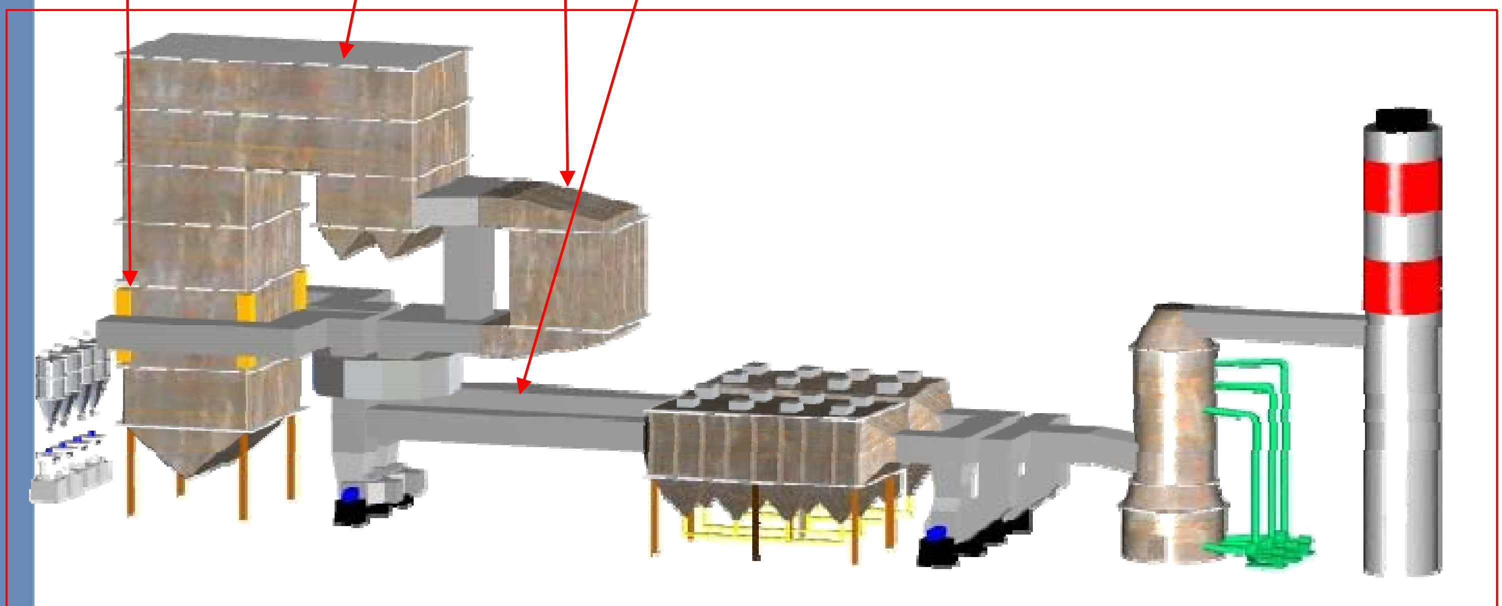
- Sulfuric acid
- Soot
- Arsenic
- Ammonium salts

