Protective Chemical Vapor Deposition Coatings for Stainless Steel Surfaces Used in Produced Water Environments

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Introduction

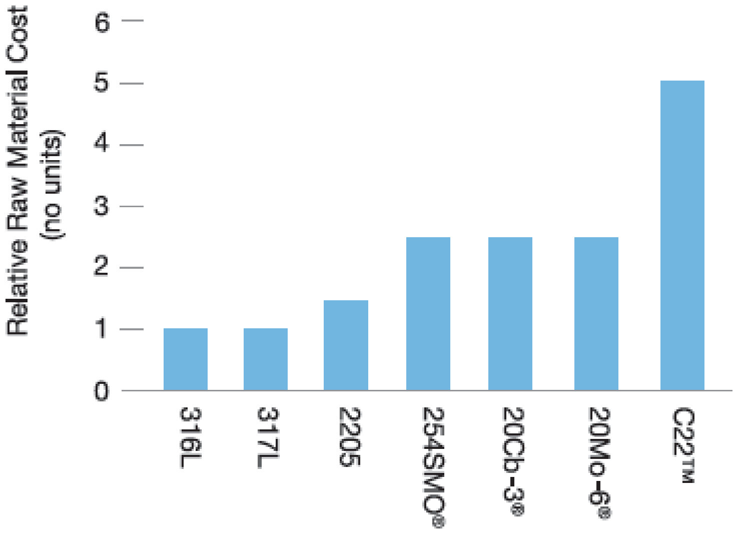
Managing produced water is a major challenge for the oil and gas industry. As wells age, water production increases and is expected to grow 50% in offshore applications alone over the next 10 years.[1] Along with increased volume, oil and gas producers must contend with potentially significant levels of corrosives such as salt or other chlorides, salinity, dissolved CO_2, and H_2S often found in produced water. The total cost of corrosion in the oil and gas industry, including costs associated with produced water, is estimated to be $1.4 billion annually.[2] Producers have limited material options in contending with severe produced water corrosion applications. Until recently, the only corrosion resistant options available were stainless steel, coatings or high performance alloys. (See Figure 1 for a complete list of materials commonly used in oil and gas exploration and production.[3])

Figure 1: Selection guidelines for corrosion resistant alloys in the oil and gas industry

Material	Comment
13 Cr martensitic stainless steel	Corrosion rates of $\leq$ 2mpy, no SSC or SCC in CO_2/NaCl, no O_2 or H_2S
Alloy 316	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/NaCl, no O_2 or H_2S
22 Cr	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/NaCl, no O_2 or H_2S
Alloy 28	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/H_2S, no elemental sulfur
Alloy 825	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/H_2S, no elemental sulfur
Alloy 2550	
Alloy 625	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/H_2S, no elemental sulfur
C276	Corrosion rates of < 2mpy, no SSC or SCC in CO_2/H_2S, no elemental sulfur

Stainless steel is a cost effective option in produced water applications, but can quickly corrode in some produced water environments. High performance alloys can provide exceptional protection, but can be prohibitively expensive, may require significant purchase lead times and may be difficult to machine. Substituting a high performance alloy such as Hastelloy C22 in a produced water system can increase the cost of the system by as much as five-fold[4] (see Figure 2).

Figure 2: High performance alloys substantially increase the cost of a produced water system

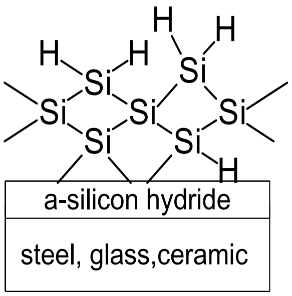


The development of silicon-based materials to prevent surface corrosion and water/surface interaction provides a low cost alternative in produced water environments. This paper will compare the corrosion rates of austenitic stainless steels, Hastelloy C22, amorphous silicon coated stainless steel and carbosilane coated stainless steel in various chloride corrosion environments. Additionally, comparative hydrophobicity data and life cycle costs will be discussed. The comparative data are generated using various ASTM methods and methodology developed specifically for coating evaluation.

