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Removing Dispersed and Dissolved Hydrocarbons from Water Using Adsorption Media Systems with Multiple Regeneration Processes

Caleb Smathers, Tommie Jackson, Scott Buckwald, Raul Gonzalo, and Ryan McPherson, ProSep

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Abstract

Clean water is a precious resource in the world. For decades, nations and companies have focused on delivering contaminant-free clean water as a byproduct of industrial processes. ProSep's Osorb Media Systems (OMS) deliver oil free water from the oil and gas industry's most challenging onshore and offshore water treatment applications. OMS not only remove challenging hydrocarbon contaminants from produced water, they do so with high efficiency over a long media life. Osorb uses a physical adsorption mechanism to remove hydrocarbons from water. Additionally, the unique structure of the media enables the adsorption isotherm to be reversed thus releasing the captured hydrocarbons from the media. The regeneration process is completed using a combination of physical and/or thermal processes that enable hydrocarbon recovery.

Two pilot tests and one field test were completed demonstrating the OMS treatment and regeneration capabilities for both dispersed and dissolved oil removal. Three different regeneration methods were found to be effective. The first pilot test demonstrated over 99% removal of dissolved hydrocarbons throughout 28 water treatment and steam regeneration cycles. A second pilot test demonstrated a 2.6:1 (wt:wt) recovery of crude oil from Osorb while maintaining efficient water treatment. The field test had eight regenerations (five with steam and three with natural gas) completed and the media maintained 98% removal efficiency and averaged <1 mg/L of dispersed oil in the effluent water.

OMS provide a proven technical solution along with the economic feasibility to treat dissolved and dispersed hydrocarbons from water which have proven challenging for the oil and gas industry.

1. Introduction

The oil and gas sector generates an estimated 70 billion bbl of contaminated water from the extraction of crude oil and natural gas (Boysen, 2013). As oil and gas reserves are reduced, production companies are forced to extract from areas that generate higher volumes of produced water as well as implement advanced recovery techniques. For example, production companies increasingly use enhanced oil recovery methods (EOR) like chemical enhanced oil recovery processes (CEOR) to increase the total oil recovery from a reservoir by as much as 30% (Walsh, 2012). The produced water generated by these advanced extraction techniques alter the water/oil mixtures in such a way that the efficiency of conventional water treatment technologies, which rely on gravity and coalescence, are reduced by as much as 50% (Walsh, 2012). Advanced water treatment technologies are needed to replace the conventional technologies that cannot efficiently treat the produced water generated by these new production techniques.

The use of adsorption media is one method being investigated in the oil and gas industry to address the growing water treatment challenges (Boysen, 2013). Osorb is one adsorption media made from organically modified silica and manufactured for water treatment applications. Adsorption media are beneficial to gravity separation techniques, especially in CEOR cases, because adsorption media do not rely on viscosity, density, and oil droplet sizes for efficient oil removal. One disadvantage of adsorption media is that most require frequent replacement due to inefficient regeneration methods or the inability to be regenerated altogether. Osorb has unique properties that allow efficient regeneration by different, effective regeneration processes, such as chemical and thermal, without damaging the media.

2. Technology Description

The unique structure of Osorb created during the manufacturing process is a highly porous, hydrophobic, and organophilic particle (Edmiston, 2016). The internal structure of the media is comprised of bonded benzene rings to a siloxane backbone, Figure 1.A. The benzene ring is an active site that adsorbs other organic species, such as hydrocarbons, through physical interactions like, pi-pi interactions and Van der Wals forces (Edmiston, 2016). The linkages within the media's pore structure are slightly flexible and expand during the adsorption process. The image in Figure 1.B shows Osorb expanding as it captures up to 6x its mass in acetone (Edmiston, 2009). Edmiston has described this expansion as increasing the active surface area for adsorption which provides higher than expected adsorption capacity (Edmiston, 2009).

The key characteristic of Osorb is the reversible physical adsorption of organics because hydrocarbons captured during water treatment can be recovered through a regeneration process. Osorb's effectiveness is retained through the regeneration and recovery process, enabling Osorb to be reused multiple times with current estimates suggesting the media can last for up to 20 years.

2.1 Technology Theory of Operation

Water Treatment using OMS is simple because all that is required is contact between the media and contaminated water. The media is supplied in 250-500 µm particles and contained using media retention screens for water treatment and regeneration. The density and hydrophobicity of Osorb results in a fixed bed that is neutral to positively buoyant during water treatment. Water treatment vessels are designed with water flow from bottom to top to ensure laminar flow and to minimize the potential for channeling. Flowing water from bottom to top benefits the regeneration process because it allows for slight fluidization of the bed which releases solid particles captured in the fixed bed. The key advantage of the physical adsorption process is the ability to reverse the adsorption during the hydrocarbon recovery and regeneration process. Osorb is selective in the hydrocarbons it removes from water and the same mechanism that determines the rate of adsorption during water treatment is reversed to remove the hydrocarbons adsorbed to the media. The recovery/regeneration process has been specifically developed using physical and/or thermal methods optimized to reduce capital and operational costs (ProSep, 2015).

