The Characterization of Novel Carboxysilane Depositions on Stainless Steel Substrates for Inertness, Wear Resistance, and Corrosion Resistance Applications

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Overview

- Use of Coatings
- Selecting Coatings
  - Coating Materials/Properties
  - Durability
  - Corrosion Testing
  - Moisture Resistance
  - Chemical Inertness
- Conclusion

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Using Coatings

- Most analytical pathways are stainless steel
  - Great structurally
  - Good corrosion resistance
  - Poor chemical properties for analytical chemists
- Coatings used to improve material properties.
- Industries are demanding harsher services for silicon coatings (like SilcoNert® 2000 (Sulfinert).
- Carboxysilane coatings (Dursan®) more robust.

Factors Contributing to Poor Sampling Reliability

- Durability/Wear
- Corrosion
- Moisture
- Design
  - Chemical & Material Compatibility/Inertness
  - Instrument Compatibility
  - Installation

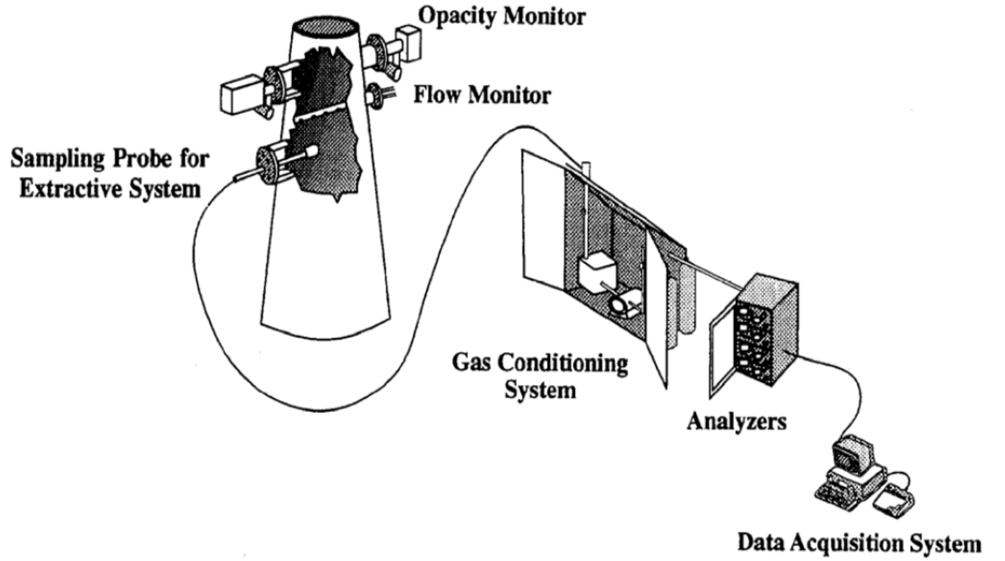

Figure 1: A typical continuous emission monitoring system (CEMS) (U.S. EPA Image)[4]

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Selecting Coatings

- Fluoropolymers
  - Very inert
  - Very corrosion resistant
  - Broad pH applicability
  - Poor adhesion
  - Poor wear resistance
  - Good to 260°C
- Silicon (SilcoNert® 2000)
  - Very inert
  - Great adhesion
  - No carryover
  - Good corrosion resistance
  - Limited pH range
  - Susceptible to steam cleaning
  - Poor wear resistance
  - Good to 450°C

New Coating

- Carboxysilane (Dursan®)
  - Good inertness
  - Great adhesion
  - No carryover
  - Good corrosion resistance
  - Broad pH applicability
  - Steam cleaning, no problem
  - Good wear resistance
  - Tested to 450°C
  - Still accumulating application data

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Coating/Material Properties

Property	Silicon (SilcoNert 2000)	Carboxysilane Dursan	PTFE, PFA
Max Temperature	450ºC	450ºC	260ºC
Min Temperature	-196ºC	-100ºC	-240ºC
Low pH limit	0	0	0
High pH limit	7	14	14
Thickness	0.12um to 0.5um	0.5um to 1.0um	25um
Adhesion	Very Good	Very Good	Poor
Wear resistance	90% of Stainless	2 times 316 Stainless	10% of SS (est.)
Moisture contact	72-90°	104-140°	125°
Inertness vs. SS	Excellent	Good	Excellent

