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Understanding the Impacts of Crude Oil H_2S Scavengers on Refinery Process Operations

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ABSTRACT

Sulfur compounds found in crude oil cause many problems. When hydrogen sulfide migrates from the liquid phase to the vapor phase, personnel, the environment, and equipment are put at great risk. H_2S is corrosive to metals, especially at high concentrations and temperatures. H_2S smells like rotten eggs at the part per billion level and is dangerous to life and health at 100 parts per million and above. Sulfur in crude oil is trending upwards. More than ever, processing companies need safe, cost-effective, and efficient handling methods with no negative impacts.

Hydrogen sulfide in crude oil is a result of natural processes occurring within the formation. Specification limits for crude oil vary widely between companies, industrial segments, and countries. Chemical scavengers such as triazines, containing nitrogen, or non-nitrogen scavengers, such as glyoxal, are often used to reduce H_2S exposure. While triazines are relatively cost-effective and efficient, processing crude oil treated with triazines introduces corrosion and fouling risks to equipment. Glyoxal requires high dosage making treatment expensive, and its low pH can corrode feed equipment.

Athlon Solutions has developed a comprehensive line of non-nitrogen and non-glyoxal H_2S scavengers for use in petroleum, each with their own unique properties. They have proven to be cost-effective and efficient at scavenging hydrogen sulfide without the long-term effects typical of triazine scavengers such as corrosion, fouling, and microbiological toxicity in wastewater plants. Crude oils treated with non-nitrogen and non-glyoxal scavengers have been processed safely, cost-effectively, and efficiently without operational restrictions or impact on finished product specifications. Safety, the chemical injection system, testing, and on-site support are also crucial for hydrogen sulfide scavenging projects in addition to chemical selection.

Keywords: crude oil, sulfur compounds, H_2S, scavengers, triazines, glyoxal, zinc, non-nitrogen, non-glyoxal, corrosion, petroleum, cost-effective, safety, chemical

H_2S OVERVIEW

As a result of eons of biological decay, H_2S is formed in liquid crude oil in the reservoir from the sulfur natural to all plant and animal life. When that petroleum is produced, the reduction in pressure forces H_2S into the vapor phase where it can accumulate in empty spaces above crude oil such as tank and barge headspaces, or in low lying areas.

H_2S has a rotten-egg odor at concentrations of 0.01 to 1.5 parts per million. At 100 parts per million, H_2S gas is immediately dangerous to life and health (IDLH). At levels in between the odor and IDLH threshold, H_2S is irritating and can cause short-term health effects. In general, exposure is limited to 10 parts per million of H_2S for an 8 hour shift (Occupational Safety & Health Administration, 2015). However, H_2S specifications for crude oil transportation and storage vary from company to company and from industry to industry.

H_2S is corrosive, especially at higher concentrations and temperatures. The United States Environmental Protection Agency (EPA) says, "The cost to repair or replace pipes, equipment, and structures deteriorated by hydrogen sulfide corrosion may exceed by many times the cost to control the corrosion and avoid infrastructure damage.

Nationally, the cost to repair corrosion damage by hydrogen sulfide is in the billions of dollars, and many communities will spend millions of dollars in the next few years to correct corrosion problems (United States Environmental Protection Agency, 1991)." When hydrogen sulfide converts to sulfuric acid in the presence of water, the attack on pipes and tanks can be devastating. H_2S can also directly react with metals such as copper, iron, and silver (United States Environmental Protection Agency, 1991). One result of this is the contamination of finished products that may not pass copper or silver strip tests if sulfur compounds are present above tolerance, which can result in the downgrade of products.

H_2S AND SULFUR COMPONDS IN CRUDE OIL

Over the years, the sulfur content of crude oil that is processed in United States refineries has increased. See Figure 1 (U.S. Energy Information Administration, 2016).