Origin of Condensable Material

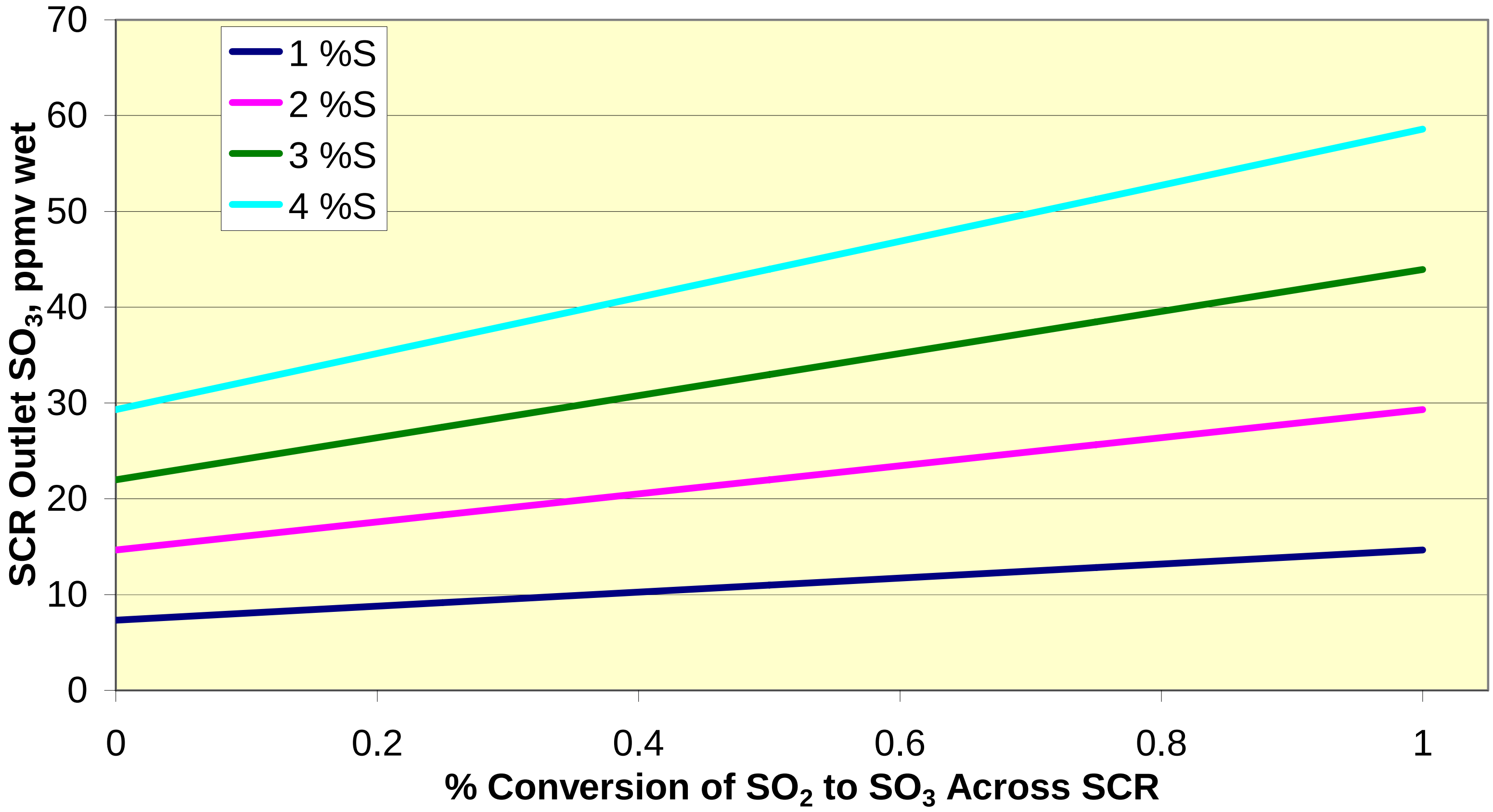
NOx, SO_3,
Arsenic
& Soot

NH_3

SO_3 & NH_3



Effect of SCR Conversion on Air Heater Inlet SO_3 Concentration*



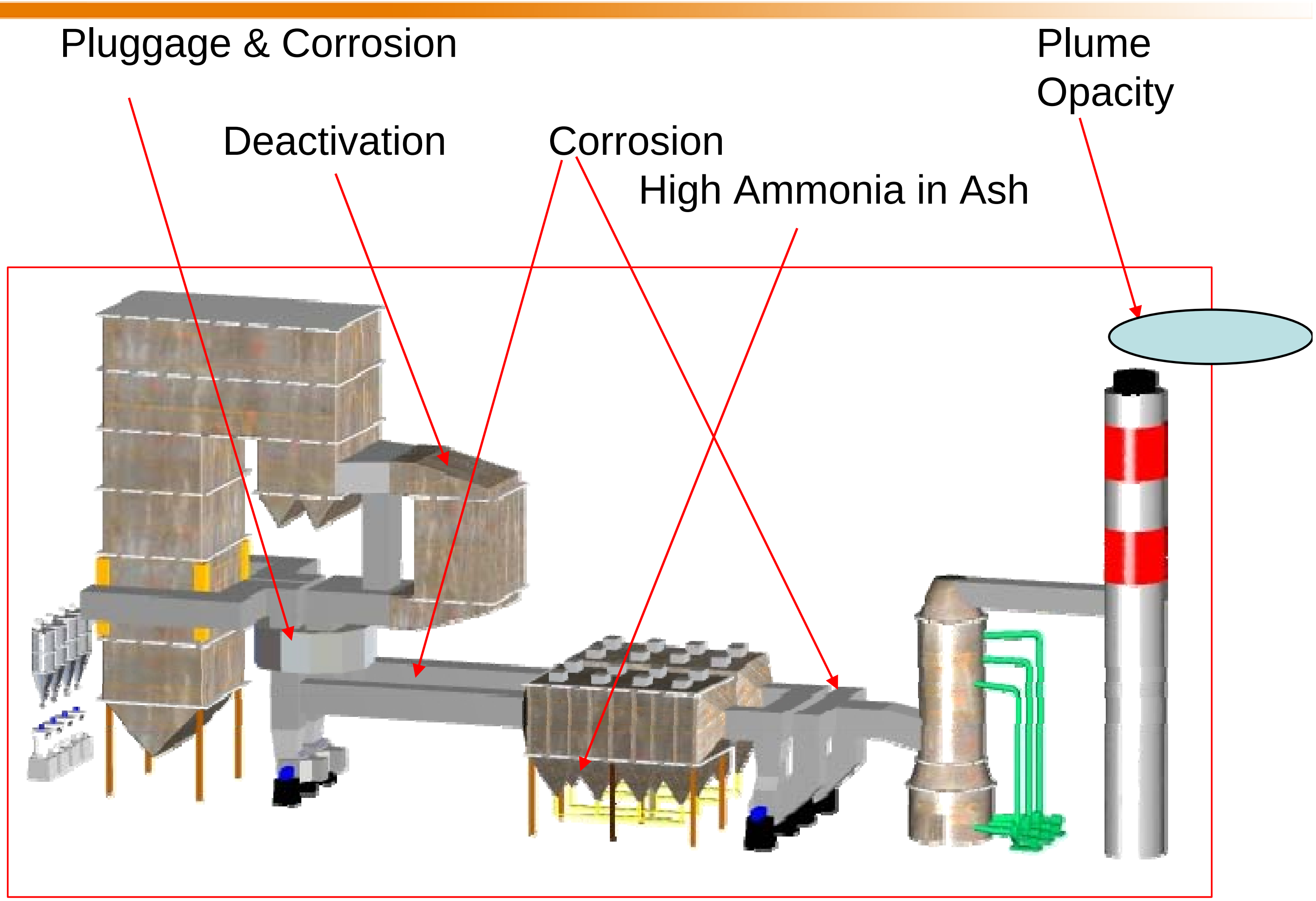
*Assumes 1% boiler conversion of SO_2

Why do you need to know?

What you don't know can hurt you.

- Impacts of condensables on equipment
- If you need a mitigation system, knowing the flue gas properties assists in designing the system
- Some condensable materials are formed in the combustion process and the quantities formed can be a function of fuel properties and how a fuel is burned
- Equipment Performance Issues:
  - SO_2 oxidation across SCR catalyst: is SO_2 oxidation expectation being met?
  - Ammonia
  - How much vapor phase Arsenic is in flue gas entering SCR?
  - Is there a plume opacity issue? If so, what are contributing factors?

Consequences of Condensables in Flue Gas Stream

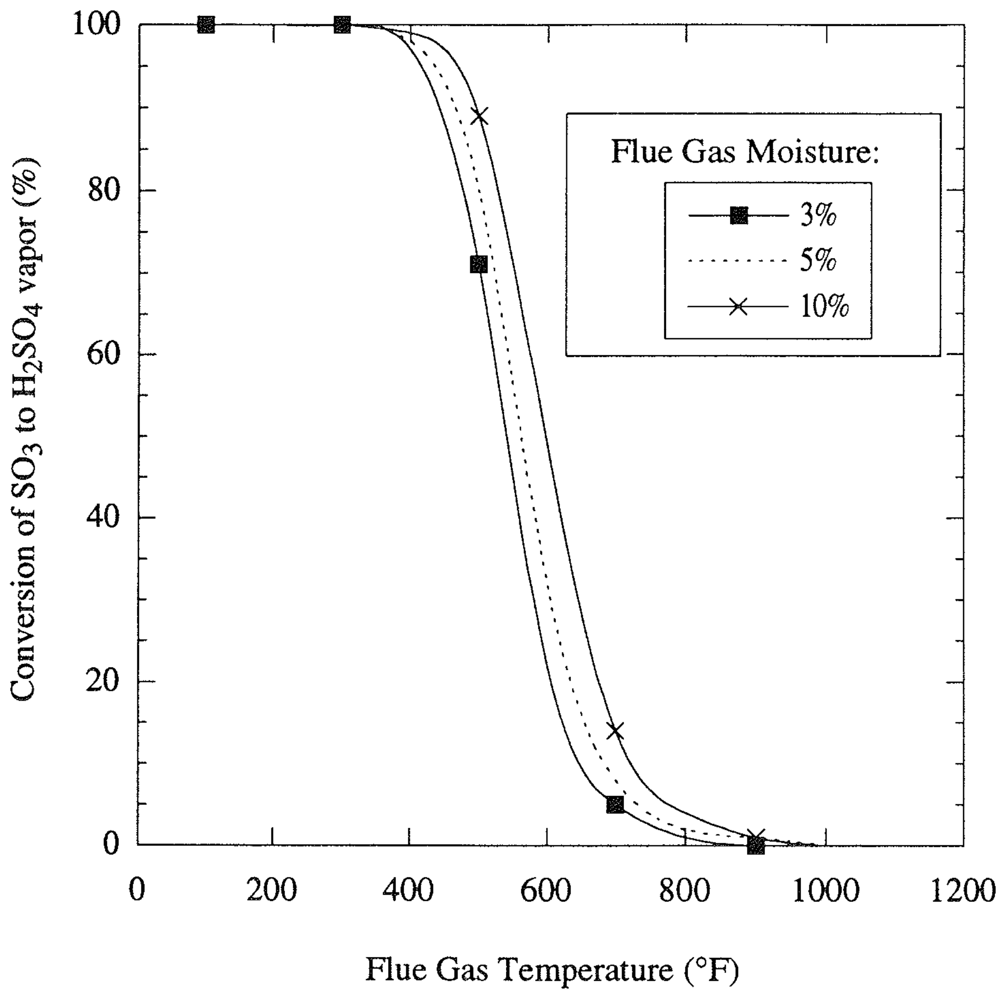


Sulfuric Acid

- As flue gas temperature drops below 800^{o}F, SO_3 combines with H_2O and forms H_2SO_4. This conversion is essentially complete when flue gas exits the air heater (~300^{o}F)

Conversion of SO_3 to H_2SO_4

(Courtesy EPRI)