The thermal regeneration process can use multiple fluids, such as steam or natural gas, to evaporate captured hydrocarbons. The physical method for Osorb regeneration uses a solvent that displaces the hydrocarbons captured and removes them from the media bed (ProSep, 2015). Typically, a solvent is selected when the application is removing heavier hydrocarbons that cannot be evaporated. The selection of the solvent is fundamental in providing an economical solution and ProSep has developed a proprietary blended solvent (ProSep, 2015). The solvent is passed through the media bed and removes the captured hydrocarbons. When the physical regeneration process is completed the media is free of captured hydrocarbons but is saturated in solvent. To remove the solvent a thermal/evaporative regeneration step is completed.

3. Testing Methods and Apparatus

3.1 Media Stability through Multiple Steam Regenerations Methods

The effectiveness and durability of the media was evaluated using accelerated life cycle tests where the media removed hydrocarbons from water with repeated regenerations. The media's capacity to remove the hydrocarbons from water was measured between each regeneration.

Water treatment was completed using a fixed media bed of Osorb as presented in Figure 2. Water was pulled from a tote tank, injected with toluene for a target concentration of 400 mg/L, mixed and pressurized in a centrifugal pump, passed through the media for treatment, and collected in a second tote. Additionally, there were sample collection points immediately before and after the media vessel. Each water treatment test looked at the efficiency and capacity of Osorb to remove hydrocarbons given a flux rate ranging from 5-10 gal/min/ft^2.

After each water treatment cycle the media was regenerated using low pressure steam (55 psig / 300°F). Regeneration was completed as shown in Figure 3. A small electric steam generator created the steam that was passed through the media from the top to the bottom. The hydrocarbons are evaporated from the Osorb and carried with the steam to a condenser. The condenser converted the steam and hydrocarbons to liquids for separation in a collection vessel.

Samples were collected at the inlet and outlet of the OMS, then analyzed for the toluene concentration using one of two methods. Some samples were extracted using chloroform to concentrate the toluene 10x and analyzed on the on the DPS Companion instrument using gas chromatography coupled with a flame ionization detector (GC-FID). Other samples were analyzed on the FROG-4000 gas chromatograph coupled with a photoionization detector using a purge and trap (P&T) method. P&T uses air to evaporate and concentrate the toluene before analysis.

3.2 Hydrocarbon Recovery using LNG Regeneration Methods

Figure 4 outlines the steps used to simulate OMS regeneration using Liquid Natural Gas (LNG). First, clean Osorb was saturated with oil to simulate the capture of hydrocarbons during water treatment and create representative media requiring regeneration. This was completed by transferring unrefined 35 API oil directly into a container of new media. The media and oil mixture were combined and gently stirred. Additional oil was added to ensure all media in the container was fully saturated.

To regenerate the media and recover the oil, a closed loop LNG circulation system was used as seen in Figure 5. LNGs are transferred from a gas storage cylinder and into the Osorb vessel. The LNG extracts and removes the oil from the media then travels to a scrubber. In the scrubber the pressure is reduced to allow the LNG to flash to vapor form and the gas and hydrocarbons separate. The hydrocarbons were collected in the bottom of the scrubber and removed from the system while the gas was recovered from the top of the vessel for reuse.

After the regeneration was completed on each batch of Osorb it was analyzed for its water treatment capabilities. To determine the water treatment capabilities of the Osorb before and after the regeneration, a representative sample of each media was loaded into a small column and a saturated toluene solution passed through the media. A ***Capture Coefficient*** was calculated using the mass of Osorb used and the mass of toluene captured after a specified volume of water was treated.

3.3 Field Trial Testing Set Up and Methods

The capabilities of the media to perform effectively have been proven inside the laboratory and through pilot studies. To evaluate the performance of Osorb with live fluids, the technology was demonstrated during a field test in Oman in collaboration with Petroleum Development Oman (PDO) and Qatar Petroleum (QP). During this demonstration, an automated pilot OMS was placed inside the Marmul WTP to treat water from a CEOR operation utilizing polymer to increase oil recovery. As discussed previously, the addition of the polymer decreases the oil removal efficiency of conventional water treatment equipment that rely on coalescence and gravity. The OMS used adsorption to remove oil from water, providing a solution to PDO to remove the oil from the water.

