Evaluation of System Surfaces in Low-Level Sulfur Analysis for the Petrochemical Industry

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Outline

- Options
- Coating process
- Performance data
- Effect of moisture on coated surface
- Other Applications

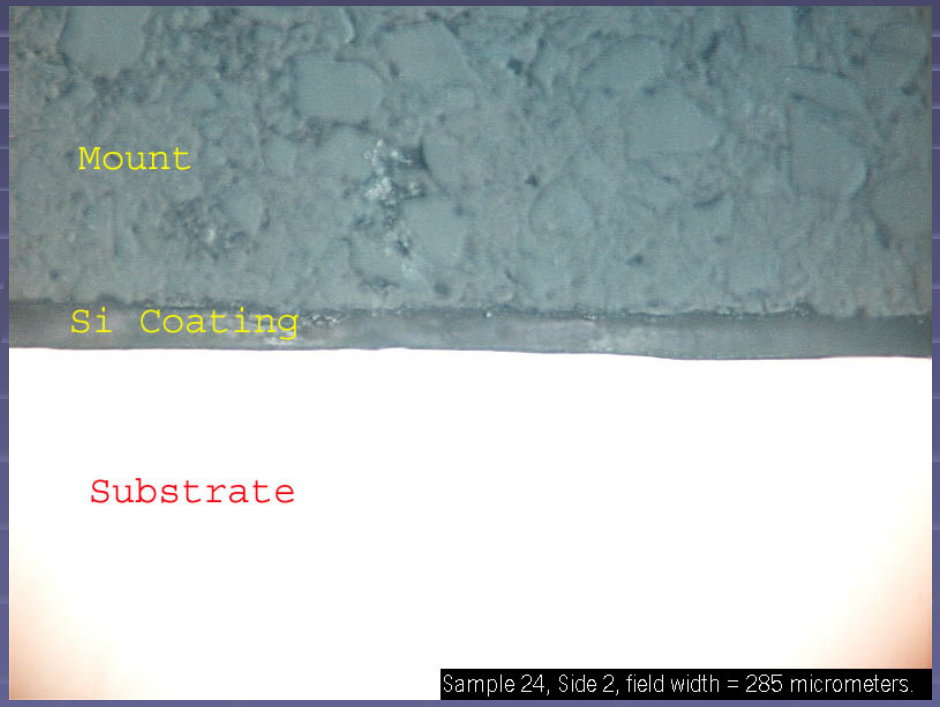
Options

- Stainless steel (welded / raw)
- Electropolished stainless steel
- Coated stainless steel (CVD)
- Functionalized coated stainless steel
- Fluoropolymer tubing

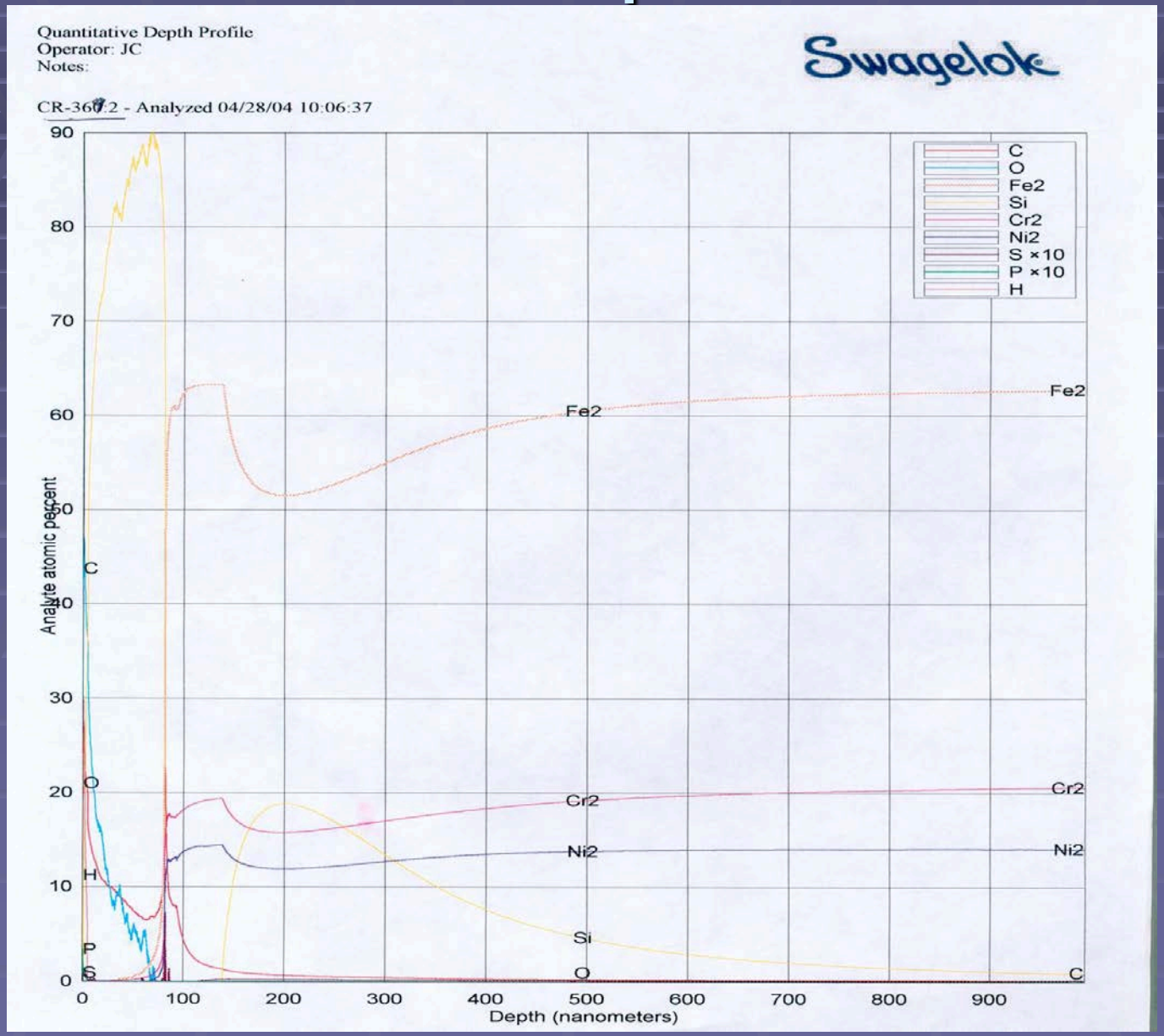
Chemical Vapor Deposition Process

- Thermal decomposition of silanes
- Amorphous silicon deposition
- Functionalization of surface if desired
- Process
  - Clean (caustic surfactant; ultrasonic)
  - Vacuum
  - 400ºC
  - Applied in vessel or oven chamber
- Total 3D coverage, not line-of-sight
- High volume (size dependent)

