

Implementation of NH₃ measurement on Post Combustion NO_x Reduction Systems.

LADCO WORKSHOP

March 24-25th, 2010

Ammonia Slip Measurement

Post Combustion NO_x Reduction:

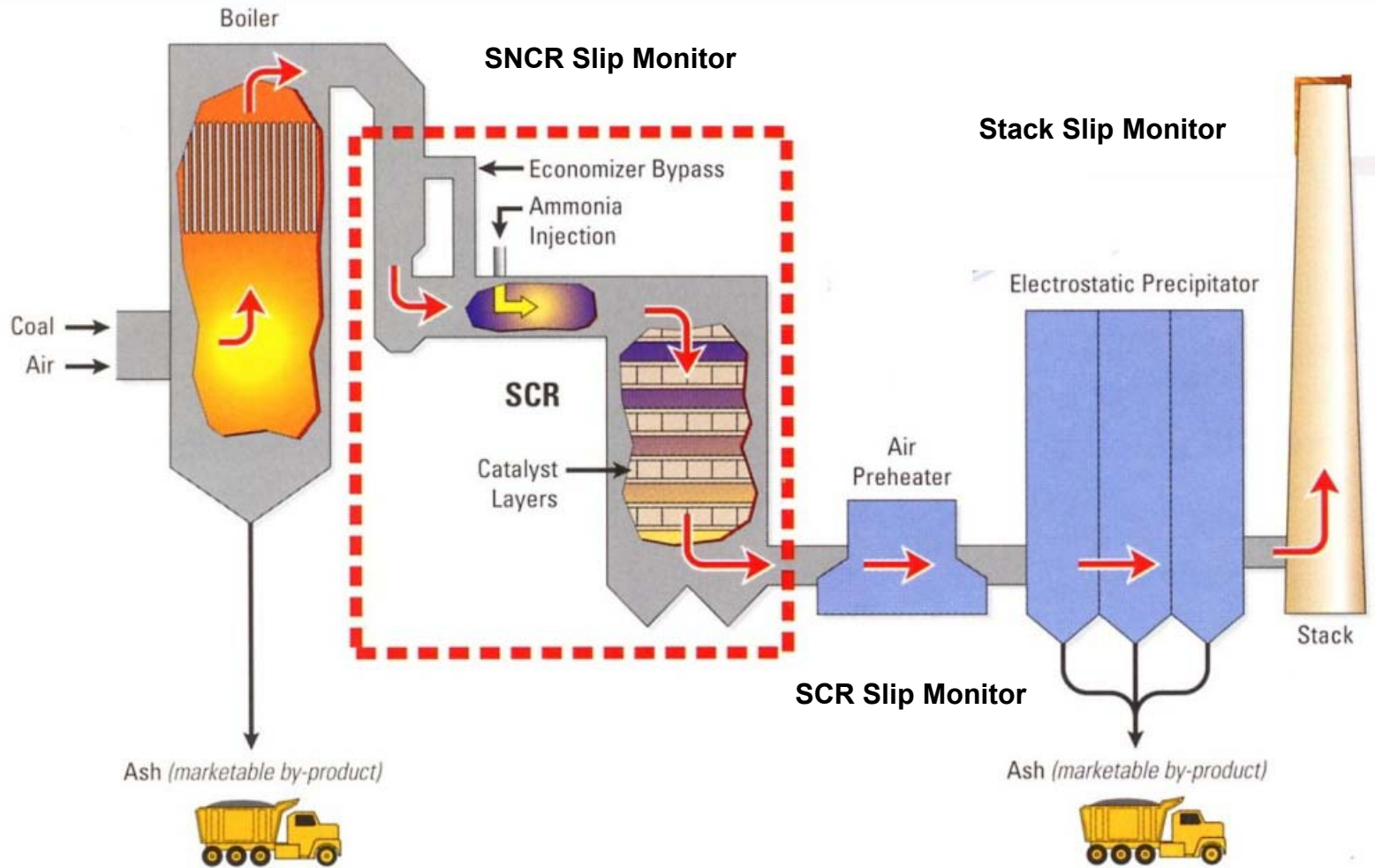
- Selective non-catalytic reduction (SNCR)
- Selective catalytic reduction (SCR)
- Common requirement: introduction of NH₃