Experimental Preparation

Test coupons of various finishes and configurations (primarily 2B mill finish (0.4um) and #8 (mirror) finish) were compared. Coupons were coated with amorphous silicon (a-Si) or carbosilane via a chemical vapor deposition (CVD) process. The CVD process thermally decomposed silane-based or carbosilane based materials to form a 3-dimensional conformal deposition on all substrate features. See Figure 3 for a diagram of the a-Si coating chemistry.

Figure 3: Amorphous silicon surface

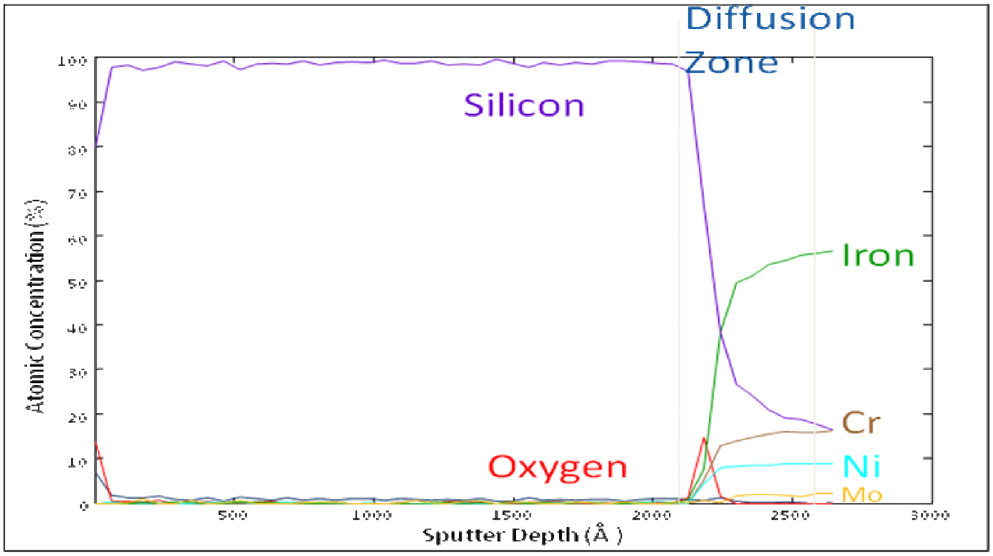


The CVD process allows for deposition onto stainless steels, high performance alloys, glass, ceramics and carbon. Advantages of the CVD process include:

- Scalable process, permits penetration into 2000ft tube coils or complex geometries 4 feet OD x 6 feet.
- Allows for various starting materials (i.e., silanes and carbosilanes)
- Additional functionalization chemistries possible
    - Change surface chemistry to make hydrophobic or oleophobic surface
- Low cost, high volume capability

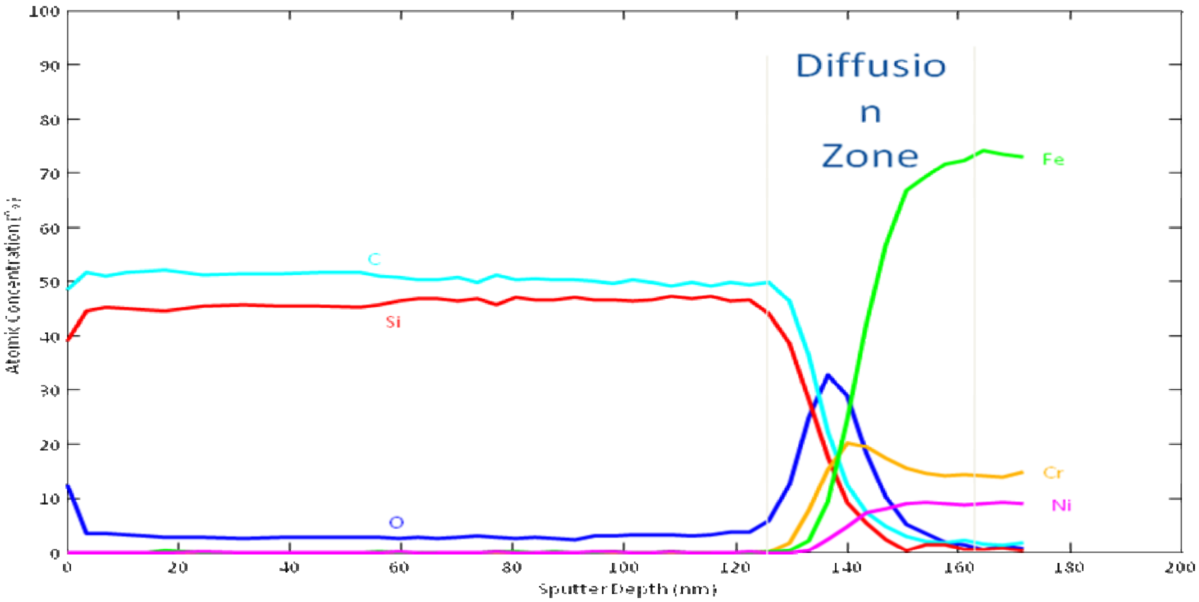
The CVD process was validated by using Auger Electron Spectrometry (AES) depth profiling to confirm adequate coating deposition thickness and verify the coating bond to the surface. Profiling of the amorphous silicon (a-Si) coated stainless steel coupon shows a silicon coating thickness of 2000A (0.2um), the a-Si coating process is capable of thicknesses ranging from 0.03um up to 3um. Additionally the AES profile clearly shows a 500A silicon-iron overlap zone. This indicates the silicon material is diffused into the stainless steel surface; making a durable bond to the stainless steel coupon. See Figure 4A.