Coating Cross Section



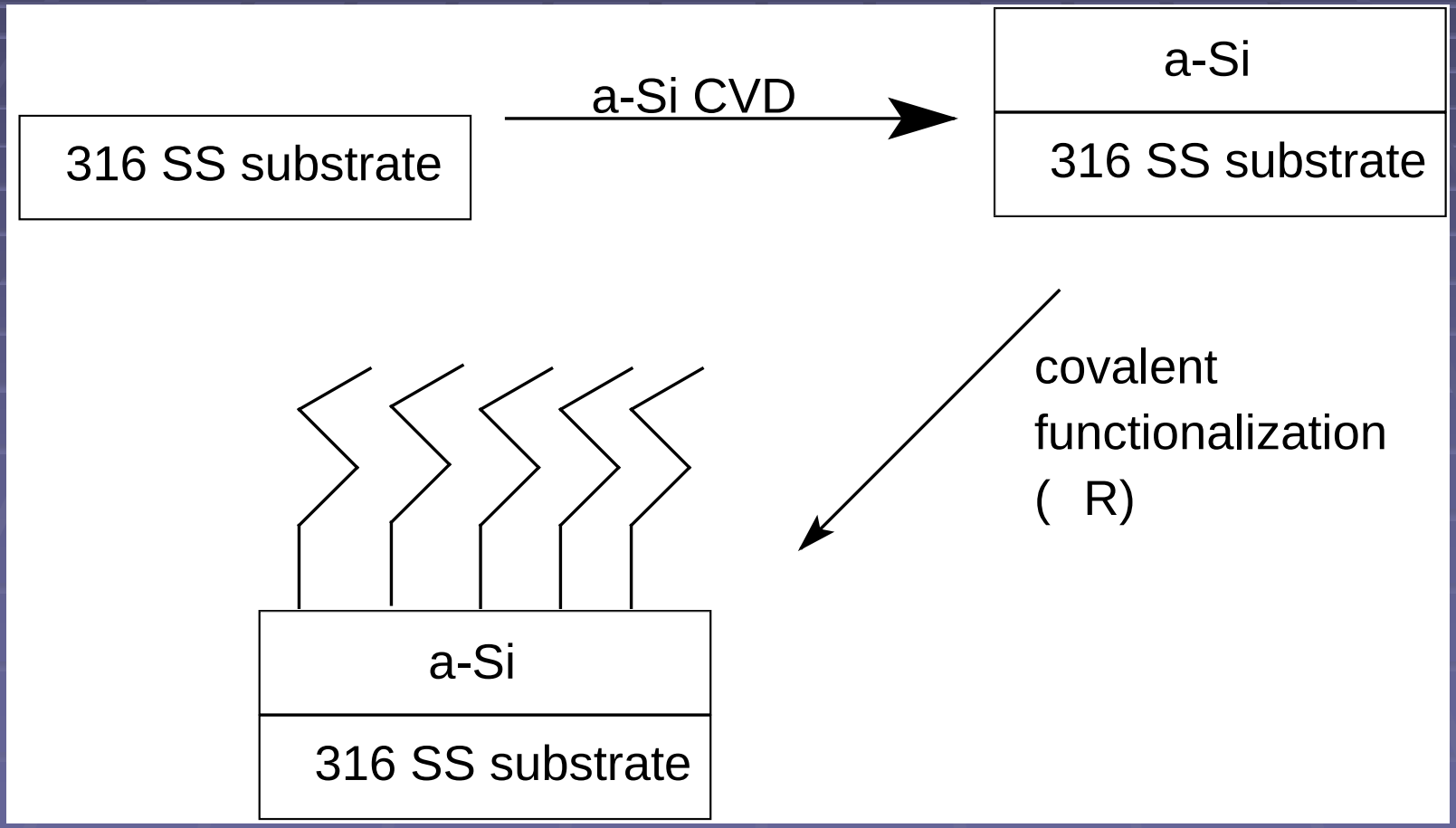
GD-OES Depth Profile



Secondary Enhancements

- Amorphous silicon deposition
  - Up to 20um in depth
  - Multiple layers to eliminate pin-holes
  - Enhances corrosion resistance
- Additional organic functionalization possible
  - Decrease of pin-holes
  - Improving surface inertness

Patented Functionalization



Coating Appearances

Common Coated Components

- Sampling Systems
- Transfer Tubing
- Valving
- Particle Filters
- Tube Fittings and Adaptors
- Sample Cylinders; Outage Tubes
- Analyzer components
- Continuous Emission Monitoring (CEM) equipment

Inertness: Amorphous Silicon and Surface-Functionalized Amorphous Silicon

- Both coatings are based on Chemical Vapor Deposition process. Similar physical properties
- Amorphous silicon
  - recommended if level of active compounds is 10-50 ppm or higher
- Functionalized
  - ideal for extremely low-level, <1ppb and up, transfer and storage of active compounds

Inertness

- Application: Reduce activity of substrate (i.e., stainless steel) to minimize adsorption of compounds
- Coated system products deliver better reproducibility and accuracy by reducing hold-up of active compounds

