

REINHOLD ENVIRONMENTAL Ltd.



2012 NO_x-Combustion Round Table & Expo Presentation

February 13-14, 2012, in Columbus, OH / Hosted by AEP

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PCUG Training: SO₃ Formation and Mitigation



Douglas P. Ritzenthaler- Environmental Equipment & Programs
February 13, 2012

Course Outline

1. Terminology
2. Plume Appearance
3. Site Overview
4. SO₃ Measurement
5. Sources
6. Sinks
7. Why Mitigate SO₃?
8. SO₃ Mitigation
9. Impacts on Downstream Equipment
10. Sample DSI Calculation
11. Questions and Comments?

1. Terminology



SO_3 or H_2SO_4 ??

- SO_3 forms in the furnace convection pass and SCR when SO_2 oxidizes to SO_3
- The SO_3 is hygroscopic and below about 1,000 °F it will begin to hydrolyze to form H_2SO_4 .
- Downstream of the air heater, i.e., below about 350 to 400 °F, the acid hydrates readily into the chemical form H_2SO_4 (vapor).
- H_2SO_4 vapor can condense to liquid aerosols.
- It is common practice to refer to the acid as SO_3 regardless of its actual form.

SO₃ and MATS

- SO₃ is often the main constituent in “condensed matter”.
- The proposed MATS limit was 0.03 lb total PM/MMBtu: condensed PM + filterable PM.
- The final MATS Rule limit is 0.03 lb filterable PM/MMBtu only.

2. Plume Appearance



Greenpeace Photo of Gavin Plant 2001

Source:<http://www.cheshiretransaction.com/town/sub/cngtown.html>

SO₃ Plume Appearance

- Low concentrations (<10 ppm) visible as blue secondary plume which does not disperse readily.
- Fine aerosols scatter light, blue haze
- Plume appearance depends on
 - Weather: sunny, clouds, rain, etc.
 - Time of day, angle of sun
- Visible to the public.
- The use of SCRs resulted in unintended increase in SO₃ generation.

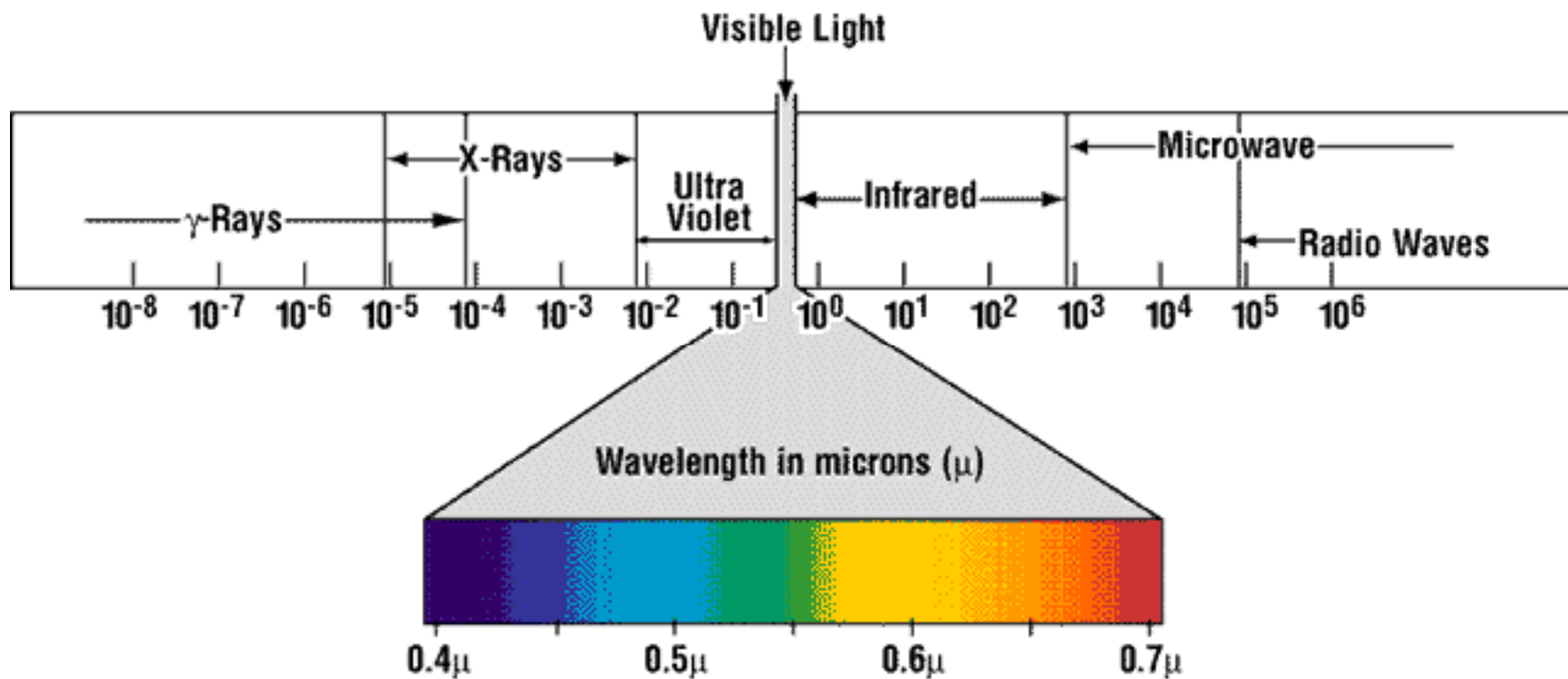


If H_2SO_4 is a clear liquid, why is the plume blue?

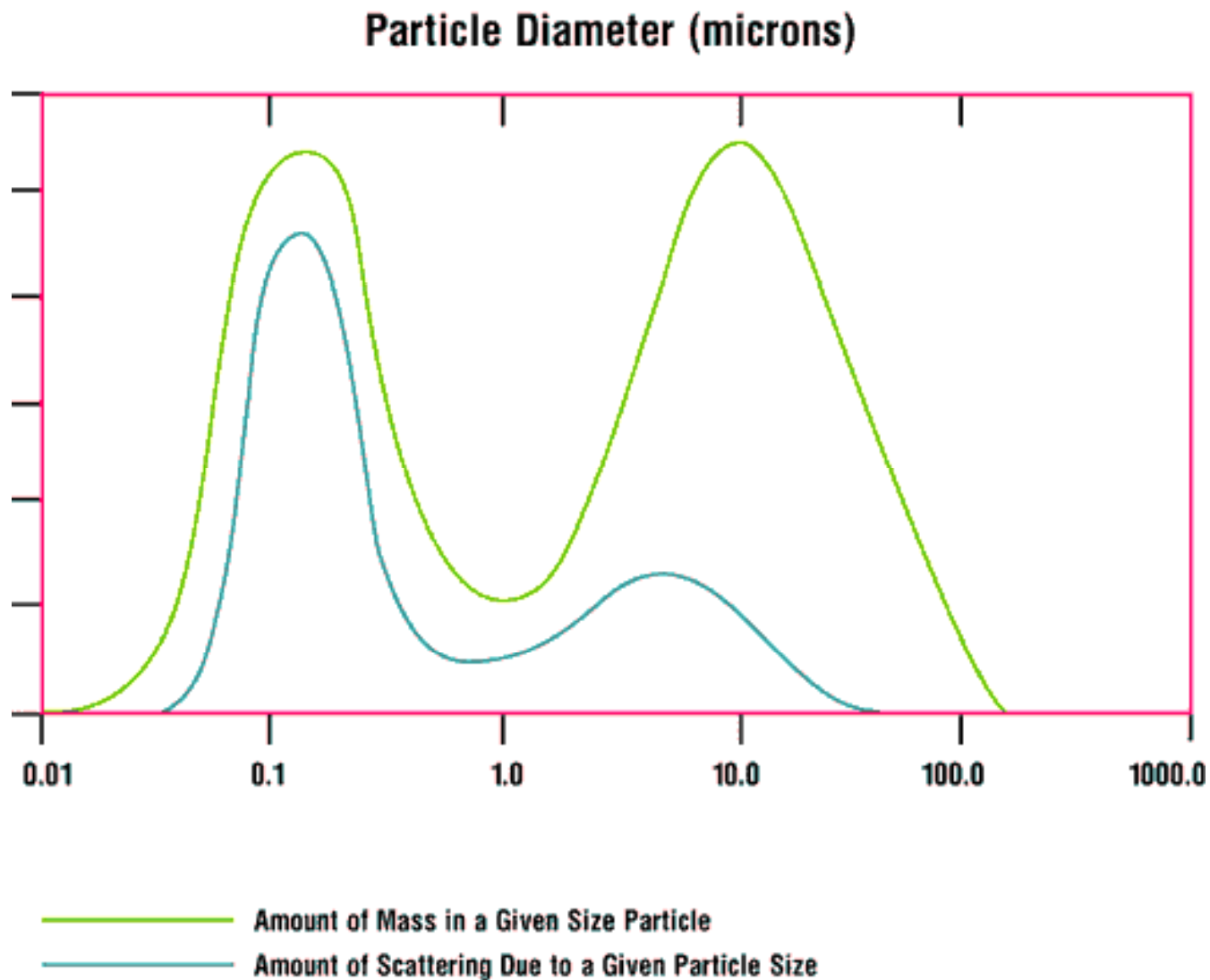
Light Scattering

- An aerosol in the size of 0.3 to 0.7 microns is ideal for scattering light.

