Difficult CEMS Applications at Refineries & Chemical Plants
Objectives

Discussion of CEMS and Process Measurement Sample Handling Issues at Refineries & Chemical Plants and Lessons Learned

• Tier 2 Diesel Sulfur Sample Preparation
• J_A Flare Rule Sample Preparation
• Oxygen Measurement of Caustic Sample
• Flare Gas Conditioning
• RSR Flare Conditioners
• Galvanic Oxygen Measurement
• FCC Sample Handling Case Study
Tier 2 Diesel Sulfur Sample Preparation
Tier 2 Diesel Sulfur Sample Preparation

Features

- Interior insulated & heated to 50°F
- Class I, Division 2, Groups ABCD compliant
- Nitrogen purge
- Low point drain
- Flow provided by process pressure
- Filtration by cyclonic side stream filter
- Parker double block & bleed for sample and calibration
- Sample returned to process
Tier 2 Diesel Sulfur Sample Preparation

Operator Comments

Process issue

• Flow thru this system is generated with a differential pressure between inlet and outlet
• When their process was upset, the DP wasn’t great enough to continue flow thru the system

Design issue

• Foil faced insulation was glued to the interior with spray adhesive
  • Adhesive failed
  • Foil facing was not resistant to physical damage
J A Flare Rule Sample Preparation
J_A Flare Rule Sample Preparation

Features

- Class I, Division 2, Groups BCD compliant
- Z-Purged enclosure with large window on front
- TIC controlled Peltier chiller
- Glass impingers
- Liquid slip sensor
- Hydrophobic membrane
- Circuit breaker
- 3 psig cal gas pressure regulator
- System / Direct calibration
J A Flare Rule Sample Preparation

Operator Comments

• Because the peristaltic pump heads weren’t lower than the impingers, the tubing trapped condensate

• Due to high vibration from enclosure mounted pump, the Teflon tubing behind the flow panel would rub and create holes in itself
Oxygen Measurement of Caustic Sample
Oxygen Measurement of Caustic Sample

Features

- Class I, Division 2, Groups ABCD via Z-Purge w/ LPS
- Flow provided by sample pump
- Caustic neutralized by water scrubber & limited to 15 psig
- Dew point to 4°C via dual stage chiller
- Hydrophobic membrane
- Water slip turns off pump
- Manual direct cal gas
- Alarm on low flow
Operator comments

- The bubbler needed in-place clean out taps; interior would foul with oily residue
- Needed a check valve on bottom of bubbler to prevent drain of contents when working with makeup water tubing
- Omega ‘spaghetti tubing’ peristaltic drive did not perform well; replaced with timed Masterflex pump
- Dip tube on bubbler needed better mechanical fixation
- Teflon tubing rubbed from vibration
Flare Gas Conditioning
Flare Gas Conditioning

Features

• Class I, Division 2, Groups ABCD via Z-Purge w/ LPS for GP components
• Flow provided by sample pump
• Dew point to 4°C via dual stage chiller certified to Class I, Division 2, Groups ABCD
• Sample pressure controlled by large area diaphragm regulator
• Water slip turns off pump
• Alarm on low flow
• Hydrophobic membrane
• Manual direct cal gas
Flare Gas Conditioning

Operator Comments

• Love it, no issues
• 100% traditional design
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RSR Flare Conditioners

Features

- Class I, Division 2, Groups BCD compliant with GP components located in customer provided area
- Reduction of dew point by 40°F
- Flow provided by sample pump
- Dual water slip turns off pump
- Enclosure heated to 160°F, insulated and faced with Al sheet
- <140°F turns off pump
- Alarm on low flow
- Isolation valves with external handles
- Hydrophobic membrane
- Double block & bleed direct cal gas injection
- Provision for H₂S leak measurement
RSR Flare Conditioners

Operator Comments

- Low point on flare probe sucked liquid, sample system didn’t shut off. I discussed setting the sensitivity on the conductivity sensor to their particular condensate.

- All zip tie anchors need mechanical attachment, not adhesive; especially in a heated enclosure

- Double the number of mechanical insulation anchors, especially around the window

- Internal temperature exceeds that of the relay; storage temperature was used as the operating temperature
Galvanic Oxygen Measurement
Galvanic Oxygen Measurement

Features

- Class I, Division 2, Groups CD
- Flow provided by sample pump
- Enclosure heated to 100°F, insulated and faced with Al sheet
- Alarm on low flow
- Isolation valves with external handles
- Hydrophobic membrane
- Manual direct cal gas injection
- Remote temperature monitoring and control
- Sample returned to process
Galvanic Oxygen Measurement

Operator Comments

• None had seen it installed in their plant; too new for feedback
Fluid catalytic cracking (FCC) is one of the most important conversion processes used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340°C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil or vacuum gas oil (HVGO). The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst.
FCC Sample Handling Case Study

FCC Unit

- A Petrochem customer has excessive sulfate/nitrate salt issues in their FCC Stack effluent. Stack maintenance requires a 100 feet climb.
FCC Sample Handling Case Study