Figure 4A: AES profile of amorphous silicon coated stainless steel



AES depth profile of the carbosilane coating showed a thickness of 120nm (1200A); with a 40nm iron/silicon carbon diffusion zone. The AES profile also validates the silicon/carbon precursors in the coating matrix. See figure 4B.

Figure 4B: AES depth profile of carbosilane coating



Carbosilane and amorphous silicon materials offer significant material property enhancements in corrosion resistance and inertness. These properties make amorphous silicon coatings advantageous for use in sample transfer, process analysis, or oil and gas exploration and refining. Figure 5 compares the material and performance characteristics of carbosilane and amorphous silicon.

Figure 5: Comparison of CVD Coating

Material	Amorphous Silicon	Carbosilane
Color	Iridescent multi-color	Flat multi-color
Application process	CVD @400c	CVD @ 450c
Coating thickness	Up to 3000nm	currently 250nm
Acid resistance	Good	Excellent
Base resistance	Poor	Excellent
Hardness	6.5 Moh	unknown
Abrasion resistance	Poor	Poor / Good (enhanced)
Maximum temperature	1000°C	currently 450°C
Minimum temperature	-210°C	unknown
Coating conformity	all surfaces by batch	all surfaces by batch
Hydrophobicity/contact angle	80°	105° (up to 144°)
Flexibility	4in bend radius	4in bend radius

Coated samples were then subjected to a series of comparative acid and hydrophobicity tests in order to characterize the corrosion capability of the various substrates.

Comparative Testing

Acid resistance

ASTM G31

316 stainless steel, amorphous silicon (a-Si) coated stainless steel and carbosilane coated stainless steel coupons were immersed in 22°C, 6M hydrochloric acid for 24 hours per ASTM G31 (Figure 6). The 316 stainless steel coupon shows significant loss of 91.9 mills per year. The a-Si coupon showed 18.43mpy loss while the carbosilane coated 316 SS coupon showed 3.29mpy loss, a 27.9X improvement over the 316 stainless steel coupon.[5]

Figure 6: ASTM G31 screening of a-Si and Carbosilane coupons (6M HCl, 24 hrs, 316 SS coupons, 22°C)

Surface	mpy	Enhancement
316 SS control	91.90	----
a-Si corr. res.	18.43	5.0 X
carbosilane	3.29	27.9 X

Additional comparative screening subjected various tubing samples to hydrochloric acid (HCl) immersion testing. The tube samples were immersed for a period of 72 hours in a 22C 6M HCl solution. 3 each of 316 stainless steel tube, a-Si coated 316 stainless steel tube, electropolished 316 stainless steel tube, a-Si coated electropolished 316 stainless steel tube, functionalized a-Si electropolished 316 stainless steel tube and Hastelloy C22 tube samples were compared. Average weight loss, mils per year corrosion rates and standard deviation were calculated and compared. The a-Si coated electropolished 316 stainless steel tube showed the greatest enhancement at 97.2 X. The functionalized a-Si coated electropolished tube also demonstrated significant corrosion resistance with a 54.6X improvement relative to 316 stainless steel. The Hastelloy C22 sample showed a 23.2X improvement over 316 stainless steel for the 72 hour immersion period. See figure 7.