Consequences of Ammonia Slip:

- If over-titrated NH_3 escapes – pollutes and wastes
- Violates permit limit if applicable
- If due to incomplete mixing – NO_x escapes
- With high sulfur fuels ammonia sulfate and bisulphate formed – can foul air pre-heater
- Ammonia contaminates fly ash making it hazardous

Ammonia Slip Measurement



Ammonia Slip Measurement

Monitoring Methods:

- FULLY EXTRACTIVE (DRY BASIS)
- FULLY EXTRACTIVE (HOT-WET BASIS)
- DILUTION EXTRACTIVE (WET BASIS)
- IN-SITU (CROSS STACK or PROBE)

Measurement Types:

- Chemiluminescence ,UV Absorption, FTIR, DOAS,
- (TDLAS)

Ammonia Slip Measurement

- **Analyzer Glossary**
- **Chemiluminescence:** (Chemical Light) a measurement technique for NO/NO_x that measures the light given off as a result of the reaction between NO and Ozone. The light output is proportional to the concentration of NO. NO₂ is converted to NO using a high temperature catalytic converter. NO₂ does not react with Ozone so it must be converted to NO.
- **UV Absorption:** a measurement technique that uses a UV spectrometer to measure a particular wavelength where the gas of interest absorbs (measurement) and a wavelength where the gas of interest does not absorb (reference). Most often used for SO₂ measurement in high concentrations.
- **Tunable Diode Laser Absorption Spectroscopy (TDLAS):** By scanning across a very narrow bandwidth in the IR region where no cross interferences occur, the absorption of the IR source by the targeted gas is proportional to the target gas concentration.
- **Fourier Transform-Infrared Spectroscopy (FTIR):** This technique measures the absorption of infrared radiation by the sample gas versus wavelength. The infrared absorption bands identify molecular components.
- **Differential Optical Absorption Spectroscopy (DOAS):** is a method to determine concentrations of trace gases by measuring their specific narrow band absorption structures in the UV and visible spectral region

Ammonia Slip Measurement



Inlet/Outlet Differential NOx Method

- First method is based on the calculation of ammonia slip using the inlet/outlet differential NOx method along with ammonia flow rate and stack flow calculation. This method has been employed successfully in many EPA permitted CEMS, the SCAQMD and many other AQMD's for control and compliance monitoring. This method is reliable and low in cost for sources where SCR inlet monitoring is a requirement.
- The inlet/outlet method is used where SCR control is also a requirement since both the SCR inlet NOx and SCR outlet NOx are measured on a continuous basis. The outlet measurement is usually the CEMS compliant system. The inlet system requires a second probe mounted on the duct before the SCR and a second NOx analyzer.
- The NOx and NH3 react on a 1:1 basis. Therefore, the amount of NH3 reacted is equal to the amount of NOx reduced in the SCR. The simplified formula is:

$$\text{NH}_3 \text{ slip} = \text{NH}_3 \text{ fed} - (\text{NO}_x \text{ in} - \text{NO}_x \text{ out})$$

Ammonia Slip Measurement

Differential NOx/NH3 Converter Method:

- An alternate ammonia method using direct measurement of differential NOx on the stack. This method utilizes two (2) NOx analyzers on the outlet (stack) CEMS. An ammonia converter is included at the stack probe which converts NH3 slip to NOx. The sample line includes an additional sample tube to transport the NH3 converted sample stream to an additional NOx analyzer.
- One analyzer is used to measure NOx emissions and the second is installed to measure the converted stream which includes the NOx and ammonia converted to NOx for the ammonia slip calculations. The NOx analyzers are identical – range, manufacturer, model number.
- A special probe is used to catalytically convert NH3 into NOx. The increase in NOx that results is NH3 slip. The probe contains an electrically heated oxidation catalyst where NH3 is oxidized with oxygen on the catalyst surface into nitric oxide (NO) and water, as follows:



