Recovering Valuable Byproducts from Oil and Gas Wastes

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ABSTRACT

An oft-neglected component of wastes generated during drilling and completion of oil and gas wells in shale plays are the drilling fluids, drilling wastes, and assorted liquids that are captured and require disposition. These streams contain substantial amounts of suspended solids and contamination from the formation being accessed, as well as potential valuable recoverable components such as crude oil and other valuable hydrocarbons. Treatment is required for these streams prior to either reuse or deep well disposal. In addition, significant revenue can be generated by recovering the valuable byproducts.

INTRODUCTION

The act of drilling oil and gas wells, conventionally or for hydro-fracturing requires the use of water based and/or hydrocarbon based drilling mud. These materials are typically defined as drilling fluids. This material lubricates drilling operations, cools the drill head, and transports drill cuttings to the surface. Various products are combined in precise quantities in order to optimize the drilling operation. This drilling mud is then recycled as much as possible before being hauled to disposal.

In the process of drilling the well, or during well completions, the treatment or disposal of wasted drilling mud and flow-back water is required. While some components of the flow-back water and drilling mud must be disposed of, there is a significant financial and environmental benefit to isolating some of the more valuable mud and wastewater components for sale and reuse.

DRILLING FLUID COMPOSITION

The drilling fluid chemistry is created specifically for each drilling operation. Not only is the chemistry specific to each drill operation, but it is changed during the operation due to bore hole depth and/or observed conditions. There are three primary classifications to these fluids; water-based, oil-based, and synthetic-based (Rehm, 2012).

Water-based mud (WBM): At its most basic, water-based mud system begins with water followed by the incorporation of clays and other chemicals to create a homogenous blend resembling something between chocolate milk and a malt (depending on viscosity). The clay (called "shale" in its rock form) is usually a combination of native clays that are suspended in the fluid while drilling or specific types of clay that are processed and sold as additives for the WBM system. The most common of these is bentonite, frequently referred to in the oilfield as "gel". Gel likely makes reference to the fact that while the fluid is being pumped, it can be very thin and free-flowing (like chocolate milk). However when pumping is stopped the static fluid builds a "gel" structure that resists flow. Sufficient pumping force is applied to "break the gel" and resume flow. At this point the fluid returns to its previously free-flowing state. Many other chemicals (e.g. potassium formate) are added to a WBM system to achieve various effects. These include controlling viscosity, improving shale stability, enhancing drill rate of penetration, and cooling and lubricating equipment. Water-based fluids are considered the most environmentally and operator friendly (Rehm, 2012). In offshore locations these fluids are typically discharged after solids removal through an NPDES permit.

Oil-based mud (OBM): Oil-based mud can be a mud where the base fluid is a petroleum product such as diesel fuel. Oil-based muds are used for many reasons, some being increased lubricity, enhanced shale inhibition, greater cleaning abilities, and reduced fluid viscosity. Oil-based muds also withstand greater heat without breaking

down. Oil based fluids drill a cleaner hole that than water based fluids as well as creating less sloughing and a smaller volume of drill cuttings (Rehm, 2012).

Synthetic-based fluid or mud (SBM): Synthetic-based fluid is a material where the base fluid is synthetic oil. Synthetic based oils include vegetable esters, olefins, ethers, and other similar type products. These products are used much in the same way as oil-based fluids in the use of weighing agents. Synthetic-based fluids also cut cleaner holes with all the same benefits of oil based fluids. However synthetic based muds can be more expensive (Rehm, 2012).

Universal Additives: Drilling fluids can contain some form of biocides, surfactants, de-foamers, corrosion inhibitors, scale inhibitors, polymers, and clays. The reclaimed drilling fluids also contain inorganic, organic, dissolved and suspended material that is picked up from the formation during the drilling operation (Rehm, 2012).

WELL HEAD DRILLING FLUID TREATMENT

Due to the volume of drilling fluids required it is most economical to reuse drilling fluids to the greatest extent possible. Drilling fluid treatment focuses on the four primary components of recovered drilling fluid. Those being drill cuttings, drilling mud, water, and hydro-carbons (oils) (Pharis 1991).

Most drilling operations include a drill rig "backyard" setup that includes facilities to reclaim the drilling mud.