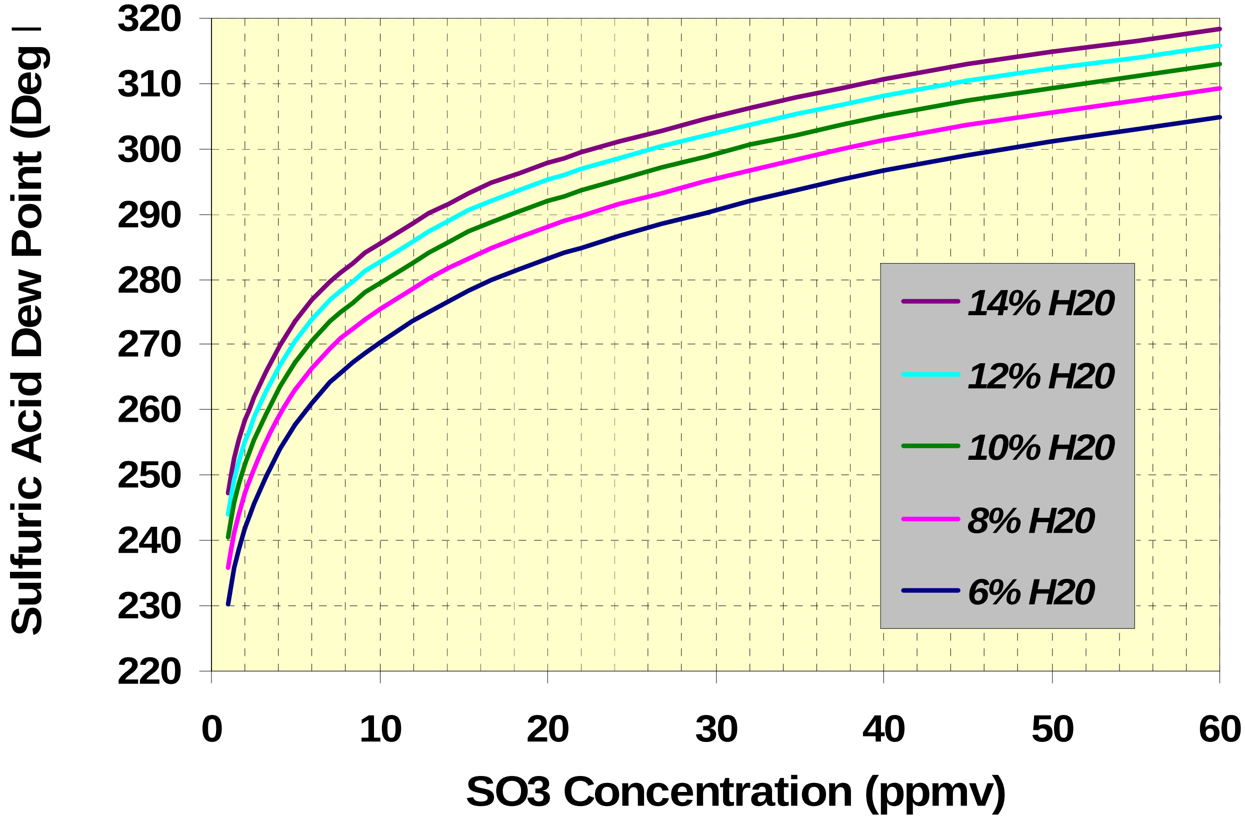
Sulfuric Acid

- Depending on the concentration, the H_2SO_4 dew point can range from 235^{o}F to 310^{o}F

URS

Sulfuric Acid Dew Point

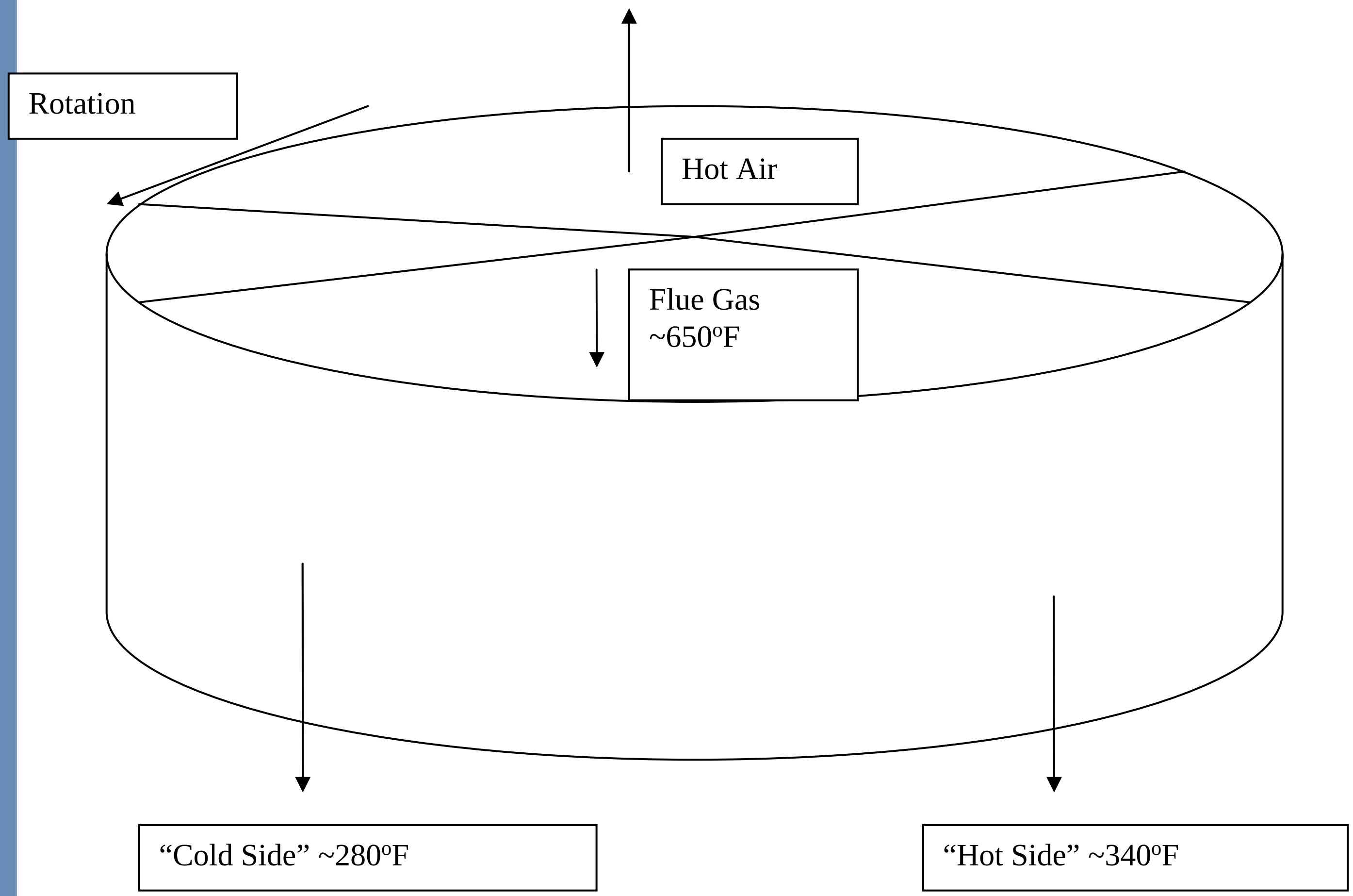
Effect of SO_3 on Sulfuric Acid Dew Point



Corrosion from Sulfuric Acid

- Lungstrom air heaters have cold spots that are below acid dew point
- H_2SO_4 condensation causes corrosion, and creates wet spots where ash/carbon can collect
- H_2SO_4 can become re-entrained in primary & secondary air streams
- Primary air containing H_2SO_4 can cause corrosion & pluggage where air enters pulverizer
- Corrosion of duct, ESP, etc. downstream of AH