The system was comprised of two water treatment vessels and all required regeneration equipment (Figure 6). The Marmul WTP operates at 20,000 m^3/day and the OMS treated a slip stream of 80 m^3/day. The system was placed downstream of the free water knockout and upstream of the primary water treatment system which consisted of induced gas floatation (IGF) vessels and nutshell filters (NSF), see Figure 7. Currently, the IGF and NSF cannot meet the oil in water (OIW) specification of <5 mg/L required by PDO because of the polymer present in the produced water. The goal of the demonstration was to reduce the OIW to <5 mg/L using only the OMS.

The field trial was set up to treat water using a single pass through one media vessel. The vessel would treat water until either hydrocarbon capture capacity or the differential pressure limit was reached. After the water treatment cycle, a regeneration was completed to remove the captured hydrocarbons and reset the differential pressure. The regeneration was a two-step process, first the heavier hydrocarbons were removed from the media using a specially blended solvent. The second step for regeneration evaporated the solvent from the Osorb using 300°F steam or a stream of natural gas.

Samples were collected before and after the OMS then analyzed by the PDO laboratory. The PDO laboratory extracted and concentrated the water samples with Trichloroethylene followed by analysis on a WilksIR Oil-in-Water Monitor.

4. Results

4.1 Media Stability through Multiple Steam Regenerations Results

The results from 28 water treatment and regenerations cycles are presented in Figure 8. The average inlet during all 28 cycles was 373 mg/L with a maximum inlet concentration of 2,072 mg/L. The average outlet toluene concentration after treatment with the OMS was 0.88 mg/L. It should be noted that 73% of the outlet samples collected recorded <1 mg/L toluene.

In Figure 8, the X-axis is the total volume of water treated by a single bed of Osorb and the Y-axis is the percent removal of toluene by the OMS. The vertical dashed lines indicate each regeneration (Regen #). The two reductions in toluene removal are attributed to a significant decrease in the inlet toluene concentration. (The average inlet during both decreases in water treatment was 11 mg/L, significantly less compared with the 370 mg/L average inlet concentration for all other sample times.) The OMS maintained its original, efficient water treatment capabilities over a four-month period of testing with 28 consecutive water treatment cycles. Additional water treatment (using a broader range of hydrocarbons) and regeneration cycles continue with the media maintaining performance.

The consistent water treatment observed after multiple regenerations support the media's ability to be reused for up to 20 years which significantly reduces the operating costs and system downtime for media replacement.

4.2 Hydrocarbon Recovery using LNG Regeneration Results

For each test 300 grams of oil contaminated media was regenerated. The process was repeated three times using three individual batches of oil laden Osorb. The oil removed from the media was recovered and measured following the LNG regeneration process. Table 1 shows that an average of 2.61 grams of crude oil was recovered per gram of media. This recovery ratio demonstrates the media's high capacity to capture crude oil. However, to determine the efficiency of the regeneration process further tests on water treatment capabilities were completed and are presented in Figure 9.

Figure 9 presents the results from water treatment testing following regeneration. New Osorb displayed a capture coefficient of 0.3 and the same media contaminated with oil has a reduced capture coefficient of 0.05. However, once the contaminated Osorb is regenerated using the LNG process the capture coefficient is restored to >0.34, as seen by samples Regenerated Batch 1, Regenerated Batch 2, and Regenerated Batch 3. The slight increase in the capture coefficient was most likely a result of media conditioning during the regeneration process. The conditioning helped prepare the surface of the media for increased interactions with the water phase as well as increased hydrocarbon adsorption.

The LNG regeneration pilot test successfully recovered the oil and restored its water treatment capabilities. Furthermore, the LNG was collected (allowing it to be reused) and a neat oil byproduct was produced. The successful regeneration and recovery using the LNG regeneration provides an alternative to the solvent regeneration method, mentioned previously. Additionally, we have also designed a closed loop regeneration process that utilizes propane and/or butane mixtures. The solvent characteristics of LNG removes the captured hydrocarbons from Osorb and operating across a small range of pressures and temperatures (P/T) separates the LNG components from the other hydrocarbons to recover the LNG for reuse. This method provides quick regeneration times at ambient temperatures with a significantly reduced operating cost because consumables are eliminated.

4.3 Field Trail Results

The field trial was completed over two years (2016 & 2017) and was split into two phases differentiated by the method of evaporation in the second step of regeneration. Phase 1 used steam to evaporate the solvent and Phase 2 used natural gas to evaporate the solvent.

