

## Practical approaches to removing thermal treatment by-products in drilling waste management.

Katerina Newman and Michael Morgenthaler, Cutpoint Inc.; Vladimir Gargoma, Quality Group Belgorod LLC.

Copyright 2018, AADE

This paper was prepared for presentation at the 2018 AADE Fluids Technical Conference and Exhibition held at the Hilton Houston North Hotel, Houston, Texas, April 10-11, 2018. This conference is sponsored by the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individual(s) listed as author(s) of this work.

### Abstract

Three issues are common to all thermal desorption processes. First, non-condensable gases containing reduced Sulphur compounds may create air emission issues. Second, contaminants, such as reduced Sulfur and nitrogen compounds, SO<sub>x</sub>, NO<sub>x</sub>, and volatile organic compounds can create pungent odors in the water phase condensate. Finally, desorbed and recovered oil has a strong odor caused by entrained thermal decomposition products that may limit its use as a drilling fluids component.

A thermal desorption unit (TDU) recovers valuable base fluids by heating contaminated drilling wastes to separate base hydrocarbons from solids. Thermal Desorption is a commonly employed technology in the drilling waste management service sector. This service sector of the upstream oil and gas industry is expected to grow substantially in the next decade as in the need for thermal treatment technology.

Thermal treated cuttings will usually meet environmental requirements for discharge or disposal without further treatment. The hydrocarbons and water distilled from the drill solids are readily condensable from the vapor stage. The relatively small footprint of a TDU compared to other technologies makes it an economical and practical choice for drill cuttings treatment. Condensed liquids are separated so that both the oil and water can be reused. Municipal and industrial facilities have long utilized solutions to address the issue of non-condensable gases and the issue of water fouling compounds. However, applying similar treatment technologies in the oilfield will require innovative engineering. This paper discusses the challenges of treating non-condensable gases and removing odor from condensate water created by TDU's in drilling applications.

### Introduction

Thermal desorption is widely used method of treating drill cuttings contaminated with non-aqueous base fluids. The main purpose of the thermal separation is to separate hydrocarbons from the cuttings. Prior to finding applications in the oilfield, thermal desorption was used in industrial environmental

applications. EPA accepted thermal desorption for removal of organic contaminants from soils, sludges, or sediment (1). Thermal desorption has been utilized to clean polluted soils at many Superfund sites in the US as well as pollution sites in other countries. Safety of thermal desorption working for EPA jobs at Superfund sites in the US was proven over many years. To further ensure safety, EPA verifies proper handling of all material at every stage of the process. Operators take measures, such as covering loose soil, to control dust and vapors during soil excavation and treatment. If necessary, gases produced in a desorber are collected and treated before release into the environment (1). Water is also collected, analytically tested, and then treated at industrial water treatment facilities. In other words, careful engineering control at every stage of the process is a key factor of process safety and efficacy. Several companies that are providing services in the oilfield have also worked at EPA sites and strongly adhere to highest levels of safety and service quality.

Oilfield service companies successfully adopted and further developed thermal desorption technologies for removing hydrocarbons, synthetics and oils from cuttings that allowed companies to move thermal desorption directly from EPA sites to the land-based oilfield waste management facilities and become players in the oilfield services market. Major oilfield service companies, however, alone with strong land-based presence, developed thermal desorption for offshore use where small footprint, use of electric power, higher capacity of the equipment and specialized safety factors were prime considerations.

Thermal desorption technologies in the oilfield today are based on low temperature indirect heating or heating from mechanical friction. Incinerators have limited application in the oilfield because incinerators do not recover oils and hydrocarbons, produce significant amounts of carbon dioxide, and require relatively large footprint.