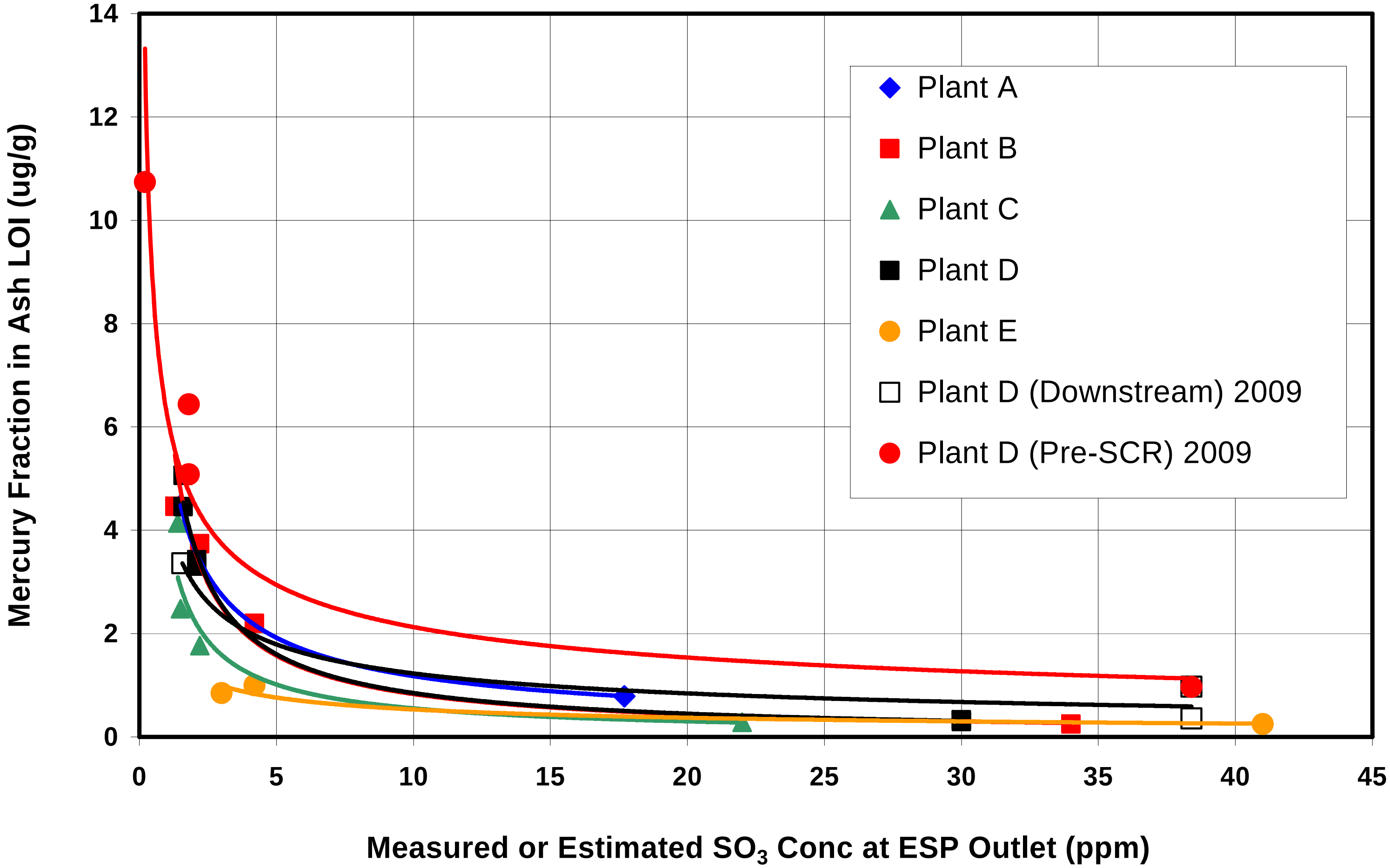
Air Heater


Rotation
Hot Air
Flue Gas
~650ºF
“Cold Side” ~280ºF
“Hot Side” ~340ºF

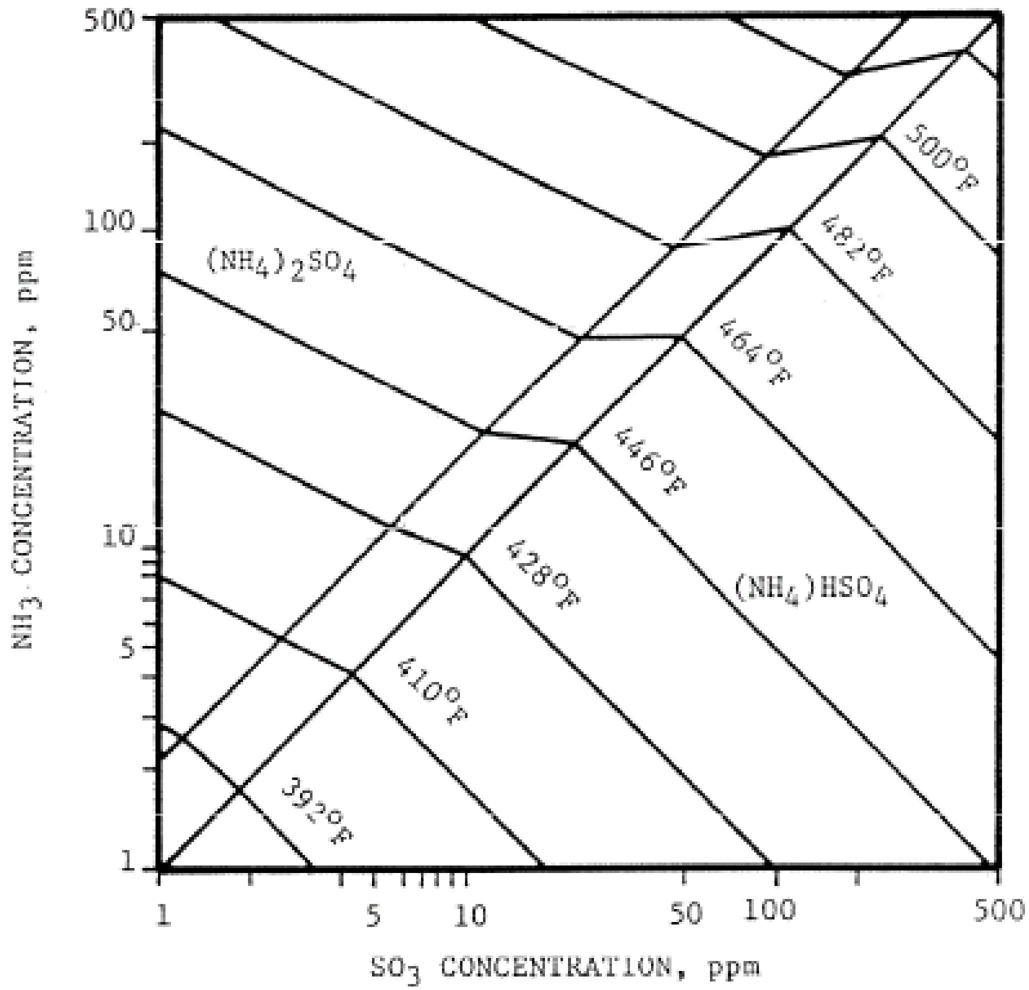
Other Effects of SO_3

- Hg removal hindered
- Contributes to plume opacity
- Air heater pluggage

Impact on Hg Capture in Ash



Ammonium Sulfate/Bisulfate



Plume Opacity

- Visible plume opacity downstream of stack
- Normally caused by sub-micron particles (most severe in 0.8 µm size ~ wavelength of visible light)
- Visible plume opacity can be > 80% for high sulfur fuels

Plume Opacity Contributing Species

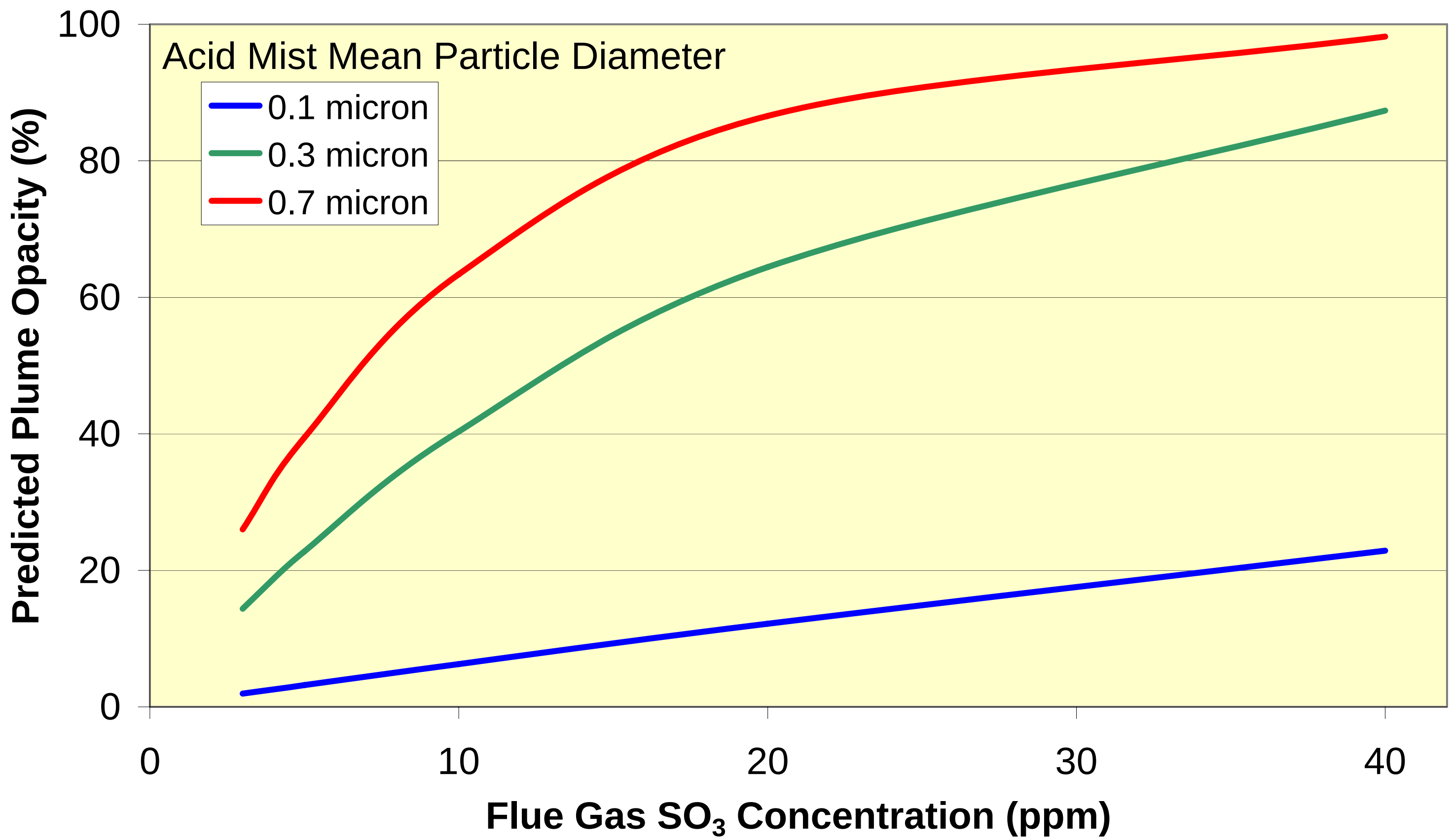
- Sulfuric acid
  - Sub-micron aerosol <0.1 µm to >0.8 µm
  - H_2SO_4 hygroscopic – gets larger as it hydrates
  - White plume with blue tint – gets more severe w/hydration
  - Visible plume evident with as little as 5 ppm H_2SO_4
- Soot
  - Sub-micron particle ~0.2 µm to 0.8 µm
  - Gray-black plume
- Metal oxides (ash, scrubber carryover)
  - White-gray plume