A total of 4,300 barrels of produced water were treated by the same Osorb with eight (8) regenerations. The reduction of OIW is presented in Figures 10. The inlet OIW averaged 59 mg/L and fluctuated from

12-202 mg/L over the eight cycles while the outlet OIW averaged <1 mg/L. The increased OIW at the outlet in Cycle 4 was due to an incomplete regeneration and that was corrected in the subsequent cycle as observed by the recovered treatment efficiency in Cycle 5. The media maintained >90% oil removal efficiency after each regeneration cycle (excluding Cycle 4 as discussed above). A majority of the OIW removal exceeded 95% and when the water treatment efficiency was below 95% it can be attributed to the decreased inlet oil concentration. The OMS exceeded the <5 mg/L specification required by PDO in each water treatment cycle (excluding Cycle 4).

Furthermore, it was observed that both regeneration evaporation methods were successful. The water treatment efficiency remained above 90% and the outlet OIW concentration <5 mg/L regardless of regeneration method used. The successful field test, along with the pilot tests, support OMS as a viable technology to treat the challenging produced waters of the oil and gas industry.

5. Discussion & Summary

The removal of hydrocarbons from water is an important process for most facilities in the O&G industry to maintain efficient operation as well as protect the environment from harmful pollutants. The increase in petroleum extraction activities is creating new challenges and amplifying old constraints for water treatment methods. The industry requires new and innovative technologies that can efficiently treat the increasing volumes of water as well as the increasingly difficult waters being created from production processes. Many technologies are available to separate hydrocarbons from water and the OMS discussed in this paper provides a new, improved water management option.

The two pilot studies demonstrate the technology's ability to effectively remove dispersed and dissolved hydrocarbons from produced water as well as flexibility of regeneration methods. Steam, natural gas, and LNG regeneration methods proved effective at removing hydrocarbons from Osorb and restoring water treatment performance. Additionally, the Osorb showed no signs of degradation and maintained consistent water treatment performance after 28 regenerations. The long life of the media reduces the overall cost of OMS and simplifies the system operation.

The results observed during the pilot studies were verified during a field trial of the technology at the Marmul WTP (Operated by PDO). During this field trial, the OMS successful reduced the oil in water (OIW) from as high as 200 mg/L to an average effluent concentration of <1 mg/L. The regeneration effectiveness was verified because the media was regenerated eight (8) times using two regeneration methods. Furthermore, throughout all the treatment / regeneration cycles the media maintained a 98% average OIW reduction. The OMS achieved these remarkable results on a produced water stream where conventional technologies have failed for many years.

The ability of OMS to achieve the water treatment efficiency required for the new, challenging waters created from CEOR operations represents a paradigm shift in oil and water separations. Furthermore, this water treatment process allows for the removal of dissolved, dispersed, and emulsified hydrocarbons from water in a single step with the additional benefit of recovering the captured hydrocarbons. OMS's water treatment capabilities combined with the flexible, efficient regeneration methods to provide operators with a cost-effective option for produced water management.

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Figures

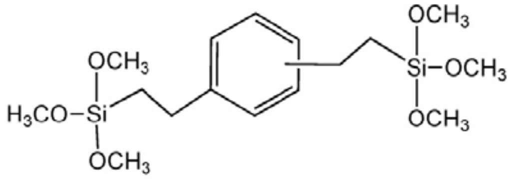

Figure 1.A – Building block of Osorb that creates a silica backbone connected by organic linkages (Edmiston, 2009).

Figure 1.B – Images of Osorb expanding as it adsorbs organics. (Edmiston, 2009)