Light Scattering



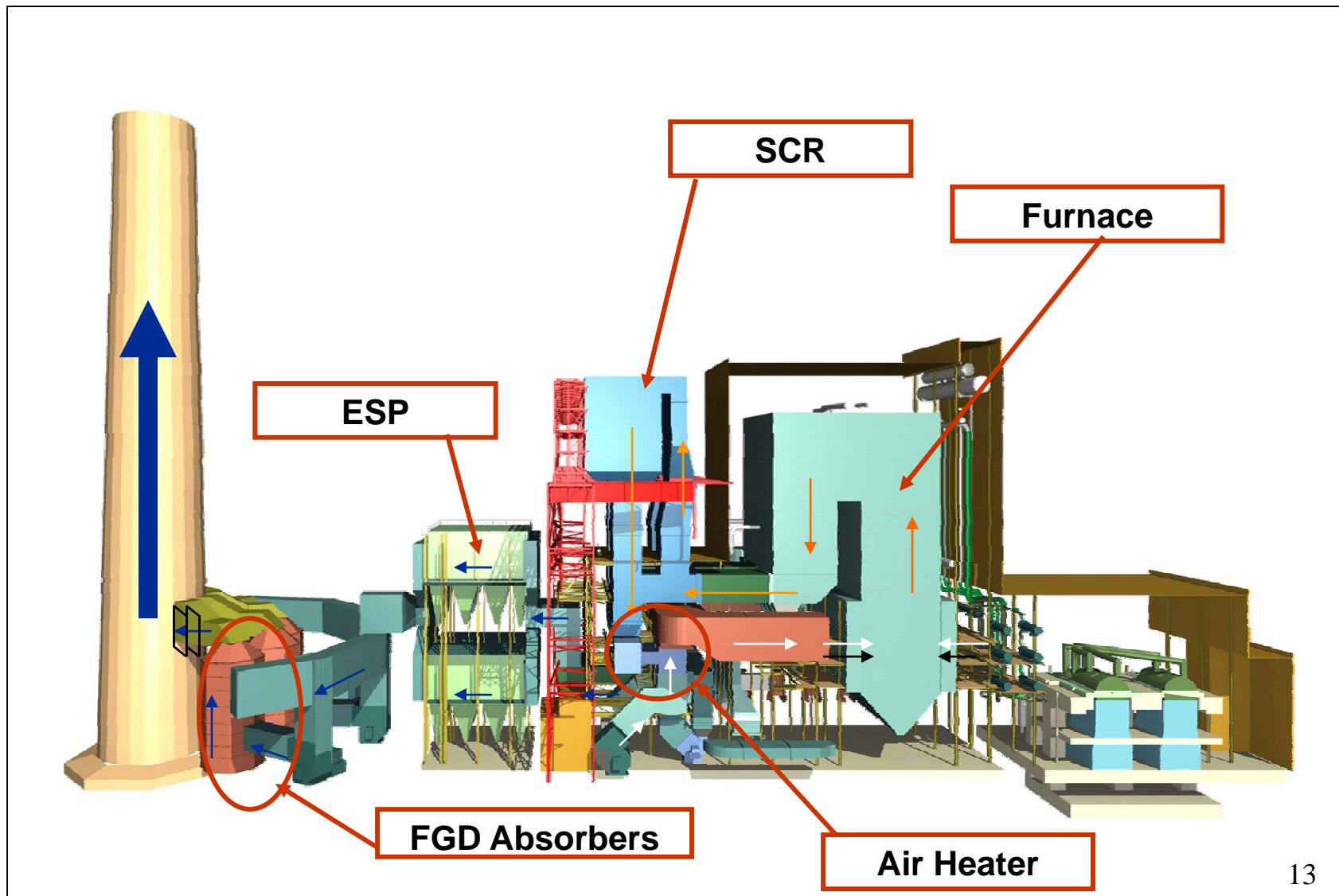
Light Scatter



3. Site Overview



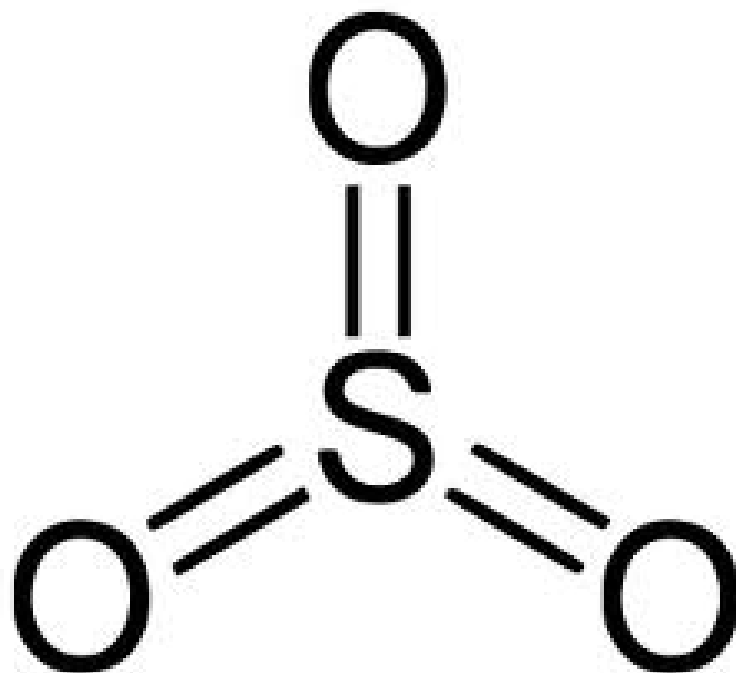
Plant Flue Gas Path Overview



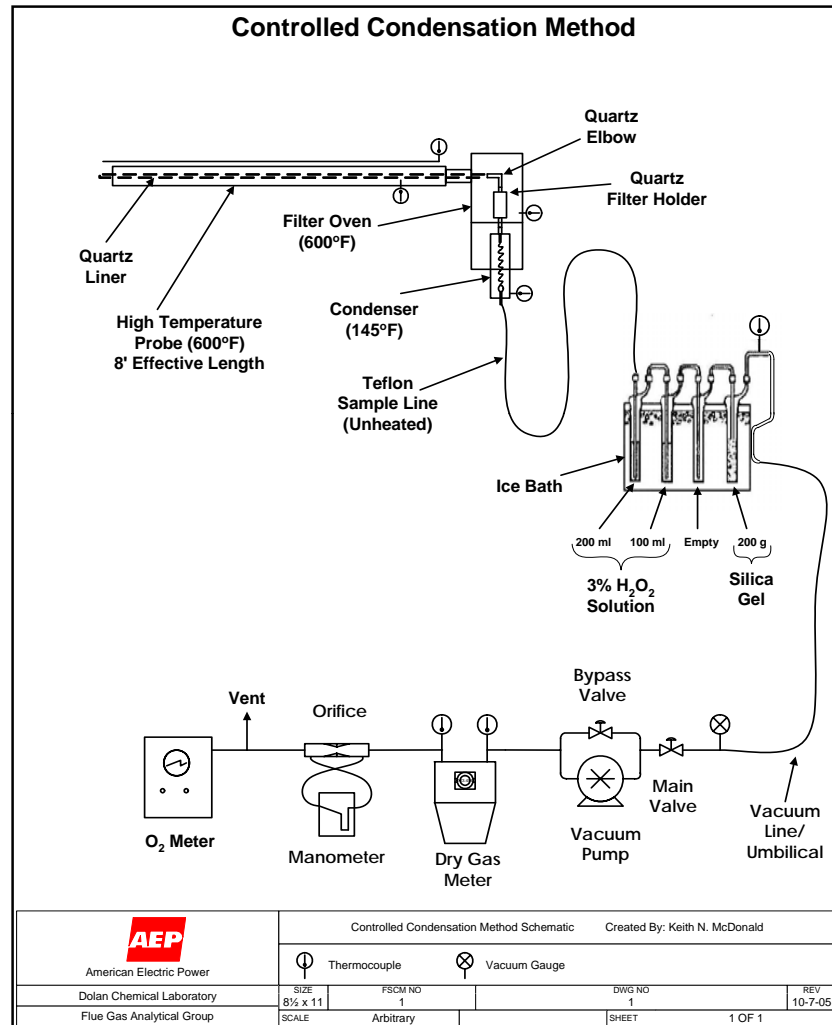
Alternate Site Equipment

- SDA, NID, or other Dry FGD
- Baghouse / Fabric Filter
- Wet ESP
- Wet vs. Dry FARS
- Tubular air heater

4. SO₃ Measurement



Controlled Condensation Method



- Controlled Condensation Method Schematic, Courtesy: Dolan Labs – Keith McDonald