Improving wear resistance & Durability

- Equipment and sample conditions can damage surfaces and increase activity.
    - Valve cycling/purging cause delamination
    - Particulate in sample streams
    - Abrasive cleaning
- Existing coatings
    - Prone to wear
    - Easily damaged
- Result: Adsorption & loss of sample

Wear and Friction Data

- **Pin on Disc: ASTM G133**
- **Base substrate is mirror-finish SS 316**

	Avg. Coeff. Friction	Wear Rate ($x10^{-5}mm^3/Nm$)
Uncoated SS	0.589	13.810
Carboxysilane (Dursan)	0.378	6.129
Silicon (SilcoNert 2000)	0.7	14.00

Load	2.0 N
Duration	20 min
Speed	80 rpm
Radius	3mm
Revolutions	1,554
Ball Diameter	6mm
Ball Material	SS 440

Courtesy of Nanovea Inc.

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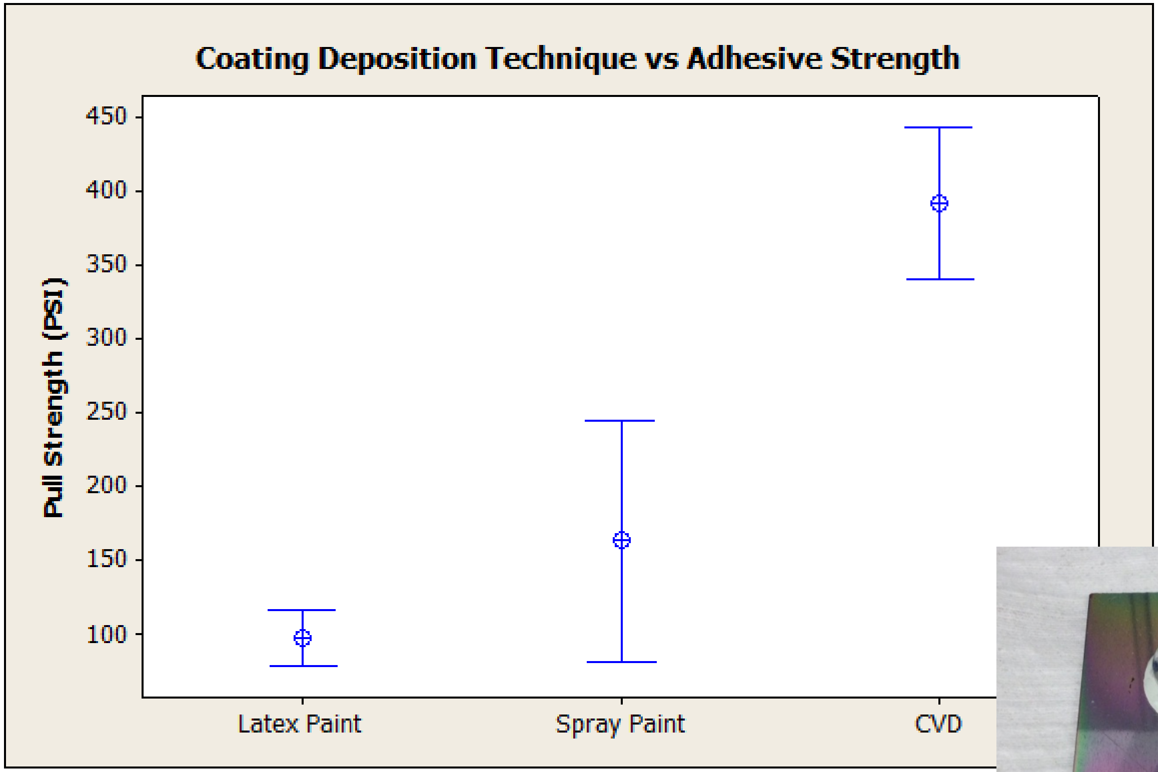
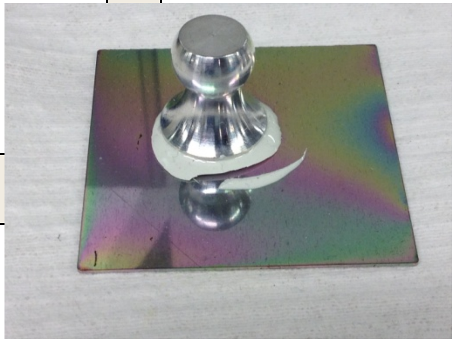
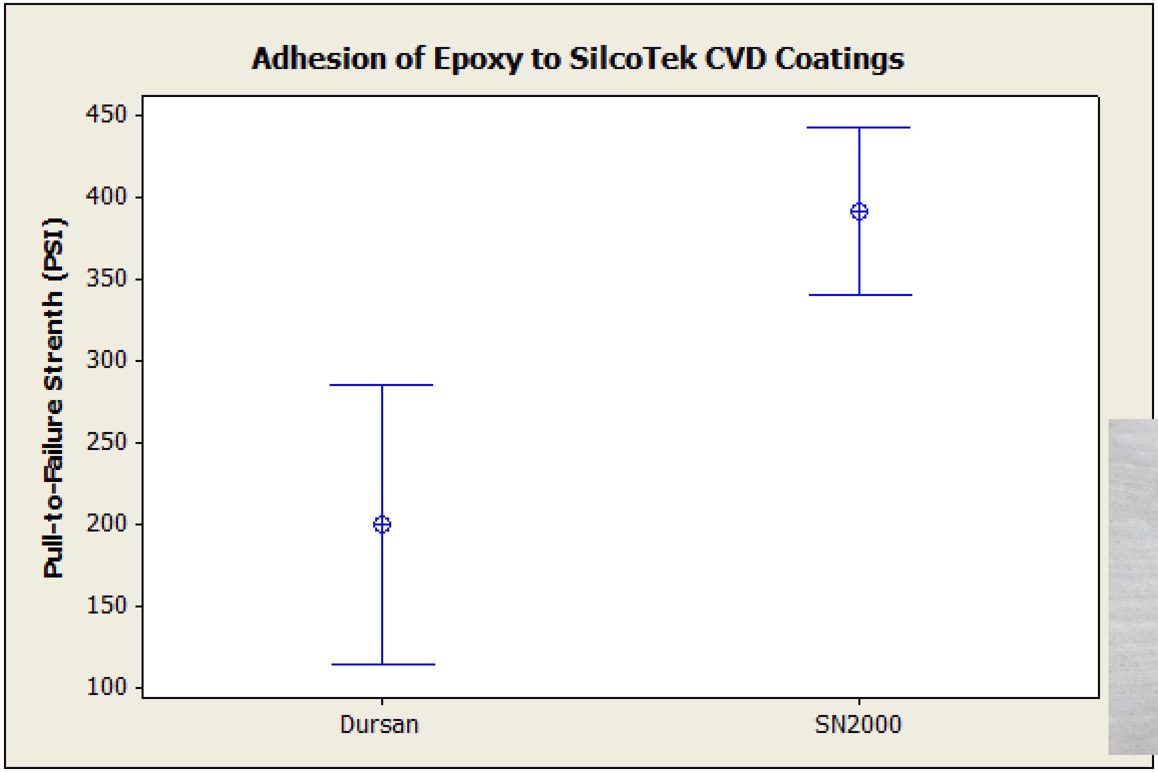
Pull Strength Measurements

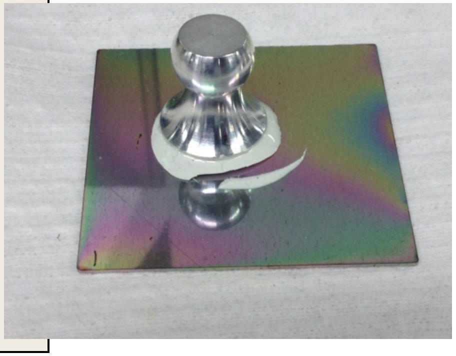




- Paints delaminated from the stainless steel

Pull Strength Measurements





- Dursan more “slippery” difficult to bond adhesive. Adhesive bond failed before coating. Demonstrating reduced friction characteristics.