FCC Unit Diagram

- Catalyst
- Carbon monoxide
- Cooling water
- Steam
- Condensate
- 1. Start-up steam turbine
- 2. Air compressor
- 3. Electric motor/generator
- 4. Turbo-expander
- 5. Cyclones
- Feedstock: 310 to 430 °C
- 6. Catalyst withdrawal well
- 7. Catalyst riser
- 8. Regenerated catalyst slide valve
- 9. Spent catalyst slide valve

Diagram details include:
- Flue gas flow paths
- Catalyst fines separator
- Electrostatic precipitator
- Boiler
- Reactor
- Distillation column
- Condenser
- Reflux drum
- Phenolic sour water
- Offgas
- Reflux
- Cracked naphtha
- Sidecut stripper
- Steam
- Fuel oil
- Slurry settler
- Pump
- Total feed
FCC Sample Handling Case Study

Customer Problem

A Petrochem customer has excessive ammonia sulfate/nitrate salt issues in their FCC Stack effluent. Stack maintenance is a 100 feet climb.

- **1st Solution Attempt-NON M&C**
  - Permapure GASS system installed
  - heated ammonia scrubber
  - heated nafion dryer
  - In series up at the stack with original 180°C heated line

Successfully removed ammonia and water vapor

- **Problem with this solution**
  - Ammonia scrubbing media is consumed by reaction and needs to be replaced.
  - media life dependent on **sample flow rate** and **ammonia concentration** in the sample.
  - media needs replacement in days or weeks when process upset conditions occurred ---Multiple heated scrubbers were added, but maintenance was still required, albeit somewhat reduced.

Real problem here is the 100 foot climb required for maintenance and the frequency that no technician wanted to perform.
FCC Sample Handling Case Study

M&C Solution Criteria

M&C identified that a successful solution would have to involve longer time between maintenance intervals or time required to do maintenance had to be greatly reduced. Varying process conditions/upsets made it difficult to determine and schedule consistent periodic maintenance.

M&C Solutions

- Includes heated sample probe filter to 250° C
- Filter non-ammonia salt particulate in probe filter without ammonia salt drop out/SO₂ reactivity issues
- Sample probe would have automated high efficiency blowback to clean non salt related particulate to minimize filter replacement
FCC Sample Handling Case Study

Probe Drawing
FCC Sample Handling Case Study

FCC Proposed M&C Solution #1

- Locate a traditional condensation based drier up on the stack (removes the majority of water soluble ammonia compounds)
- Followed by an unheated ammonia scrubber located on the stack, prior to the original sample line entry point
- Media replacement would be easier with the unheated scrubber with maintenance be decreased as the majority of ammonia would be removed at the drier.

The customer did not select this solution due to concerns of drier/condensate removal device maintenance required on the stack and concerns about $\text{SO}_2$ scrubbing in the condensation based drier.

- This solution would have allowed the maintenance interval time to be longer
- The customer perception was that cooler and condensate removal (peristaltic pump) would result in increased maintenance time with system subsequently being “off-line” for a longer period of time when maintenance was performed.
- In addition the customer also had the concern of $\text{SO}_2$ scrubbing in the drier which would not give accurate $\text{SO}_2$ reportable emissions from the stack.
FCC Sample Handling Case Study

FCC Proposed M&C Solution #2

- Replace the existing ammonia scrubber with a heated ammonia scrubber containing acid injection in reactor vessel to replace the solid ammonia scrubbing media.
- Chemical reaction for scrubbing the ammonia would be the same with acid injection rate and acid concentration tuned to reduce maintenance intervals to quarterly or annually.
- Customer would reuse the existing sample line.

The customer rejected this idea because they did not want liquid phase acid up on the stack in a storage container.
FCC Sample Handling Case Study

FCC Proposed M&C Solution #3

• Replace sample line with stainless steel tube sample line heated to 250 deg C, which keeps ammonia salt from creating compounds in the vapor phase.
• Ammonia will be scrubbed with the ammonia scrubber on the sample conditioning panel in the instrument shelter.
• Alternatives for condensation and permeation based driers to be installed on a panel in the instrument shelter with the solid ammonia scrubbing based media.

The customer selected the above solution and permeation membrane drier to minimize the potential for SO₂ loss in condensation based drier.
FCC Sample Handling Case Study

Final Solution #3 - Panel
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FCC Sample Handling Case Study

FCC Panel Heated Oven with Solid Ammonia Based Scrubbing Media
FCC Sample Handling Case Study

Final Solution #3

- Ammonia Scrubber Media Replacement
- Parallel Ammonia Scrubbers
- Replacement Takes a few Minutes
- System Remains On Line During
- No Stack Climb Required
FCC Sample Handling Case Study

Final Solution #3 – Lessons Learned

• Customer required a solution that will solve the problem with the minimum maintenance and minimum missing data.
• Customer will not accept a solution that could cause other problems in the future, such as potential emission integrity ($SO_2$).
• Customer will not accept a solution that would require additional chemicals, that could cause perceived dangerous conditions to health and safety manager.
• M&C had to offer many different solutions and options before the final solution with detailed description of benefits/pitfalls of each option.
• Continuous communication and the willingness to “think outside the box” was required to meet the customers needs.
• M&C selected optimal solution for application which is specific to each sites preferences and unique circumstances.
Thanks for Listening
Questions?

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