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Potential Effects of Upstream Additives on Refinery Corrosion and Fouling

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Foreword

The objective of this technical committee report is to provide guidance to refiners on the potential impact of additives used in oil production (including well drilling, completion, and stimulation) and transportation on refinery fixed assets. The report draws on the knowledge and operating experience of the global refining community in processing a wide variety of feedstocks including conventional and nonconventional oil sources. It is intended to aid refinery and corporate staff in evaluating and mitigating the impact of existing, new, and changing feedstock additives on their process units, while not prescribing a crude selection process.

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NACE technical committee reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be recommendations for general application of this technology, and must not be construed as such.

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Introduction

It has long been recognized that certain additives used in oil and gas production ("upstream") field development and operations can impact downstream refining processes. Likewise, chemicals are sometimes added or cargo mixing can occur in transportation of crude oil from the producer to the refiner, also altering the processing properties. Production processes, such as deepwater production, bitumen mining, heavy oil production using steam, hydraulic fracturing of tight formations ("fracking") are highly dependent on chemical additives during production. For hydraulic fracturing, chemical additives also play an integral role during well completion / stimulation and the large number of wells per unit of production cause the likelihood of drilling, completion, and stimulation additive carryover to increase.

Refining of the various Canadian heavy oils and synthetic crudes derived from those sources has become common in Canadian, upper Midwest (pipelined), and Gulf Coast (railcar transport) US refineries. Also, output from the primary light tight oil (LTO) producing fields, Eagle Ford and Bakken, has increased more than tenfold since 2010 and US refiners have altered their strategies to include significant refining of LTO because of the pricing advantages of those crudes. Global development of such resources lags that in the US, but is also increasing rapidly.

As an example, since 2010, ad hoc discussions indicate the organic chloride contamination is potentially increasing. Organic chloride contamination was found in pipeline crudes in western Canada and California. A South American refinery suffered multiple failures in their naphtha hydrotreater (NHT) in mid-2010 as a result of organic chloride contamination in their pipeline crude source. This refiner had processed nominally the same crude from this pipeline for many years without incident. Organic chlorides have also been detected in crudes supplied from West Africa and offshore Brazil. Taken together the above facts demonstrate an increasing likelihood of drilling, completion, maintenance (cleaning fluids) and/or production additives being present in the crude oil delivered to refineries.

Many additives, even if present in the crude, are innocuous at the levels commonly used. Others can have a large impact on refining operations. These effects are not limited to the crude distillation unit (CDU), but can affect many downstream and conversion units as well. While there has been some systematic study of the effects of upstream and midstream additives on refining including the development of analytical methods; most of the knowledge has been derived from inference, experience, and nonstandard test methods. It is a purpose of this technical committee report to collect such knowledge and experience and to serve as an aid to refiners in evaluating the impact of new or changing crude diets relative to crude additives on their operations especially as it relates to asset integrity.

The scope of feedstocks to be discussed in this report includes: conventional crude (or pool) oils, unconventional oils (such as bitumens, synthetic crudes derived there from, dilbits, synbits, etc), shale or tight oils, and natural gas condensates. More complete definitions and characterizations of these feedstocks are included in the report.

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This section is not meant to be a complete description of upstream and midstream operations, but rather to describe specific aspects of those operations and the feedstock types that have the greatest potential to affect refinery processing because of contamination of, or additions to the crude oil that is produced or transported. Each phase of oilfield operations makes extensive use of many chemicals to increase the efficiency of the operation or to increase the production rate from a given well or field. In many oilfield operations (especially drilling, completion, and stimulation), additives are not directly added to the produced oil. Improper segregation or phase distribution of those additives can still result in contamination of the produced oil. While transportation relies less on additives, any additives used are supplied directly to the refinery with the delivered crude oil. In oil and gas production, many types of chemicals are added to the production fluids. Most notably, hydrate inhibitors or foaming additives are usually added in somewhat higher concentrations compared with other oil field chemicals such as scale or corrosion inhibitors. It is common to add other types of inhibitors and additives to prevent corrosion, scale formation, foaming or emulsions, etc., downhole and/or in topside pipelines. For example, most mid-stream oil transportation pipelines introduce corrosion inhibitors to the oil stream to prevent corrosion. These chemicals have a much higher probability to end up as contaminants at the refinery stage. This is especially true for chemicals that are oil soluble.