A thermal desorption unit's (TDU) main components are feed hopper, process module, scrubber, condenser, heat exchanger, cooler, and separator (Figure 1). The design of these components differs as does the source of power used for

heating. The process module may be heated using burners that reuse the desorbed oil as a fuel source (Figure 1) which lowers fuel cost and minimizes the need for fuel to be delivered to the TDU location. Other designs use induction heating and thermo-mechanical technology but will rely on mobile generators or the electrical grid power. The thermal desorption process starts when the feed is loaded into the process module via the feed hopper and then heated. During the heating phase, liquid components vaporize separate from solids. Next, vaporized liquids are cooled and condensed. Oil and water are separated into separate streams and leave the unit. Desorbed solids are transported out of the process chamber and cooled to allow safe handling after these solids leave the unit.

### **Influences of chemical composition and treatment goals**

Mineralogy and chemical composition of formations drilled obviously vary, yet these cuttings form the inert portion of a thermal unit feed. Fluids associated with drill cuttings may contain salts, man-made chemicals, naturally occurring organics and dissolved minerals. Small amounts of slop water or wash water can also be part of the feed. The amount of oil and water in the feed is usually limited to ensure required capacity and prevent process upsets. Units that based on thermomechanical, friction are generally more capable of processing mid-weight invert emulsion drilling fluids. Characteristically, the capacity of any TDU decreases with increasing concentration of oil and water content in the feed.

The heat applied during thermal desorption will separate volatile compounds like oils, synthetic oils, and water are vaporized. Some hydrocarbons, oils, chemicals, and minerals may change form or composition when heat is applied. Due to the chemical composition of the original feed, some gases made not condense in the condenser unit and may require additional treatment to comply with regulations to be safely released into the environment.

The ability of a base fluid used in invert drilling fluids to withstand heat decomposition is important. Olefins are known to be more stable when subjected to thermal desorption and usually have minimal by-products in terms of decomposition of the carbon-chains. Esters decompose more readily and undergo significant change during thermal treatment. Odor and darkening of the color in all types of oil is usually occurs.

The nature and composition of the feed will define the concentration thermal treatment by-products, such as non-condensable gases (NCG), water pollutants, bacteria, and solids particle sizes. While the concentrations of such contaminants may be wide, the final goal for minimization of these unwelcome components is always narrow, particularly, if the goal is a “zero discharge” (Table 1).

### **Microbiological influences and its mitigation**

Bacteria are found everywhere. Drilling fluids and oilfield waters are source and a host for a variety of microorganisms. Drill cuttings carry bacterial load of the original formation drilled and any fluids and soils it encountered. Both, aerobic and anaerobic bacteria can be present in the thermal treatment

feed.

Aerobic bacteria need oxygen but can survive in dormant stage in the oxygen deficient environments. Aerobic bacteria generally are not a concern in recovered after thermal desorption fluids. Water after treatment contains minimal amounts of aerobic bacterial food sources, aerobic bacterial count is usually acceptable. If the water stream after thermal unit has little or no contact with outside environment, chances for re-contamination are limited. However, SLYM were reported in water storage vessels downstream of TDU's. These bacteria form protective membranes commonly described as “slime” and can live in the oxygen-deprived environments in a wide range of pH. SLYM can form beneficial co-existence with some anaerobic bacteria allowing it to survive and thrive in relatively oxygen rich environments (3).

Anaerobic bacteria, apparently, often survive thermal treatment processes in a dormant form, or spores, and may reappear in the active form when conditions are favorable. Favorable anaerobic conditions are created in the water storage tanks when tanks are closed to the environment. The use of closed tanks, in some cases, are directed by local regulations to prevent contamination to and from the outside environment. Furthermore, liquid/liquid separation efficiency in any thermal unit is always less than 100% and any recovered water will contain some oil. An oil layer forms when water is placed in a tank allowing dispersed and dissolved oil to further separate from the water. A thick oil layer may form in the tank over time. This oil layer “seals” the water creating anaerobic conditions for the water substrate. Third, water contains food sources, such as Sulphur and other compounds utilized by anaerobes (4).