Controlled Condensation Method

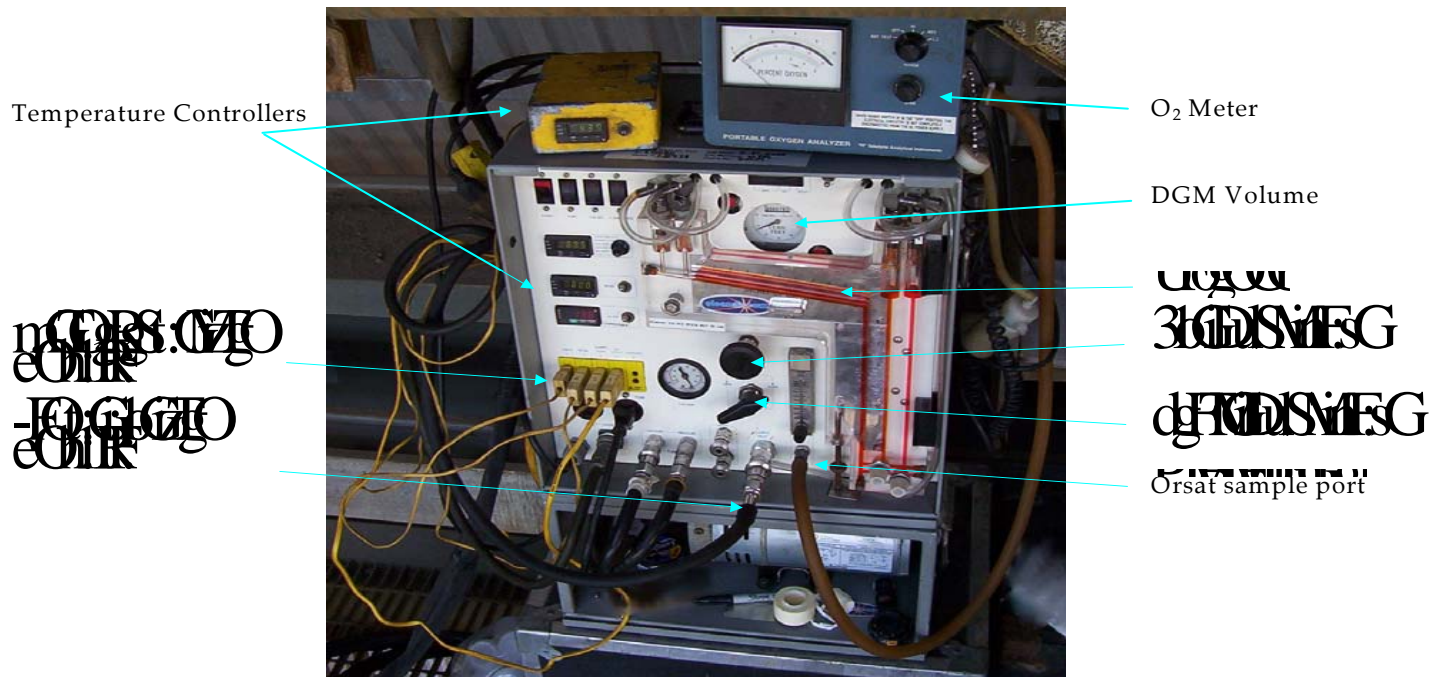


- SO₃ Sampling, Courtesy: Dolan Labs

Controlled Condensation Method

Continued – Slide Courtesy Dolan Labs, Keith McDonald

CCM Procedure - Operation



Controlled Condensation Method

Titration

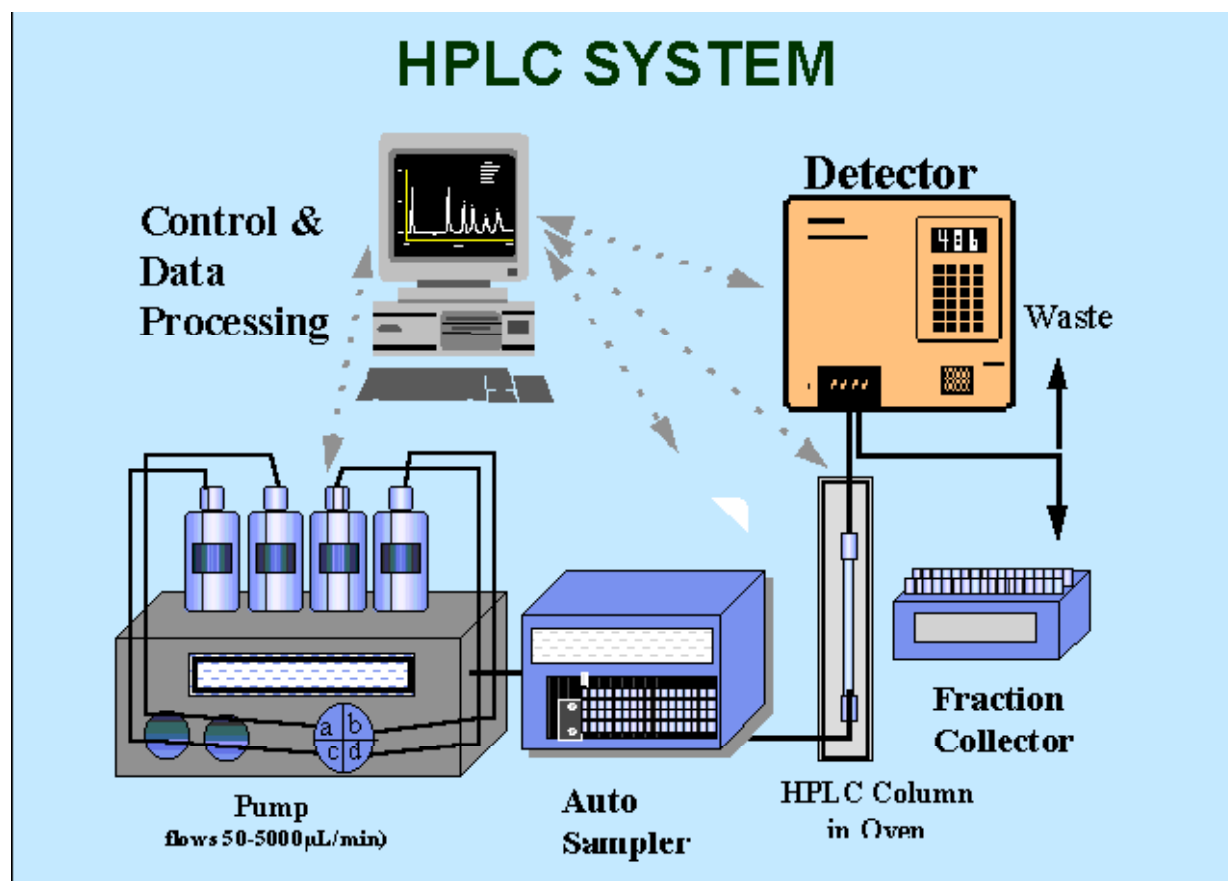


- Titration for determining SO₃ Concentration,
- Courtesy: Dolan Labs

Ion Chromatography

Illustration from http://www.forumsci.co.il/HPLC/ion_chrm.html

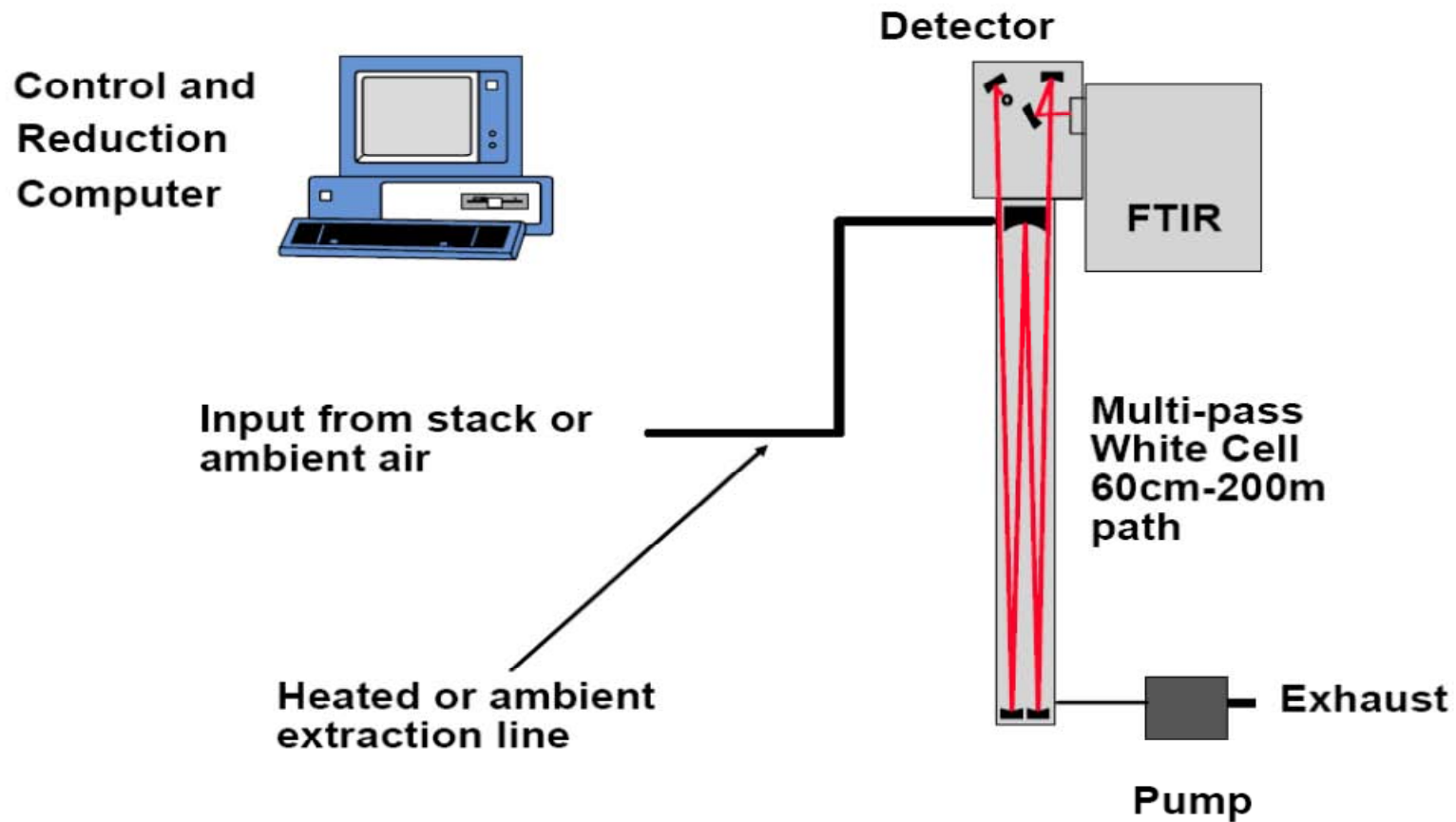
- An analytical technique for the separation and determination of ionic solutes in water.



FTIR

Slide From EPRI/IMACC Presentation May 2006

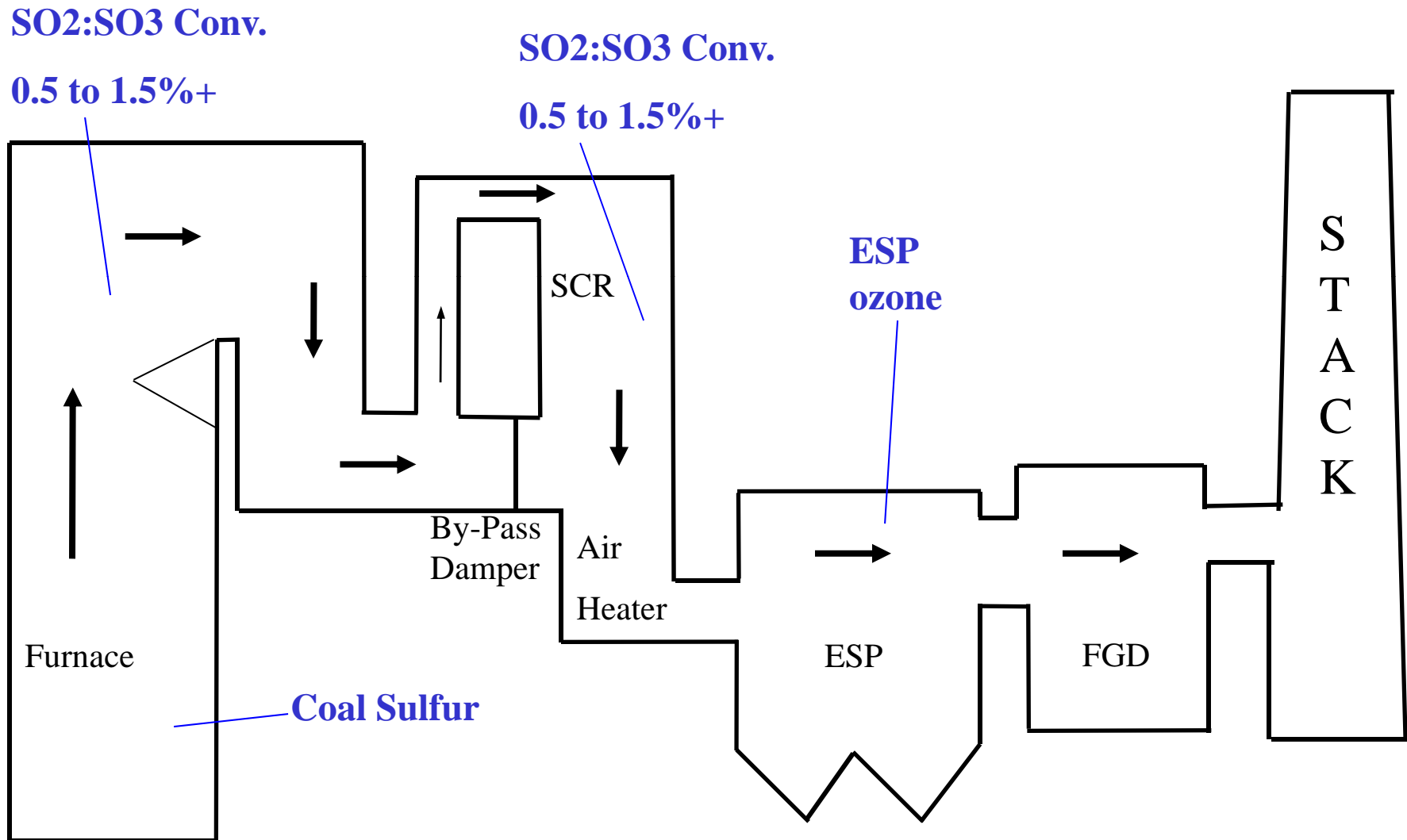
Typical Extractive FTIR System



SO₃ Monitor

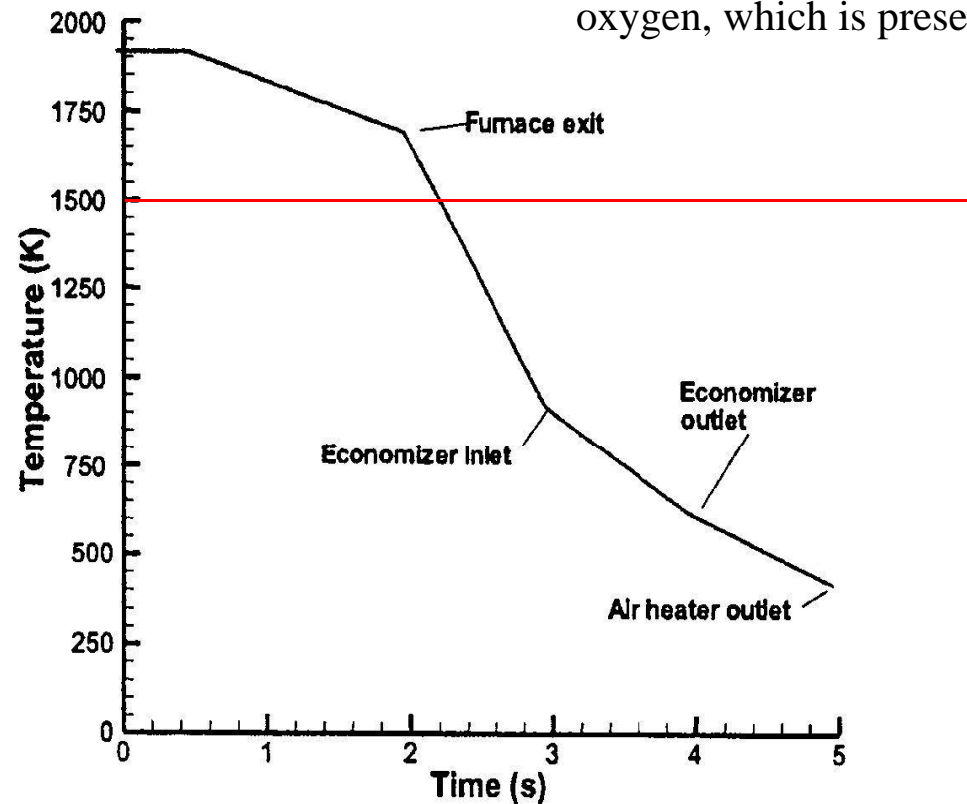
- In-situ laser diode technology is showing promise, but is not commercially available yet.
- Breen probe measures the presence of condensables such as SO₃.