Fate of SO_3/H_2SO_4

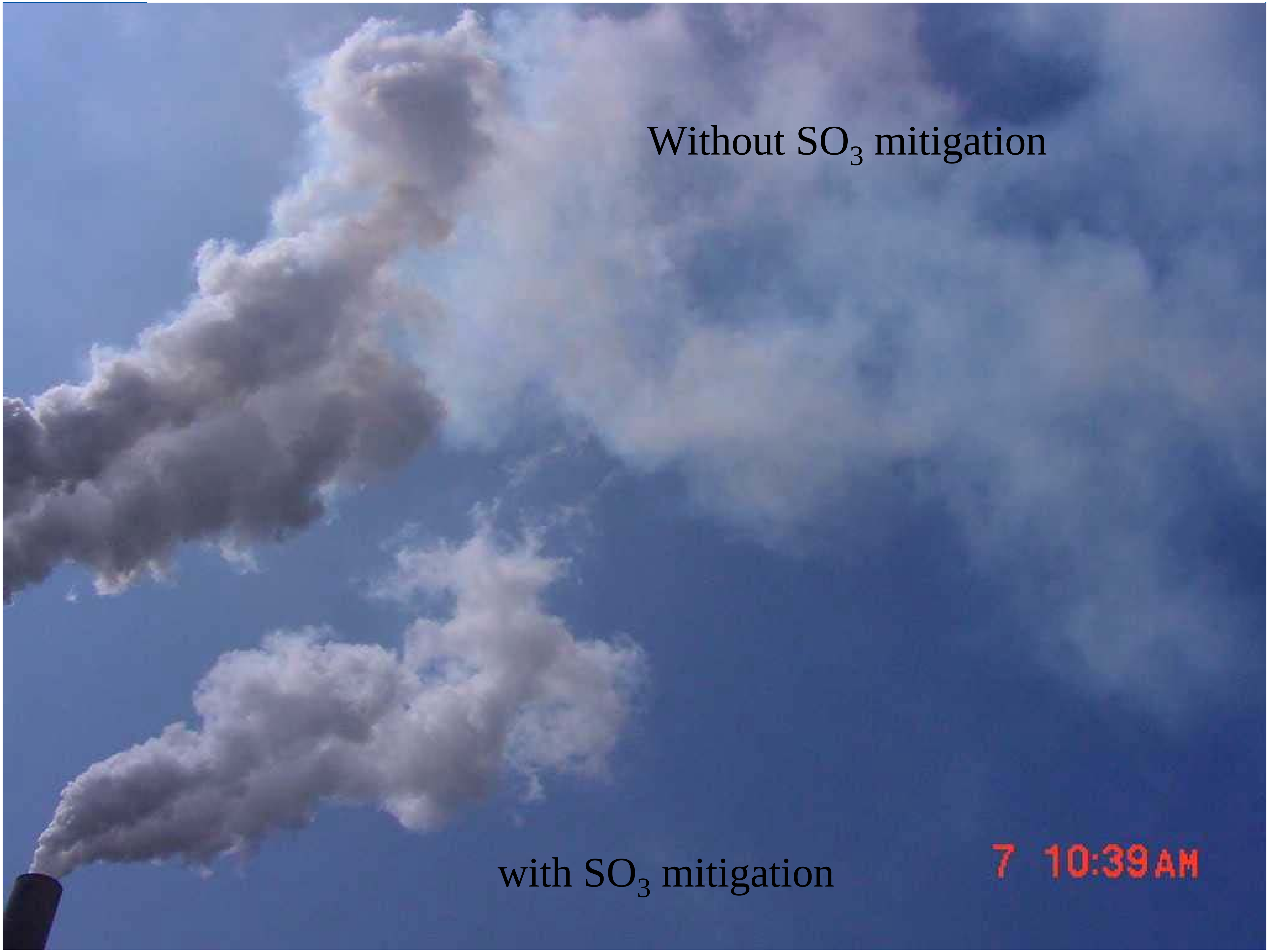
Existing air emission controls do not collect SO_3/sulfuric acid at high efficiency:

- 10-20% removal typical across air heaters and cold-side ESPs
  - Mostly adsorption, condensation
  - Actual percentages vary significantly
- Widely varied removal across wet scrubbers
  - Measured range <10% to >80%

Predicted Effects of SO_3 on Plume Opacity*



*25-ft stack diameter


Without SO3 mitigation
with SO3 mitigation
7 10:39 AM

Measurement Techniques to Determine Condensable Levels in Flue Gas

- SO_3/H_2SO_4
- Ammonia
- Arsenic
- Soot

Sampling System Components Common to Most Methods

- Probe
- Condenser Train (impingers) – determine flue gas moisture (engineering data & sanity check)
- Pump
- Dry Gas Meter
- O_2 at DGM exit recommended

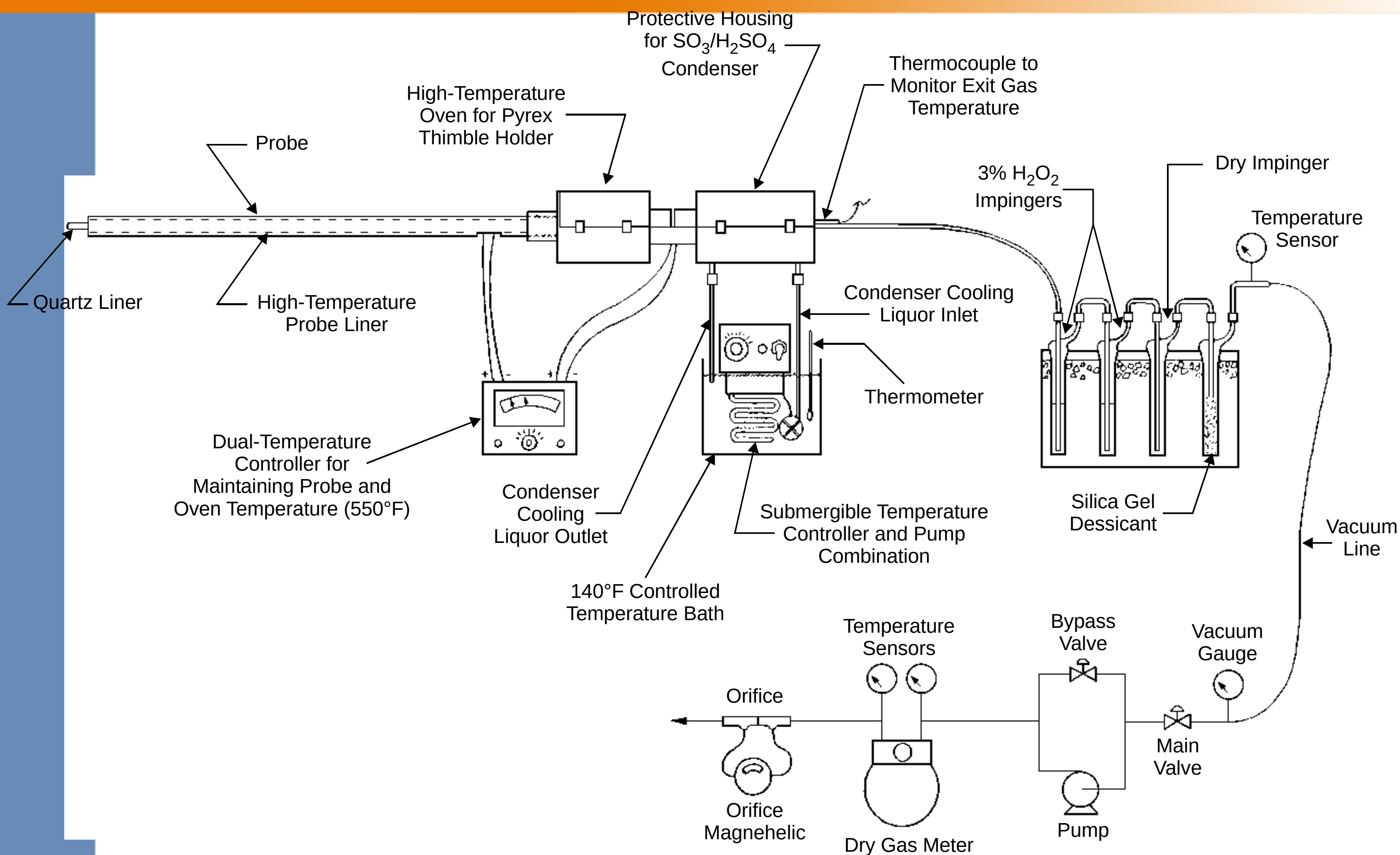
SO_3 Measurement

- EPA Method 8 – not appropriate for flue gas streams with high moisture – ASTM committee working on method based on Controlled Condensation
- FTIR
  - Expensive
  - Can be difficult to operate
- Controlled Condensation System (CCS)
  - Preferred method
  - Single point, non-iso-kinetic sampling
  - Several variations (CTM-013/M-8A – Kraft Recovery Furnaces)
- Cascade Impactor (wet/cold stack)
- Analysis of samples by Titration or IC