Figure 7: 72 hour immersion of amorphous silicon, 316 stainless steel and Hastelloy C22 coated coupons in 6M HCl, 22°C

Tubing Type	Average Weight loss (g)	Mpy corrosion / Standard dev.	Enhancement
316 welded	0.3085	29.94 / 0.98	
a-Si coated 316 welded	0.0492	4.76 / 4.45	1.9
Electropolished 316 seamless	0.1669	15.57 / 1.09	1
a-Si EP 316	0.0019	0.17 / 0.06	97.2
Functionalized a-Si EP 316	0.0031	0.29 / 0.03	54.6
HP Alloy	0.0075	0.67 / 0.05	23.2

ASTM G48 method B

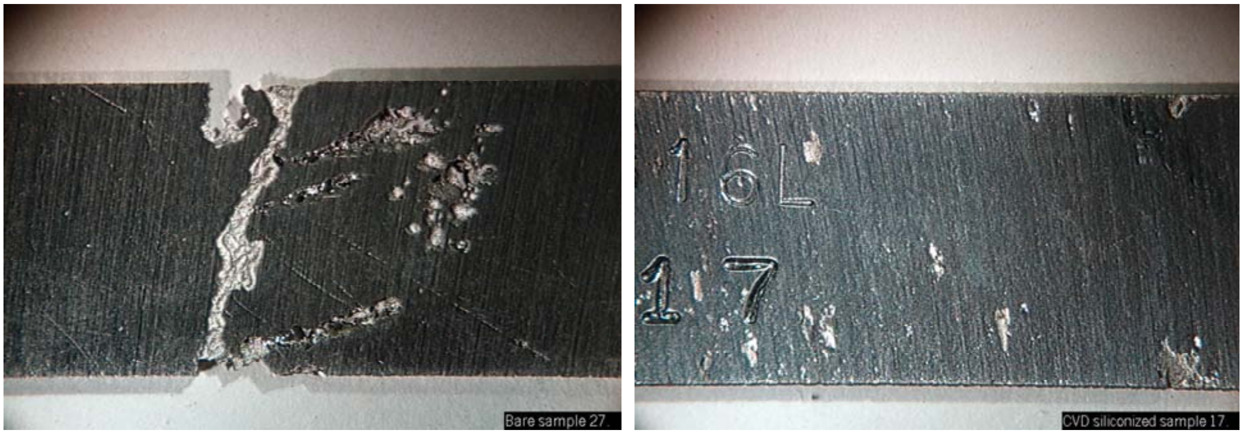
316 stainless steel and amorphous silicon (a-Si) coated stainless steel coupons were immersed in a 20°C 6% ferric chloride solution for 72 hours. Per ASTM G48 method B, the coupons were wrapped with a gasket to promote corrosive attack. The amorphous silicon coated 316ss coupon showed a 10x reduction in weight loss. (Figure 8).

Figure 8: ASTM G48 Method B comparison of amorphous silicon and stainless steel coupons. 6% ferric chloride solution, 20°C, 72 hours[6]

Sample	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Weight Loss (g/m^2)
a-Si Sample 17	10.4105	10.3710	0.0395	19
a-Si Sample 28	10.1256	10.0743	0.0513	25
a-Si Sample 47	10.1263	10.0742	0.0521	25
316L SS Sample 27	10.0444	9.5655	0.4789	231
316L SS Sample 34	10.1265	9.6923	0.4342	209
316L SS Sample 37	10.1007	9.6276	0.4731	228

Figure 9 shows the untreated 316ss coupon exhibited significant pitting and severe corrosion at the gasket area. The a-Si coated 316ss coupon shows some pitting with no apparent corrosion at the gasket interface.