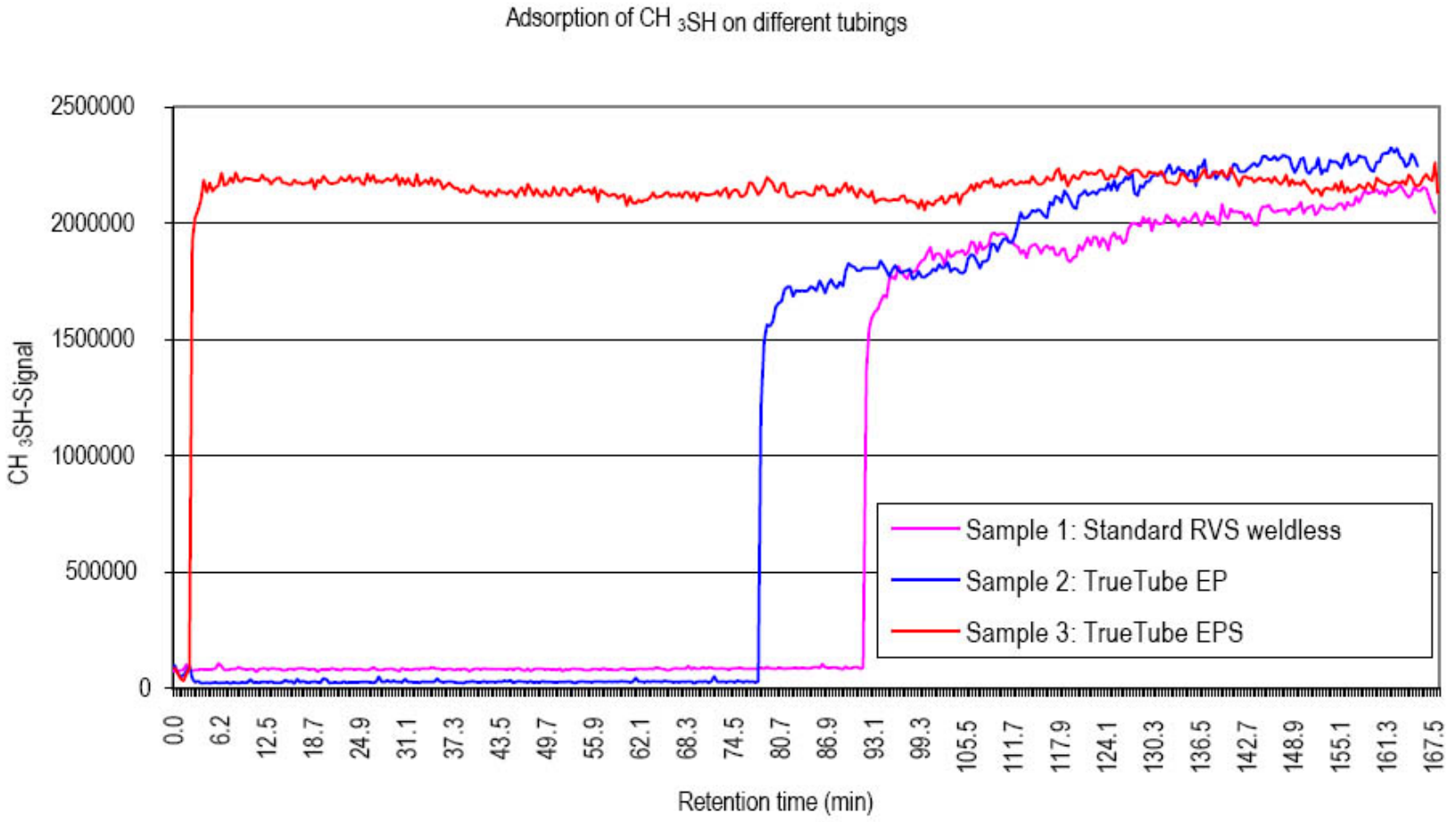
Current Applications

- Sulfurs: Application areas
  - Natural Gas; LPG
  - Ethylene; Propylene
  - Fuel Cells
  - Petrochemical process Streams
  - Beverage Grade CO_2 (Soda/Beer)
  - Flavor (Wine/Beer)