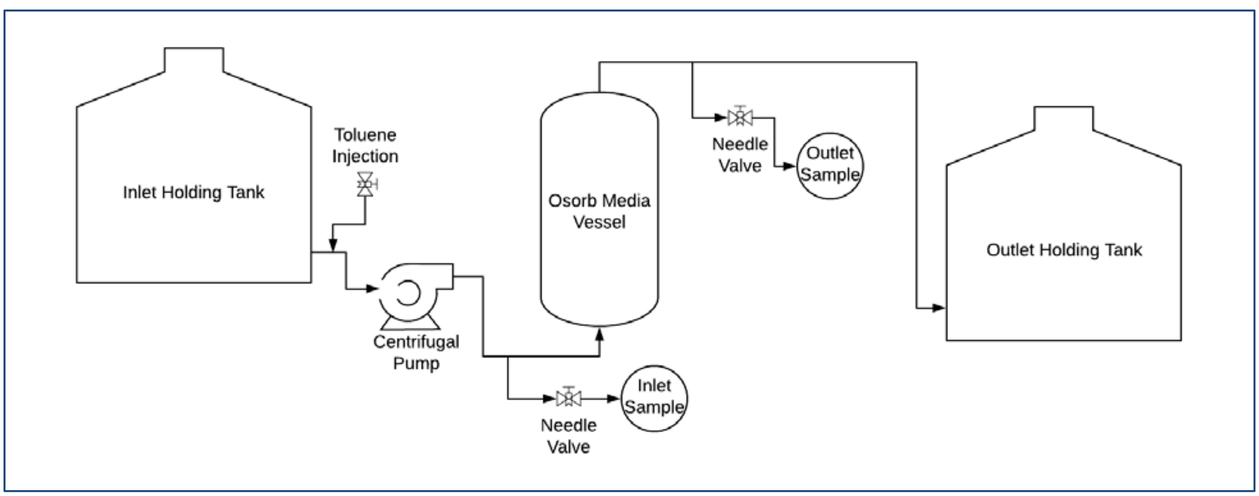

Figure 2 – Pilot Scale Water Treatment Flow Diagram

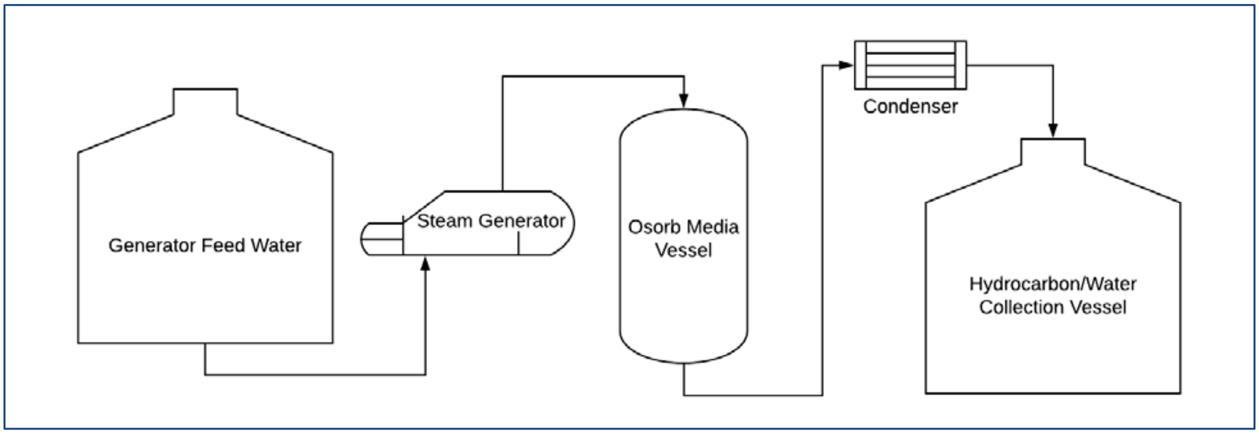

Figure 3 – Pilot Scale Steam Regeneration Flow Diagram

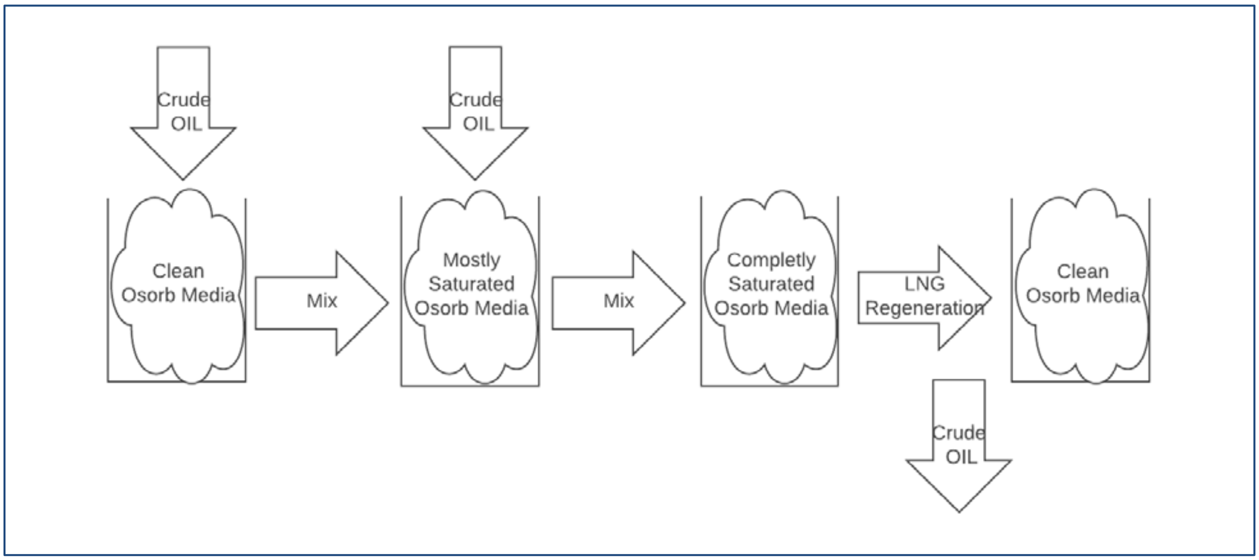

Figure 4 – Experimental testing steps for LNG regeneration of saturated Osorb.