5. SO₃ Sources



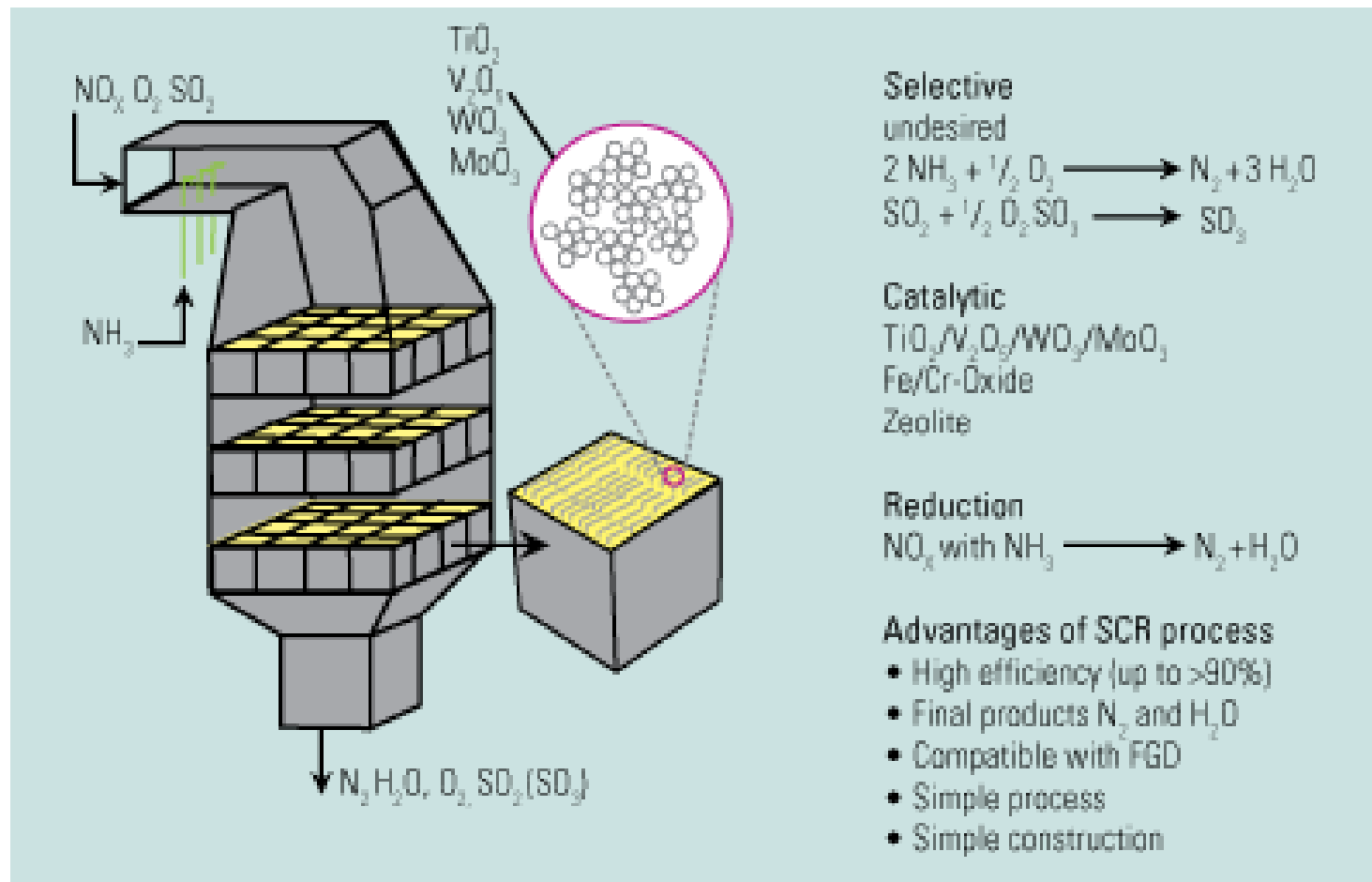
Time/ Temperature & SO₃ Formation

SO₃ formation is dependent upon atomic oxygen, which is present above 1500 °F



Temperature-time history for a coal-fired power plant (from Senior et al., 1999)