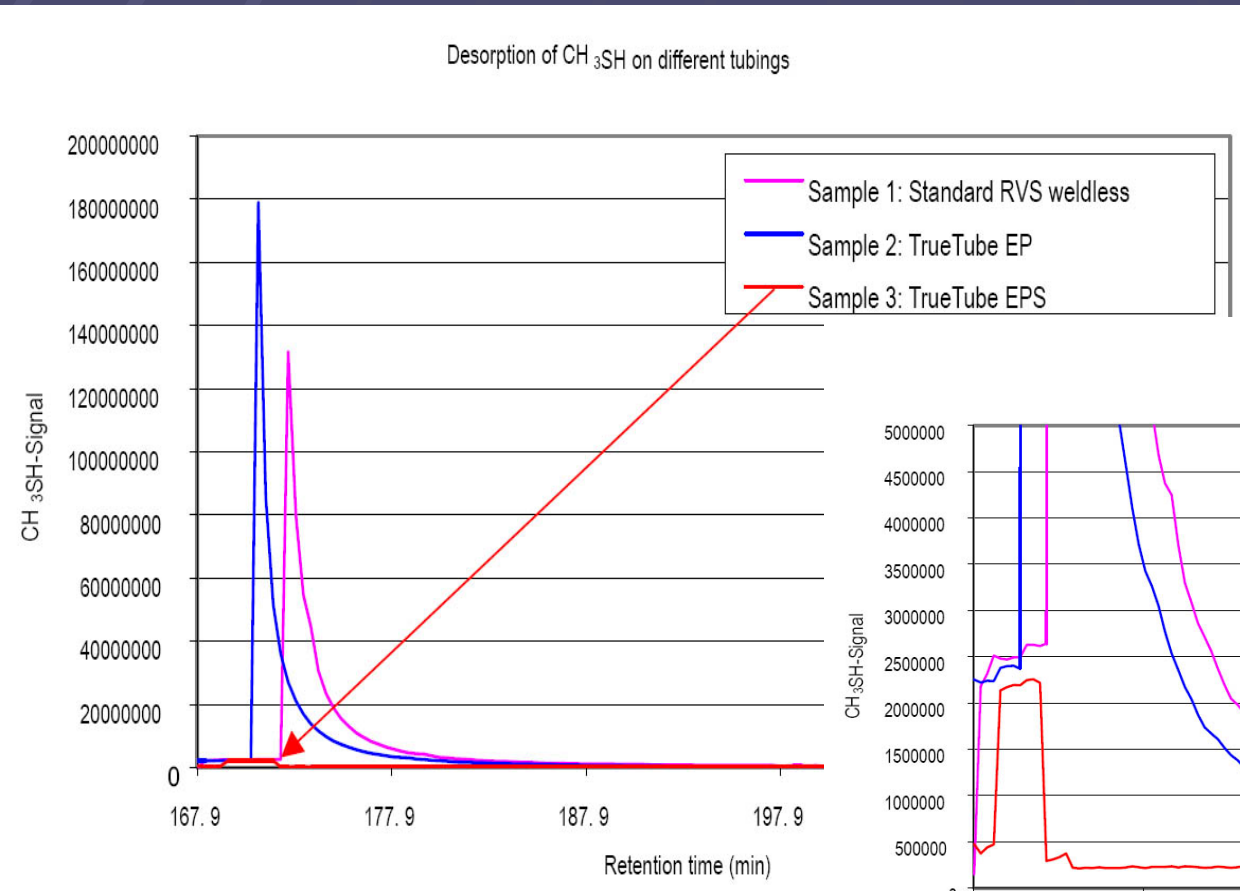
Flow-through data

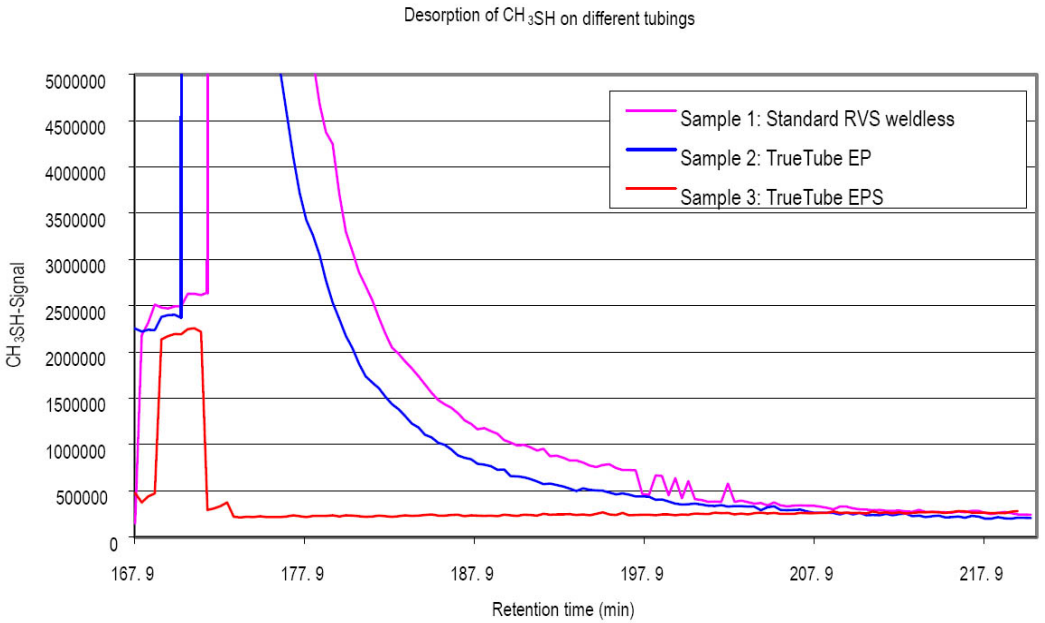
- 100’ 1/8” x .020” tubing
  - Standard weldless 316L
  - Electropolished 316L
  - a-silicon coated EP 316L
- 0.5ppmv methylmercaptan in He
- SCD detection

Effectiveness of coated transfer systems to reduce hold-up: Methyl Mercaptan



Inert surface eliminates “memory” effect common with transfer of active compounds

