Performance Update and Review of Coatings Used to Improve Reliability and Accuracy of Sulfur, Mercury and NO_x Sampling and Analysis Equipment.

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Introduction

- Use of coatings
- Material compatibility results
- Uses and applications
  - Ja
  - others
- Field results and data
- Upcoming

Applications

- Coating have long history of use in petrochem/refining for inert sampling starting with Teflon lined sample cylinders, fittings, tubing
- ULSD & ULSG standards accelerated need for coated systems and components
- Needed alternatives to Teflon for high temperatures and to avoid delamination

Applications

- SilcoSteel and Sulfinert brought new inert coating technology to application.
- Combining with material improvements of electropolished surfaces, trace ppb levels of transport and analysis possible
- Expanding needs from just reduced sulfurs:
  - Ammonia
  - Mercury

Sulfurs and Steels

- Most pathways consist of steel and stainless steel
- Over time, in contact with sulfurs, these surfaces will equilibrate to help with analytical results
- Part per billion level analysis not possible and very slow change times to signal given concentration change
- Coatings are great for these materials to improve reliability and analytical results
- The smoother the better. Reduce surface area, less chance of contact points and more efficient and effective coating.

Sulfurs and Copper

- Complete Loss
- H_2S and sulfurs will be scrubbed from sample streams with high copper alloys such as
  - Monel®
  - Brass
- Problem: Monel® commonly used in HF containing streams (alkylation units)
  - This is a prevalent problem facing integrators and analyzer manufacturers with Subpart –Ja taking hold
  - Recommend use of Hastelloy in the HF containing streams with SilcoNert coating

Sulfurs and Copper

- Brass substituted for stainless in cost cutting efforts
- No sulfur data from a systems containing these materials is to be trusted.
- Copper alloys cannot benefit from the Silicon/Silco- based coatings.
- Test data on Monel® and sulfurs well-presented by Hashem, et. al.,[1] from Schlumberger-Oilphase DBR
  - Samples at 50ppm (relatively high nowadays) are scavenged in Monel® tubing

[1]Hashem, et. al, "Low-Level Hydrogen Sulphide Detection using Wireline Formation Tester", International Petroleum Technology Conference, IPTC 11582, (2007)

What about sampling a stream in carbon steel pipes?

- Common in Natural Gas and Refinery streams, samples are being sent through long carbon steel piping
  - Doesn't this adsorb the sulfur compounds?
  - How can the results be reliable in a process system even with coated stainless components?
  - Contamination, moisture, other issues
- It's all about the sampling

Sampling from Carbon Pipes

- Studies and presentations by Welker Engineering throughout the years[2] demonstrate a good sample point is required
  - Away from the wall
  - Away from turbulent flow
  - From center of stream if possible
  - Away from any flow disruptions
- Wall sample points are poor because of “zero velocity” flow profile, lot’s of contact with wall, moisture, contamination
- Laminar stream samples in the middle of the flow profile will give a real time representative sample of the stream
- Then with an inert sample probe and transfer equipment it is possible to get an accurate, and real time analysis of the stream.

[2] Fish, D. J. “Techniques of Composite Gas Samplings”; Welker Engineering Technical Note

Applications

- Subpart –Ja, refinery flare gas testing
- Oil and Gas well downhole sampling
- Ethylene/Propylene catalyst poisons
- Coal Fired Boiler Flue Gas testing
- Ammonia slip
- NOx

Refinery Flare testing

- Rule 1118 now Subpart –Ja regulation
  - All new and modified refinery flares to be monitored by November 2015
- Given stream compositions need for inertness for trace level analysis of reduced sulfurs, ammonia slip and even mercury
- Stream may even have HF from Phillips Alkylation units

Refinery flare gas

- Davidson, et. al.[3] published data on refinery flare gas monitoring systems for stability over a year.
- This was then California Rule 1118, which is direct predecessor of Sub Part –Ja regulations
- System showed great stability over period.
- No impact from upsets on system performance
- Monitoring range from 1 to 150,000 ppm total sulfur
- Vent gas measure at middle 50% of flare with angled coated probe to get representative sample
- Concluded need for stable instrumentation, heated sample system and inert coating