SCR

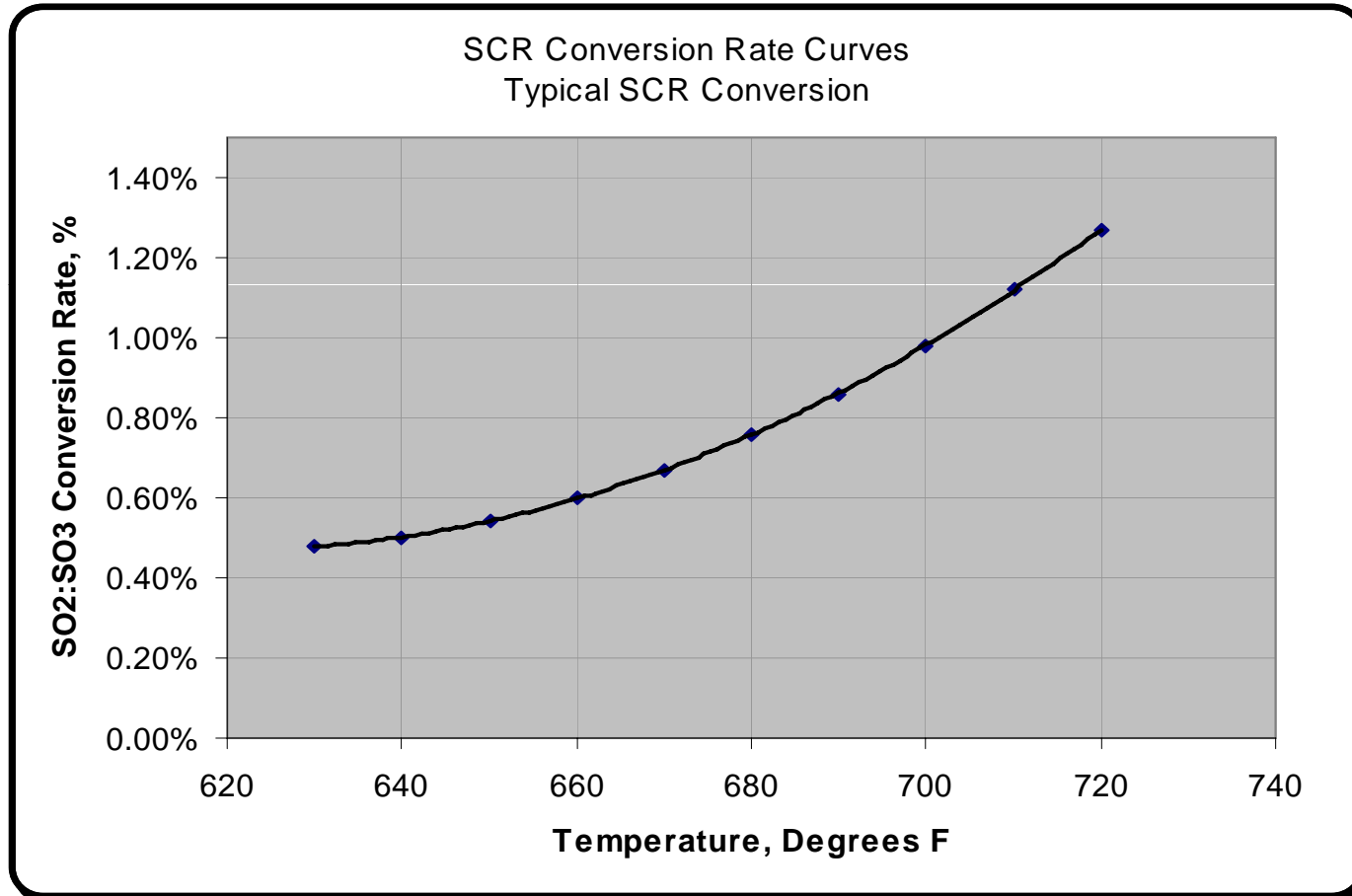


SCR



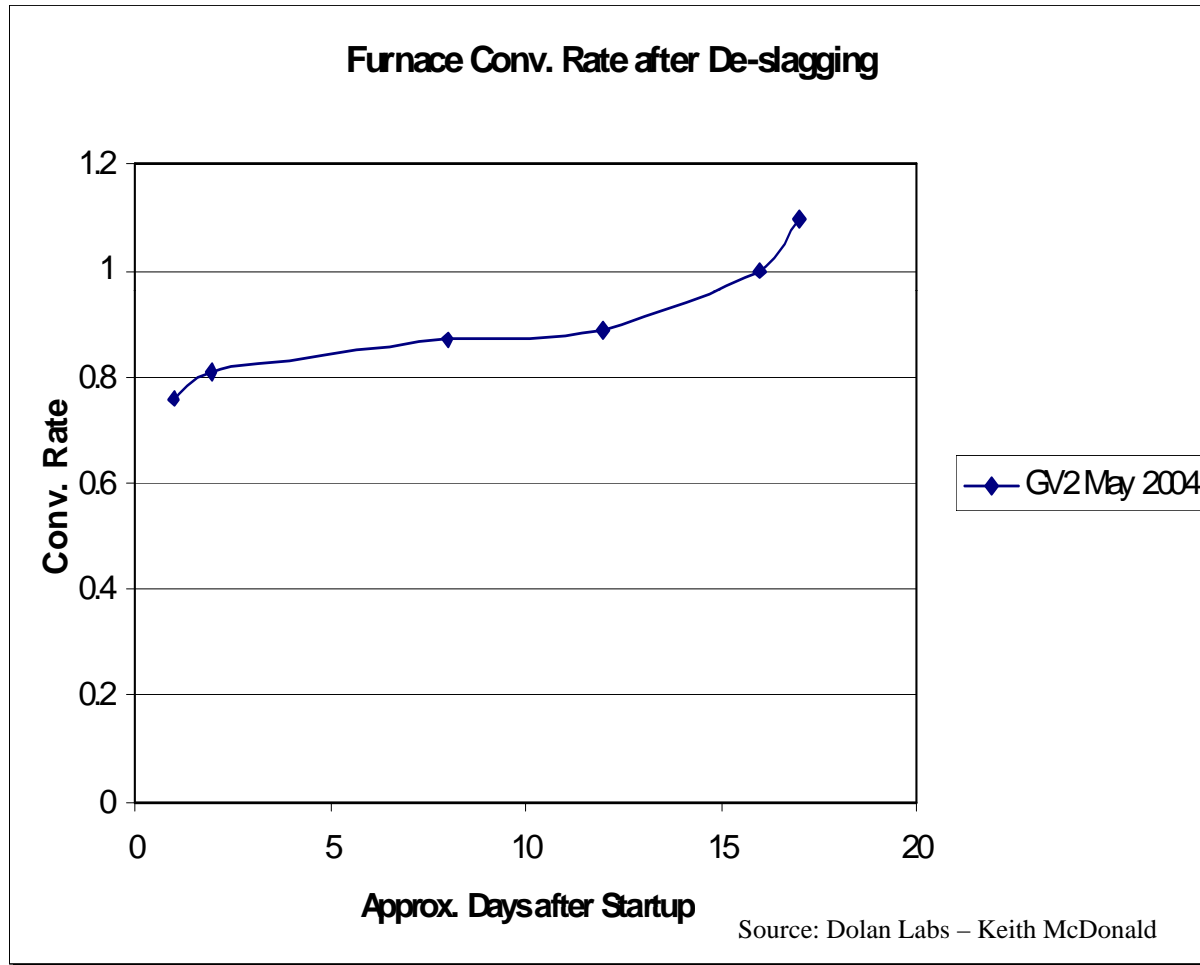
- SCR Catalyst Being Installed

SCR



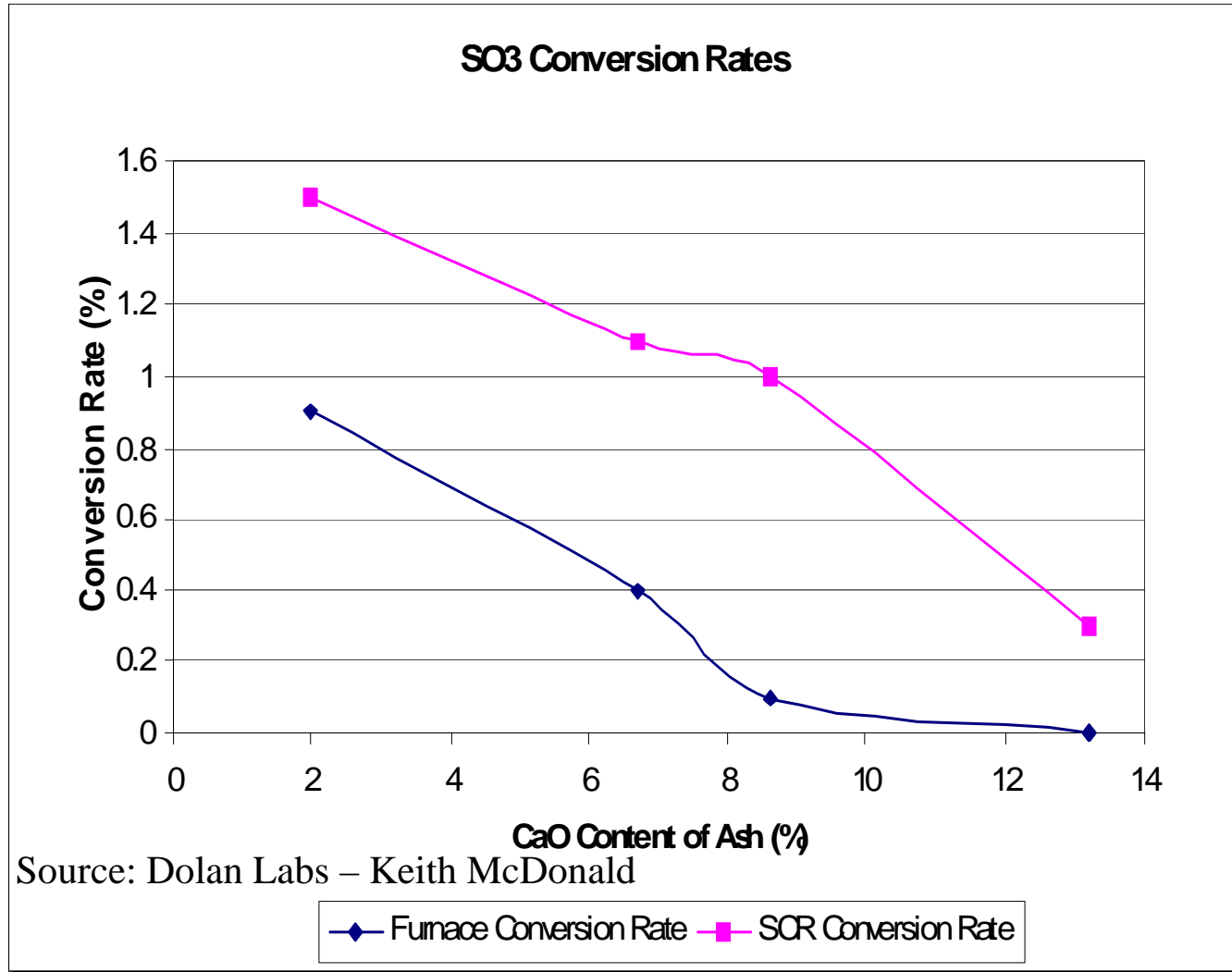
- Conversion Through 3 Layers

SCR



Fuel

Impact on Conversion Rate



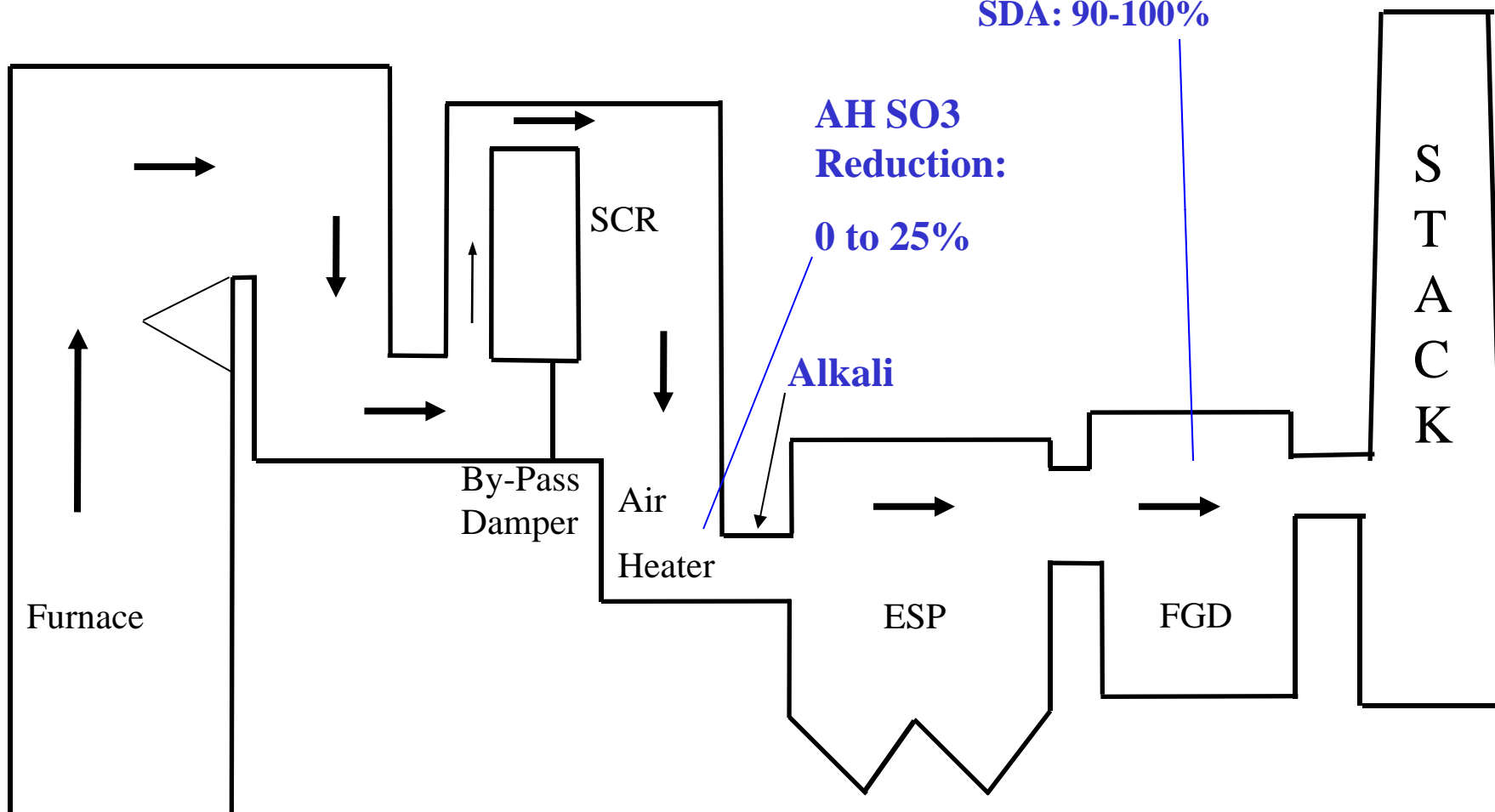
6. SO₃ Sinks

WFGD SO₃ Reduction: 10-50%

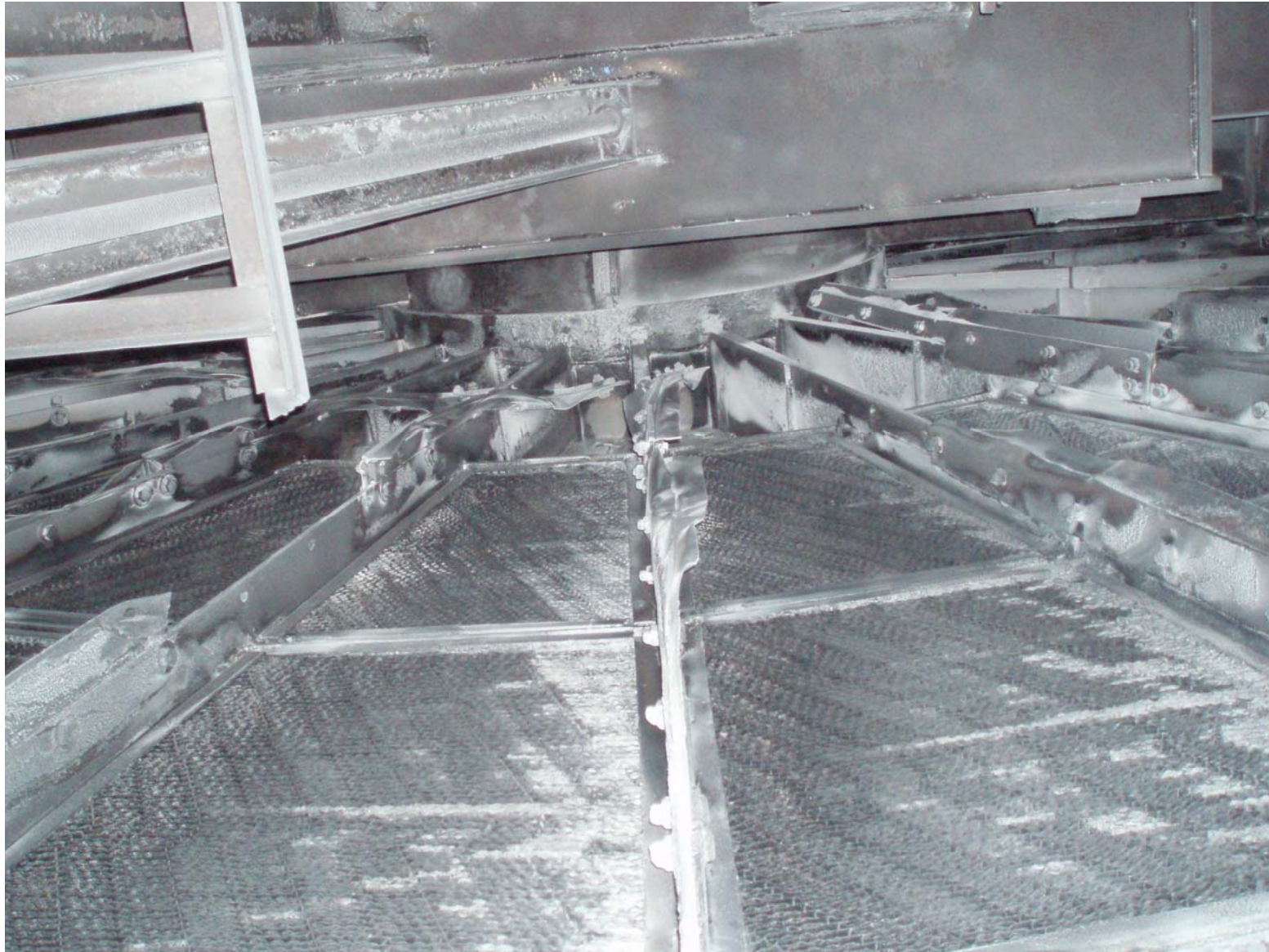
SDA: 90-100%

AH SO₃
Reduction:
0 to 25%

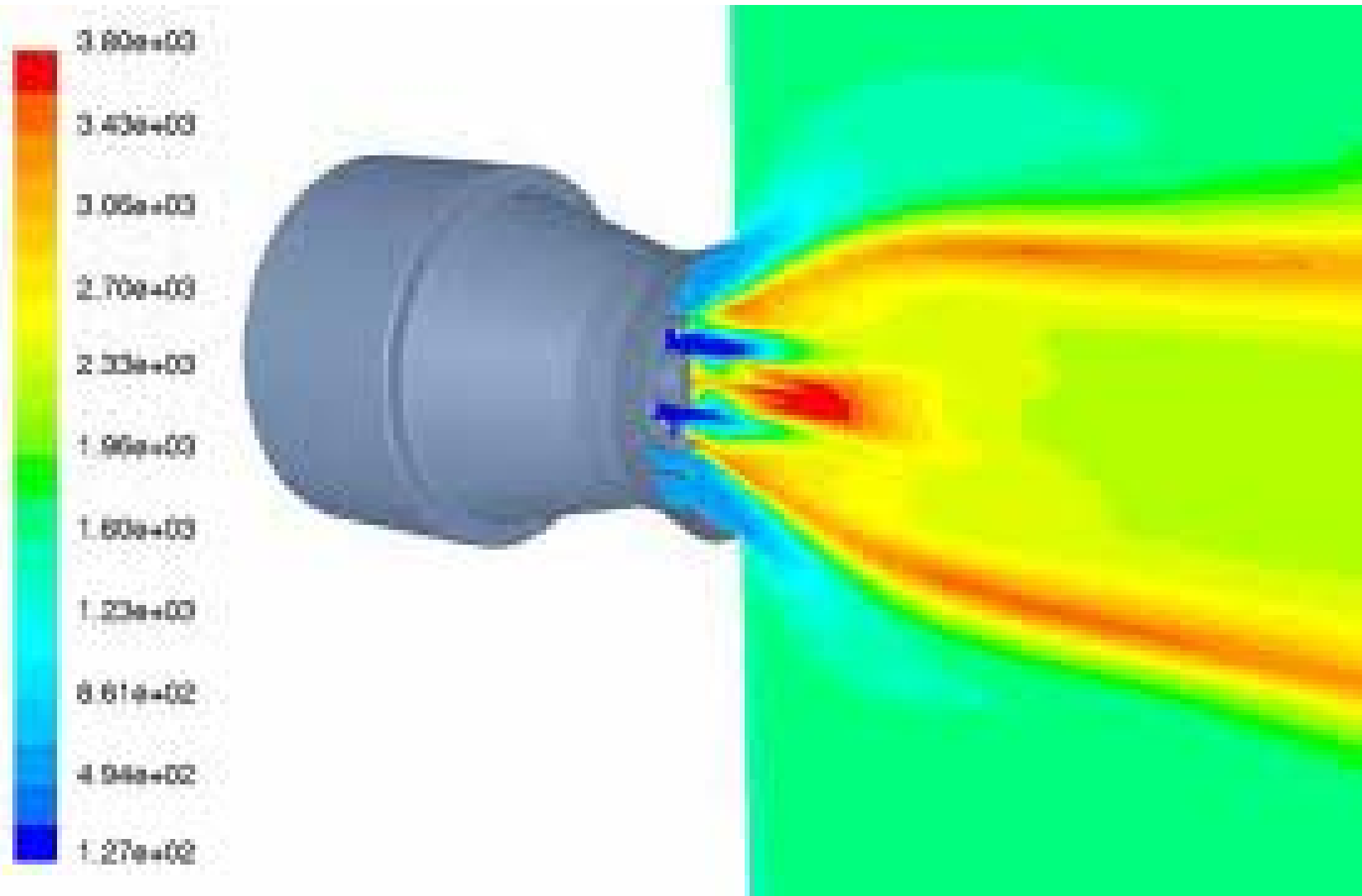
Alkali



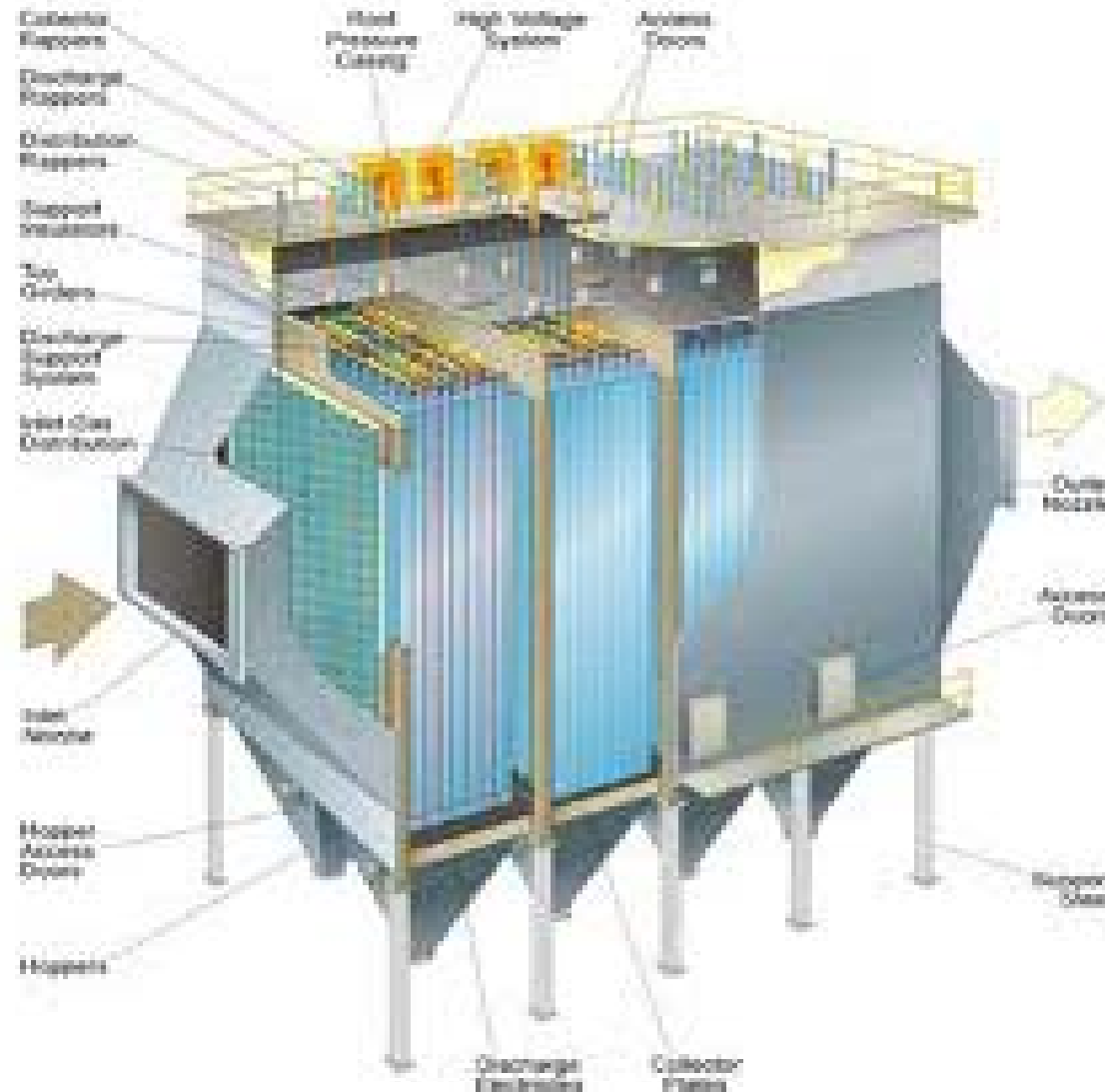
Air Heater Removes 0-25% SO₃



SO₃ Destruction in High Temp. Zone

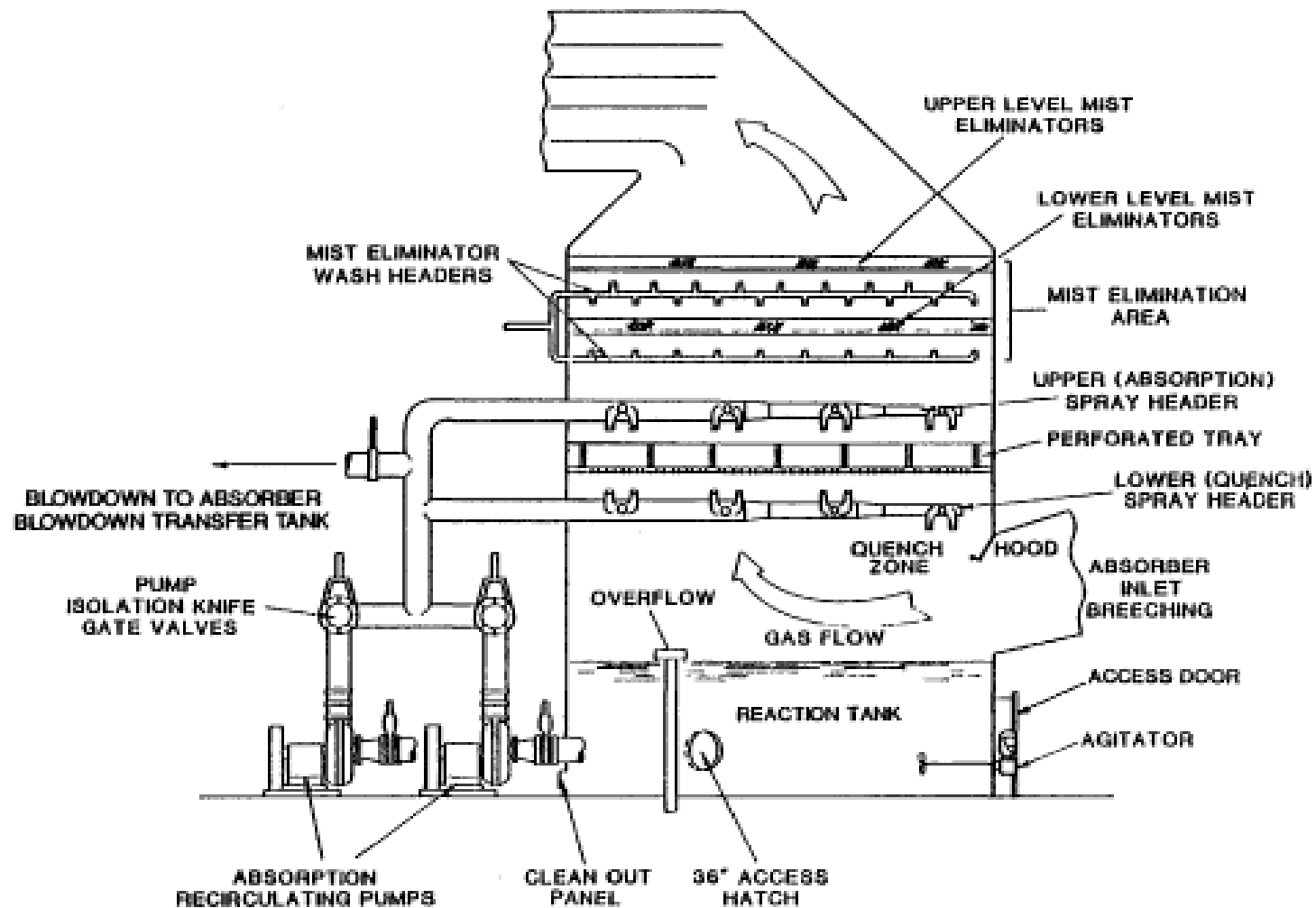


ESP



Native SO_3 capture with alkaline ash

Wet FGD Can Capture 15-75%



7. Why Mitigate SO_3 ?



This is a “no-brainer”

Why Mitigate SO₃?

Continued