Anaerobic bacteria, such as sulfate reducing bacteria will create significant issues when recovered water is collected and stored in tanks and vessels. SRB produce acetic acid and reduce sulfate ( $\text{SO}_4^{2-}$ ) to form sulfides, like hydrogen sulfide ( $\text{H}_2\text{S}$ ). Alkalinity is also produced in the same chemical reaction. Although many anaerobic bacteria can produce sulfide, SRB is usually relatively rapid sulfide producer capable of reducing other sulfur oxyanions ( $\text{SOx}^-$ ), such as sulfites and thiosulfates (4,5). Favorable conditions for SRB can be formed, for example, if the water is collected and stored in closed or pressurized tanks and the water depth is greater than approximately 1 ft.

The first step of bacteria mitigation is to assess and recognize the presence of bacteria. This can be done by properly sampling freshly desorbed water and water stored in tanks. Sampling for anaerobic bacteria and testing is rather involved and complex. Because samples are collected in small volumes, it is easy to expose samples to the air, sun light, chemicals, changing of pH and other, sometimes accidental factors and kill bacteria. If bacteria are killed during sample collection and transportation to the laboratory, expensive laboratory test cannot give any useful result. All samples must be collected anaerobically, using aseptic techniques, and delivered to the laboratory capable of performing anaerobic plate count testing in timely manner at optimum conditions.

The anaerobic plate count is the trustworthy test for anaerobic bacteria. Use of other methods can be problematic

because the desorbed water may interact with test broth composition turning the broth black much faster than SRB can grow and react with the broth. Two different anaerobic plate counts, for bacteria and for spores, are recommended. Alternatively, other tests may be used in the field, but results of these tests must be viewed as indicators only. SRB both reduce sulfate to sulfide and simultaneously produce alkalinity. Therefore any increase in alkalinity of the stored water can serve as an indicator or warning to check for bacteria presence.

Bacterial issues are mitigated by removing bacteria, removing bacterial food, or creating conditions incompatible with the bacterial life. Chemical biocides and oxidizers are added to disinfect the water and obtain residual effect. These chemicals are highly effective if properly applied. These chemicals can be difficult to handle and present some ecological dangers.

Process design should minimize or eliminate the use of chemicals for bacterial control to minimize overall cost. Newly developed treatment systems (Figure 1) use air as a first step for bacteria reduction and degassing of recovered water condensate. The water may be pumped through series of orifices to provide efficient contact with the air and then piped downstream. Any residual gases released in the process are collected in a separate stream and piped away. Storage tanks for water are aerated. The system includes provisions for use of chemicals to control wide range of bacteria. Hypochlorites, such as sodium hypochlorite and calcium hypochlorite, may be practical choice as an effective and readily available even in distant field locations disinfectants. Other chemical-free options for disinfection include UV light if the water to be disinfected has the adequate transmittance for the UV light to be effective.

### Removal and treatment of gaseous by-products

NCG are a common issue in industries that use similar thermal processes. NCG treatment units typically employ scrubbing, chemical treatment, and adsorption. Most of these technologies are incompatible with the oilfield requirements due to the large footprint or the need for large amounts of reagents. The pulp and paper industry's NCG treatment methods come the closest to be considered practical to work with TDU.

NCG is a concern because of its composition, properties as well as the ability to emit distinct foul odor. NCG are highly toxic. These gases contain Reduced Sulfur compounds that involve hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide that are usually responsible for foul odor. NCG may also contain other pollutants, e.g. methanol, that are regulated by some local environmental regulations. Reduced Sulphur gases, e.g. hydrogen sulfide and mercaptans, are acidic and adsorb into water phase condensate creating water quality issues and odors. Moreover, NCG are corrosive to carbon steel. Some components of NCG, e.g. methanol, can soften plastics and resins. Thus, NCG can cause significant issues if carbon steel, plastics or fiberglass reinforced plastic piping and vessels are used for equipment construction. NCG components are typically flammable in the presence of

sufficient oxygen and can be explosive if contained in a pipeline or vessel at specific conditions (5). Thermal desorption systems and auxiliary equipment are engineered to eliminate perilous conditions keeping NCG outside of flammable and explosive range.