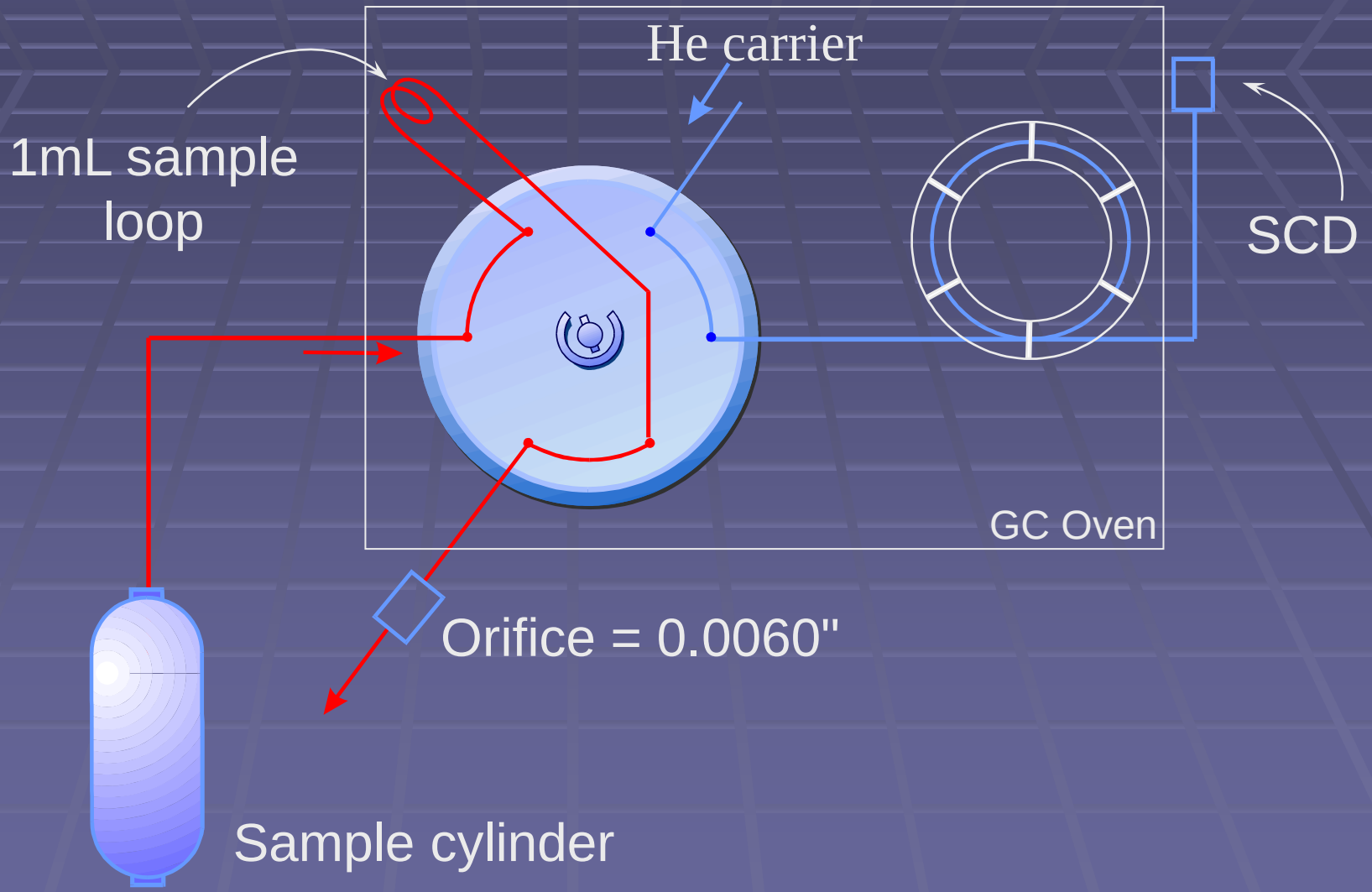




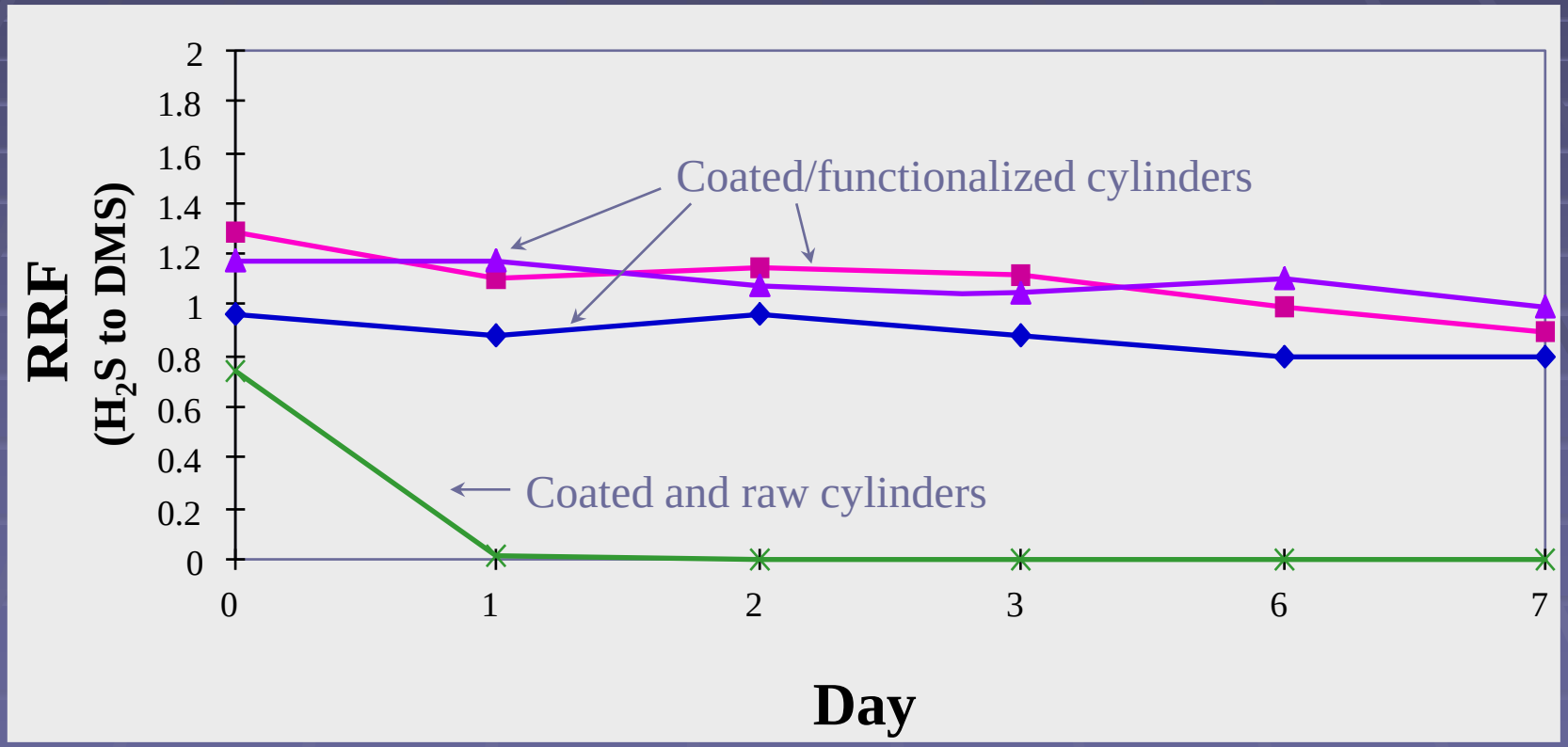
Testing System for Sulfur Gas Storage & Transfer

- Coated/uncoated sample cylinders and sample valves
- Coated sampling system (transfer line, sampling valve, 1ml sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard

Complete Sulfur Analysis System



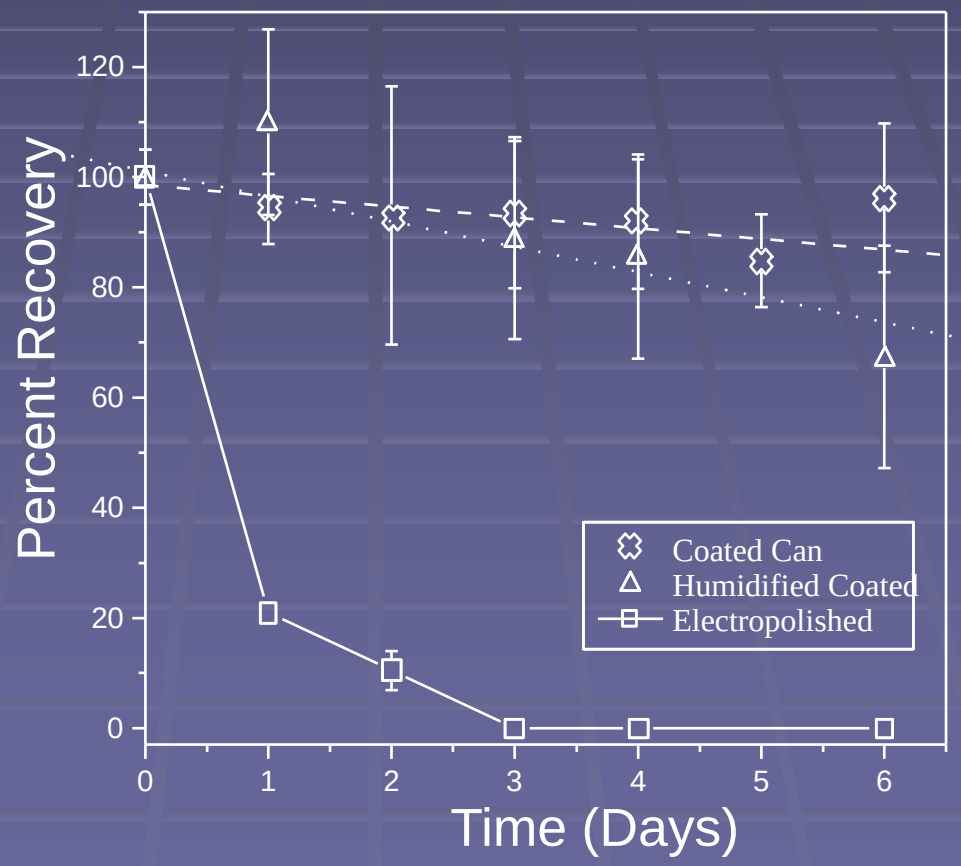
17ppbv H_2S Containment in 500ml Cylinders