Initially, oil production came from onshore wells under gas pressure with relatively porous formations that allowed the light oil to freely flow to the well bore and into the above ground equipment. As this "easy oil became less common, various methods have been developed to increase production from low pressure, tighter formations with heavier, viscous oils both onshore and offshore. Furthermore, nontraditional sources such bitumen and upgraded products derived from bitumen have become economical to produce. Finally, light, tight (or shale) oils from extremely low porosity formations have recently become a major source of refinery feedstocks. Each of these feedstocks is discussed below in light of the commonly observed contaminants associated with each.

Common Feedstock Types and Associated Contaminants

Onshore Oil Production

Onshore oil production is taken as the baseline to compare other production methods against. In many cases, this represents the "easiest" production with the fewest constraints upon facilities and hardware. Primary production, where the reservoir is under pressure and oil freely flows through the well bore to the surface has a lower potential for contamination compared to secondary or tertiary production where various techniques are used to stimulate the flow of oil into the well bore. Secondary and tertiary productions methods (water, steam, caustic, alkaline/polymer/surfactant flooding, etc.) vary widely and can affect the produced oil in many ways. A complete description of these methods and effects is beyond the scope of this technical committee report. Refiners typically educate themselves about the production methods for oils that they process in order to be aware of the potential routine and episodic contaminants.

Chemicals used during well drilling, completions, work-overs, and cleaning are separated from normal production, but separation is not always perfect. Initial production with high levels of contaminants is usually segregated for disposal or treatment to remove those contaminants. This treatment sometimes does not completely remove the contaminants (drilling muds, gellants, mineral or organic acids, paraffin solvents, chlorocarbons in some parts of the world), asphaltene dispersants, etc) or the contaminated oil is "bled off" into normal production. Also, there is a period of time after segregation where these chemicals can contaminate the produced oil at lower levels.

Of potentially higher concern are production chemicals added continuously or periodically directly to the produced fluids either via the well bore or on the surface. These are primarily used to prevent or reduce the effects of corrosion; mineral scale formation; hydrate, wax, or asphaltene precipitation; improve flow efficiency; separate oil, water, and gas phases; etc. Other chemicals added to treat produced water are of lesser concerns as these are typically added after oil/water separation. If the produced water is used for water flooding, these chemicals enter the produced crude via entrained water (brine) or partitioning to the reservoir oil.

Offshore Oil Production

Significant oil production comes from several offshore production regions such as the North Sea, the Gulf of Mexico, Brazil, etc. One of the features of this method of production is the small size of the platforms and consequent need to reduce equipment size/footprint. This makes phase separation a challenge given the relatively low retention time in the separation vessels. Because of this situation, there is a greater need to use chemicals to improve the rate of separation. This results in increased antifoam and demulsifier use. This can also result in the use of high temperatures for oil dehydration. This can lead drying of brine droplets with the formation of salts. These solid salts are more difficult to remove at the refinery desalter, but can still hydrolyze to form HCl in the crude preheat train and furnace.

Another feature of offshore production is the low temperatures at depth below the water surface. Any slowdown or disruption in production can require the use of hydrate inhibitors to prevent blockage of the production system. Also, paraffins or other organic deposition can be more problematic than situations where the production system is warmer.

Given the expense of platform construction and installation, satellite production wells from different producing zones can be pipelined to the primary platform. This can result in changing oil characteristics over time as new production comes on line and older field decline. On a larger scale, production from multiple platforms is usually blended into one pipeline to shore, resulting in the same effect. The increasing use of FPSO (Floating Production Storage and Offloading) facilities partially offsets this effect with cargoes from specific platforms being shipped directly to refiners. However, inadequate cleaning of these storage facilities or inadequate draining of maintenance fluids sometimes results in contamination of subsequent crude cargoes.