CCS Equipment

- Heated quartz or glass lined probe
- Thimble filter in oven
- Modified Graham condenser coil
- Circulating hot water bath (maintain coil temperature ~20^{o}F > moisture dew point)
- Transfer tube from coil to impinger train
- Moisture condenser containing DI or hydrogen peroxide
- Meter box & pump

CCS Train Schematic

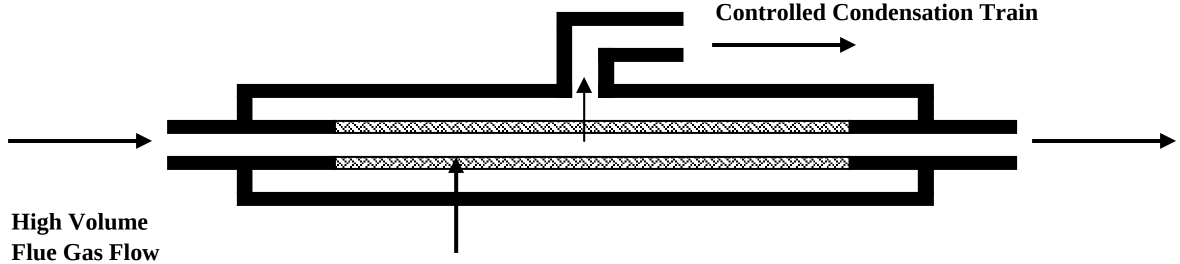


CCS Equipment

CCS Pre-Test Procedures

- Use equipment arrangement that allows coil to be observed during operation (some methods have heat blanket covering coil)
- Modified sampling procedures might be required for certain situations (wet stacks, sorbents/reactive solids bias: high alkali ash, trona, lime, SBS – might require inertial gas separator)
- Conduct pre-test leak check (glass-to-glass connections in CCS oven make this challenging – unable to use Teflon[r] tape because of high temperature)

Inertial Gas Separator



CCS Pre-Test Procedures

- Establish probe and filter temperatures at approximately 550ºF or hotter, depending on sampling location (prevents condensation of H_2SO_4/formation of ammonium salts)
- Circulating water bath temperature should be approximately 170ºF (depends on conditions)
- Record initial dry gas meter reading

CCS Sampling Procedures

- Establish and maintain sampling rate at ~0.3 cfm (some conditions require other rates)
- Maintain probe and oven temps. ~550°F +
- Maintain modified Graham condenser coil exit temperature at approximately 20°F – 25°F above moisture dew point (~150°F – 160°F)
- Collect sample for 25 to 60 minutes
  - depends on concentration of SO_3
  - observation of sulfuric acid collection in coil
- Measure flue gas sample O_2
- Observe coil
  - Sulfuric acid appears as "frosting" on coil, white deposit (ammonium salts), large drop (high SO_3 concentration)

CCS Sample Recovery Procedures

- At completion of sampling, stop pump, record final meter volume
- Stop hot water circulating pump
- Remove coil, filter end first
- Rinse coil with DI water
- Replace with new coil
- Repeat sampling procedure (3 times)
- Analyze recovered sample for sulfate using titration or IC

Ammonia Sampling

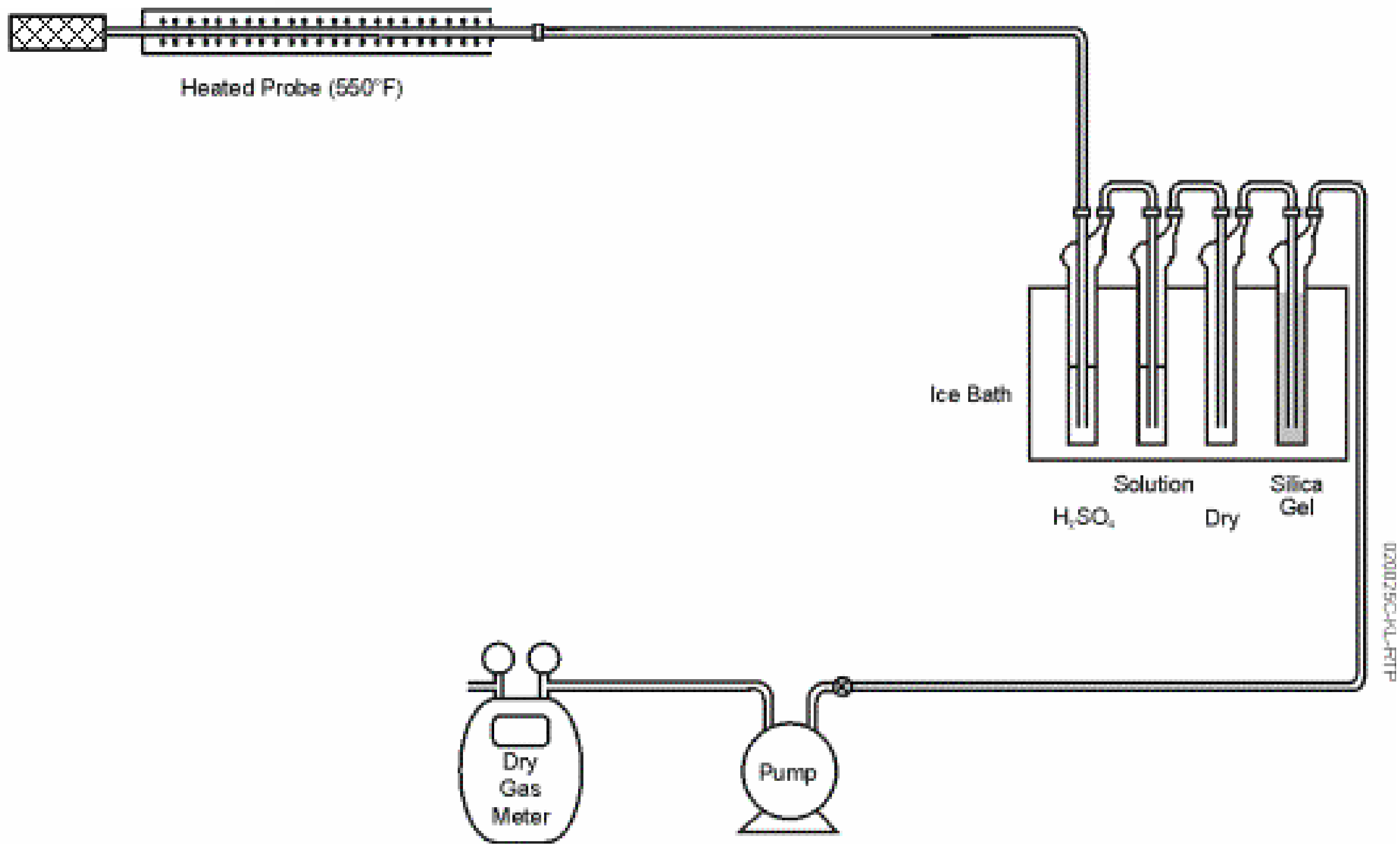
- FTIR
  - Expensive
  - Can be difficult to operate
- EPA CTM-027
  - Standard method: iso-kinetic with EPA Method 17 in flue duct filter (iso-kinetic not necessary for vapor phase sampling upstream of air heater)
  - Initially developed for stack measurements
  - If SO_3 present, much of ammonia is collected as ammonium salts in transfer tubing
  - Impinger train containing 0.1 N H_2SO_4 collects vapor phase NH_3
  - Modified method (external filter @ 248^{o}F +/-25^{o}F) could be used to determine “free” ammonia (downstream of AH)
  - Altering method might be necessary depending on the purpose of measurement
- Analysis of samples by Ion Selective Electrode or IC