Figure 9: Comparison of 316L coupon (left) and a-Si coupon (right) after ASTM G48 Method B testing. The a-Si coupon shows significantly less corrosion and pitting compared to the 316L coupon.



ASTM G61

316L and 304L stainless steel coupons were compare to an a-SI coated 316L coupon in acid, neutral, and basic aqueous solutions with varying Cl- ion concentrations (ranging from 100, 3000, and 5000ppm). The electrochemical potential was measured per ASTM G61 using an EG&G VersaStat System. Solution temperature was held at 23°C. Figure 10 compares corrosion potential (Ec), current density (Ic), pitting potential (Eb) and corrosion (CR) rates of the uncoated stainless steel coupons and the a-Si coated stainless steel coupon. The data show a 50X reduction in corrosion rate (CR) for the a-Si coated coupon in a neutral, 3000ppm Cl- solution. In an acidic 1N H2SO4, 3000 ppm Cl- solution, the a-Si coated coupon demonstrated a 10x improvement in corrosion resistance. In a basic 1N NaOH 3000 ppm Cl- solution, the a-Si coated coupon performed marginally better with an overall corrosion resistance improvement of 4x. The data demonstrates the limitation of a-Si coatings in basic solutions while showing good performance in acidic or neutral chloride environments.

Figure 10: Comparison of corrosion potential of 316L, 304L and amorphous silicon coated coupons in various chloride solutions.

Neutral solution, 3000 ppm Cl- 50x improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-418	0.096	370	0.04
a-Si 316 L	-533	0.002	1460	0.0009
304 L	-435	0.145	361	0.06

Acidic solution, 1N, H2SO4, 3000 ppm Cl- 10x improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-662	1.920	370	0.83
a-Si 316 L	-843	0.123	927	0.05
304 L	-639	2.650	587	1.14

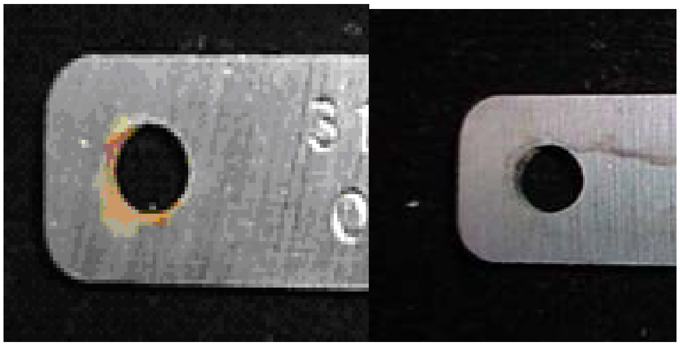
Basic solution, 1N, NaOH, 3000 ppm Cl- 4x improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-419	0.193	265	0.08
a-Si 316 L	-816	0.036	618	0.02
304 L	-388	1.120	668	0.48

ASTM B117

316L stainless steel and a-Si coated 316L stainless steel coupons were subjected to ASTM B117 salt spray testing. The coupons were installed in a salt spray (fog) apparatus per ASTM B117 specifications. 100°F 3.5% by weight sodium chloride salt solution fogged the coupons for a duration of 4000 hours. The 316L stainless steel coupons showed some light surface rust, but no signs of pitting corrosion. The a-Si coated 316L coupon showed no signs of bleeding, rusting, or pitting corrosion. See Figure 11 for a visual comparison of the coated and uncoated coupons.

Figure 11: Comparison of 316L SS coupon (left) and a-Si coated coupon (right) after 4000 hour B117 salt spray testing. The 316L coupon shows corrosive attack while the a-Si coated coupon shows no signs of corrosion.