Light, Tight Oil (LTO) Production

LTO have become a significant feedstock to many refineries since 2010. These oils tend to be light and low in total sulfur, nitrogen, and TAN (total acid number). Accordingly, they had been viewed as easy to process feedstocks. However, experience has shown several problems associated with LTO.

LTO are produced from very low permeability formations. This requires hydraulic fracturing to open channels in the rock and allow oil to flow to the well bore. Production rapidly decays and requires refracturing of new producing zones to regain high production rates. The wells are closely spaced to more efficiently recover the oil in place. Finally, these producing regions in the USA (Eagle Ford, Bakken, Niobarra, etc.) are poorly served by port or pipeline infrastructure, so transportation is in small batches via railcar, truck, and barge. These factors combine to cause high variability of LTO quality from cargo to cargo. Large differences in gross crude properties such as API gravity, yield structure, even color have been documented.

As a result of environmental regulations, water used in the fracturing process is more often recycled than in the past. This can increase the headspace H_2S concentration because of partitioning of H_2S between the recycled water and new (sweet) production. The storage and recycling of water can also lead to increased microbiological growth. This can lead to additional H_2S production if sulfate-reducing bacteria are present in the water. Also, the microbiological growth in the water can contaminate the LTO, leading to potential for increased microbiologically-induced corrosion (MIC) in refinery tankage, logistics, and transportation equipment.

LTO tend to be light and paraffinic exhibiting incompatibility when blended with heavier, more asphaltenic crudes. Cases of severe desalter upsets or crude preheat fouling were observed when LTO were blended into existing crude diets. Because of this experience, many refiners process LTO in dedicated crude distillation units with little blending or have carefully evaluated crude compatibility to create stable blends. Despite dedicated processing, organic fouling can still be an issue with LTO. The paraffinicity of LTO can also lead to wax deposition, high cloud point, and high pour points.

LTO tend to have high solids content and the solids tend to be finer than most other refinery feedstocks. The solids are thought to result from the fracturing process and are particles from the formation or the proppants used to maintain open cracks in the rock.

Bitumen-Based Feedstocks

Several global feedstock producing areas are based on bitumen. These near surface deposits are also referred to as oil sands. The most developed area of exploitation of these deposits is in western Canada and an entire industry has developed to convert the oil sands into various refinery feedstocks. Large mining operations are used to gather the oil sands which are then subjected to various processes to separate the bitumen from the sand. As a result of the viscous nature of the bitumen a diluent (naphtha, natural gas condensates) is used to reduce the viscosity and allow pipelining of the dilbit (diluted bitumen) to upgrading facilities or rail transport of railbit to refineries. The diluents are recovered at the upgrading facilities and reused for bitumen transport or become part of the naphtha production stream of the refinery. Rail transport is typically via heated railcars, so less or no diluent is needed to reduce bitumen viscosity. The diluent can become a means to cycle-up certain contaminants such as mercaptans that are corrosive to upgrading or refinery equipment.

Thermal methods are also used to produce bitumen deposits that are too deep to mine and heavy crude oils. The primary method in use today is known as Steam-Assisted Gravity Drainage (SAGD). This method injects low pressure steam into a hydrocarbon reservoir via a horizontal well. The heat from the steam reduces the viscosity of the hydrocarbon and allows it to drain into a lower horizontal well from which it can be pumped to the surface. Environmental pressures to reduce the amount of surface water used for SAGD production has resulted in the use of more saline groundwaters and recycling of produced waters. This, in turn, increases the salt and other water-soluble impurities content of water entrained in the produced hydrocarbon.

Much of the bitumen produced today is upgraded. Upgrading can use thermal (coking) or catalytic (hydrocracking) processes to convert the bitumen to products that can be directly processed in a refinery or blended with traditional crude oils for refining. Some refineries have processed dilbit as well, although product has a dumbbell-shaped yield curve and is blended with other feedstocks rich in middle distillates.