Front Page Article 3/16/04:

Pollution unites town, but solution tears it apart

By Rick Hampson, USA TODAY

CHESHIRE, Ohio — Jennifer Harrison stands in the ruins of her old kitchen, looking out the hole where the window used to be, past the lots where the houses used to be, at the power plant that devoured her village.

Source: http://www.usatoday.com/news/nation/2004-03-15-pollution-ohio_x.htm

Why Mitigate SO₃?

- Higher SO₃ levels with SCR operation.
- Higher SO₃ levels with higher sulfur coal.
- Less buoyancy with wet (cooler) plumes.
- Blue plumes are readily visible to the public at very low concentrations.
- Your plume is being watched.

Why Mitigate SO₃?

Continued

- Although SO₃ is not currently regulated, experiences at Gavin Plant and other sites are well publicized.
- Risk of public complaints: Blue plumes are readily visible to the public at very low concentrations. 6-8ppmdv is visible on a clear day.
- New permits are typically issued with an SO₃ emissions limit.

8. SO₃ Mitigation



Utilities are the underdog.

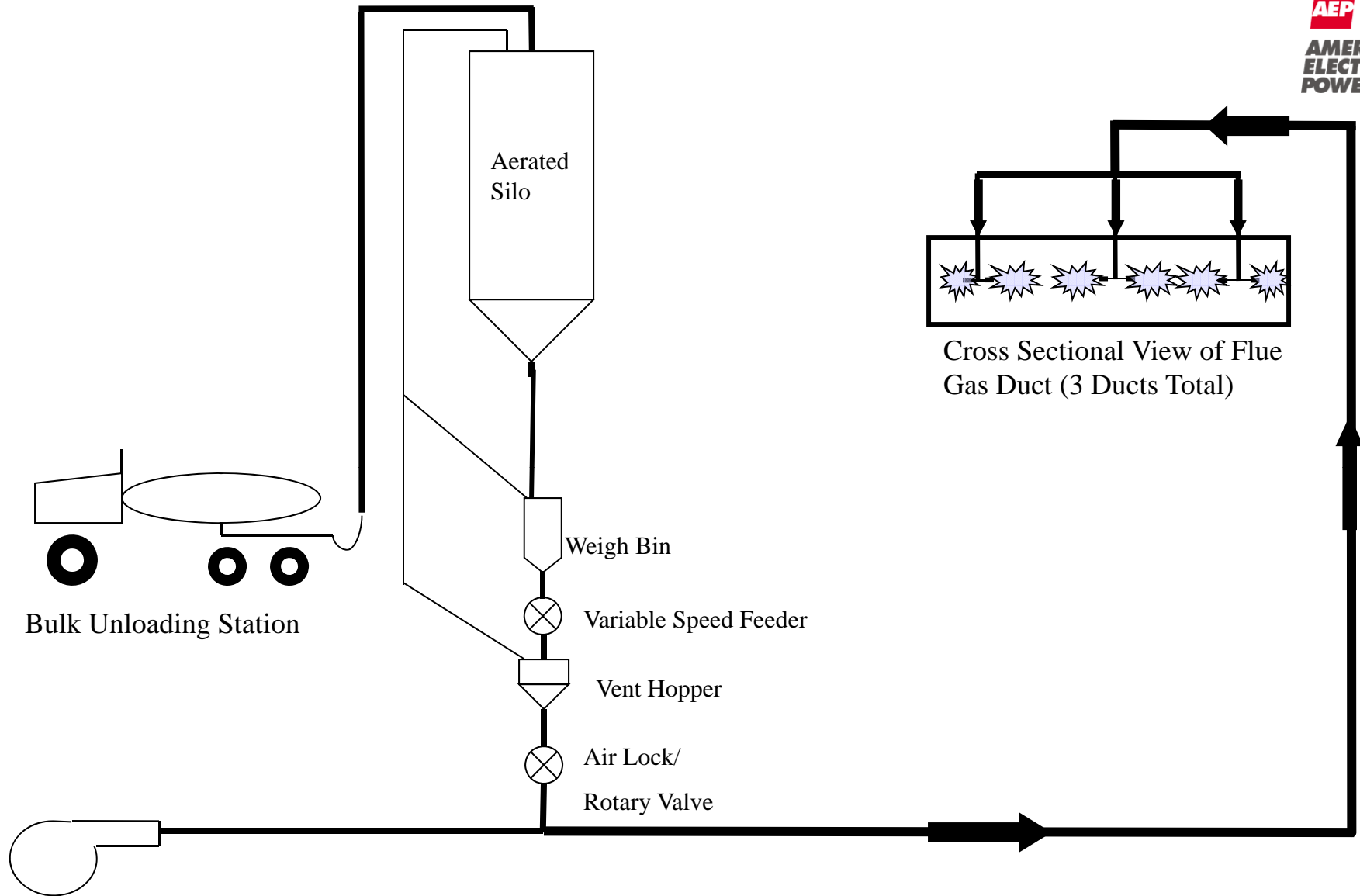
SO₃ Mitigation Options:

Partial List of Chemicals Tested:

- Trona
- Magnesium Hydroxide: Mg(OH)₂
- Hydrated Lime
- High Surface Area Hydrated Lime
- Magnesium Hydroxide Silicate (Talc)
- Magnesite: MgCO₃
- OmniClear: Proprietary Calcium-based product
- Soda Ash: Na₂CO₃
- Magnesium Oxide: MgO
- SBS
- Morpholine (Evaluated)
- Others

Trona Injection System





Simplified Trona Injection Schematic

9. Impacts on Downstream Equipment



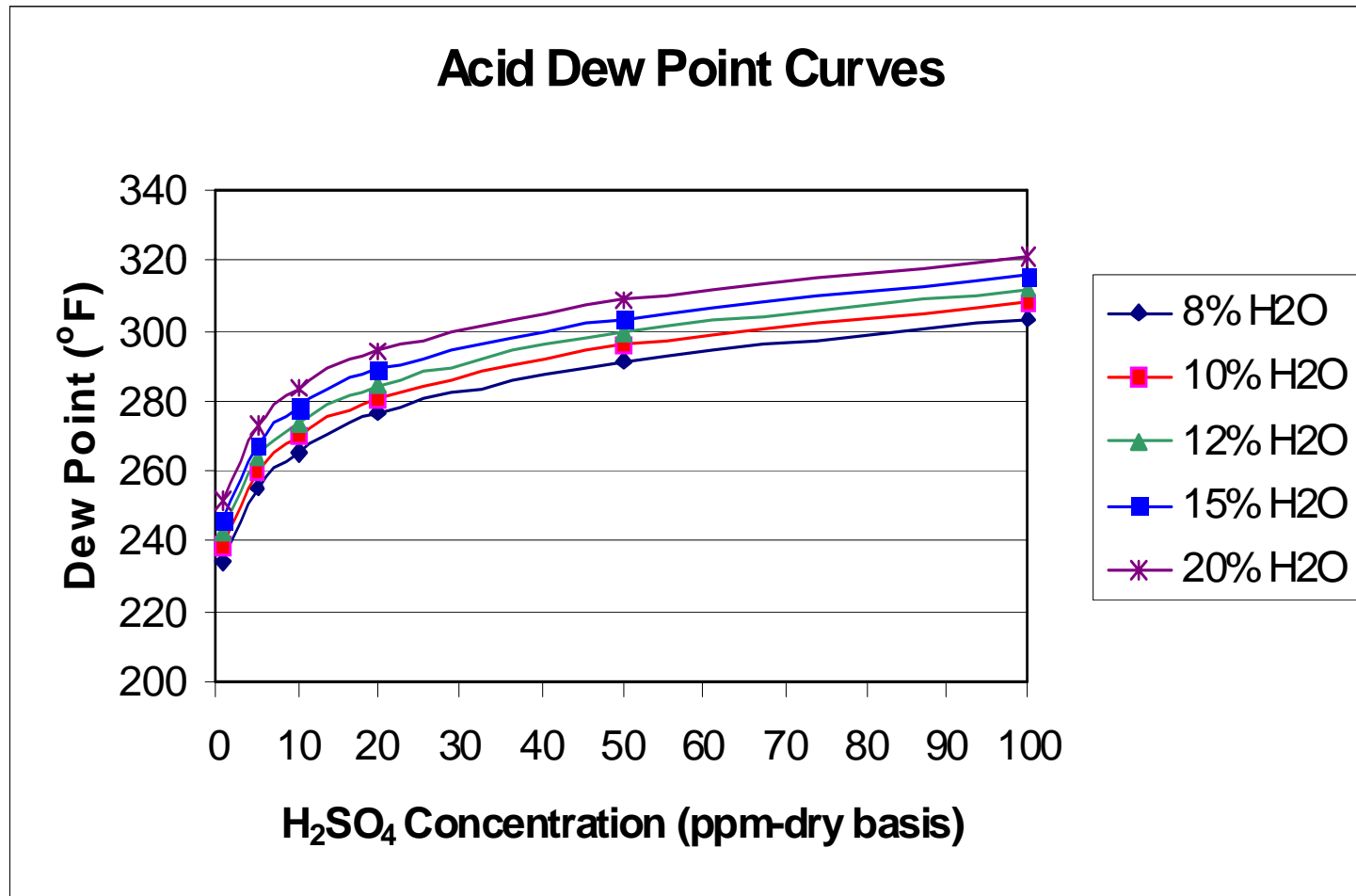
Don't get bit!