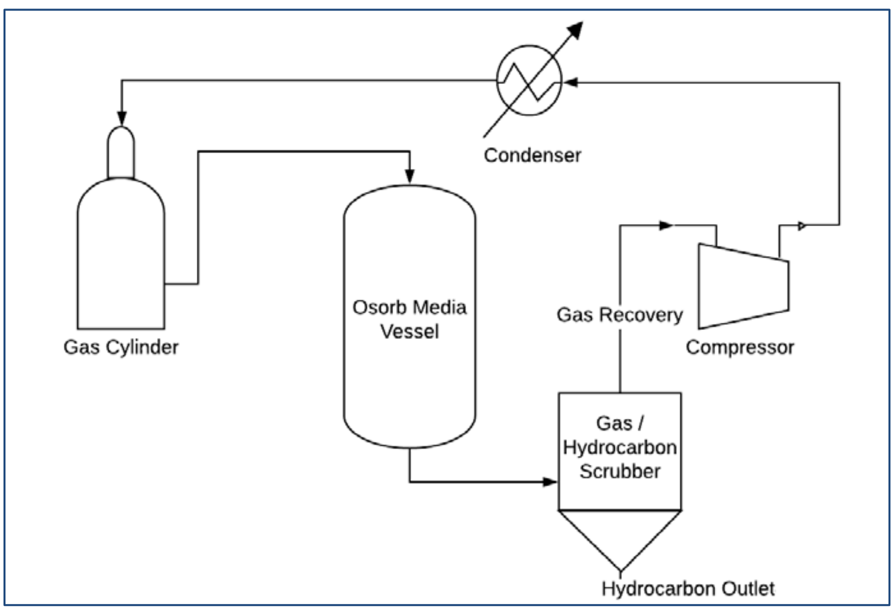

Figure 5 – LNG regeneration process flow used for pilot testing.