One of the primary upgraded products transported to refineries is syncrude (synthetic crude). Syncrude is produced by combining various distillate products from the upgrader to create a wide boiling hydrocarbon which contains very little residuum. Synbit combines syncrude with bitumen to create a product more like traditional crude oil in terms of yield curve.

Besides the unique yield structure of some of these products, thermally cracked materials can have higher concentration of olefinic materials leading to fouling. Thermal upgrading removes less of the heteroatom content of the bitumen compared to hydroprocessing upgrading. Products containing raw bitumen can contain high solids loading from the original hydrocarbon source. Catalytic upgrading can add to the bitumen-derived solids loading because of entrained catalyst fines. These solids can also contribute to fouling and stabilize desalter emulsions.

As a result of the price-advantaged nature of bitumen-based feedstock and LTOs, refiners have considered blending these feedstocks. The different chemical compositions of these feedstocks provides a high likelihood of incompatibility upon blending. This is carefully considered before pursuing this feedstock strategy.

Transportation Additives

The traditional modes of crude oil transportation from oil producing areas to refineries are ships (tankers of various capacities) and pipelines. With the advent of light, tight oil (LTO) production, these methods have been supplemented by truck, rail, and barge. These smaller cargo means of transport have traditionally been used for inter-refinery shipments of intermediate products, other feedstocks, and/or finished products. Because of the rapid development of fragmented onshore production in the shale plays, pipeline infrastructure and access to large water-borne ships is lacking. If development continues to be favorable for LTO, the potential exists for such infrastructure to develop, but would require time to be implemented. Delays in approval of a pipeline from western Canada to the US Gulf Coast makes rail transport of crude, bitumen, and synthetic crudes from Western Canada likely in the near future. Gulf Coast refiners are beginning to put the infrastructure in place to receive shipments by rail.

While significantly less additives are used by the transportation industry compared to oil production, any transportation additives are present in the crude oil when it arrives at the refinery. The mode of transportation, crude properties, transport temperature, and jurisdictions involved are among the important factors in determining the type of additives likely to be present in crude oil received at the refinery. For example, the most important oil properties for pipeline transportation include: viscosity, density, and pour point. Thus, most additives are those that prevent wax precipitation, reduce drag during flow, depress the pour point, etc. Corrosion inhibitors are also likely to be used. On the other hand, H_2S scavengers are less likely to be used in pipeline transport. There have been incidents where pipeline additives continued to flow when the pipeline was down. When restarted, a slug of oil with a much higher than normal additive content can make its way to the refinery.

In the case of heavy oils and bitumens, transportation via pipeline might include the use of diluents (e.g., up to 30 vol% naphtha) or even emulsification of the heavy oil into a water continuous emulsion. There is little control over the potential contamination of the naphthas being used for bitumen diluent and these can be a potential source of contaminants (e.g., mercaptans and reactive sulfur species).

Even with the use of the various additives, foreign material accumulates in the pipeline and are removed periodically. While the material removed via pigging is segregated and disposed of, there is a potential for it to get into the crude supply. The contaminants in this case would consist primarily of solids, including: sand, dirt, rust, waxes, asphaltenes, and water. These contaminants primarily affect tank sludge accumulation and possibly carryover, affecting desalting and heat exchanger/heater fouling. The addition of oil soluble chemicals such as corrosion inhibitors, emulsion breakers, paraffin inhibitors to oil carrying pipelines can accumulate in the oil stream and potentially be harmful to the refinery operations. For example, phosphate esters in oil soluble corrosion inhibitors can be transported with the oil stream to the refinery and have a negative effect on the refinery catalysts. This is also true for sulfur containing components such as mercaptans. A gelled solution between pigs is used to assist in the cleaning and also to place additives (corrosion inhibitors, drag reducers, biocides, etc) onto the pipe walls. The appearance of these contaminants is completely episodic and unpredictable, but can result in significant sludge accumulation in refinery tanks (decreasing residence time for dewatering) and/or desalter upsets.