Challenge of Corrosion

- Samples can contain corrosives that quickly attack stainless
  - Hydrochloric acid (HCl)
  - Sulfuric acid (H_2SO_4)
  - Saltwater
- Physical loss of equipment due to corrosion
  - Maintenance
  - Replacement cycles
- Corrosion increases surface activity and particulates
- Silicon coatings susceptible to caustics

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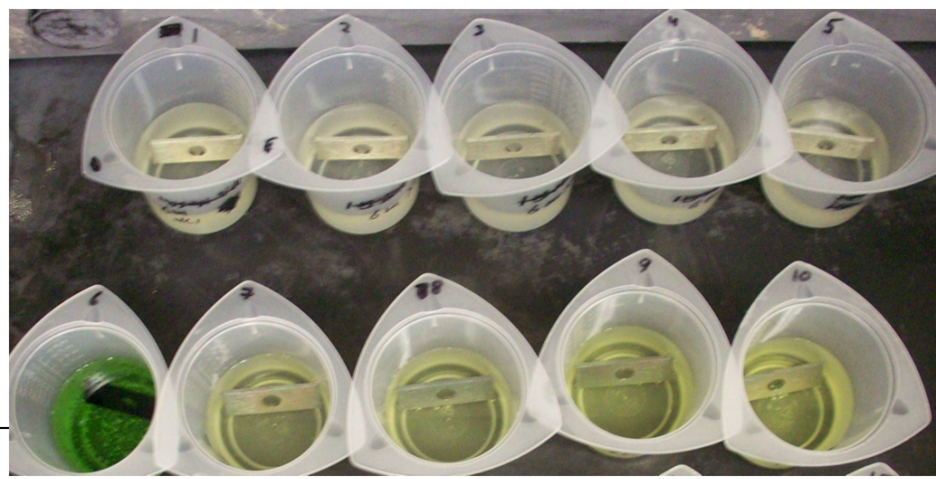
Acid Corrosion Resistance

- ***ASTM G31 Guidelines: 6M HCl; 24hr; 23ºC***

	316L SS	Silicon	Carboxysilane
MPY	**181.98**	**4.32**	**0.44**
Improvement Factor over 316L stainless	**---**	**42**	**411**

Photo after 19hr exposure



Dursan coated

Silcolloy coated

Acid Corrosion Resistance
ASTM G31

	5% HF		70% Nitric		85% Phosphoric		25% Sulfuric	
	MPY rate	factor	MPY rate	factor	MPY rate	factor	MPY rate	factor
316 SS	120.00	-	0.78	-	0.62	-	54.64	-
Carboxysilane	80.38	1.49	0.10	7.50	0.08	8.00	5.36	10.19
Silicon	44.26	2.71	0.36	2.14	0.28	2.18	23.62	2.31