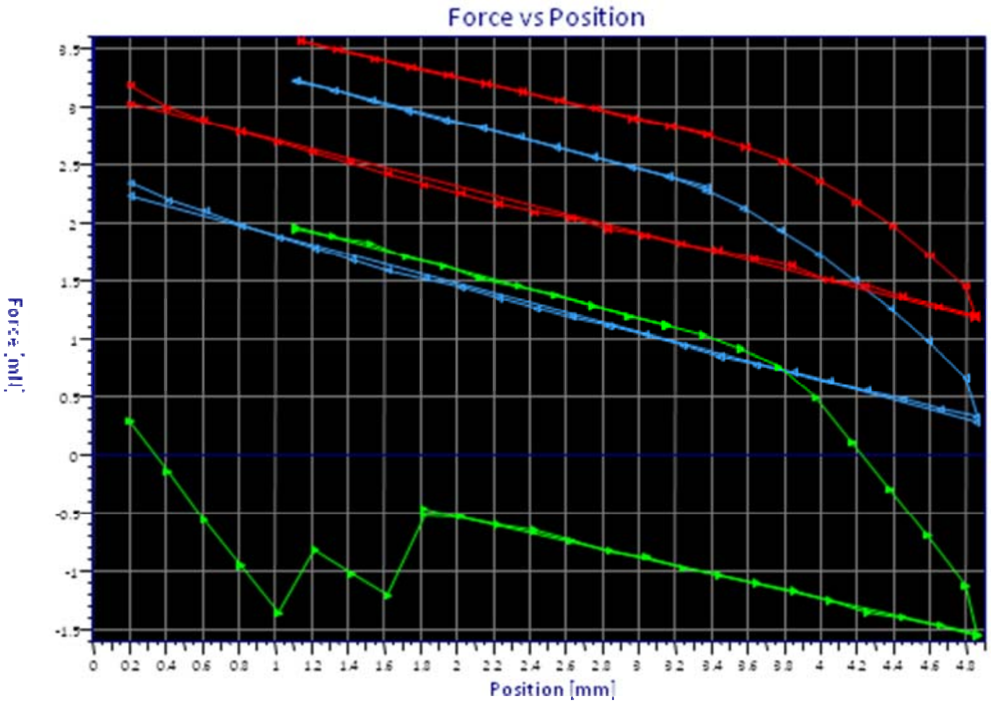


Hydrophobicity comparison

A hydrophobic surface can be beneficial in produced water applications. High contact angle, hydrophobic, surfaces are easier to clean, tend to resist fouling, and in extreme examples, have less than 1% of water in contact with the surface. This limits corrosion, extends the life of the part and improves system and instrument performance.

Tensiometric measurements were used to derive Contact angle/surface energy measurements for 316 stainless steel, a-Si coated stainless steel, functionalized a-Si stainless steel, carbosilane coated stainless steel, and functionalized carbosilane coated stainless steel coupons. A Kruss model K100 tensiometer recorded advancing and receding contact angle measurements as exemplified in Figure 12.

Figure 12: Example of Kruss model K100 tensiometer measurement. The instrument utilizes water surface tension to compare surface hydrophobicity of materials. This example compares hydrophobicity of 316 stainless steel to amorphous silicon and functionalized amorphous silicon. The functionalized amorphous silicon demonstrates significantly greater hydrophobicity compared to 316 stainless steel.



Bare 316ss: 37.2° advancing; 0° receding
a-Silicon coated: 53.6° advancing; 19.6° receding
Functionalized a-Si: 87.3° advancing; 51.5° receding

The advancing and receding contact angles of various surfaces are compared in Figure 13. The functionalized carbosilane coatings demonstrate a significant improvement in surface hydrophobicity with a narrowing hysteresis gap to approach an extreme hydrophobic state (Cassie-Baxter state). Greater hydrophobicity contributes to reduce corrosion, improved surface cleaning and less contamination of instrumentation.

Figure 13: Comparison of surface hydrophobicity of various silicon coated 316 coupons vs. uncoated 316 stainless steel. The functionalized carbosilane coating demonstrated a 3x improvement in hydrophobicity compared to 316 stainless steel. [5]

Surface	Advancing / Receding
a-Silicon	53.6 / 19.6
Funct. a-Silicon (HC)	87.3 / 51.5
carbosilane	100.5 / 63.5
Funct. Carbosilane (HC)	104.7 / 90.1
Funct. Carbosilane (F)	110.5 / 94.8
316 SS	37.2/0

Figure 14 visually compares the extreme difference in hydrophobicity of stainless steel vs. the functionalized carbosilane coupons. The carbosilane coated coupon demonstrates a significant reduction in wetted area while reducing corrosion potential, improving drying capability and reducing potential contamination of instrumentation due to corrosion or surface interaction.