Ammonia Sampling Equipment

- Heated quartz or glass lined probe
- Filter at tip of probe inside flue (standard) or outside flue in oven (modified)
- Teflon transfer tube
- Moisture condenser containing 0.1 N H_2SO_4
- Meter box & pump

CTM-027 – "Standard" Non-isokinetic Method w/In-Flue Filter

Glass bell with quartz fiber filter material



Ammonia Sampling Procedures

- Conduct pre-test leak check
- Heat probe to approximate temperature of flue gas
- Record initial dry gas meter reading
- Collect sample from single point or multiple points (traverse) for 1 to 2 hours (sampling time depends on sensitivity desired), rate ~ 1 cfm
- Measure O_2 at meter exit (recommended)
- Record final dry gas meter reading
- If SO_3 is present in flue gas, some/all ammonia will collect in transfer tube as ammonium salts (visible to observer)

Ammonia Sample Recovery

- After probe cools, rinse probe, transfer tubing and combine with contents of impingers containing 0.1 N H_2SO_4
- Analyze sample for ammonia: ion specific electrode (ISE) or ion chromatography

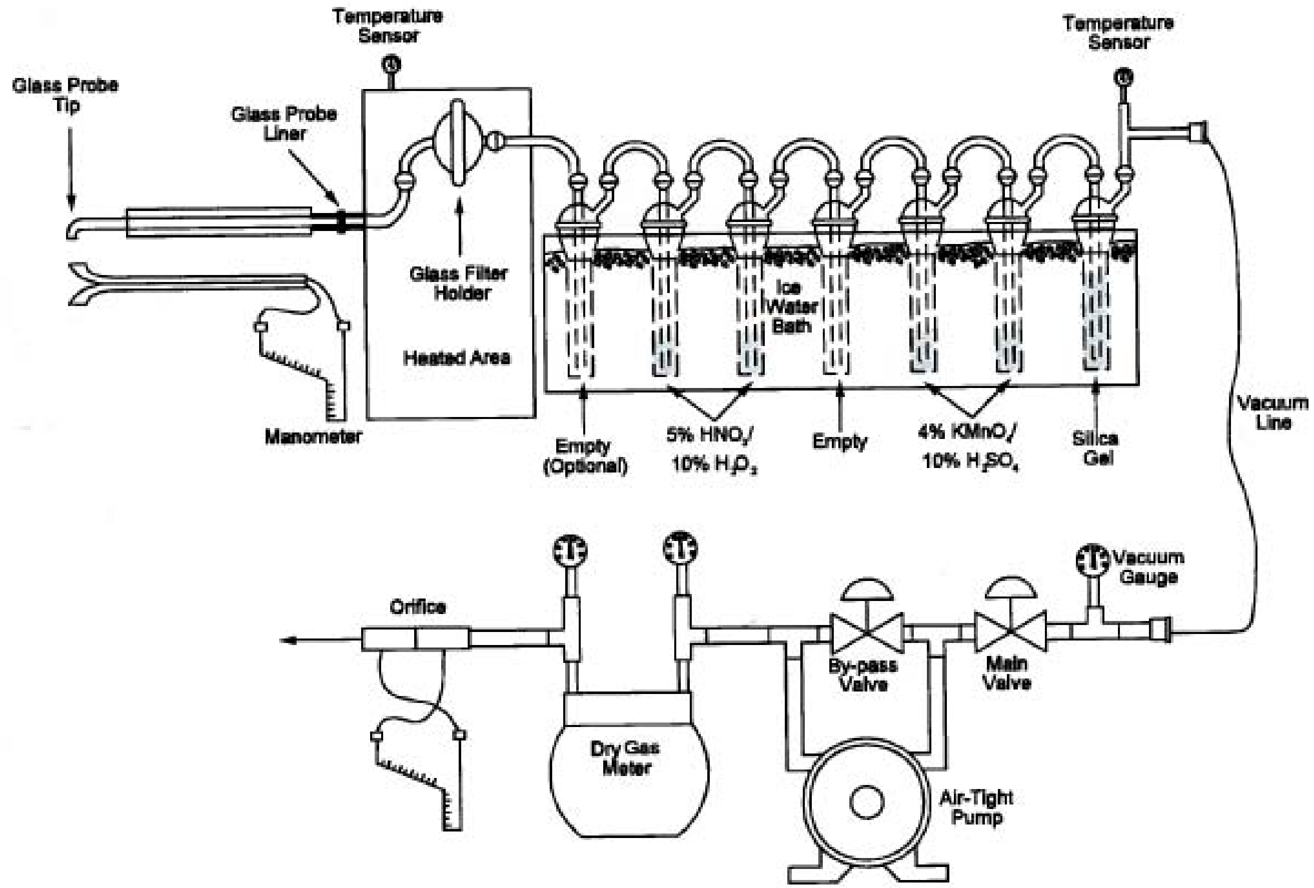
SO_3, Ammonia (ABS)

- FTIR (expensive, difficult to operate)
- Breen probe
  - Modified acid dew point probe
  - In-situ, single point, batch analysis
  - Ammonia Slip (as ABS)
  - SO_3 (condenses H_2SO_4 on probe tip)
  - Indicates relative levels of ABS/SO_3
  - Should be calibrated against test methods that yield known results

Arsenic

- EPA Method 29 – Metals Train, uses external filter at 248°F +/- 25°F
- Can modify approach to incorporate in flue filter in order to segregate vapor & solid phase Arsenic (measurements taken up-stream of SCR); might require use of IGS
- For determination of As only, M-29 impinger train is modified to eliminate impingers 4 – 6

Standard EPA Method 29



Method 29 Procedures

- Iso-kinetic sampling method
- Initial leak check
- Record initial dry gas meter reading
- Sample iso-kinetically for 1-hour while traversing flue (single point sample optional, non-iso-K optional – depends on whether total As or vapor phase As is to be determined)
- Measure sample O_2
- Record final dry gas meter reading

Method 29 Recovery & Analysis

- Rinse nozzle, probe, filter housing (“front-end” sample)
- Recover filter (“front-end” sample)
- Recover impingers 1 – 3 (“back-end” sample)
- Analyze samples using inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS)
- “Front-end” yields solid/liquid phase As
- “Back-end” yields vapor phase As

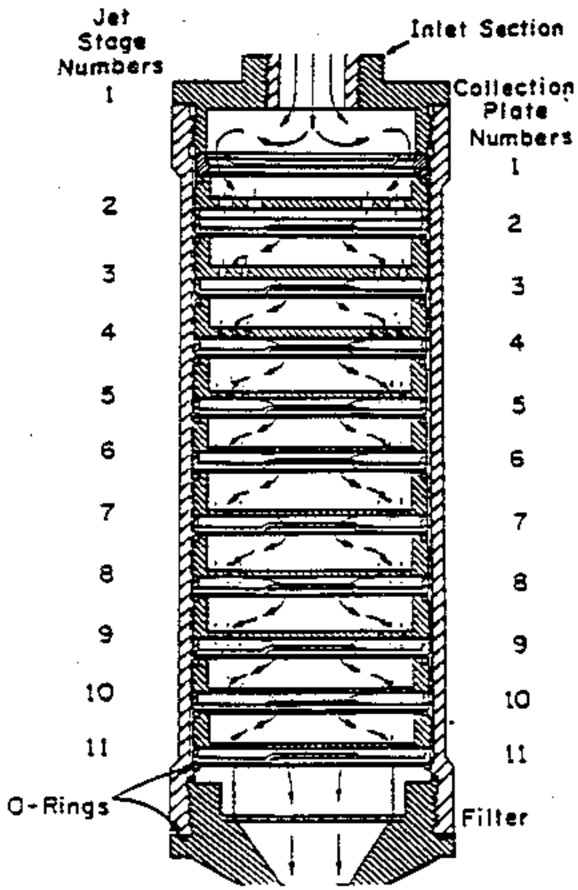
Stack Measurements: Plume Opacity Analysis or Engineering Data

- Sulfuric acid
  - CCS (operate at elevated temperature)
  - Cascade impactor
- Soot
  - Cascade impactor
- Metal oxides (ash, scrubber carryover)
  - Cascade impactor
- PM mass loading
  - M-17