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Exposure to Caustic Base

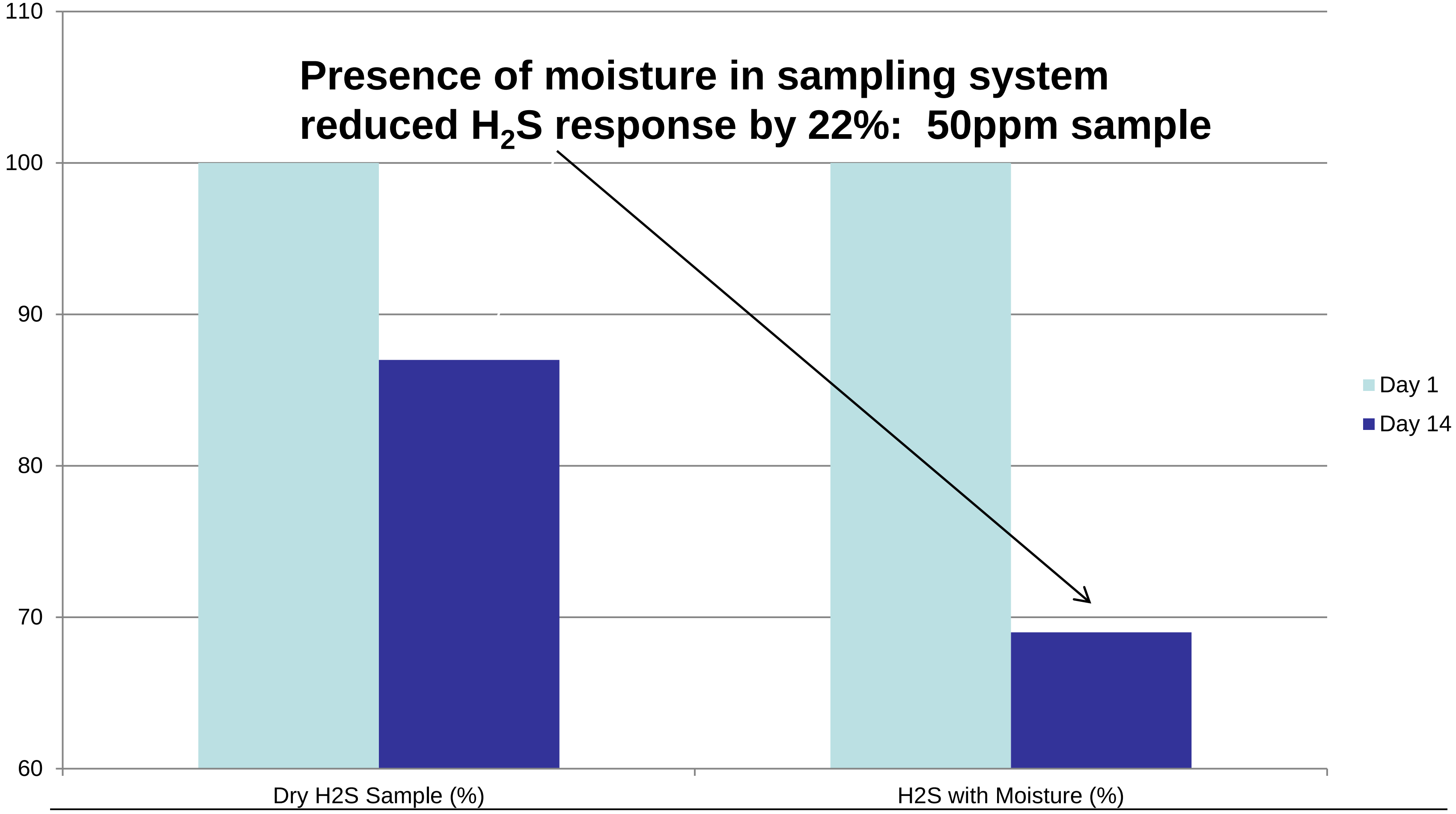
- ***1M KOH; 24hr; 22ºC***

ASTM G31	**316L SS**	**Silicon**	**Carboxysilane**
MPY	0	3.40	0.01
Improvement Factor Over Silicon	Infinite	Dissolution	261

Challenges of Moisture

- Benefits of coating that help release water faster
  - Components less susceptible to corrosion
  - Faster cycle times
  - Increased accuracy
  - Eliminate moisture/sample interaction

Impact of Moisture



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Measuring Hydrophobicity

Kruss K100 Tensiometer Testing on 304 SS ¼" OD tubing

DI Water	304 SS	SilcoNert 2000	Dursan	PTFE
Advancing	36.0	87.3	105.5	125.4
Receding	5.3	51.5	85.3	84