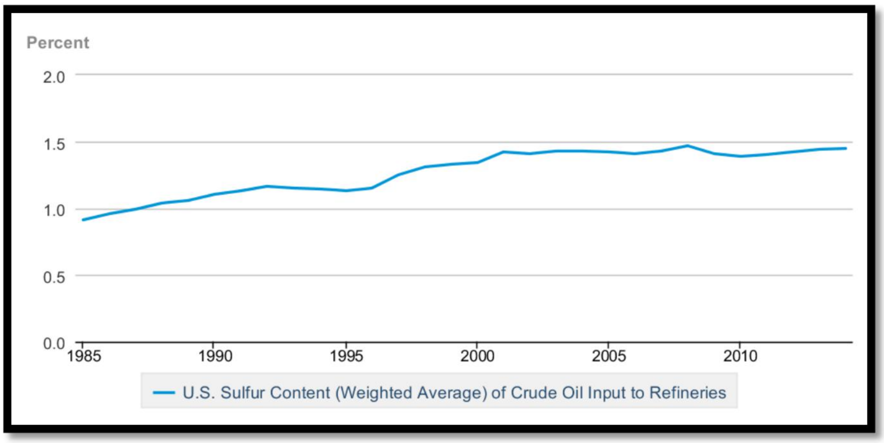

Figure 1: According to the U.S. Energy Information Administration, the U.S. sulfur content (weighted average) of crude oil input to refineries has been increasing over the years.

Sulfur compounds may already exist as H_2S, or they can be larger sulfur containing compounds that could potentially break down to form H_2S. This upward sulfur trend, as well as a sharper focus on safety in the industry, continues to drive a need to control the H_2S in crude oil.

TRIAZINE

One cost-effective, commonly used way to control H_2S is to apply a nitrogen-based chemical scavenger such as triazine. One mole of MEA-triazine, for example, can react with 2 moles of hydrogen sulfide. Theoretically but unlikely, a third mole of H_2S could potentially react (Contreras, Green, Patel, & Wodarcyk, 2015). However, corrosion and fouling issues while processing crude treated with triazine scavengers have been attributed to the chloride salts formed from the use of nitrogen-based scavengers. Studies show that a 5% solution of MEA hydrochloride at 225°Fahrenheit corrodes carbon steel at 414 mpy and even Hastelloy C276 at 4.9 mpy. It has also been confirmed that the byproduct of the reaction between MEA triazine and H_2S, dithiazine, can polymerize. This may result in fouling of trays and overhead systems (Contreras, Green, Patel, & Wodarcyk, 2015). In light of this, many refiners are no longer willing to accept the risks associated with processing crude oils that have been scavenged with nitrogen-based scavengers.

GLYOXAL

Due to the increased demand for non-nitrogen scavengers, the industry began to use glyoxal as an H_2S scavenger. Glyoxal is the simplest di-aldehyde chemistry. This alleviated the corrosion and fouling concerns in towers and overhead systems caused by nitrogen containing scavengers; however, glyoxal is slow to react with H_2S, unstable at high temperatures and pressures, and the common 40% glyoxal in water solidifies at 7°F (-14°C), making handling potentially difficult. Due to its low pH of 2 to 3.5, glyoxal must be applied and handled with caution (BASF, 2008). In addition, it is not cost-effective due to the high dosages usually required (Amonsa, Mohammed, & Yaro). See Figure 2 for a dose response example.

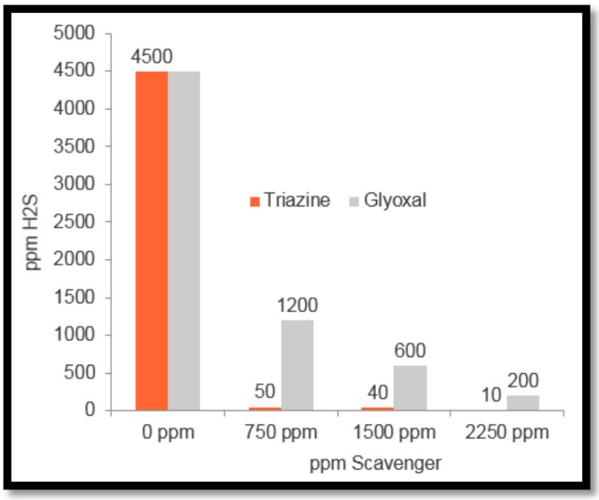

Figure 2: H_2S in the vapor space is on the y-axis and chemical dosage is on the x-axis. A sample with a starting concentration of 4,500 ppm H_2S was dosed with varying quantities of glyoxal and triazine. Unlike triazine (orange bars), glyoxal (taller grey bars) was unable to reduce the H_2S concentration to an acceptable level even at high dosages.