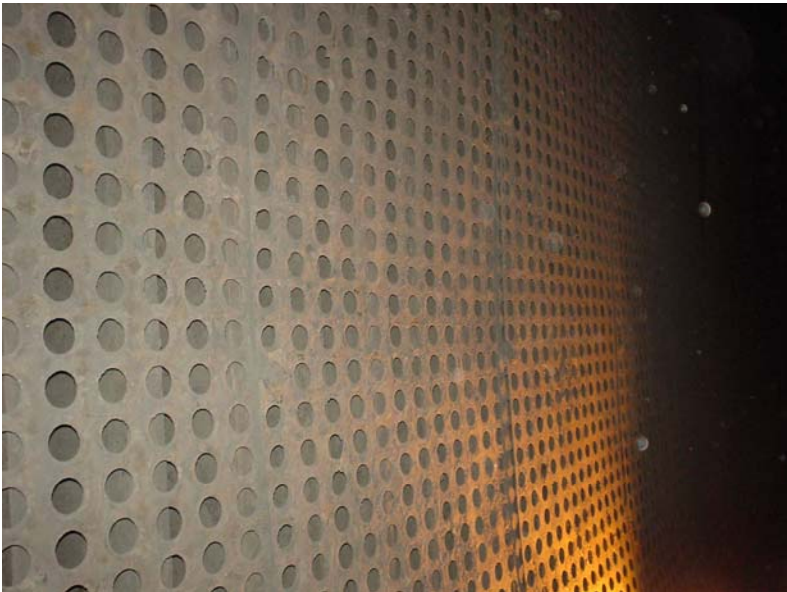
Duct Corrosion



SO₃ Dew Point

Continued





Lower Precipitator Inlet Flow Distribution Plates
Gavin 1 - 5/17/04

Turning Vane Deposits



Test of Spray Lances



10. Sample DSI Calculation



Proper Sizing is Critical

Sample Calculation

- Givens:
 - 1300 MW Unit
 - 6.5 lb SO₂/ MMBtu coal
 - Design Heat Input: 11,936 MBtu/hr
 - 1.2% SO₂ to SO₃ Boiler Conversion Rate
 - 3 Layer SCR
 - 0.25% per layer SCR Conversion Rate (at design temp.)
 - Cold Side ESP
 - B&W Wet FGD
 - 2.47 x 10⁶ SCFMd flue gas flow from the furnace

Sample Calculation

continued

- Calculate ppm of SO₂:
 - 11,936 MBtu/hr x 6.5 lb SO₂/MBtu = 77,584 lb SO₂/hr.
 - Using Ideal Gas Law: 77,584 lb./hr SO₂ → ppm_{dv} SO₂
 - PV=nRuT → V = nRuT/P,
 - where p=14.69psia, T=530 degree R, and
 - Ru= Ideal Gas Constant=10.73 (psia ft³)/(lbmol degree R)
 - n= (77,584 lb SO₂/hr) / (64.066 lb/lbmol) = 1,211 lbmol SO₂/hr
 - V=7,814 SCFM SO₂
 - PPM SO₂ = 7,814/2.47E6 = 3,163 ppm_{dv} SO₂

Sample Calculation

continued

- Calculate PPM SO₃ at furnace exit:
 - 1.2% SO₂ to SO₃ conversion in furnace
 - 3,163 ppm SO₂ x 1.2% = 38 ppmdv SO₃ exiting furnace.
- Calculate PPM SO₃ at SCR exit
 - 3 layers at 0.25% per layer = 0.75% conversion
 - Remember that conversion rate is temperature dependent!
 - 3,163 ppmdv SO₂ x 0.75% = 24 ppmdv SO₃ added by SCR
 - Total ppmdv at SCR exit = Furnace + SCR =
=38+24 = 62 ppmdv at SCR exit

Sample Calculation

continued

- Calculate SO₃ at Air Heater Exit
 - Assume 20% SO₃ sink by AH (site specific)
 - AH removal is dependant upon AH set point and other factors
 - Actual sink will depend on operating conditions that can change with changes in fuel, etc.
 - Test results would be better than assuming removal
 - Ignores AH In-leakage, which may be significant
 - 62 ppmdv x 0.8 =
=50 ppmdv SO₃ at air heater exit

Sample Calculation

continued

- Assume 30% SO₃ sink by wet FGD
 - 50 ppmdv x 0.70 = 35 ppmdv – with no mitigation
 - To obtain 10 ppmdv at stack, need $10/0.7 = 14$ ppmdv at ESP outlet (FGD inlet).
 - Test data is preferred to assuming a removal.
 - Long term testing is required to determine the consistent SO₃ removal by the FGD. Expect large variations in data.
- Mitigation needed: $50 - 14 = 36$ ppmdv, or...
 - $36/50 = 72\%$ Removal with Trona

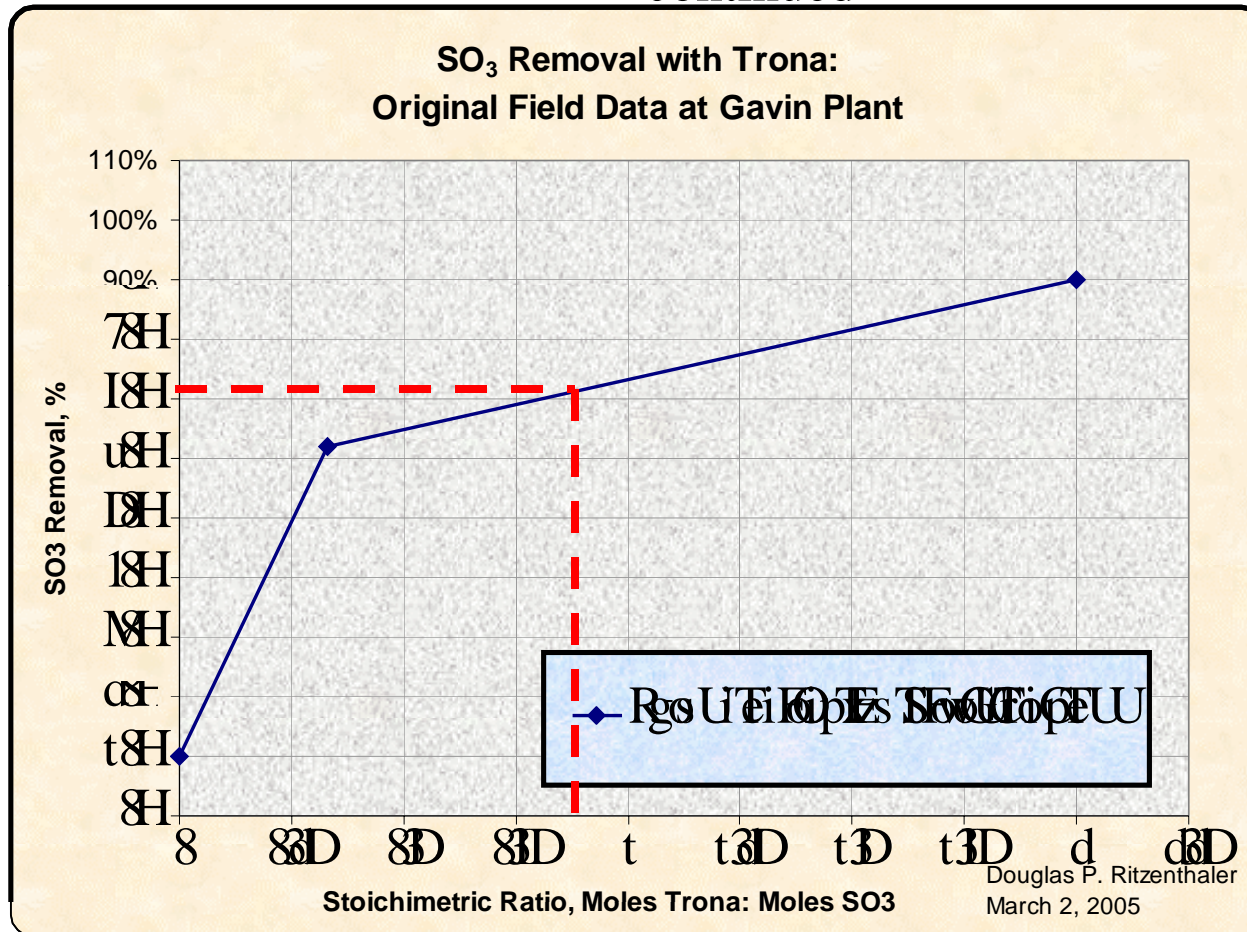
Sample Calculation

continued

- Mitigation needed: 50-14 – 36 ppm_{dv}, or...
 - $36/50 = 72\%$ Removal with Trona
- Use Sorbent Utilization Chart (obtained from field testing) to determine injection stoichiometric ratio (SR) needed for a given removal.
 - $TPH = SR \times ((\text{lb SO}_3/\text{hr}) / M_{\text{WSO}_3}) \times (M_{\text{WTrona}}) / (2000\#/\text{Ton})$
 - Lb SO₃/hr derived from ideal gas law: $n = PV/RuT$ to obtain moles of SO₃, from which mass can be obtained.

Sample Calculation

continued



SR = ~0.88

Sample Calculation

continued

- Calculate TPH Trona for a 72% removal
 - Moles/hr SO₃:
 - » $n = PV/RuT = 14.69 \text{ psia} \times \text{SCFMD} / 10.73 \times 530 \text{ Rankine}$
 - » V in derived from SO₃ ppm_{dv} and flue gas SCFMD
 - » $V = 50 \text{ ppm}_{dv} \text{ SO}_3 \times 2.47 \text{ E6 SCFMD} = 123.5 \text{ SCFMD}$
 - » $n = (14.69 \text{ psia} \times 123.5 \text{ SCFMD}) / (10.73 \times 530 \text{ Rankine})$
 - » $n = 0.319 \text{ lbmol SO}_3 / \text{min} = 19.1 \text{ lbmol SO}_3 / \text{hr}$
 - $\text{Lb SO}_3 / \text{hr} = n \times \text{MWSO}_3$
 - $\text{TPH} = \text{SR} \times ((\text{lb SO}_3 / \text{hr}) / \text{MWSO}_3) \times (\text{MW Trona}) / (2000 \# / \text{Ton})$
 - $\text{TPH} = \text{SR} \times n \times \text{MW Trona} / 2000$
 - » $\text{MW Trona} = 226.051$
 - » $n = \text{lbmol/hr of SO}_3$
 - $\text{TPH} = 0.88 \times 19.1 \times 226.051 / 2000$
 - $\text{TPH} = 1.9 \text{ TPH for a 72\% Removal of SO}_3$

Sample Calculation

continued

- 1.9 TPH does not take into account HCl, HF, or other strong acids.
- A separate calculation for these other strong acids needs to be completed and the required injection rate added to the 1.9 TPH calculated above.

Sample Calculation

continued

- After establishing the calculated Trona injection rate, add a service factor to compensate for
 - Variations in Sorbent Quality (+10%)
 - Dispersion problems or plugged nozzles (+10%)
 - Operational Margin (+15%)
- $\text{TPH design} = \text{TPH} \times 1.35 = 1.9 \times 1.35 = 2.6$
- **2.6 TPH Estimated Design Trona Flow Rate**

Final DSI System Size

- 2.6 TPH includes a service factor
- What about the future?
 - Low conversion catalyst?
 - Operating temperatures?
 - Fuel variations?
 - Will higher removal rates be needed?
- Turn down ratio?
 - Using a 10:1 turn down ratio the system design is:
 - 0.3 to 3 TPH

11. Questions / Comments?



An engineer's work is never done.