

Reduce Downtime and Ensure Accurate Sulfur Results with Sulfinert[®]-Treated Sampling Path

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Accurate analysis of part-per-million and part-per-billion levels of sulfur-containing compounds is critical to effectively managing process streams and meeting regulations for low-level sulfur. Many organo-sulfur compounds, like hydrogen sulfide (H₂S), methyl mercaptan, and ethyl mercaptan, adsorb to metal surfaces during sampling, resulting in false negatives or artificially low values. Additionally, these compounds are slow to desorb from untreated metal surfaces, which can lead to unpredictable levels of carryover between samples. Both scenarios contribute to inaccuracies and compromise the ability of operators to optimally manage process streams. Using Sulfinert[®]-treated sampling and transfer equipment results in more accurate sulfur sampling and faster cycle times, ultimately improving productivity and preventing costly process upsets.

Sulfinert® Coating Ensures Sulfur Detection

Sulfinert® is a proprietary (U.S. Patent #6,444,326), silicon, chemical vapor-deposited coating, specifically designed to improve the inertness of steel, stainless steel, alloys, alass, and ceramics. It is used to passivate sampling vessels, transfer tubing, fittings, and custom parts to prevent sulfur adsorption along the sample path. As shown in Figure 1, Sulfinert® treatment significantly improves the recovery of sulfur compounds, such as hydrogen sulfide, compared to untreated cylinders. Here, a gas containing 17 parts-per-billion (ppbv) hydrogen sulfide was stored for 7 days in both untreated and Sulfinert®-treated stainless steel high pressure sample cylinders. The relative response of hydrogen sulfide to dimethyl sulfoxide was measured over time to indicate level of inertness. Data show that adsorption occurred rapidly in the untreated cylinder, with complete loss occurring within 24 hours. In contrast, the Sulfinert®-treated cylinders reliably stored low levels of active sulfur compounds for the entire 7-day test period.

A similar benefit is seen when Sulfinert®-treated tubing is used; the inert surface created by this treatment prevents adsorption and delivers a representative sample without delay (Figure 2). In this case, the sulfur transport properties of 100 foot (30.5 meter) lengths of Sulfinert®-treated, electropolished, and raw commercial grade stainless steel tubing were compared using 500 part-per-billion (ppbv) methyl mercaptan. The Sulfinert®-treated electropolished tubing did not adsorb the methyl mercaptan to any measurable extent, whereas the untreated electropolished tubing totally adsorbed methyl mercaptan for more than 75 minutes and the sulfur gas level did not stabilize until 130 minutes. Conventional 316L seamless tubing totally adsorbed methyl mercaptan for more than 90 minutes, and the sulfur gas level did not stabilize until 140 minutes. Compared to untreated material, the use of Sulfinert®-treated vessels and tubing clearly reduces sulfur adsorption, resulting in more accurate sampling and less downtime due to process upsets.

Treatment Eliminates Memory Effects

In addition to preventing adsorption of sulfur







Figure 2: Sulfinert®-treated tubing does not adsorb methyl mercaptan (500 ppbv) compared to electropolished and standard stainless steel tubing. Tubing dimensions: 100 foot lengths, 1/8in OD x 0.020" wall. Data courtesy of Shell Corp. and O'Brien Corp. (2).

compounds, Sulfinert® treatment eliminates memory effects. When adsorption of sulfur-containing compounds is prolonged, desorption from the surface can occur slowly, causing disruptive false readings over time. This "memory" of adsorbed sulfur compounds can cause long delays in equilibrating a sample stream. Figure 3 demonstrates the memory effects of three types of tubing used to transfer streams containing sulfur compounds. The Sulfinert®-treated tubing shows less retention of sulfur compounds by several orders of magnitude, indicating very high sulfur inertness. Sulfinert®-treated sample pathways can eliminate costly refinery product losses due to false or delayed readings.

Value of an Inert Pathway

Using Sulfinert®-treated sampling and transfer equipment results in more accurate sampling and faster cycle times, which translate directly into increased productivity and cost savings. Shorter sampling cycles mean more samples can be collected and analyzed in a given period of time, improving productivity. Also, significant savings can be achieved when false readings are eliminated because process upsets can be detected faster. Typical savings can be calculated by looking at average per-hour cost of operating a process that relies on accurate quantification of sulfur compounds. For example, a 1-hour delay in operations can cost an 800,000 tpy ethylene plant \$50,000. Similarly, a 250,000 tpy LDPE unit will cost operations \$36,000 for a 1 hour upset, while an EBSM styrene plant will cost \$33,000 (Figure 4).

Summary

Sulfinert®-treated sampling and transfer systems allow oil and gas exploration, chemical and petrochemical plants, and refineries to obtain accurate sulfur data the

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Figure 3: Sulfinert[®]-treated electropolished tubing shows no memory effects. Sulfur memory is prolonged in raw commercial grade stainless steel tubing. 500 ppbv methyl mercaptan in helium. Data courtesy of Shell Corp. and O'Brien Corp. (2).



Figure 4: Estimated losses resulting from a 1-hour delay in operations due to sulfur adsorption in sample and transfer systems.

first time, every time—with no delays, sample errors, or false readings. In addition to providing the analytical benefits of inertness, the coating is ideal for these applications because it reliably conforms to intricate surfaces, does not interfere with threaded or compression joints, and is not damaged when tubing is bent. Analysts charged with monitoring sulfur levels in process streams can save thousands in improved yields, better test cycle times, and improved system reliability by using rugged, inert Sulfinert®-treated sampling vessels and equipment.

References

- D. Smith, D. Shelow, G. Barone; "Instrument and Sampling Equipment Passivation Requirements to Meet Current Demands for Low-Level Sulfur Analysis"; Presented at Gulf Coast Conference, 2001; Restek Corporation, Bellefonte, PA 16823.
- 2. Application of TrueTube™ in Analytical Measurement Cardinal UHP, August 2004.

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