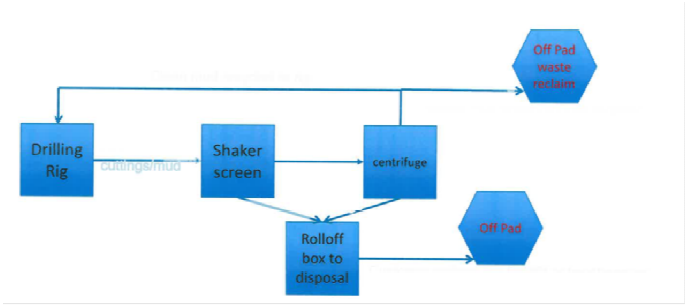

Figure 1 – Backyard Drill Rig Process Flow Diagram

The first step in treating drilling fluids at the rig is to run the fluid recovered from the hole through a vibrating screen known as a shaker screen or shale shaker. This screen separates most drill cuttings, which are then stored for disposal or to be treated for reuse.

Photograph 1 – Backyard Drill Rig

The fluid passing through the screen can still contains a large amount of solids. This fluid is typically run through one or more hydro-cyclones or centrifuges for additional solids removal. The higher solids fraction or the mud from the equipment is then sent to the source tank or pit to create the reclaimed drilling fluid (Pharis 1991).

The amount to which drilling mud is reused is limited. As the clay solids are passed through the hydro-cyclone the particles are sheared into smaller particles. When the clay particle size shrinks then the amount of chemicals required increases due to the larger surface area of the aggregate particles (see Table 1). This means that mud must be wasted at such a rate to maintain a satisfactory large particle distribution, observed by chemical usage, in the drilling fluid. Wasted drilling mud is then stored for offsite treatment and/or disposal (Pharis 1991).

	Mud entering system	Mud returning to system
Solids Content %	6.0	4.0
Avg Particle Size (µm)	50	10
Surface Area (acre/bbl)	5	16

Table 1 - Particle Size of Drilling Mud
(Pharis, 1991)

The clean water from the hydro-cyclones or centrifuges is either recycled in the drilling operation or stored for treatment and/or reuse offsite. It should be noted that clean drilling fluid water is significantly different in characteristics from flowback or produced water that is generated from oil/gas well development and oftentimes reused during hydraulic fracturing. The drilling fluid is typically lower in volume and dissolved solids, but higher in solids and drilling chemicals (Pharis 1991).

Oils and other hydrocarbons in the water following the shaker screen are removed by a skimmer or in an oil and water separator. These oils can be of good quality for immediate reuse or may become emulsified with the water and solids. Emulsified oils must be treated, typically offsite, before they can be reused.

Photograph 2 – Emulsified Oil

DRILL CUTTINGS TREATMENT

Treatment of drilling fluids during drilling at the rig location is based on optimizing usage of drilling fluid for the creation of the borehole and minimizing the need to transport waste materials. The waste cuttings removed by the shaker screens require treatment before the materials are of a suitable quality for disposal in a landfill of for their reuse. In addition, there is typically a “high suspended solids” wastewater volume that can be treated for reuse.

Drill cuttings can be reclaimed with proper treatment. If hydro-carbons such as diesel are used during drill operations then the drill cuttings can be blended with coal and burnt for energy recovery. Alternately the drill cuttings can be heated in an anoxic environment which vaporizes the hydro-carbons removing them from the drill cuttings. One such system manufactured by Thermtech is a thermo-mechanical cuttings

cleaner (TCC), The TCC is based on the basic principle of thermal separation. The oil based mud (OBM) cuttings are heated to a temperature sufficiently high to evaporate the oil (and water) from the mineral solids. By heating the waste to a temperature higher than the evaporation point of the base oil in the OBM. The oil and water will be condensed back to liquids in later process steps. A common name for such technologies is “thermal desorption” technologies.

There are different ways of heating the waste. In a TCC the heat is created by friction as opposite to indirect heating.

The TCC is based on a completely different principle than the indirect thermal technologies. The TCC converts kinetic energy to thermal energy by creating friction in the waste. A drive unit sets a series of shaft mounted hammer arms in motion inside a barrel shaped process chamber (also referred to as the hammermill or just the mill). The solid particles are forced towards the inner wall of the process chamber where the kinetic energy from the rotating arms will be transformed to heat by friction. The unit can run continuously, automatically controlled by an advanced Programmable Logic Controller (PLC) system. Frictional heat is constantly created by the hammering and motions.