- The NH3 conversion process has an efficiency of 90-98% depending on the sample flowrates, age of converter, and NH3 concentrations. Conversion efficiencies of 95%+ can be expected on typical combustion turbine applications.

$$\text{NH}_3 \text{ slip (ppm)} = \text{NOx (ppm) (total converted)} - \text{NOx (ppm) (unconverted)}$$

Ammonia Slip Measurement

Direct measurement of NH₃:

- This can be done using several methods, both across the stack or duct measurement or Insitu probe type systems.
- Typical across duct measurements use the Tunable Diode Laser method, or DOAS monitor.

Ammonia Slip Measurement

In-Situ...Advantages:

No gas transport

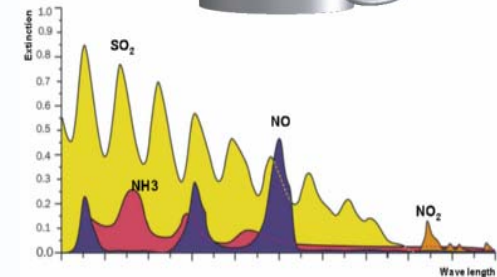
- : Fast response time
- : No loss of components in a sample system
- : No filters, sample lines, pumps to clean

Lower planning expenses

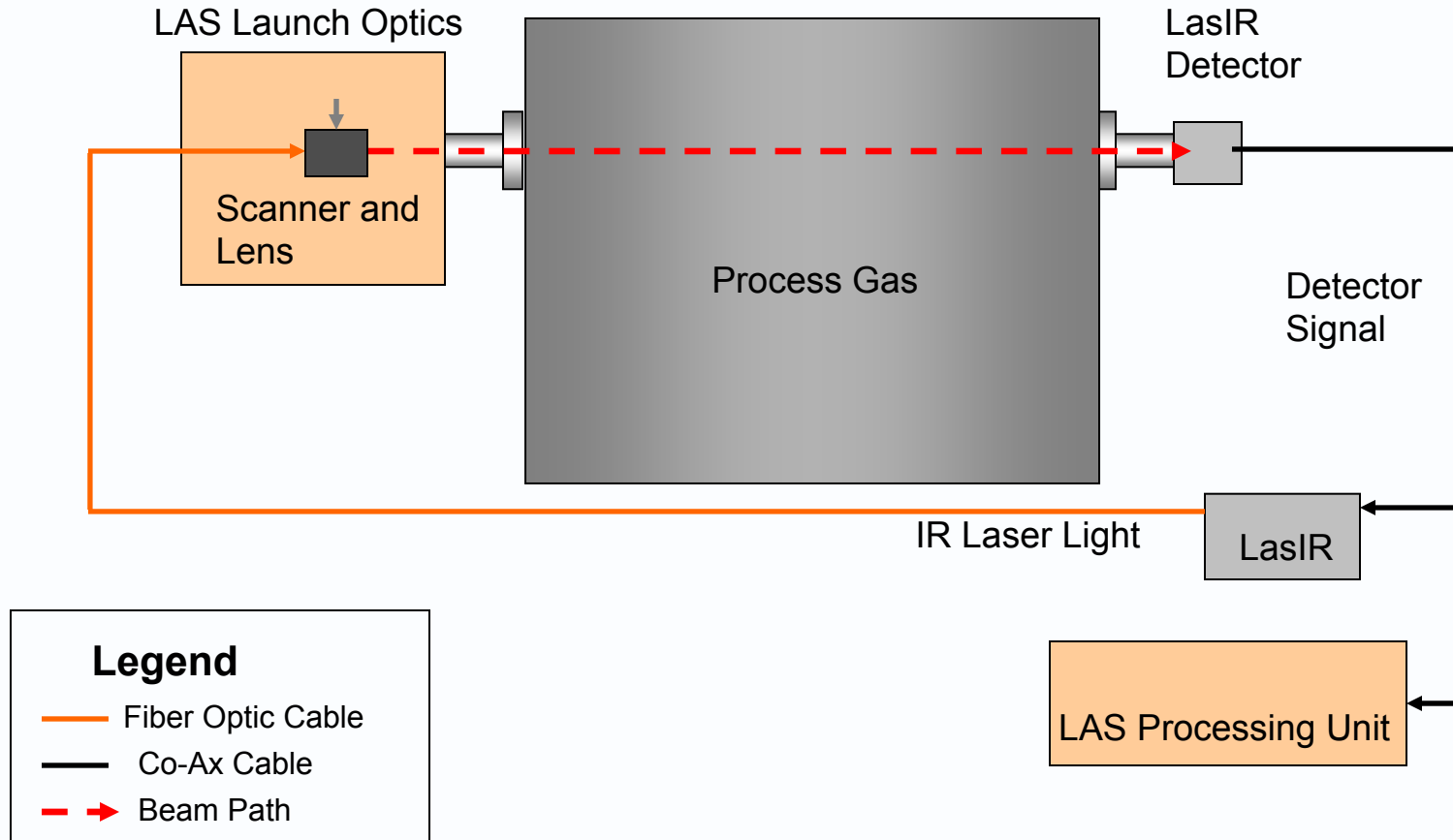
- : Support for heated sample gas lines
- : Analysis container
- : Disposal of sample gas and condensate