DI Water Contact Angle Illustrations (advancing) on flat surfaces

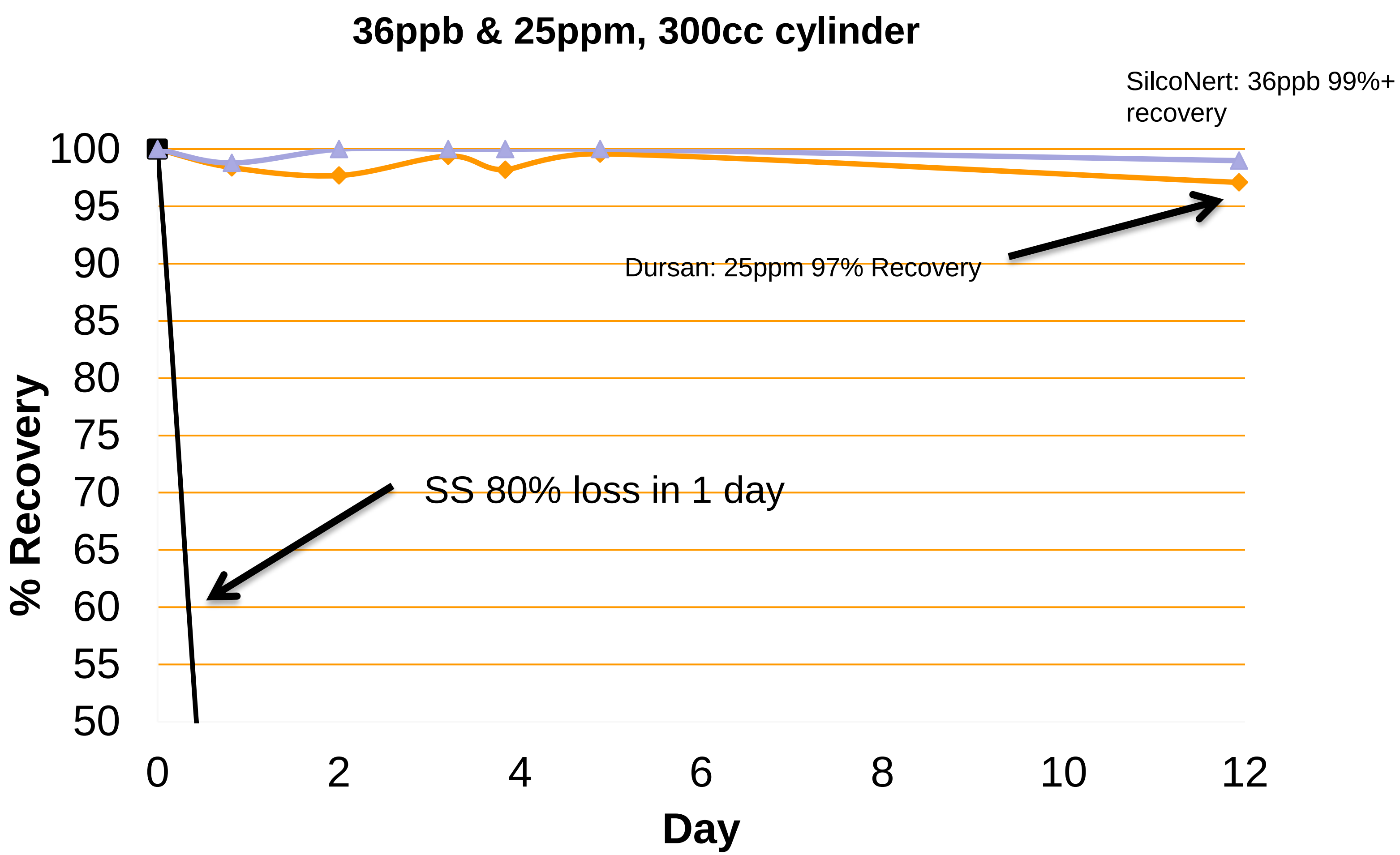
304 SS SilcoNert 2000 Dursan

Chemical Inertness

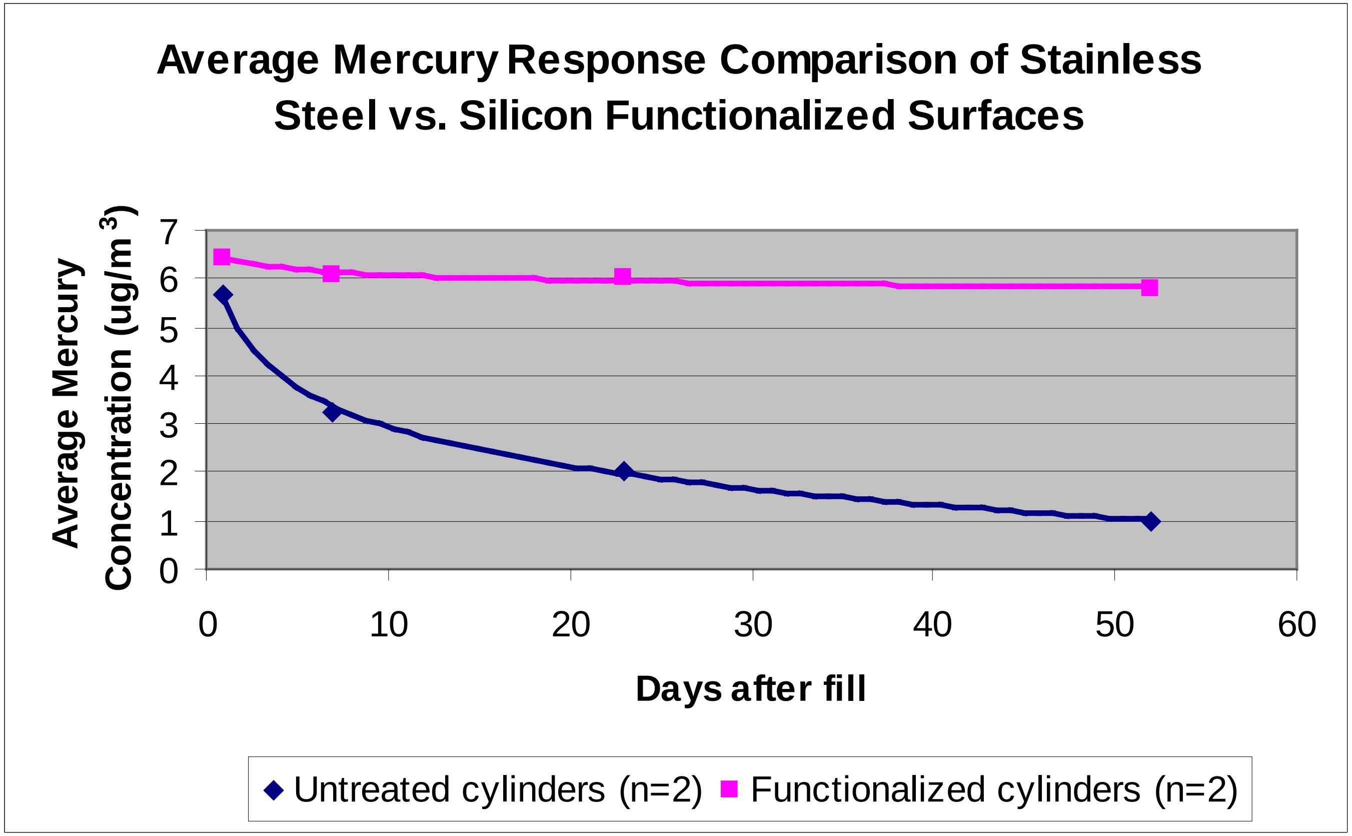
- Stainless Steel:
  - Adsorbs sulfur compounds
  - Causes loss of mercury
  - Demonstrates poor transportability (tailing) of polar organics such as alcohols
  - Adsorbs ammonia