Collection and burning of NCG approach was taken for oilfield system design. Gas treatment module (Figure 1) was included in the design to clean the solids from NCG. All desorbed stream, oil, water and solids were cleaned from NCG prior to exiting outside the system into the environment (Figure 2). Once collected, options for burning NCG may include, for example metered addition into TDU fuel stream that can yield a "fuel" with significant heating value, dedicated equipment, e.g. flares, regenerative thermal oxidizers, or other equipment capable to safely provide basic conditions for thermal destruction of NCG compounds. These basic conditions are temperature of 1600°F (871°C), residence time of 0.75 sec. and excess oxygen content of 3-4%. Notably, if any of these basic conditions are exceeded, the others can be reduced (6).

### Removal of contaminants and odors from desorbed water

Removal of contaminants from desorbed water started with separation of non-condensable gases away from the water stream. The aim of de-gassing is not only to collect and take away free gases, but also is to separate, or off-gas, gases that may still be dissolved. Pumping through an orifice, variety of orifices, or spraying, exposes the most surface area assisting dissolution. Chemicals suitable to assist this dissolution either as a gas or as suspended solids can be injected into the water stream prior to the passing the water through these orifices. The example of the treatment option designed for natural gas fueled thermal desorption unit (Figure 1), separated and collected non-condensable gas could be flared or be burned as an addition to the fuel. Next, water could require additional chemical treatment to coagulate, flocculate dissolved solids and then remove suspended solids. Later, microfiltration via self-cleaning filters or membranes was chosen to remove suspended solids to eliminate use of consumables. In a different step, oil could be removed using oil-water separators or oil removal filters. However, different treatment option was offered if storage tanks are used for desorbed water storage. When desorbed water is stored in tanks, it separates into layers where top layer is oil and the lowest layer is settles solids. In this case, small amounts of demulsifiers and settling agents can be added into the water to assist separation, destroy emulsions and settle solids. It is beneficial to store water in a tall tank that has small footprint on the ground and equipped with several draining ports to be able to drain out, in laminar flow fashion, separated oil, water and settled solids. If the water is released into the environment, advanced filtration, such as nano-filtration or reverse osmosis, conditions water to practically drinking water specifications. Notably, some of above steps can be used in different order depending on feed requirements and process conditions.

Electro-chemical treatment of desorbed water remains an open opportunity and has significant technological challenges

to be overcome. This technology of oilfield water gained popularity in the near past for treatment of flowback and produced water. However, different designs of electro-chemical water treatment units enjoyed different levels of success in terms of efficacy of treatment. Mainly, the technology application is to remove dissolved solids, oils and, at some extend, disinfect the treated water. These objectives are justly achievable only if electrodes materials are selected specifically for the specific ions to be removed. Electrochemical technologies work well in stable environments, when water quality is very consistent in terms of type and concentration of contaminates. Because desorbed water went through the thermal desorption, or thermal distillation, it may present an opportunity for successful use of electro-chemical treatment. The drawbacks, on the other hand, are that electrodes are the costly consumables; off-gas issues during electrochemical reactions in the electrolytic cell need to be mitigated; the use of strong acids for electrodes cleaning may create chemical hazards; high voltage related issues may be present, etc. Moreover, the electrode material selection would remain the greatest challenge for technology success.

### Removal of odor and color from recovered oil

Distinct strong order and darker color if compared with new base oil are typical for recovered desorbed oil. Apparently, if the recovered oil is used as a fuel for the TDU, no odor, or color, removal is needed. However, if the oil is reused for drilling fluids preparation, strong specific odor triggers mistrust in oil quality. Two basic steps may be essential to re-gain oil quality assurance and verify fluids performance expectations. First one is to analyze comparable samples of oils before and after thermal desorption in the analytical laboratory to compare oil conditions in terms of C-chains lengths and quantities. Colors also may be measured as per ASTM D1500 standard (7) and compared to Quality standards for the oil. If the recovered oil passed the test for its decomposition, next, odor and color can be removed.