ZINC

Zinc-based H_2S scavengers are very effective. Zinc scavengers have high selectivity for H_2S, react instantly and irreversibly, and have been used in the upstream for removing H_2S during the drilling process (Amonsa, Mohammed, & Yaro). Zinc compounds are also introduced into crude via reclaimed oil that contains zinc lubricants. While effective, industry studies indicate that zinc may lead to desalting issues and have potential to create tight emulsions (Crude Oil Quality Group, 2004) leading to poor salt removal, oil under carry to the wastewater plant, and water carryover into the crude unit. The zinc also aggravates fouling in a preheat train and can poison catalysts.

ALTERNATIVE OPTIONS

By process of elimination, when considering a crude oil H_2S scavenger, a non-nitrogen, organic but effective, or non-harmful metallic chemistry should be preferred.
Athlon Solutions has developed two different lines that meet such criteria.

Product A

Product A is a water-soluble, multi-blend hydroxyl solution. The product is extremely effective in removing H_2S. Figure 3 shows that PRODUCT A is 5 times as efficient as triazine and scavenges 15% more H_2S at initial contact.

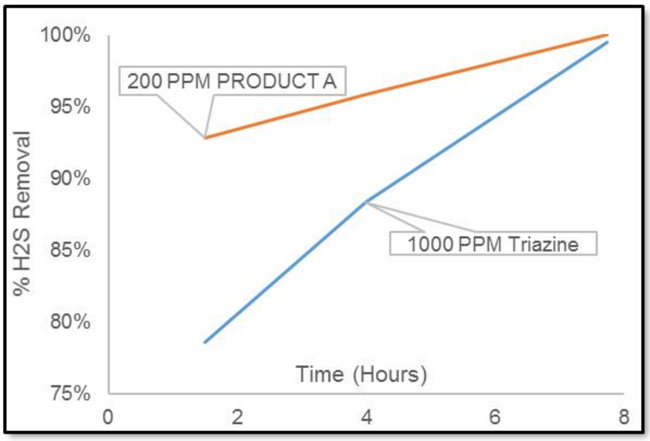

Figure 3: PRODUCT A removes more H_2S faster at lower doses than triazine. The y-axis is % H_2S removal in the vapor space and the x-axis is elapsed time in hours.

There are several other properties of PRODUCT A that make it an excellent product for crude oil, including:

- Converts H_2S into a stable non-hazardous sulfate salt
- Targets H_2S and reacts instantaneously upon contact.
- The chemical also removes light mercaptans from liquids in the same manner.
- PRODUCT A has a much higher specific gravity than crude oil and most other hydrocarbons
- Uses a proprietary catalyst to increase reaction rate

The properties of PRODUCT A not only make it a very effective H_2S scavenger but also eliminates several issues in the crude processing system often associated with amine- based scavengers. Due to the product's density, it will settle from crude oil very rapidly, and this is important because the water soluble reaction products and unreacted scavenger will settle out in tankage. They can then be drained and removed from the process, but should the unreacted product and water soluble reaction products not have ample time to settle in the tank farm, it can then be removed by the desalter. Worst case scenario: the product is carried into the crude unit where, in actual use, PRODUCT A has not shown any corrosion or fouling tendencies.

Another variable that should be considered when evaluating a system is the chemical impact on a wastewater treatment plant. Studies and experience have shown that PRODUCT A is nontoxic to biological systems.