For transportation by a means that includes a vapor space and the potential for worker exposure to that vapor is treated using an H_2S scavenger. Differing environmental regulations for various jurisdictions can result in differences in H_2S scavenger use rates to assure suppression of H_2S vaporization. Likewise, regulations for inshore water transport versus offshore water transport, can result in different H_2S scavenger dosage rates.

Pumpability and preventing deposition of waxes and other crude oil constituents is also important in these modes of transportation. For those issues, however, temperature control and heating can be used in place of additives, especially in the cases of rail or truck transport.

Understanding the entire supply chain to a particular refinery assists the corrosion engineer in anticipating the potential for contamination by various additives and in developing plans to mitigate the potential effects.

Common Additives Associated with Refinery Corrosion and Fouling

Table 1 below lists common upstream or transportation additives that have been associated with refinery process corrosion and/or fouling problems highlighting feedstocks subject to such contamination and refinery units affected. Each of these additives or contaminants are discussed in detail in Section 3.

Table 1
Common Upstream and Transportation Additives Associated with Refinery Process Corrosion and/or Fouling

Additive/Contaminant	Feedstock Where Seen	Units Affected	Effects
H_2S Scavengers	Light Tight Oil (LTO), Sour Synthetic Crudes, and most others as determined by transport methods and jurisdictional requirements	Crude Distillation Unit (CDU), Wastewater Plant	Elevated brine & overhead water pH, salt fouling and/or corrosion, increased COD[A]/effluent plant bacteria "bug" kills
Organic Chlorides	Onshore, offshore	Naphtha Hydrotreater (NHTU), Kerosene Hydrotreater (KHTU)	Increased HCl in reactor effluent stream, increased risk of amine or ammonia salt fouling, dewpoint corrosion
Other Halides (Bromides, Fluorides)	LTO, onshore wells undergoing work overs	NHTU, KHTU	Increased HBr or HF in reactor effluent stream, increased risk of amine or ammonia salt fouling, dewpoint corrosion
Silicon (organic forms, usually from antifoams)	Off-shore	Coker, Fixed Bed Conversion Units	Heater fouling,[B] catalyst activity loss
Phosphorus	Off shore/on shore (currently LTO and light western Canadian)	CDU, Fluidized Catalytic Cracker (FCCU), Fixed Bed Conversion Units	Fouling of jet draw tray, lower tower sections, furnace, catalyst activity loss
Methanol	Off-shore	Wastewater Plant	Increased COD; inhibitory impact on biological treatments
Corrosion Inhibitors/Scale Inhibitors/Biocides	All	CDU, Wastewater Plant	LTO: Rare impact with fouling; Biocide impacts waste plant
Organic Acids	Offshore	CDU, Wastewater Plant	Low brine & overhead water pH, increased neutralizer demand and salt fouling / corrosion risks
Filterable Solids	LTO, mined bitumens, synthetic crude	CDU, Residuum and Gas Oil Conversion Units	Desalter upsets, CDU & Conversion Unit heat exchanger fouling, Conversion Unit catalyst activity loss

A: Chemical Oxygen Demand
B: Coker heater fouling was observed when processing a crude blend containing a both silicon-based antifoam and high calcium.

Section 2: Feedstock Surveillance Strategy

Surveillance of crude oils and other feedstocks brought into the refinery is necessary to proactively identify threats in advance of processing or early in the processing cycle. These programs usually operate on at least three levels: first is evaluation of new feedstocks to be processed at the facility, second is surveillance of individual feedstock cargoes, and third is monitoring of process streams. The first assessment has historically entailed an assay of crude oils to understand its basic properties and characteristics. While this identifies some corrosion and fouling threats due to bulk crude oil components such as TAN and sulfur compounds, it is usually not sufficient as it does not usually capture contaminant issues nor changes in the crude over time. These are usually captured by special, non-routine testing during the assay phase or ongoing cargo surveillance. Some contaminants are present at potentially problematic concentrations in most or all cargoes (eg: H_2S scavengers), while others are episodic and rare contaminants (eg: organic chlorides). Also, assay results for the values of certain properties (such as TAN) in crude fractions may not accurately reflect the values observed when processing the crude in the refinery.