Compounds responsible for odor and color are usually present in a fluid in very low concentrations, often measured in ppb. Odorous compounds most likely dissolved in the liquid that maybe both, oil and water, or only one at a time. Fine advanced filtration or treatment using activated charcoal, diatomaceous earth, organophilic clays or similar materials removes both odors and color. Obviously, different absorbers have different degrees of effectiveness and should undergo engineering selection prior to best fit for the application cleaning media. On practice, the recovered oil should be properly placed in contact with the cleaning media, allow for residence time and then mechanically separated from it. Desired result should be lighter in color and practically odorless oil. Variety of mechanical separation, in this case filtration, equipment is available on the market allowing selection of economically suitable equipment. Selected equipment should deliver acceptable media dryness after filtration and have suitable operating and handling requirements. To reduce waste streams, the cleaning media may be regenerated or cleaned in TDU for reuse or responsible disposal.

### Conclusions and Discussion

Treatment of NCG are common in many municipal and industrial thermal treatment processes. Thermal treatment facilities used in the oilfield are smaller and must adapt municipal and industrial technologies to meet the specific challenges for the oilfield both technical and economic.

In the oilfield, treatment of NCG, water and solids depend on the local environmental regulations that govern rules allowing release of gases, water, and solids into the environment. Meeting, but rather exceeding, local regulations and company environmental standards is a driving force behind environmental treatment technologies. Zero-discharge requirements already stipulated in some areas around the globe may be substantially extended in the near future.

Understanding environmental regulations, emission testing and process design will mitigate NCG treatment issues. Use of smaller capacity, smaller footprint, designed with by-products treatment systems on-board thermal treatment units close to the point of drill cuttings generation may mitigate or eliminate emission issues. A variety of technologies exist that can be used as a “building blocks” to achieve suitable solutions for the oilfield market can be engineered. Process engineering expertise is necessary to realize potential of thermal treatment technology for drill cuttings and oil-rich slurries.

Regulatory requirements and economic considerations play the key role in the waste management decisions. Any by-products or any process can be treated to required standards, however, in many cases such treatment is economically challenging. Equipment manufacturers should be encouraged and supported by the industry users to develop thermal desorption, or any other separation, equipment that consider whole cycle of life of drilling fluids and its constituencies.

### Acknowledgments

Authors would like to thank engineers of Quality Group Belgorod for assistance with this paper.

### Nomenclature

<i>NCG</i>	= <i>Non-Condensable Gases</i>
<i>EPA</i>	= <i>Environmental Protection Agency</i>
<i>SRB</i>	= <i>Sulphur Reducing Bacteria</i>
<i>SLYM</i>	= <i>Slime Forming Bacteria</i>
<i>NCG</i>	= <i>Non-condensable gases</i>
<i>UV</i>	= <i>Ultra-violet</i>
<i>ppm</i>	= <i>part per million</i>
<i>ppb</i>	= <i>part per billion</i>
<i>cfu/mL</i>	= <i>colony forming unit per milliliter</i>
<i>cgs</i>	= <i>gram per cubic centimeter (g/cm<sup>3</sup>)</i>
<i>ND</i>	= <i>non-detectable</i>