Figure 14: Visual comparison of hydrophobic carbosilane coupon (left, center) vs. stainless steel coupon (right). Greater surface exposure of water leads to increased surface contamination and corrosion.

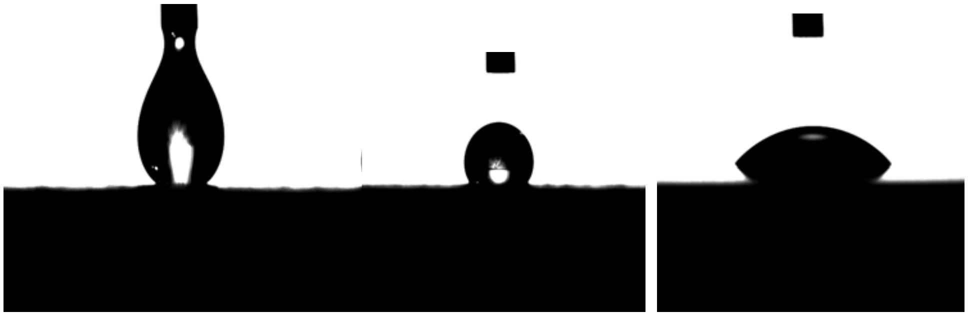
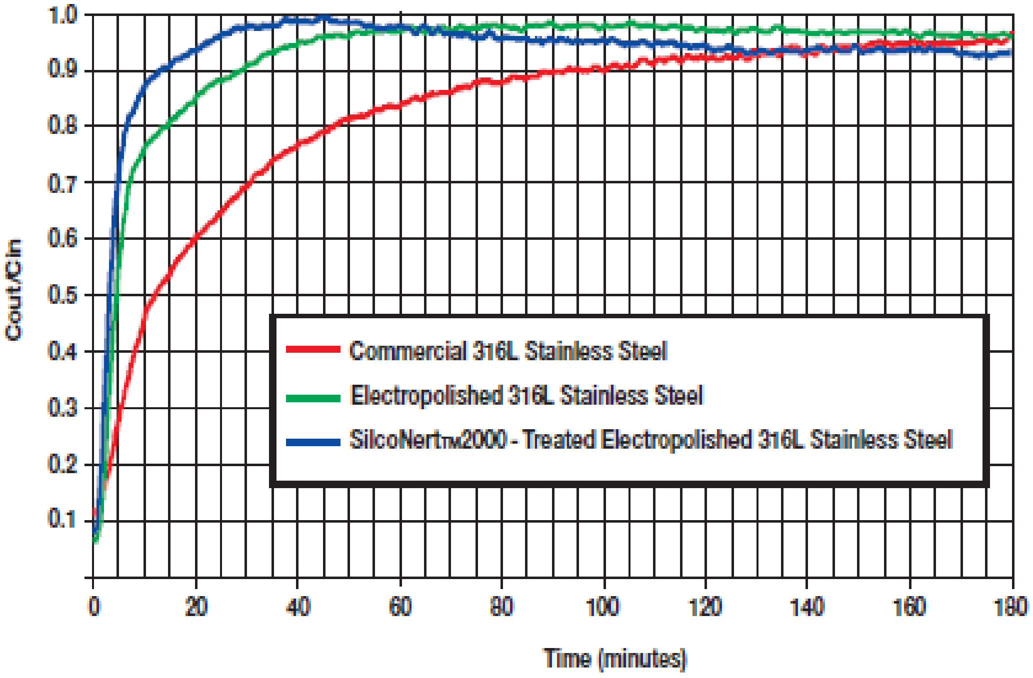


Figure 15 demonstrates a more practical application of hydrophobic surfaces. Hydrophobic surfaces minimize the adsorption of water, thus minimizing corrosion by limiting water/surface contact. Adsorption rates of water in 100 foot x 1/4in OD hydrophobic a-Si coated and uncoated stainless steel tubes are compared. The a-Si coated and uncoated tubes are exposed to 0.35slpm of saturated water/nitrogen. The time required for the water/nitrogen flow exiting the tube to reach saturation is measured for each tube. The longer the duration until saturation, the more moisture is adsorbed into the tube surface.