The surveillance program must be sustainable. It is difficult to justify continued expense of analyses for episodic contaminants in crude oil when most times the contaminants are not detected. A balance between crude assays, cargo analyses, and process monitoring must be developed to provide a sustainable and successful program in light of the high likelihood threats to a given refinery. These attributes and considerations determine how to design a surveillance program.

The details of a refinery feedstock surveillance program depend on the feedstocks being processed and specific unit present of each refinery. Examples are given below for several contaminants to illustrate the concepts of designing a robust feedstock surveillance system. Details concerning analytical methods are given in the individual contaminants discussion in Section 3 below.

Example 1: H_2S scavengers are a frequent contaminant of many feedstock types as the use of these additives is driven by the regulatory and safety requirements of many feedstock transportation systems. The amines liberated by H_2S scavenger treatment are not measured by crude assays and require non-standard test methods after aqueous extraction of the amines from the feedstock. Some refiners routinely conduct such testing, while others impose limits on the type and concentration of H_2S scavenger treatments they will accept. During processing, high level contamination is readily detectable by increased desalter brine and CDU overhead sour water pH values. On-line pH analyzers monitoring the CDU overhead sour water or desalter brine are very useful for rapidly detecting H_2S scavenger contamination. Some refiners routinely analyze CDU overhead sour water for amines and chlorides to assess salt deposition potential. If concentrations of amine and chloride are sufficient to cause salt deposition, high rates of localized corrosion can result. This damage is difficult to detect and manage by routine inspection programs, so many refiners prevent salt deposition by the above means (feedstock limits), feedstock blending to dilute the amine, chloride management, or process controls (eg: overhead temperature).

Example 2: Organic chlorides are less frequent contaminants in feedstocks processed by refineries, at least at concentrations that cause rapid corrosion in the naphtha and / or kerosene hydrotreaters. However, there have been numerous high consequence incidents where loss of primary containment due to organic chlorides has been documented. These species are not measured in crude assays as they are not inherent components of crude oil. Due to the episodic nature of significant organic chloride contamination, such data would be of little value in managing this threat. Some refiners chose not to process crudes that have a history of organic chloride contamination. Other refiners conduct cargo analyses of suspect crudes at some frequency including analysis of each cargo. Many refiners use process monitoring in addition to or in place of feedstock analysis. Process monitoring usually consists of analyzing the feed to potentially affected hydrotreaters for total or organic chlorides or measuring chlorides and / or pH in the cold separator sour water of those units. Reliance on sour water monitoring requires a response procedure to mitigate the immediate risk and to identify the source of the organic chlorides for long-term mitigation. This is difficult to accomplish without a robust logistics system where individual crudes can be segregated and fed to the unit at controlled rates.

Section 3: Discussion of Specific Additives and Contaminants

3.1 H_2S Scavengers

Hydrogen sulfide (H_2S) is a naturally occurring compound dissolved in many crude oils as produced. It is also formed in the refining process by the degradation of sulfur compounds in crude at high temperatures. Government regulations and finished product specifications are dictating greater removal of H_2S from produced crude. As a result, producers and end users of crude oil employ H_2S scavengers to reduce hazardous levels of the toxic gas from the vapor space and from the liquid phase. H_2S scavengers are added to crude cargoes to lower H_2S level measured in the head space of tanker cargo holds to legally acceptable levels. Some ports now require levels of < 10 ppmv of H_2S in the head space to ensure the safety of workers.

Three major classes of H_2S scavengers that can be used in treatment of oil include – water soluble, oil soluble, and metal based products.

Description

Water-soluble scavengers are among the most common scavengers and are often the product of choice for applications at temperatures below 93 °C (200 °F). Economical costs and fast reaction rates make them attractive options. Moreover, because of their water solubility, they add a minimum amount of nitrogen to the fuel. These are the preferred additives for use in LPG, residua and crude oils.