Product B

A second series of H_2S scavengers was developed. PRODUCT B is an organic, non- metal, non-glyoxal, and non-amine water soluble H_2S scavenger. It is an aqueous base polyhydric ether and like PRODUCT A, is also effective at removing H_2S without any harmful side effects. PRODUCT B requires longer to react and settle than PRODUCT A (depending on crude properties and temperature). Though it will contribute water to crude oil, the water is easily removed in the desalter. If there is product carryover from the desalter, no corrosion nor fouling is expected or been observed. However, due to the low dose requirement, the water contribution should be minimal. Unlike glyoxal, PRODUCT B is cost-effective, efficient, and has a more neutral pH of about 6. A simplified reaction mechanism is summarized as:

PRODUCT B + H_2S -------> Cyclic Sulfur and Sulfide Compounds

CASE HISTORY 1: PRODUCT A

A major United States refinery had an opportunity to sell crude oil. The crude oil was expected to be heavily laden with H_2S and needed to meet a specification of 100 ppm or less H_2S in the vapor space above the crude in order to be shipped. The crude was first loaded into tanks before being loaded onto barges. The H_2S specification was met as each tank was filled, and the crude was able to be quickly loaded into barges to make room for additional incoming crude. The water and reaction products remained behind in the tank. Every barge that was loaded met the maritime specification of less than 100 ppm of H_2S in the compartment's vapor space, and no personnel were exposed to H_2S during the treatment, loading, or unloading process. Figure 4 shows data from the 5 times tanks were filled. Treated crude oil H_2S ranged from 0 to 60 ppm in the vapor, while the average untreated crude oil was as high as 5,000 ppm. Individual samples of untreated crude oil at times contained H_2S as high as 18,000 ppm.

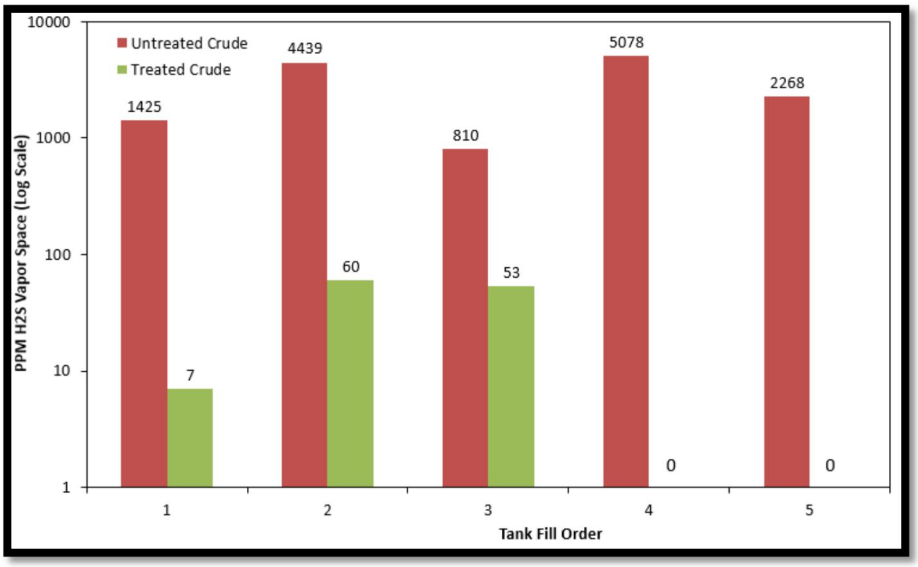

Figure 4: H_2S in the vapor space is represented exponentially on the y-axis. The x-axis represents each time a tank was filled and then shipped. The untreated crude oil (red, taller bars) contained high levels of H_2S while the treated crude (green, shorter or no bars) met the shipping specification of 100 ppm or less.

Nearly 800,000 barrels of crude oil were successfully treated, and the shipping refinery enjoyed several million dollars in net benefits to their organization as a result. The receiving refinery processed the crude with no throughput restrictions nor upset incidents attributed to PRODUCT A.

CASE HISTORY 2: PRODUCT B

Similar to Case History 1, a major United States refinery needed to store and ship crude oil that was expected to have high levels of H_2S. The H_2S vapor limit for tankage and shipping was 100 parts per million. For this crude oil application, Athlon Solutions recommended PRODUCT B. The product would have time to react and would allow the project to be cost-effective.