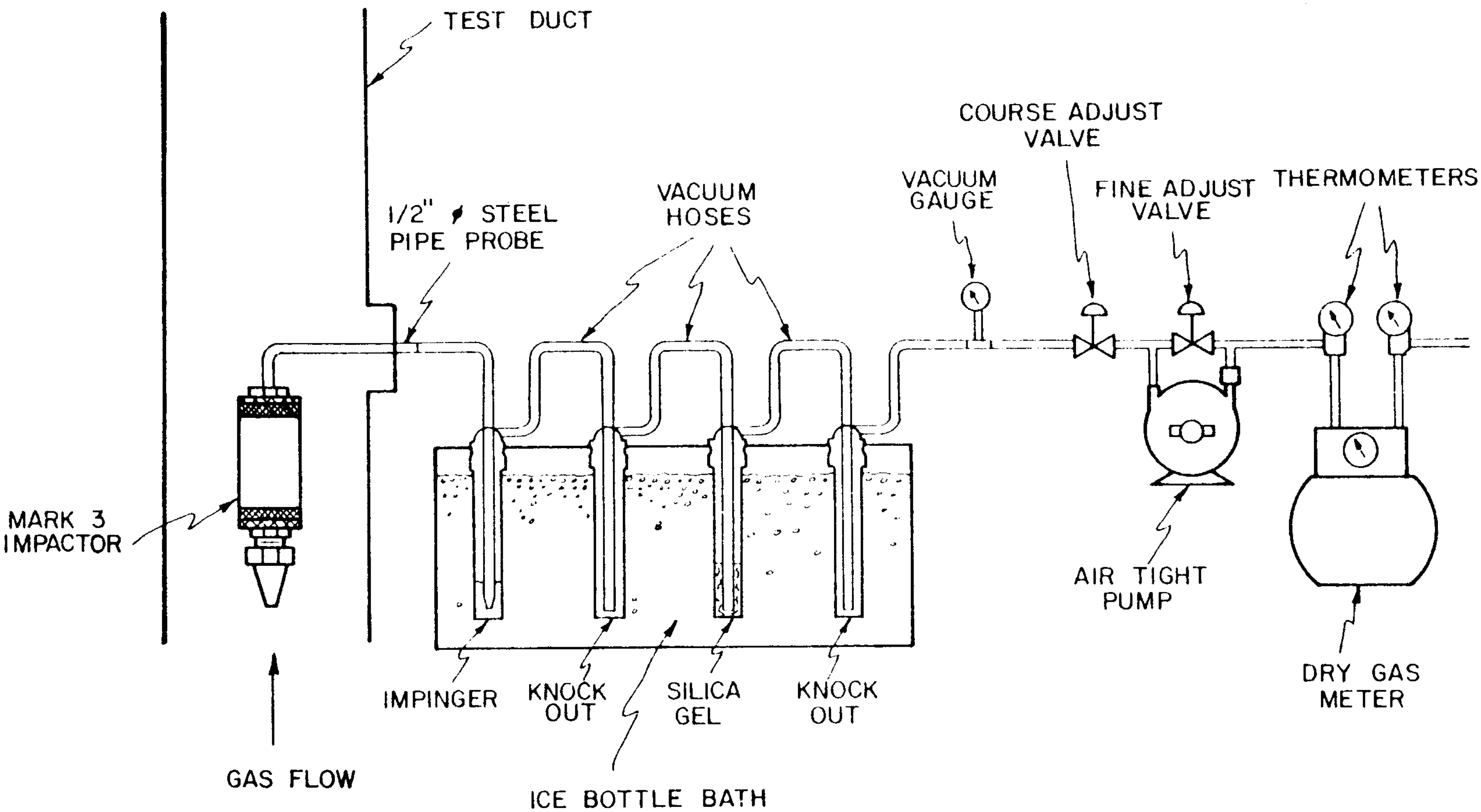
Cascade Impactor

- U of Washington Mark V
  - 12 stages
  - 0.15 µm to 10 µm
  - Single point sample, point of average velocity in stack
  - Quartz substrates
    - Gravimetric analysis
    - Carbon (soot) analysis by stage
  - Kapton (plastic)
    - Metals analysis by PIXE by stage
    - Sulfate (H_2SO_4) analysis by IC by stage

U of Washington Mk V Cascade Impactor

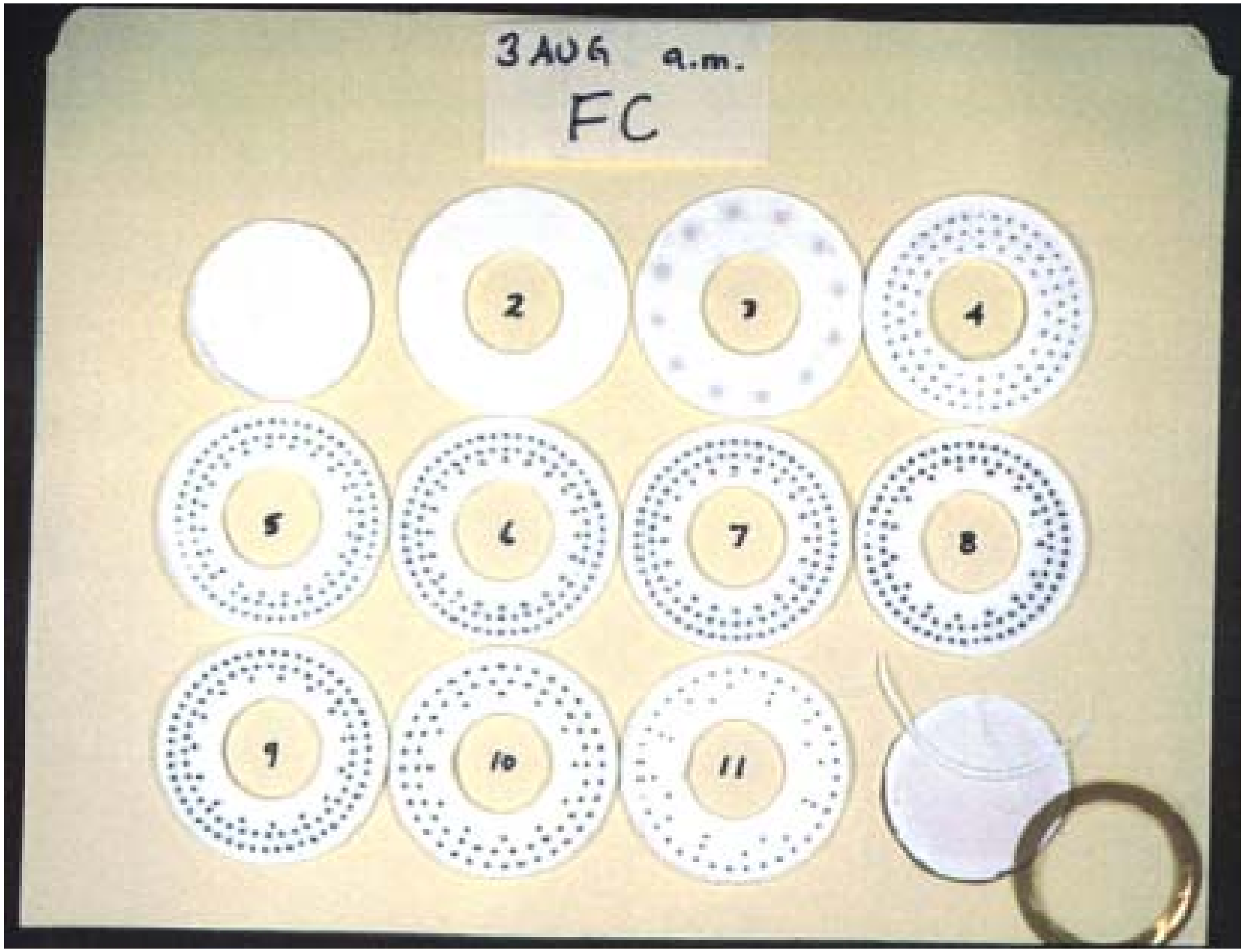


U of W Mark V Cascade Impactor



U of W Cascade Impactor

U of W Mark V Cascade Impactor Quartz Substrates



Concluding Comments

- Use the appropriate adaptation of the sampling method for the particular application/sampling condition
  - Hot flue gas stream (upstream of AH)
  - Cool flue gas stream (downstream of AH)
  - Interference from reactive components (use of IGS) – can significantly bias results
  - Wet stack
- Observe sample collection
  - CCS coil
  - Ammonia sample transfer tube
  - DGM exit O_2
  - Sampling system data – temperatures, pressures, flow
- Since most of these measurements are for “Engineering Data” – can “bend the rules” to adapt a sampling system to collect the information desired