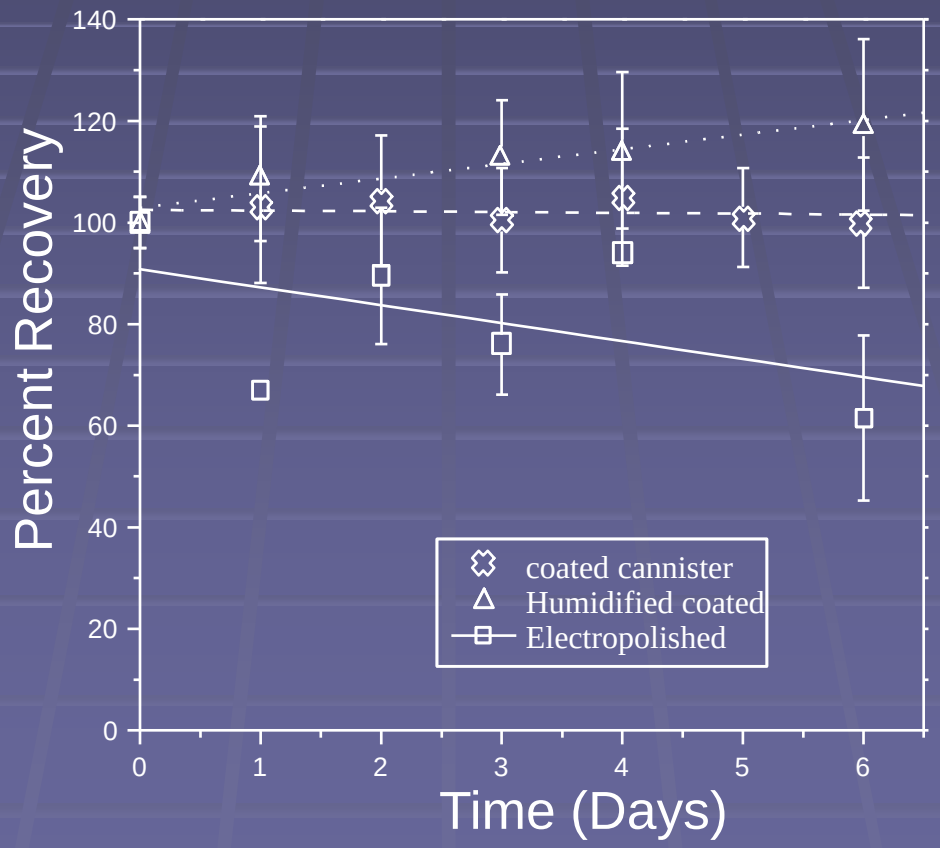
Stability Study Test

- 11ppbv
- 6 days stability study
- Reference std is at 55ppbv
- Dimethyl sulfide as internal standard
- Coated Sampling Cans (n=18)
- Humidified (rh=50%) Coated Sampling Cans (n=5)
- Electropolished Cans (n=2)