The liquids evaporate and leave the chamber, new waste is pumped in, and solids are discharged through a cell valve. The hottest spot in the process is the waste itself. The base oil is under influence of high temperature for maximum a few seconds. The oil is re-used by all the largest mud companies as a component in new OBM.

Compared to other thermal desorption technologies most of the TCC benefits are related to the way the TCC is heating the waste.

An alternative thermal desorption technology is the Therma-Flite Holo-Scru® thermal desorption systems which volatilize and recover 99.5% of hydrocarbons from drilling mud. Holo-Scru® processes can accept feed stock with hydrocarbon percentages greater than 70%, effectively collecting and condensing water, diesel and other hydrocarbon vapors. In applications such as natural gas drilling where diesel and water constitute the liquid phase diesel is typically filtered and then resold or reused as a lubricant for future drilling.

Therma-Flite units in operation in the U.S. process drill cuttings from shale drilling. This feed stock is generally 10% to 30% diesel, and 20% water. Recovery rates for diesel typically range from 97% to 99.5%.

The standard Therma-Flite system includes a feed screw with loading trough, or for applications when feed storage is required, a feed hopper with integrated live bottom. For low viscosity drill cuttings containing diesel and water a positive displacement pump is used to feed the unit. Feed stock is discharged from the feed screw into a double knife-gate airlock. The airlock cycles to allow feed to enter the airlock chamber while maintaining a seal to the desorption chamber. For added safety the airlock includes optional fittings for a nitrogen or CO_2 purge which can be used to insure any air remaining in the airlock is displaced prior to the airlock cycling, and discharging the feedstock into the desorption chamber.

The heart of the system, the desorption unit, includes intermeshed Holo-Scru® rotors. In

this chamber feed stock is heated under a slight negative pressure in a sealed, anaerobic environment. Heating in this system is indirect. Thermal fluid is circulated throughout the Holo-Scru® rotors and outer jacket of the desorption chamber. The proprietary Holo-Scru® dual rotor design is self-clearing and feed stock which might otherwise bake on to the rotors and is easily removed. Different mixing programs may be set in the PLC which will increase the heat transfer into the feed stock.

A variety of heat transfer fluids may be used to heat product up to 850-degrees Fahrenheit. A second stage system can be incorporate to heat the product to above 1,200-degrees Fahrenheit. Most feed stocks may be de-volatilized to less than 0.05% remaining hydrocarbons. As the heated solids exit the desorption chamber they pass through a second airlock and into a cooling screw conveyor. In the cooling screw solids are indirectly cooled by circulating water through the jacketed wall of the screw. The temperature is further reduced by direct-contact quench cooling via atomizing sprays along the top of the cooling screw housing. The vapors exit the unit into a Venturi-effect, multi-stage condenser. Cooled and filtered condensate is used as the condensing fluid. The Venturi-effect condenser is highly-efficient with less than 0.01% hydrocarbons remaining in the non-condensable stream. The non-condensable stream is released through a duct to the air intake on the diesel generator providing power. The drill cuttings after these processes are clean and can be disposed of or reused. Typical reuse applications can be in asphalt or concrete aggregate or for road base construction.

Photograph 3 – Thermal Treatment System

DRILLING MUD TREATMENT

The waste drilling mud and other high-suspended solids wastewater must be treated for the removal of the large amount of suspended solids. The treatment process typically begins with chemical addition of an oxidant to break down any surfactants or de-foamers which would negatively impact the downstream treatment process. The pH is then adjusted to optimize coagulation and solids removal. Coagulants used can be iron, aluminum, or carbonate based. Carbonate based coagulants can serve a dual purpose of adsorbing oils and other hydro-carbons from the drilling mud.

The removed solids at this point are usually of sufficient concentration that they can be dewatered in a filter press, centrifuge, or similar treatment process. The filtrate from dewatering operations can then be sent to a treatment facility that handles drilling fluid water. While the mud solids can be disposed of in a landfill they can also be reused in various applications. Favorable

data has shown that drilling mud could be used to line landfills, be land farmed, or mixed with organic mater to aid in wetland restoration. However regulatory approval for some of these options is still an obstacle (Stewart 2012).