The crude was delivered and treated directly from pipeline before being sent to tankage and finally to ships. H_2S levels were similar to those described in Case History 1. With time, PRODUCT B continuously reduced H_2S to progressively lower and lower concentrations in the tanks and barges. Dosage of PRODUCT B was calculated at 0.27 ppm product used per 1.0 ppm H_2S in vapor. Such a treat rate is comparable and lower than dosages for triazine based products, but without the corrosion and fouling concerns. See Figure 5 for data.

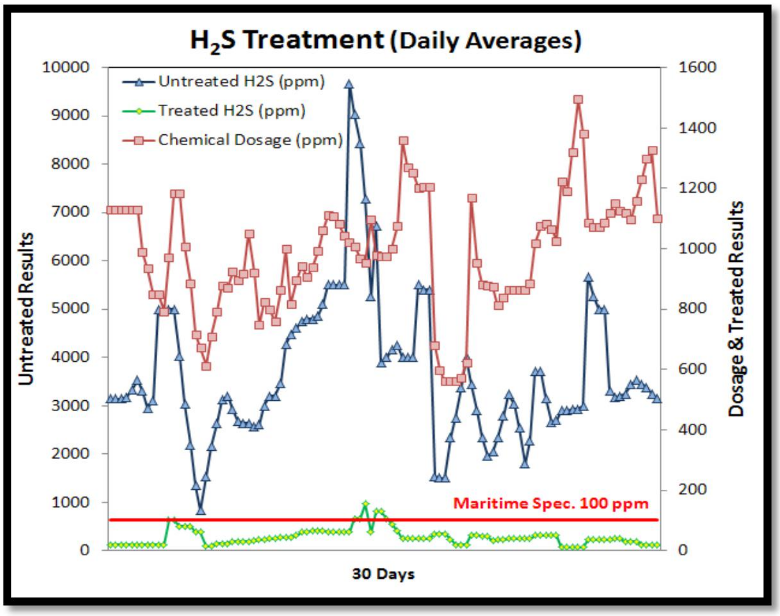

Figure 5: Untreated H_2S concentrations (blue line / triangle markers) in the crude oil are plotted on the left y-axis while the treated crude oil H_2S concentrations are plotted in green on the right y-axis with small circular markers. PRODUCT B dosage is plotted in red with circular markers also on the right y-axis.

After treatment operations were completed at the refinery, the PRODUCT B treated crude was run through the refinery process. The treated crude was blended in at increasing percentages over the course of several months. No unit upsets attributable to the treated crude were observed. Over 1 million barrels of crude oil were treated, and the refinery enjoyed increased margins from the treated opportunity crudes. Most importantly, no one was exposed to hydrogen sulfide gas in either case.

APPLICATION CONSIDERATIONS

Athlon Solutions has had great success with their crude non-amine and non-glyoxal H_2S scavenger chemistries. However, product injection and monitoring is critical for a successful application.

Greater residence time and mixing efficiency of the scavenger lead to a reduction in chemical usage and increase in H_2S removal.

Any scavenger needs ample opportunity to contact H_2S. Contact is less likely in a laminar flow system. The Reynolds number can be used to determine whether flow in a pipe is laminar, transition, or turbulent, with higher values representing higher turbulence. The Reynolds number depends on the fluid velocity, the diameter of the pipe, and the kinematic viscosity of the fluid. Viscosity is temperature and density dependent, and is an important consideration.

Generally speaking, variables such as crude oil density, temperature, and pipe size probably cannot be controlled. For maximum effectiveness, H_2S scavengers should be injected into the oil stream at the warmest locations, into a section of line with the smallest diameter (greatest pressure drop and turbulence) and as far upstream from the final destination as possible, to maximize mixing time. Less than optimum injection locations can require increased dosage to overcome the flow challenges, or require modifications to the pipe, such as the installation of static mixers. Table 1 shows Reynolds numbers for three crude oils with different viscosities and API gravities.