Lower installation and operation cost

- : No Heated sample gas lines (\$50/ft)
- : Larger component Inventory and Replacement requirements
- : Cost for shelter or space in existing analyzer rooms.



Ammonia Slip Measurement



Tunable Diode Laser Analyzer

Ammonia Slip Measurement



TDLAS Ammonia slip Monitoring:

- In-situ measurement avoids loss of sample integrity, to Minimize NH₃ Slip
- Single Indicator of direct measurement of Slip for compliance or performance of DeNO_x system
- Fast response better than 60 seconds allows better feedback for control, less violations.

Ammonia Slip Measurement

EXTRACTIVE :

- ❖ Sample delivered to analyzer mounted in typical cabinet , possibly integrated with CEMS.
- ❖ Useful for Dirty Applications such as certain Coal Fired Plants.
- ❖ Measurement type: Chemiluminescence, UV Absorption, FTIR
- ❖ Minimal performance at low concentrations
- ❖ Easy to calibrate, since standard calibration gas procedures are incorporated.
- ❖ Not the most cost effective when equipment, install and maintenance costs are accounted for.



Ammonia Slip Measurement

UV photometer
DEFOR



For measurement of
1 to 3 UV components
Including O₂

Ammonia Slip Measurement



Certification of NH₃ Slip Measurements

- There are no performance standards against which NH₃ monitors can be certified, and there are no adopted methodologies for the certification of continuous NH₃ monitoring.
- CTM-027 defines how best to obtain representative stack test samples for verification of stack conditions, against which any analyzer system would be referenced,.
- In addition, there are no NIST traceable Protocol calibration gases for NH₃ at lower levels. The most accurate calibration gas for NH₃ is a working class gas with an accuracy of +/- 5%. Also, the lowest level that can be commercially obtained is 7 ppm.
- Spiking is an accepted method by which relative accuracy data can be obtained but once again no standards are set on how to achieve this.
- Most Insitu analyzers have built in calibration standards either by filters or calibration gas cells. All have the ability to do self check zero and span, and most can be checked against a standard gas at a higher value working class

Ammonia Slip Measurement



SUMMARY:

- ❖ Until a clear acceptable method for accurate measurement of NH₃ at the lowest concentrations now seen (less than 2ppm) is commercially available, and one that can be applied to all applications, then Industry must rely on the vendors to assist in meeting their needs whether it be permit verification or process optimization.
- ❖ Insitu while giving the best accuracy will be considered the front runner for most applications, but without the ability to do all applications at the low level measurements will struggle for acceptability.
- ❖ Extractive surrogate measurements will continue to dominate the Utility market for now because of the ease of acceptability as part of a CEMS.
- ❖ Tunable Diode Laser technology is proving to be the most accurate method, but will have to wait until a suitable calibration method has been defined and accepted.