DRILLING WASTWATER TREATMENT

Wastewater from drilling operations undergoes a similar chemical treatment regiment as mud processing. Oxidants, pH adjustment, and coagulants are added in a staged series of treatment vessels. Biocides may need to be added as well. Gravity separation can then be used to remove solids. A skimmer on the gravity separation process can serve to remove any oils in the wastewater. Alternatively a dissolved air floatation (DAF) process can be used instead of gravity separation. Since the oils and solids will be combined in the solids from the DAF it will not be possible to reuse any oil.

Following gravity or DAF solids removal the wastewater is filtered either through sand, mixed media, or bag filters. The filtered water can then be re-used for drilling water makeup or for hydro-fracturing.

Oil treatment is only typically necessary if the oil recovered from drilling operations has become emulsified. Emulsion breaking is typically done in a batch process where acid is added to the rag oil before it is heated. This breaks the hydro-carbons and oil from water and solids. The oil and hydro-carbons can then be skimmed off for reuse. The solids-laden wastewater is then sent to the head of the wastewater treatment process, typical of that described above, for treatment and reuse.

EXAMPLE TREATMENT FACILITY AND DATA

The Marcellus shale region has led the industry in treating and reusing water and wastes generated during the drilling, completion, and production phases of well development. One commercial facility has been operating in Masontown PA, since 2010, servicing the industry within a 150 mile radius. When customers determine that their water or wastes cannot be reused on the well location they transport the drilling wastes, flowback water and production water to the plant via vacuum tanker trucks. Plant personnel pre-screen the incoming material for various contaminants prior to entry into the system to determine if the material can be adequately treated, and if so, the appropriate treatment regime.

Typical contaminant levels are provided below for the incoming waste water. As can be seen from the data, the influent waters to be treated are extremely variable, which poses operational challenges in treatment.

Parameter	**Influent Range (mg/L)**
Calcium	150 - 7,000
Strontium	10 - 1,500
Sulfate	0 - 1,500
Barium	25 - 2,000
TSS	200 - 2,000
TDS	3,000 – 80,0000

Table 2 – Typical Influent Wastewater Characteristics

The plant has a hydraulic capacity of 1 MGD. The facility consists of chemical mix

tanks, clarifiers, oil skimming, finished water storage, sludge preparation tank, and sludge dewatering equipment. The incoming material is fed into one of three chemical mixing tanks where its pH is adjusted with sulfuric acid, hydrochloric acid or sodium hydroxide to be near neutral.

The treatment process for most wastewaters into the system begins with adding potassium permanganate in the mix tanks oxidize metals to a higher valence state and to increase the ORP to minimize anaerobic conditions. Produced water, containing barium, may be added to the other wastewater stream so that ba0rium sulfate can be precipitated in the clarifiers.

After the mix tanks the wastewater is pumped to a primary clarifier for settling of heavier solids. Coagulant aid and emulsion polymer is added to assist in proper settling. The effluent from the clarifier is then pumped into a second mixing tank where soda ash is added. This will help precipitate calcium and remove it from the return water. The wastewater then flows by gravity to a secondary clarifier where emulsion polymers are added to aid in the removal of additional solids.

Effluent from the secondary clarifier flows by gravity through a trough that is quiescent enough to allow oil and other hydrocarbons to float to the surface and be skimmed off using a belt skimmer. In the hotter summer months, bleach may be added at this point to prevent biological growth. If required, the pH may be adjusted following the removal of oil. The trough flows into a finished water tank, where it is temporarily stored prior to sale.

Settled solids from each of the two clarifiers are pumped to a sludge storage tank. This sludge is then pumped through a plate and frame filter press which produces a solid cake. This cake passes the paint filter test prior to disposal at an approved landfill.

The primary contaminants removed in the process are sulfate, iron, barium, calcium, strontium and various other suspended solids. Oil is recovered from the clarifiers and skimming trough it is transported for reuse at other wells. Currently additional facilities are being added to enhance the removal and recovery of natural gas liquids from the water generated from the Marcellus gas production.

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