Figure 6 – OMS with Treatment and Regeneration Equipment

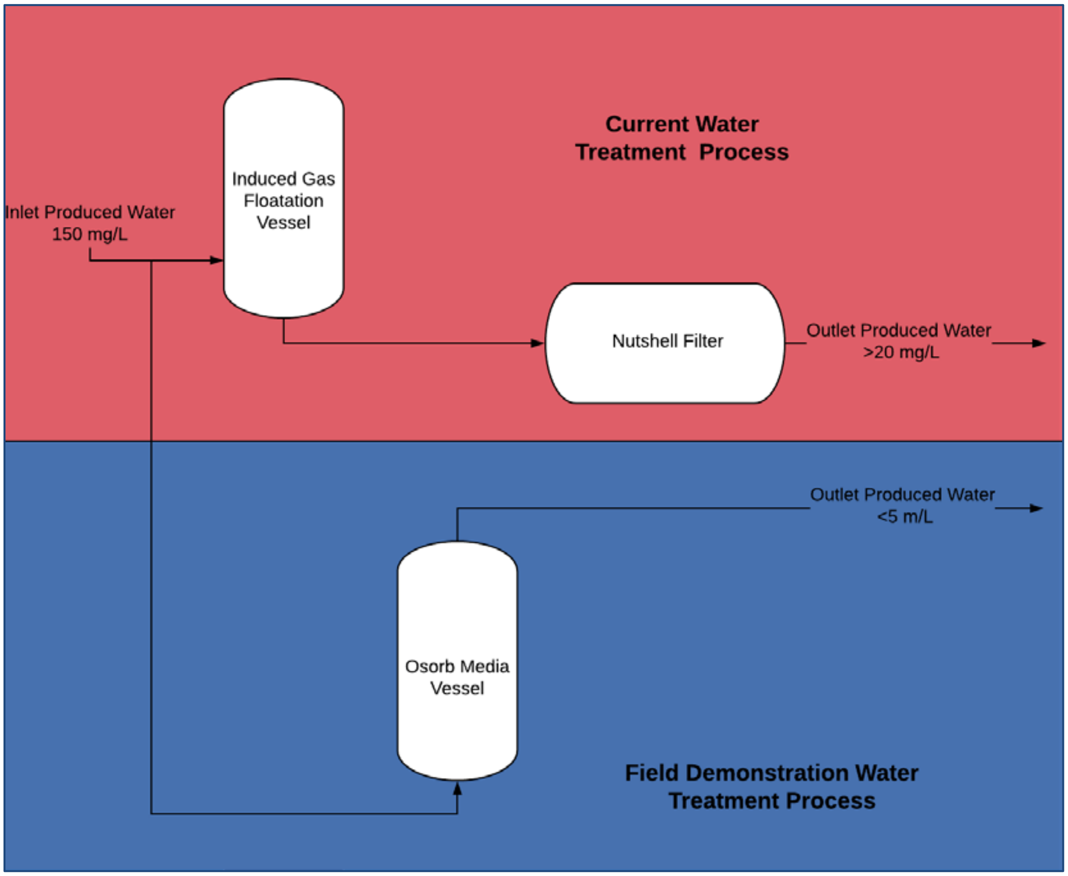

Figure 7 – Current Water Treatment process at PDO Marmul WTP (top/red) and OMS Water Treatment Process (bottom/blue) during Field Demonstration at Marmul WTP

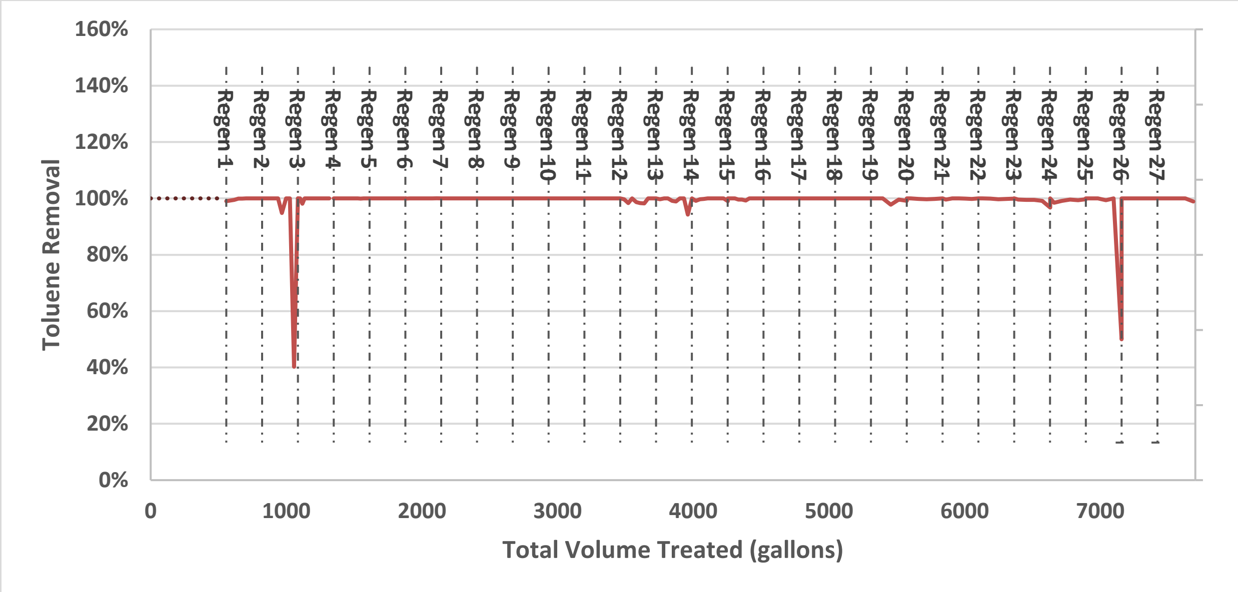

Figure 8 – Percent reduction of toluene using OMS after subsequent steam regeneration cycles

Table 1 Recover of Crude Oil from Osorb using LNG

Charge #	Initial Charge (g)	Crude Oil Recovered (g)	Ratio Recovered Oil/OM
1	302	221	2.65
2	308	226	2.58
3	325	244	2.59

