Question 42: What are your typical H_2S (hydrogen sulfide) detection and monitoring methods used on heavy oil fractions being transported via truck, rail, or barge? What are the mitigation options you employ?

SAM LORDO (Nalco Champion)

We see typically dragger tube testing and head space H2S monitors being used. Mitigation is still done, for the most part, with chemical additives. The most commonly used additives are from the triazine family. As a result of the concerns that refiners have with some of the existing triazine and non-triazine (e.g., glyoxal) being used with respect to the impact on downstream equipment, Nalco Champion has developed both non-triazine, non-acidic (non-glyoxal), and low nitrogen alternative H2S scavengers. These products are currently being introduced to the market, both upstream and downstream.

JAMIE McDANIELS (Athlon Solutions)

Heavy oil fractions should always be assumed to contain H2S, which can substantially concentrate in heavy cuts, putting the health and life of those transporting the oil in danger. Key detection and monitoring methods are as follows:

***H2S monitors** should always be worn by any party involved in the transfer, but monitors should not be relied upon as the sole detection or monitoring device.

***Test for H2S in the vapor space** prior to loading to understand the safety hazard for oils meeting the scope of ASTM D-5705[i.e., viscosity of 5.5 mm2/s (square millimeters per second) at 40°Cto 50 mm2/s at 100°Cor those conforming to Specification D 396 grade numbers 4, 5 (heavy), and 6]. Conduct modified testing using the actual storage area and transportation temperatures for hydrocarbons not meeting the scope of ASTM-D5705.

***Handheld gas “sniffers "can** also be used to monitor the air around the transportation vessel and the vapor space above the hydrocarbon where H2S can migrate to and reach dangerous levels.

Mitigation options include three techniques.

1.Nitrogen blanketing can be used to keep H2S out of the vapor space. However, once the oil is moved from the vessel that is blanketed, the exposure risk is present again.

2.Vapor scrubbing techniques can be used. Such a process moves the concentrated H2S vapors away from storage where they are converted to a safer form. Like nitrogen blanketing, this is only effective for a static environment and also requires capital. If there were temperature increases or agitation, more H2S could potentially evolve.

3.Chemical scavengers that react with H2S in the liquid phase and permanently prevent the deadly gas from migrating to the vapor space are the safest option. Such scavengers should have thermally and time-irreversible reactions with H2S. The chemical should be added as far upstream and ahead of the transportation process as possible to eliminate the risk. The chemistry should also be able to scavenge H2S to safe limits and not pose any harm to the process to which the oil is destined. Chemical scavengers can be the most cost-effective option, too. The oil can be tested for H2S before and after chemical treatment, as per the procedures mentioned above, to verify that the residual concentration is safe for transportation.

EDWARD NARANJO (Emerson Process Management)

There are two common methods for H2S detection suitable for gas monitoring in the transport, loading, and offloading of petroleum fluids: solid state and electrochemical gas detection. Both techniques offer sensitivity in the parts per million, are robust, and have a rich history of use in the oil and gas industry. Electrochemical sensors are an electrochemical cell that employs a two-or three-electrode arrangement and in which concentration measurements can be performed at transient or steady state. These sensors are highly sensitive, consume low power due to their intrinsically safe operation, and have good specificity to hydrogen sulfide. The devices have a working pressure range of 10% within atmospheric pressure and, consequently, require no recalibration if used at high elevations. By contrast, solid-state sensors usually consist of a gas-sensitive resistive film, a platinum heater element, and an insulation medium. Most commercial gas sensors make use of tin oxide or tungsten oxide combined with other oxides, catalysts, and dopants to increase device selectivity. Solid-state sensors are among the most rugged devices used for gas monitoring, making them an ideal choice for monitoring gases in harsh environments.

Gas detection, however efficient, is only one of several tools employed to mitigate the consequences of a gas leak. Active methods, such as the use of fans in loading and offloading stations, transport gas in open and uncongested areas to help dissipate the gas cloud and dilute the gas. Stronger car structures also prevent leaks caused by collisions and train derailments. More importantly, gas detection should not take precedence over safe plant design. Principles of intensification or minimization, substitution, attenuation or moderation, and simplicity should be applied to the transport of crude oil, natural gas, and its derivatives. With fewer leakage points or opportunities for error, for example, gas leaks may be avoided, reducing the need to control the hazard by added equipment.

RON PARISE (Nalco Champion)

For fast field analysis, typical field tests follow the ATSM D-5705 method or “Can Test” for vapor-phase H2S measurements. More accurate liquid-phase measurements typically follow the ASTM D-7621 or UOP-163 methods. These latter procedures require laboratory space and are not field friendly. There have been recent developments with anew rapid field test method using IP-570 that have proven effective. Online crude sulfur analyzers have also been introduced into the industry. Mitigation strategies typically employ the use of an amine based H2S scavenger to react with the H2S in the crude oil to generate a non-reversible sulfide derivative and mitigate H2S concerns. Care must be used in selecting the right type of amines as we have seen certain types of amines end up in a crude overhead and lead to accelerated salt deposition and potential corrosion or fouling.

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