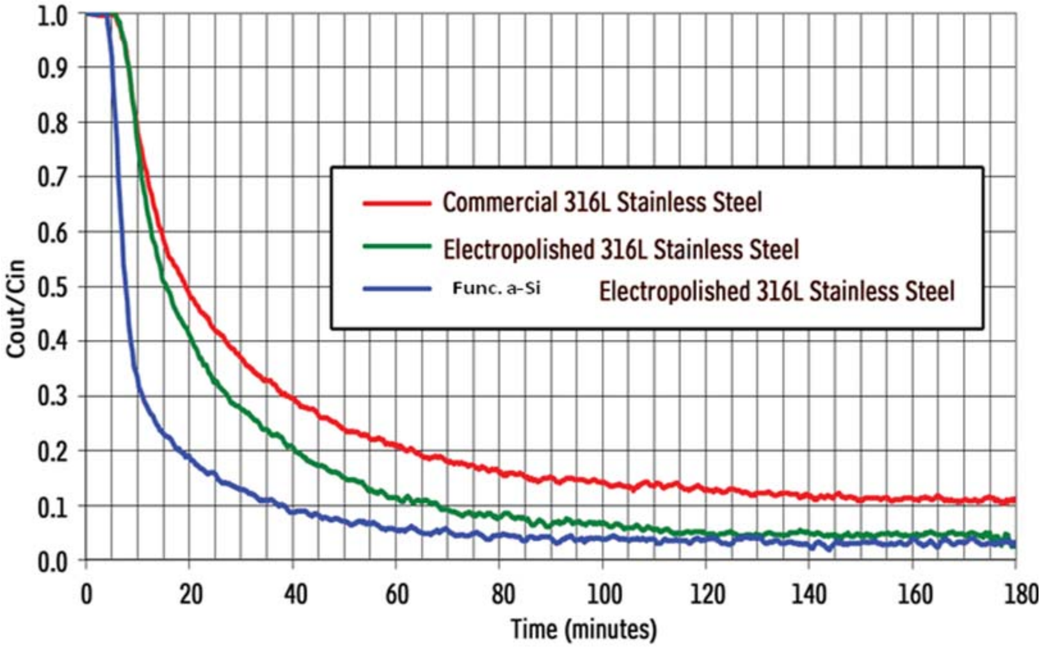
Figure 15: Comparison of water adsorption rate in amorphous silicon (a-Si) coated and uncoated tubes. The a-Si tube adsorbed 9x less water compared to 316 stainless steel.[7]



Commercial stainless steel tube adsorbed the most water requiring 180 minutes to achieve 95% saturation. Electropolished stainless steel required approximately ¼ the time, 40 minutes, to achieve saturation. Electropolished tube minimized adsorption by reducing surface area that can trap moisture. a-Si coated electropolished tube further reduced adsorption by 50%. Saturation was achieved in 20 minutes demonstrating that hydrophobic surfaces minimize water adsorption into steel surfaces, thus minimizing corrosion potential.

Drying rates of coated and uncoated tubing (100 feet, 1/4in) were also compared (figure 16). Commercial 316L tube dried to a 96% equilibration in 180 minutes while electropolished 316L tubing dried in 60 minutes and a-Si coated electropolished stainless steel tube dried in 30 minutes. The a-Si coated electropolished stainless steel tube dried in 83% less time; demonstrating a more hydrophobic surface releases moisture faster and minimizes corrosion potential.

Figure 16: Dry-Down comparison of amorphous silicon tubing vs. 316 stainless steel tubing. The a-Si coated tubing dried in 83% less time compared to commercial 316L stainless steel tubing.[7]



Conclusion

Test data indicate that amorphous silicon and carbosilicon coatings are effective in extending the corrosion resistance of stainless steel in produced water environments. Silicon coatings can delay the onset of corrosion in stainless steel by 10x or more in produced water applications. Instrument, filtration, valve, fitting and pump manufacturers have a cost effective alternative to high performance alloys in produced water applications. Silicon coatings can reduce costly maintenance and field failures due to system corrosion while avoiding the high material costs associated with high performance alloys. Silicon coatings demonstrate significant life cycle cost savings, compared to unprotected stainless steel or high performance alloys.

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