Flow and Line Size Parameters			Crude A - 41 API	Crude B - 20 API	Crude C - 19 API
Flow Rate (BPH)	Line Size (in)	Velocity (ft/sec)	8.788 cSt	408.1 cSt	957.3 cSt
3500	16	3.91	55133	1187	506
4000	16	4.47	63010	1357	578
4500	16	5.03	70886	1526	651
5000	16	5.58	78762	1696	723
5500	16	6.14	86638	1866	795
6000	16	6.70	94514	2035	868
6500	16	7.26	102391	2205	940
7000	16	7.82	110267	2374	1012
7500	16	8.38	118143	2544	1085
8000	16	8.94	126019	2714	1157
8500	16	9.49	133895	2883	1229
9000	16	10.05	141771	3053	1301

Table 1: Three different crude oils were tested for API gravity and viscosity. Reynolds numbers were calculated for each crude at varying flowrates through the same line. Turbulent flow is highlighted in green, transitional in yellow, and laminar in red. Turbulent flow would be expected in Crude A at all flow rates, laminar flow would be expected in Crude C at all flow rates, and Crude B would experience both transitional and laminar flow. Such data helps to predict chemical dosages.

As seen from the data, just small changes in crude oil properties with a change of crude such as API gravity, can have an effect on turbulence. As expected, heavier crudes don't mix as easily, i.e., are more viscuous, and are often more difficult to treat.

The use of a properly designed quill helps to disperse chemical into the hydrocarbon stream. Due to the relatively small chemical requirement, a water carrier stream, such as firewater, can be utilized to force small droplets into a wider pattern in the flowing crude oil to help disperse the chemical. As mentioned in the previous case histories, the water will either remain with the crude oil or settle out and remove the reaction products and unreacted chemical. In either case, a water carrier has not been seen to be problematic.

Due to the criticality of crude oil treatments, injection system design is important, and it is advisable to remove any potential barriers prior to treatment. Backup pumps should be onsite or in some cases, an eductor can be used to eliminate additional moving parts all together. A delay in or intermittent loss of treatment could permanently affect the H_2S content in tankage. Tank mixers are often unreliable and do not guarantee effective mixing. For this reason, a primary sampling station should be set up to establish treatment rate and a secondary sampling point post treatment but prior to storage should be set up to verify the treatment and removal of H_2S. Flow meters should also be used to ensure proper dosage.

SAFETY AND TREATMENT OPERATIONS

Hydrogen sulfide in crude oils can exceed immediately dangerous to life and health (IDLH) levels by a factor of 10 to 100. For that reason, the most important thing to consider during a treatment is safety. Best practices for sampling include using a supplied air breathing apparatus, DOPAK sampling stations (DOPAK Sampling Systems, 2014), and "the buddy system". The use of a DOPAK may eliminate the need for SCBA because it guarantees zero emission sampling and keeps the process closed. Of course, a job safety analysis must always be performed prior to beginning work.

Additional best practices are to have someone onsite monitoring treatment, plus a second person, the buddy as mentioned above, anytime the pumps are on and crude oil is being transferred during a project. This second person observes as the first person samples and adjusts the pump as necessary. This is typically done every half hour during a treatment, because, as explained, any sudden increase in H_2S can put the entire project behind if the pumps are not quickly adjusted accordingly. This second person is to ensure that if there is an accident, help is immediately called for. Treats often occur in remote locations and at all hours of the night. In the event primary means of communication is not available and a personnel exposure incident occurs, another person in full PPE is ready to assist.

MEASUREMENT CONDITIONS

ASTM D5705 is often the default test method to test crude oil for H_2S. The scope of this test method, however, is limited to residual fuel oil and similar fuels. It is also limited to H_2S that ranges from 5 to 4,000 ppm of H_2S. The test is designed to be performed at 140°F. Under the conditions of this test method, H_2S is equal in the liquid and vapor phase, so by measuring the vapor space with a length of stain detector tube, the liquid phase is indirectly measured (Standard Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils, 2000).