Primarily, water soluble H_2S scavengers used in H_2S abatement of crude oils are nitrogen-based. Triazine chemistry is most often employed throughout the petroleum and refining industry. Worldwide, the most versatile and economical of the triazine family used to abate H_2S are monoethanolamine (MEA) triazines. The most common product in this service uses hexahydro-1,3,5-tris(hydroxyethyl) triazine, commonly known as triazine or MEA triazine, as its active ingredient. There are various other products used for H_2S scavenging as well, including another less commonly used form of triazine (1,3,5-trimethylhexahydro-1,3,5-triazine) made from methylamine (MA) instead of MEA. The chemistry is very similar to the MEA-based triazine except the byproduct formed is MA, which is more volatile than MEA and thus more likely to weather off in the process.

The general formula and reaction schemes for MEA and MA triazine chemistries with H_2S are shown in Figure 1. A paper by Bakke[1] et al sheds some insight on the triazine H_2S scavenging reaction mechanism, kinetics and efficiency. Both MEA and MA triazines react with two moles of H_2S to form the respective MEA or MA dithiazine derivatives splitting off the corresponding amine as a reaction product. Theoretically, a third mole of H_2S could potentially react with the remaining amine group in the dithiazine derivatives to form the trithiane, but it is kinetically slow and not a viable reaction as discussed in the paper.

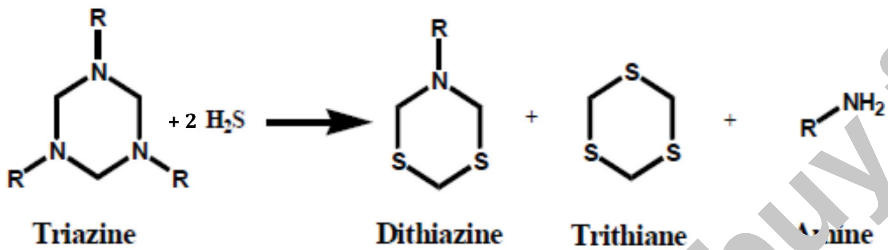

Figure 1: General Reaction of Triazine with H_2S (R = MEA or MA)

Oil-soluble H_2S scavengers are used in high-temperature applications or when water content is minimal. These scavenger products could be triazines with alkyl amine functionality. These products react with H_2S irreversibly to form a thermally stable, oil soluble alkyl sulfide. They can be applied at a wide range of temperatures, from ambient up to 176 °C (350 °F), and are often the product of choice for viscous heavy oils and residua.

Metal-based scavengers answer the specific needs of very high temperature and high-H_2S concentration applications. These additives can be used at temperatures in excess of 176 °C (350 °F) to form thermally stable products and are able to provide H_2S reduction levels that other H_2S scavengers cannot achieve. These are mostly used in H_2S treatment of residua or asphalt when its transported. No major reports that these are used for crude oil treatment.

There are other non-nitrogen based scavenger chemistry that can be used for H_2S abatement including aldehyde-based. These chemistries are not widely accepted for treatment at this time because of generally higher costs and lack of field demonstration of performance. The aldehyde-based products tend to be acidic in nature and cause corrosion, especially at injection points or in tankage if they are not entirely miscible.

Sources

World demand for crude oil along with the increasing concentration of H_2S in the oil and products formed from processing hydrocarbon is placing greater emphasis on the safety, environmental and operational concerns associated with hydrocarbon management. H_2S treatment of crude oil can happen during production or transportation of the crude. The treatment of the crude can begin at several possible locations listed below before the crude enters the refinery. These locations include:

Oilfield Production

A paper by Garcia[2] describes H_2S scavenger applications in crude oil production systems that exist in the oil field or offshore systems consisting of floating production systems positioned strategically near a FPSO. For FPSO applications, sour crude oil is treated as production is transferred to the FPSO or during the lifting operation onto transport shuttle tankers before shipping to the marketplace. In addition, crude oil producers often assess the feasibility of applying H_2S scavengers to abate the toxic and corrosive gas from produced fluids originating from subsea oil production and platform systems. In these applications, injection of scavenger occurs in the gathering lines before or after the separators effectively abating the H_2S from oil and gas export systems. In-line injection can be used to meet export gas H_2S specifications.