3 Davidson, T.; et. al. "Performance of Environmental Monitor For Total Sulfur and High Heating Value of Refinery Flare Gas System." ISA 56th Analysis Division Symposium 2011, League City, TX (2011)

Refinery Flare Gas

- Lessons applied to Subpart –Ja demand
- Sample system stability:
  - Heated transfer lines
  - Surface finish considerations
  - Metallurgy
  - HF or not HF
- Can achieve the regulatory standards and provide stable performance

Oil and Gas Well Sampling

- Need to quantify sulfur content of new wells
- Growing concerns now requiring monitoring of mercury content as well
- Presentation by Schlumberger in 2007[1] and 2013[4] highlight the application of coatings to provide stable sample bottles.
- Any level of mercury (measured in $\mu g/m^3$) is of interest because of mass volumes being pumped
- Need to quantify sulfur content of all wells for quality and safety standards

[4] Harfoushian, J. "Quantification of Low Levels of Mercury in Gas Reservoirs Using Advanced Sampling and Analysis Techniques" Society of Petroleum Engineers Annual Conference, SPE166220 (2013)

Oil and Gas Well Testing

- Inertness needs:
  - Mercury necessitates clean handling and inert sample bottle or risk losing all mercury to adsorption
  - Sulfur results dependent on system design downhole and of sample bottle conditions on surface

Ethylene/Propylene

- Study presented by Biela, et. al. from Air Liquide[5]
- Sulfur contamination causes catalysis poisoning relating directly to reduced yields
- H2S (hydrogen sulfide) and COS (carbonyl sulfide) coming over in polymer-grade Ethylene and Propylene
- Conversion of COS in furnace to H2S and then contact with catalysts.
- Poison levels very low (Propylene)
  - 10ppb COS
  - 50ppb CS2
  - 1ppm Dimethyl Sulfide (DMS)
- Manufacturing Specifications for monomers: 50ppb H2S (ethylene); 20ppb COS (propylene)
- Sampling systems and standards are necessary to keep yield high

5 Biela, B.; et. al. "The Do's and Don'ts in the Analysis of Sulfur for Polyolefin Producers"; Gulf Coast Conference, Galveston, TX, Paper 081 (2003)