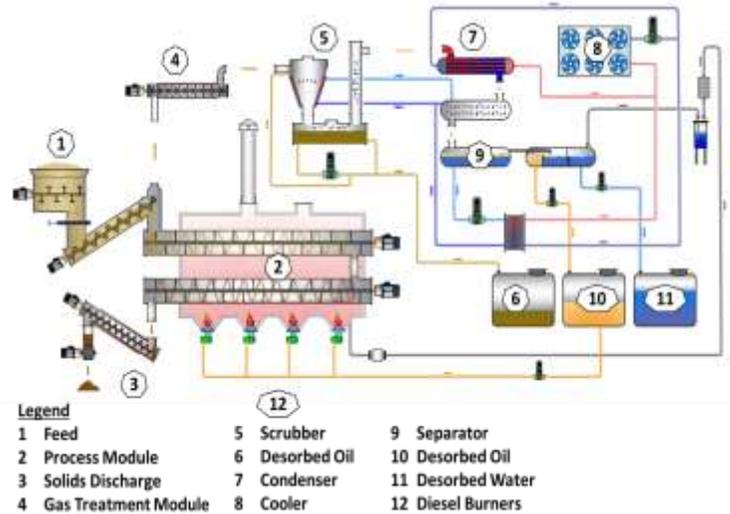
### References

1. A Citizen's Guide to Thermal Desorption, United States Office of Solid Waste and EPA 542-F-12-020 Environmental Protection Emergency Response September 2012 Agency (5102G), [www.epa.gov](http://www.epa.gov)

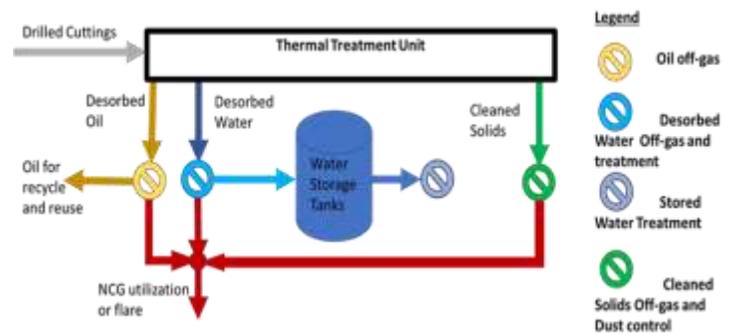
2. Cullimore, Roy: Microbiology of Well Biofouling, 1999 CRC Press LLC., 1999.
3. Widdel, F., and Hansen, T. A.in: A. Balows, H. G. Trüper, M. Dworkin, W., Harder and K.-H. Schleifer, (eds.): The prokaryotes, 2nd. Edn., Springer-Verlag, New York, 1992.
4. Cypionka H., Sulfate-Reducing Bacteria. In: Reitner J., Thiel V. (eds) Encyclopedia of Geobiology. Encyclopedia of Earth Sciences Series. Springer, Dordrecht, 2011.
5. Sax, N.I.: Dangerous Properties of Industrial Materials, Fourth Edition, Van Nostrand Reinhold, 1975.
6. Green D.W., Perry, R.H.: Perry's Chemical Engineering Handbook, Eight Edition, McGraw-Hill, 2007.
7. ASTM D1500 - 12(2017), Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale), ASTM Volume 05.01 Petroleum Products, Liquid Fuels, and Lubricants (I): C1234-D3709, 2017.

**Table 1.** Variety Water Quality Before Treatment and Zero Discharge Targeted Treatment Goals.

Analytes	Unit	Assumption for the Range of Initial Water Quality Directly after TDU	Assumptions for the Range of Initial Water Quality from Storage Tanks	Required Treatment Goals. Assumptions for of the Final Water Quality After Treatment
pH		6 - 8	6 - 8	7
Density	g/cm <sup>3</sup>	~ 1	~ 1	~ 1
Total Hardness	mg/L	<1	<10	<10
Total Alkalinity	mg/L	100 - 900	100 - 900	< 300
Nitrates (NOx)	mg/L	0 - 1000	0 - 1000	<100
Sulfates (SOx)	mg/L	1 - 1000	1 - 1000	<100
Total Sulfides	mg/L	<200	<100	<10
H <sub>2</sub> S	mg/L	0 - 40	1 - 40	ND
Hydrocarbone/Oil	mg/L	50 - 800	50 - 800	< 2
Anaerobic Bacteria	cfu/mL	< 100 or N/D	1K - 100K	ND
COD	mg/L	100 - 5000	100 - 7000	<100
BOD	mg/L	100 - 1000	100 - 5000	<100
VOC	mg/L	< 1000	< 1000	ND
Odor		Strong	Strong	Practically ND



**Figure 1.** Schematic diagram of Thermal Treatment Unit design with indirect heating using recovered desorbed oil energy source.



**Figure 2.** Schematic diagram of by-products treatment placement.