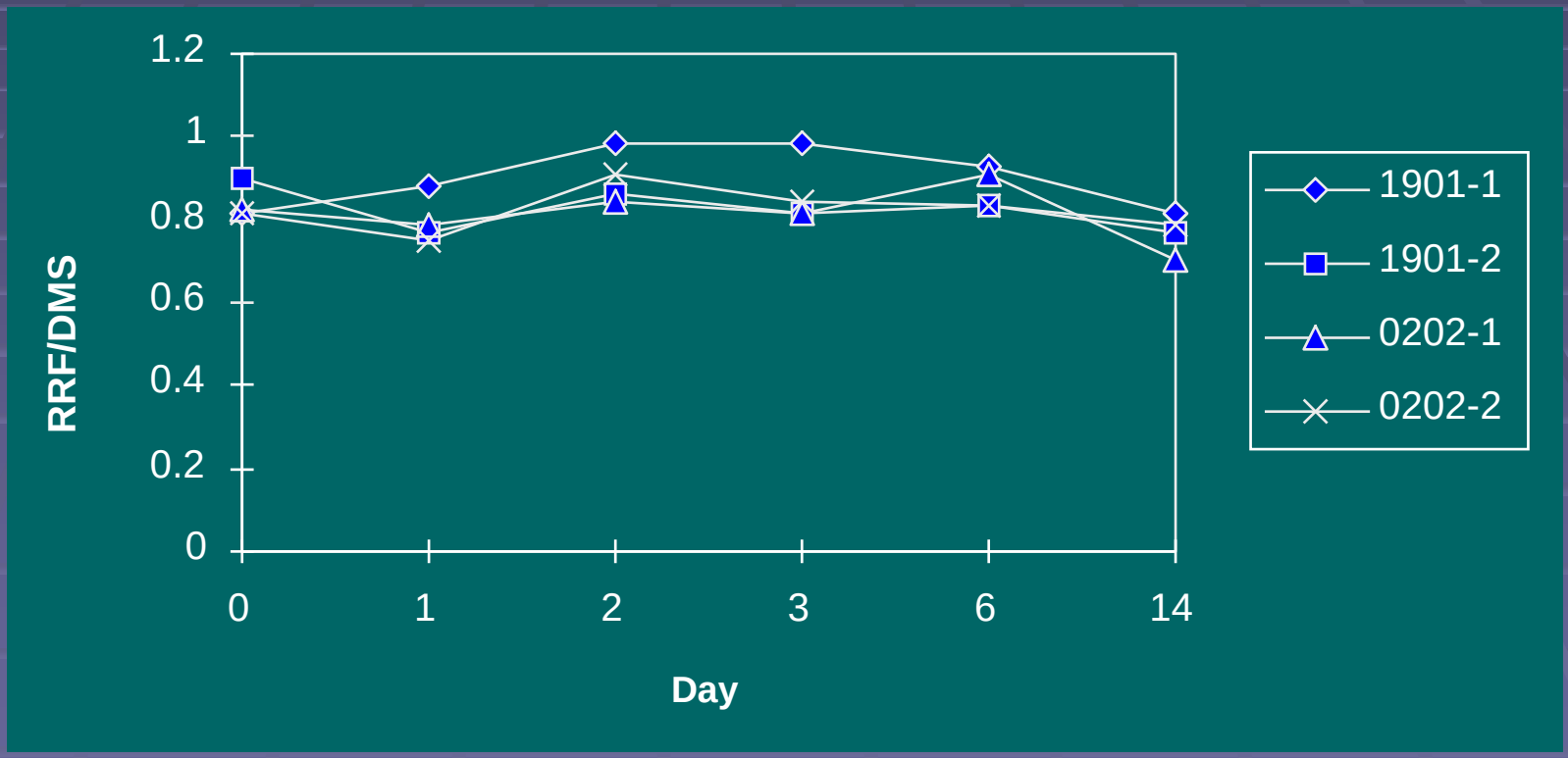
H_2S at 11ppbv in 6l Air Sampling Cans



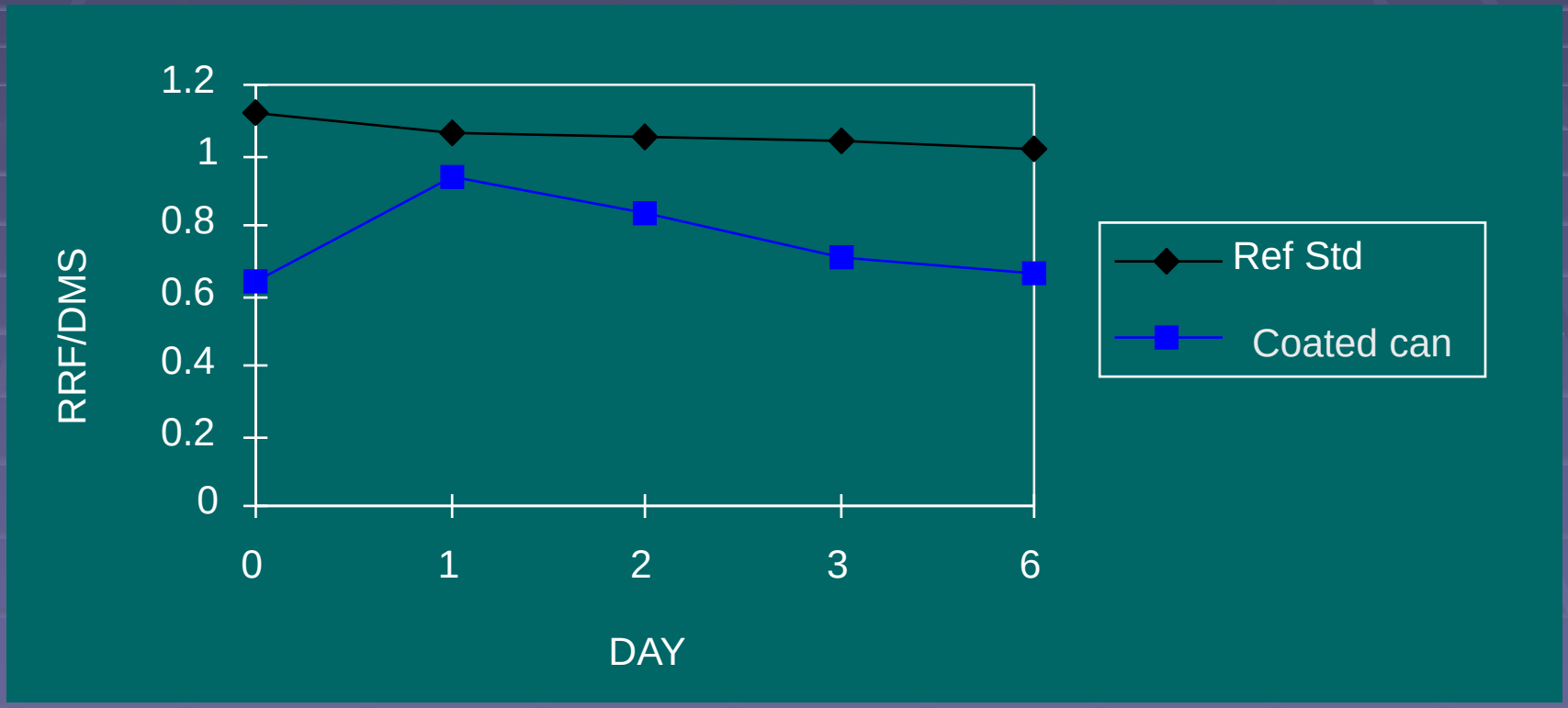
Methyl Mercaptan at 11ppbv in 6l Air Sampling Cans



H_2S at 11ppbv for 14 days



H_2S at 1.5ppbv



Effect of moisture

- Coatings decrease adsorption of water, hydrophobic
- Leads to quicker removal of moisture through sampling lines
- Components less susceptible to corrosion
- Faster cycle times and increased accuracy with less moisture hold-up in tubing
- Several coatings and surfaces available

Moisture Data

- 1ppm moisture, 0.35slpm
- Amount of time to equilibrate a 1ppm moisture sample through 100 feet of dry tubing:
  - Commercial Seamless 316L tubing:
    - 180 minutes (96% equilibrated)
  - Electropolished Seamless 316L tubing:
    - 60 minutes (98% equilibrated)
  - a-silicon coated e-polished seamless 316L tubing
    - 30 minutes (98% equilibrated)

Moisture Data (cont)

- Time to dry 100’ tubing wetted with 1ppm of moisture when connected to a dry purge
  - Commercial Seamless 316L tubing:
    - 175 minutes
  - Electropolished Seamless 316L tubing:
    - 65 minutes
  - a-silicon coated e-polished seamless 316L tubing
    - 35 minutes

Additional Benefits of a-silicon layer

- Corrosion Resistant. a-silicon layer improves corrosion resistance in
  - Acidic environments
  - Marine environments
- Anti-Coking. Coating barrier eliminates catalytic effect of substract.
- Ultra-High-Vacuum (UHV). Reduces outgassing of vacuum components.