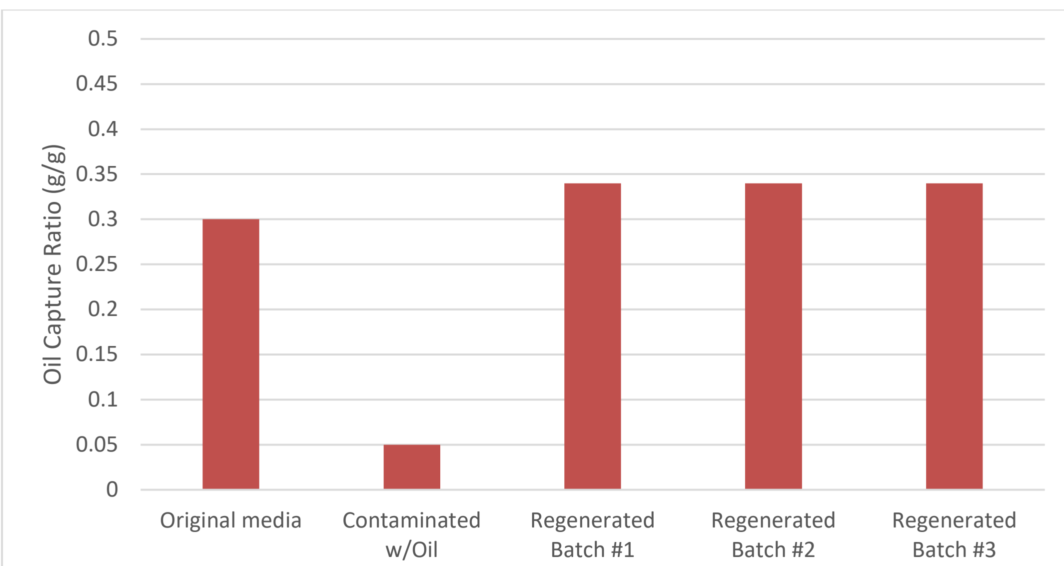

Figure 9 OMS Water Treatment Capacity before and after Regeneration using LNG Process

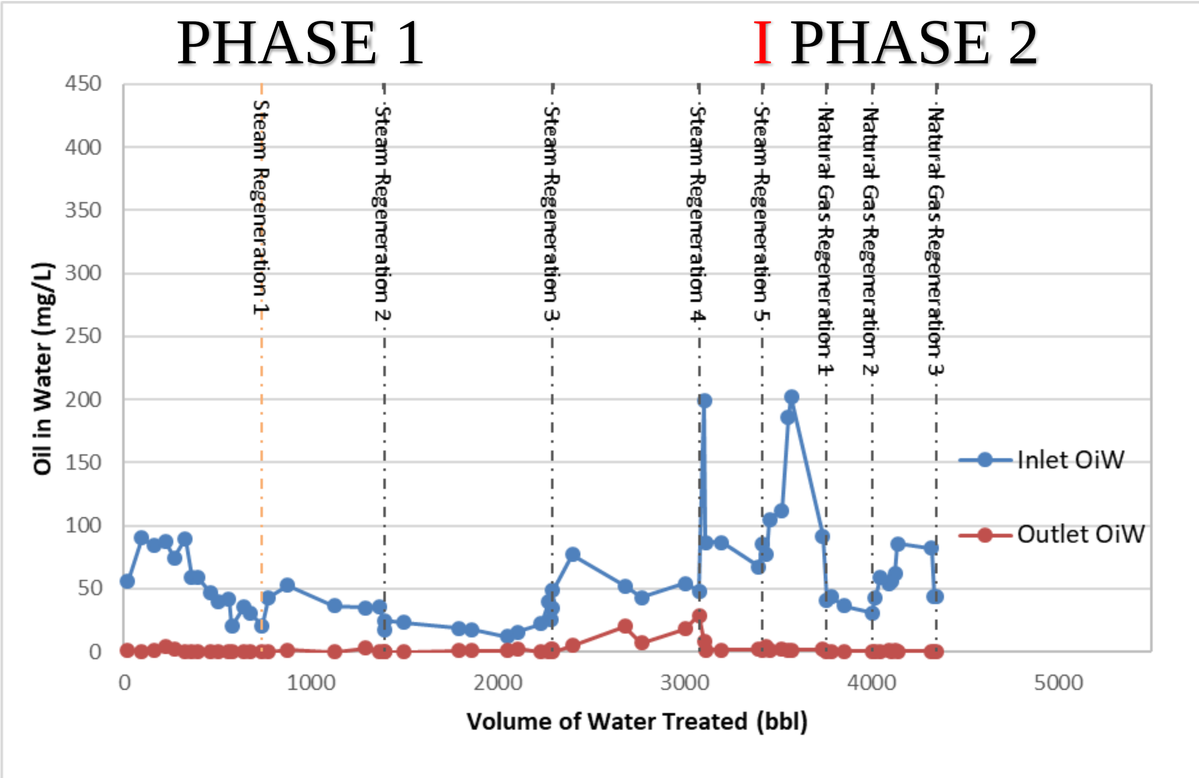

Figure 10 – Inlet and Outlet OIW Concentration across OMS during Field Trial