Coal Flue Gas

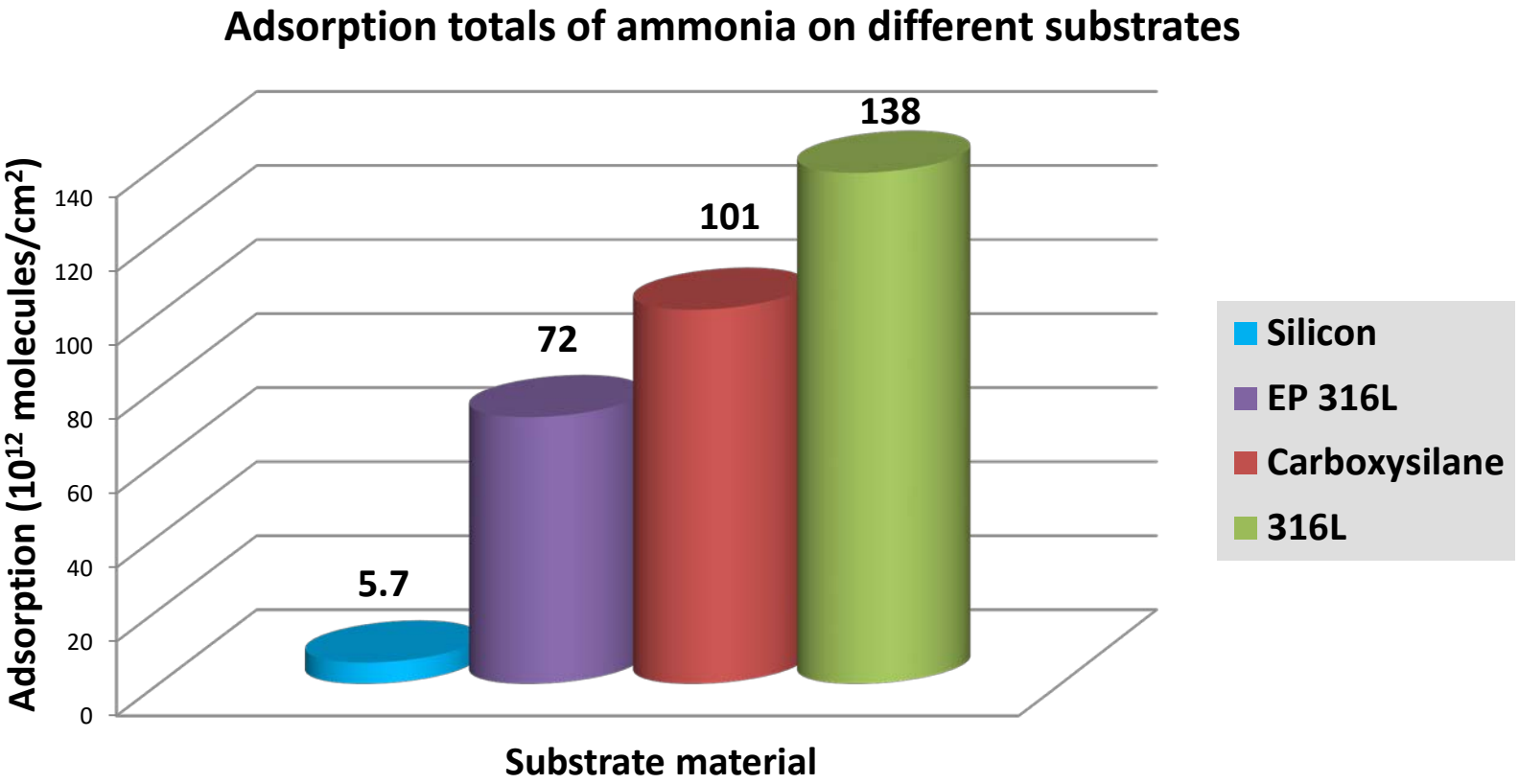
- Emissions of mercury in Coal Flue Gas from Boilers is now a monitored pollutant
- Also effluent from refining, petro activities that are monitored
- Problem is the oxidation of mercury and inability to analyze due to loss
- Coatings applied to sample probes, transfer lines, inertial filters eliminated adsorption
- Studies done on oxidized mercury Hg^{+2} demonstrate 100% transfer of these adsorptive compounds in coated transfer lines[6].

[6] Lan, X.; et. al. "Seasonal and Diurnal Variations of Total Gaseous Mercury in Urban Houston, TX, USA"; Atmosphere, 5, pgs. 399-419 (2014)

Ammonia

- Ammonia slip is release of ammonia through treatment process and pollution control equipment. Sulfur Reduction units, NO_x reactors, mercury control units
- Necessary to accurately monitor the levels of ammonia as this slip can now be considered a pollutant

Modified Silicon deposition reduces adsorption of ammonia[7]



[7]Vaittinen, et. Al., "Adsorption of ammonia on metal and polymer Surfaces", University of Helsinki, 2013

NO_x compounds

- Common pollutant from combustion process
- Monitoring for boilers and automotive need to look at NO_x emissions.
- Mixed samples of Nox compounds along with ammonia and moisture common for automotive exhaust, very difficult application
- Silco-based coating performing as well as Teflon-lined with no adsorption, change or loss[8]

[8] Fitz,D.; et. al. “Quantification Of Uncertainties In Continuous Measurement Systems For Low-NOX Emissions From Stationary Sources” California Energy Commission; Consultant Report P500-01-018F; 2003

Upcoming Challenge: Tier 3 Fuel Standards

- Sulfur in Gasoline from 30ppm to 10ppm
- Old tricks of priming sample system will not work as well at low ppm
- Coatings will play important role in providing stable, responsive on-line and process monitors.
- Components commonly causing sulfur adsorption:
  - Probes
  - Tubing
  - Metal filters
  - Sample Cylinders
  - Regulators
  - Fittings
  - Valves
- Get testing systems ready now.

Conclusion

- Trace and active compound analysis are getting more accurate and reliable.
- Impact of substrate that are smoother, coatings that are better and sampling techniques that are robust
- Subpart –Ja will require the biggest deployment of these technologies in order to meet regulatory requirements
- The technology is there and there are experts at all OEM's deploying improved equipment.
- As more requirements emerge, more technologies are going to be required to meet the growing standards of a changing world.