Corrosion Resistance

- Stainless steel surfaces susceptible to attack from hydrochloric acid, sulfuric acid and nitric acid
- Is it possible to Enhance Corrosion resistance by deposition of an amorphous silicon layer?
- Silicon is insoluble in hydrochloric acid, sulfuric acid and nitric acid

Benefits

- To extend lifetimes of equipment exposed to corrosive environments and/or process streams
- Protection of high value equipment in corrosive environments

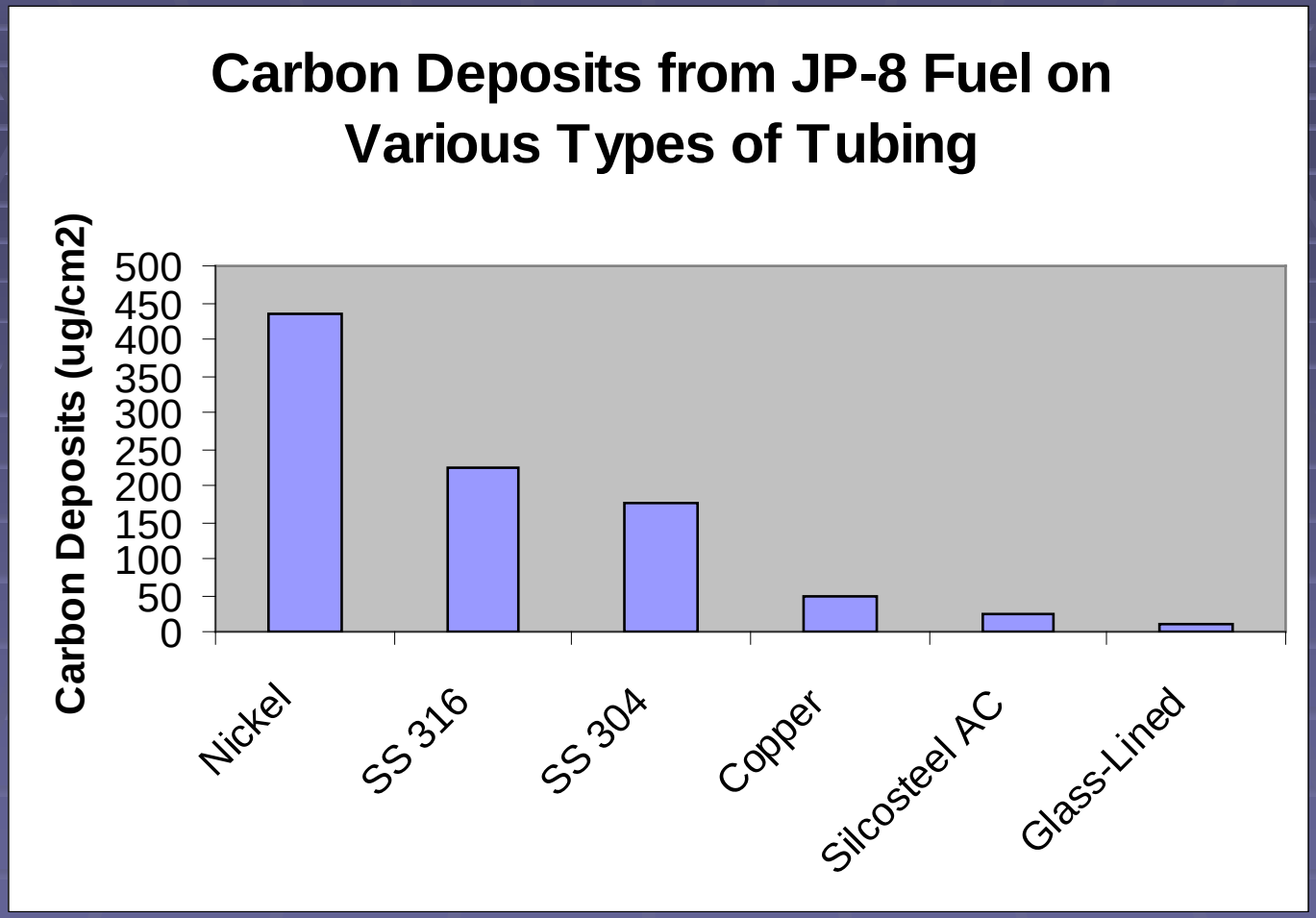
Known Applications

- Enhancing corrosion resistance in Marine environments
- Process streams containing HCl
- Protection of Continuous Emissions Monitoring Equipment (Nitric and Sulfuric acid)
- Use in Automotive Exhaust test equipment (Nitric and Sulfuric acid)

Anti-Coking

- In applications of heated hydrocarbon transfer, carbon deposits can form
- Carbon deposits are catalyzed by nickel, sulfur and carbon in steel lattice
- The functionalized a-silicon coating produces a barrier that eliminates catalytic carbon buildup

Anti-Coking Data



- Semih Eser; PSU Prof. Fuel Sciences
- 8x improvement over raw 316L

Ultra-High Vacuum applications

- a-silicon layer releases moisture from surface more readily in vacuum
- Layer acts as a boundry to reduce outgassing of hydrocarbons and moisture from coated components used in vacuum systems
- Reduced outgassing rate by 14x @10 hrs of pumping
- Consistently outperforms cleaned parts
- Eliminates bakeout
- Faster pump down
- Lower base pressure with smaller pumps


R&D
100

Conclusions/Future

- Continual process improvement and new product development
  - Hardness
  - Improved corrosion resistance
  - Customized surfaces
- Develop Corrosion data comparing coating on different substrates
  - Enhancement of Carbon Steel
  - Protection of high nickel alloys
  - Value of coating in marine environments
  - Application of coating to valves & fasteners

Acknowledgements

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