- Need coating that is chemically inert for analytical systems

Total Sulfur Recovery



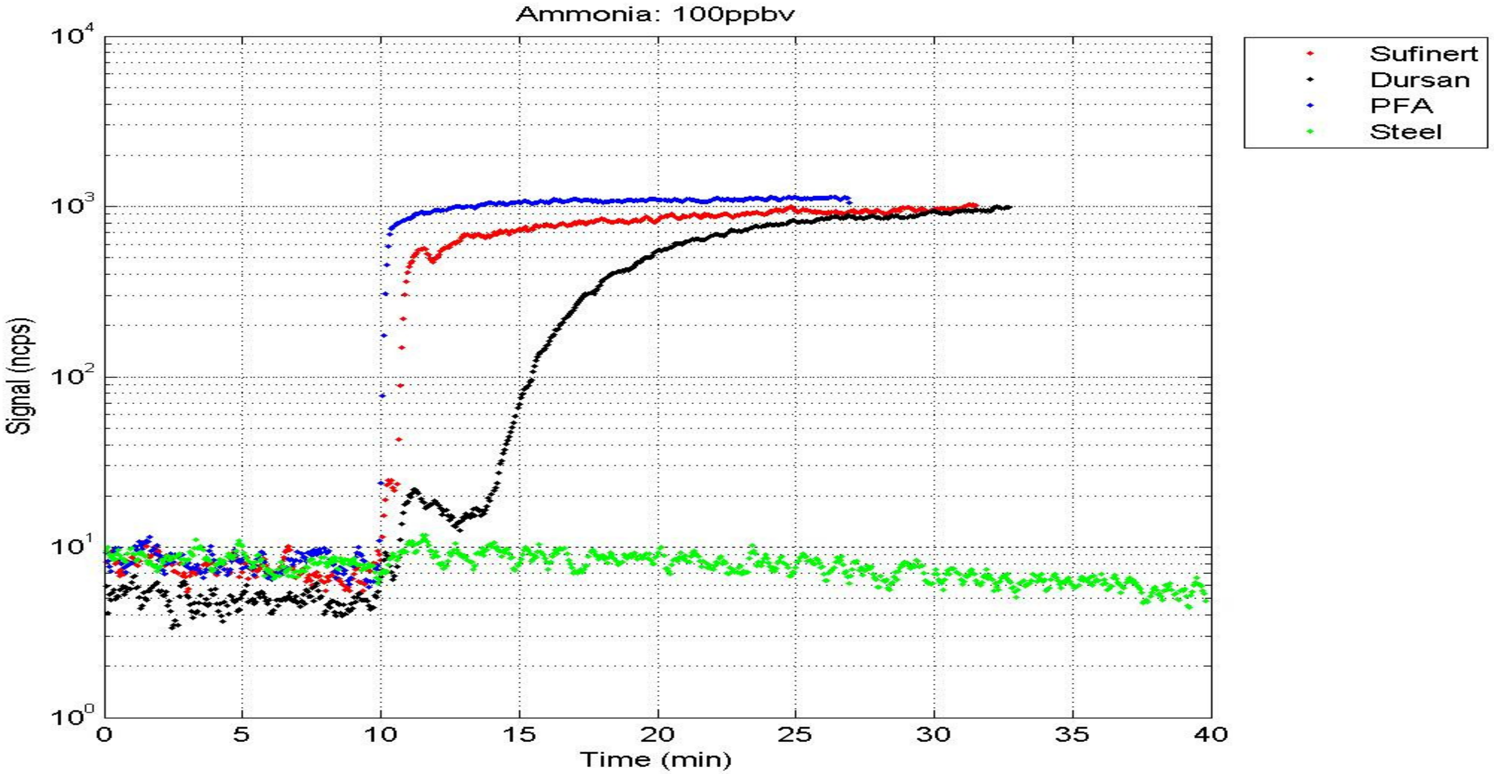
Mercury 50 Day Stability



Courtesy of Spectra Gases Inc.

Ammonia Adsorption

100PPV, 500sccm, 1.8m tubing, min



- *Measured PTR-MS signals of ammonia (m17). At t=10min the gas stream was switched in a way*
- *that it passed additionally the different 1.8m long lines. The PFA line seems to be best for Ammonia, while*
- *the steel line completely adsorbs the 100ppbv of Ammonia in the sample gas for hours. All lines were 1.8 m,*
- *not heated (30°C), sample gas flow was 500 sccm (std. ml/min) of 100 ppb of ammonia in N2.* **Courtesy of IONIMED Analytik**

Selecting Coatings

Factor	Fluoropolymers	Weight	Silicon (SilcoNert)	Weight	Carboxysilane (Dursan)	Weight
Durability	Poor wear resistance		Fair wear resistance		Good wear resistance	
Corrosion	Excellent		Good		Good	
Moisture	Excellent		Good		Excellent	
Inertness	Excellent		Excellent/ no carryover		Good	
Chemical / Material Compatibility	Poor adhesion/ Broad pH range		Excellent adhesion		Excellent	
Instrument Compatibility	Good		Good		Excellent	
Installation	260c max		450c max		450c max	

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Conclusion

- Analytical and Process industries demanding increased performance from coating
- Coating selection dictated by application
  - Corrosion resistance
  - Moisture resistance
  - Inertness
  - Wear
- Broad spectrum environments and applications may involve a tradeoff in performance.
  - In field applications, carboxysilane coatings (Dursan) may be the best overall performer.