The "H_2S in Crude Measurement Report" published by the Canadian Crude Quality Technical Association (CCQTA) states several important facts (Lywood & Murray, 2011):

1. ASTM D5705 is not suitable for crude oil
2. There is great variability between analytical methods testing for H_2S in crude oil (because H_2S in the vapor space above crude oils is dependent on many variables including density, temperature, and H_2S concentration in the liquid)
3. UOP 163 has the lowest standard deviation and is the recommended method to determine H_2S values in cargoes and tanks

UOP 163, however, is a liquid phase measurement and does not help us understand how much of that H_2S will migrate to the vapor space. Stanhope Seta published a report titled "Measurement of Hydrogen Sulfide in Crude Oil" in which they were able to correlate a modified liquid phase test method with a modified ASTM D5705 test method. In the modified ASTM D5705 method, the crude was heated to 77°F. They found that the vapor phase H_2S concentration was 66 times that of the liquid phase. HOWEVER, that is only applicable to that particular crude oil at that particular test temperature (Mylrea, 2014).

Disproportionate behavior of H_2S in crude oil has been observed. In an 85% heavy crude blend, there was an almost linear increase in H_2S with increasing temperature. In stark contrast, with a different 90% heavy crude blend, H_2S in the vapor phase declined as temperature increased. H_2S evolution from crude oil to the vapor phase is more than temperature and density dependent.

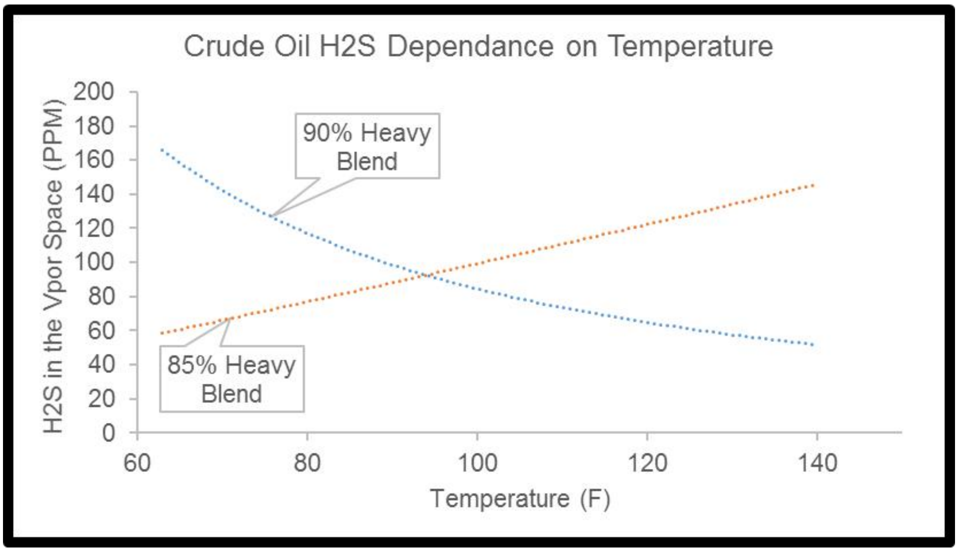

Figure 6: H_2S concentration (PPM) in the vapor is on the y-axis and temperature is on the x-axis. H_2S in the crude oil blend composed of 90% heavy crude decreased with an increase in temperature, and the exact opposite was true for the 85% heavy crude blend.

Due to the volatile nature of H_2S and its dependence on many factors, it is recommended to use a modified ASTM D5705 test to as closely resemble tankage and shipping conditions as possible. This includes temperature and agitation. Alternately, if the crude blend is fairly consistent, the worst case scenario should be determined for that crude oil (whether it be a high or low temperature), and should be tested and treated accordingly. Understanding the test methods is vital for safety and important for controlling to the appropriate chemical treatment rate.

CONCLUSION

Though it is cheap and effective to use triazine scavengers in crude oil, they can often lead to corrosion and fouling issues in the refinery. Glyoxal scavengers are relatively inefficient, and zinc scavengers are prone to cause fouling and desalting issues. Athlon Solutions has developed two lines of non-nitrogen and non-amine crude oil H_2S scavengers that are efficient, cost effective, and harmless to refinery or wastewater processes. Chemical application, proper testing, and, most importantly, safety are vital to making treatments cost-effective and efficient. Scavenging H_2S from crude oil can be financially opportunistic for refiners using the proper scavenging chemistry and application techniques.

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