Osorb®: A Novel Technology in the Treatment of Produced Water
PW Unit #1 and Skid Unit #1

Jay Keener

Production Chemist and PW Unit #1 Program Manager
ABSMaterials, Inc. and PWA, LLC

Abstract

Osorb is a silica-based, swellable glass which can effectively capture 96-99.9% of organic compounds from a produced water stream. The glass is hydrophobic, allowing it to absorb up to eight times its own mass in hydrocarbons and VOCs without absorbing any water. After each use, the organics can be removed from the Osorb for recycling or disposal, and the glass can be reused hundreds of times. In bench testing, Osorb has been successfully used to treat samples of produced water from Wyoming, Canada, and the Gulf of Mexico. In testing the Wyoming produced water, the concentration of hydrocarbons was reduced up to 99.5% after treatment with Osorb. It was determined that this reduction remained effective when using as little as 1.25% w/v (kg glass/L water) Osorb and 60 seconds of contact time. Testing on the Wyoming produced water also indicated that sub-0° C temperatures do not inhibit the ability of Osorb to effectively absorb organic contaminants from the water. The treatment of the Alberta produced water resulted in a ~94.15% reduction in hydrocarbon concentration, though this treatment was carried out using 15% w/v Osorb. A pilot system, PW Unit #1, completed a successful field test in 2010, treating Clinton formation produced water. The use of Osorb in the system resulted in the successful reduction of the 277 ppm hydrocarbons in the Clinton water down to 0.1 ppm, a 99.9% reduction in hydrocarbon concentration. PW Unit #1 is undergoing final stages of development and fabrication and will be deployed in March 2011 to treat produced water in the gas fields in Wamsutter, WY. A second pilot system, Skid Unit #1, has completed two successful treatment tests on produced waters in Texas and Ohio, effectively targeting oil and grease, and BTEX compounds. Skid Unit #1 will be deployed to south Texas in February 2011.

Osorb glass is a new class of silica-based materials that have the capability of swelling and absorbing up to eight times their dried mass of neat, dissolved, or gaseous organic species. Osorb has been shown to possess the following attributes:

1. The rate of swelling is often mass transport limited.
2. Swelling is completely reversible if absorbed species are removed by evaporation or rinsing.
3. Absorption is non-selective and can be induced by non-ionic organic species.
4. The material is hydrophobic and does not swell in the presence of water or water vapor.
5. Swelling and absorption is driven by the release of stored tensile force rather than chemical reaction.

A formulation of Osorb which has proven very effective at treating highly contaminated produced water has been developed. Since much of the structure of Osorb is composed of aromatic rings, the glass has a particularly high affinity for the contaminants typically present in most produced waters: BTEX, VOC's, and hydrocarbons. Also, the high salinity of produced water increases the polarity of aqueous medium. Since the hydrocarbons and VOCs in the water are hydrophobic, this increased polarity causes the compounds to have a higher affinity for Osorb, which is also highly hydrophobic.

To date, multiple lab tests and initial field tests of the PW Unit #1 and Skid Unit #1 pilot scale systems have been completed. The lab tests examined the use of Osorb for the treatment of produced water. The field testing of PW Unit #1 was conducted to analyze a fluidized bed treatment system for larger scale produced water management. Field testing of Skid Unit #1 was conducted to analyze the ability of Osorb to treat produced water in a fixed bed treatment system.

Wyoming Produced Water Laboratory Testing

A sample of Wyoming produced water was collected for bench scale testing. Oil sheen was visible on top of the water sample, indicating the presence of high concentrations of hydrocarbon. A 20 mL aliquot of the water sample was agitated with 2 g Osorb (10% w/v) for 60 seconds. The removal of organics was immediately observable after the addition of Osorb. The Osorb particles, initially clear, swelled and turned brown. The treated produced water became clear and odorless. This physical observation indicates the transfer of organics from the water to the Osorb matrix. The produced water/Osorb solution was filtered to separate the Osorb from the resulting aqueous solution. The Osorb-treated and the untreated produced water were tested using a modified ISO 9377-2 method. The primary deviation from the ISO 9377 was the use of a mass spectrometer rather than a flame ionization detector. This was done so each organic component could be identified by comparison to a NIST98 mass spectral library.

Osorb was highly effective at removing the organic components from the produced water. Using 10% w/v Osorb (kg glass/L water) with a 60 seconds contact time resulted in ~98% extraction of organic species as measured by gas chromatography-mass spectrometry. As suggested by the visible sheen, most of the organic components were hydrocarbons. The post treated results showed some residual benzene and xylene compounds at 4 and 9 minutes.

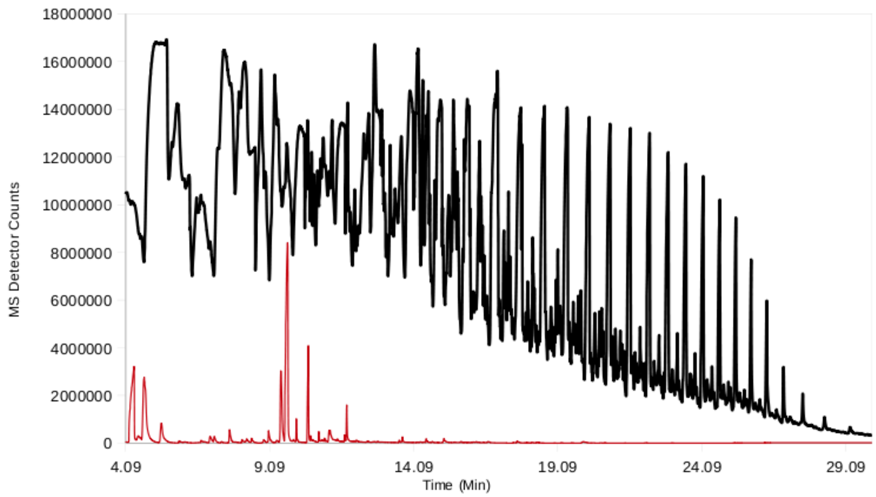

Figure 1. Gas chromatograph-mass spectrometry analyses of (black) untreated produced water and (red) water after 60 second treatment with 10% w/v Osorb.

After the initial analysis of the Wyoming produced water was complete, additional testing was conducted to analyze the effects of: variations in the exposure time of the water with Osorb, variations in the Osorb % w/v used to treat the water, and treatment at relatively low temperatures. To analyze variations in exposure time, three samples of the produced water were exposed to 2 g of Osorb for 30, 60, and 120 seconds, respectively. The results are shown below in Table 1.

Table 1. Correspondence between contact time of Osorb with the water and the % extraction.

Contact Time	% Extraction
30 s	96.0%
60 s	99.0%
120 s	39.5%

These results indicate that having the correct exposure time has a significant effect on the extraction of organic species from produced water, in part due to the surface interactions between the organic species and glass material. The chromatograms from these three tests are shown below in Figure 2. In order to quantify the reduction in contaminant concentration, mineral oil was used as a standard. Using this mineral oil standard, approximate concentrations were obtained for the untreated and treated produced water. The untreated produced water has an approximate total organic concentration of approximately 4.86 mg/L (4.86 ppm), while the sample treated for 60 seconds has a concentration of approximately 0.41 mg/L (0.41 ppm).

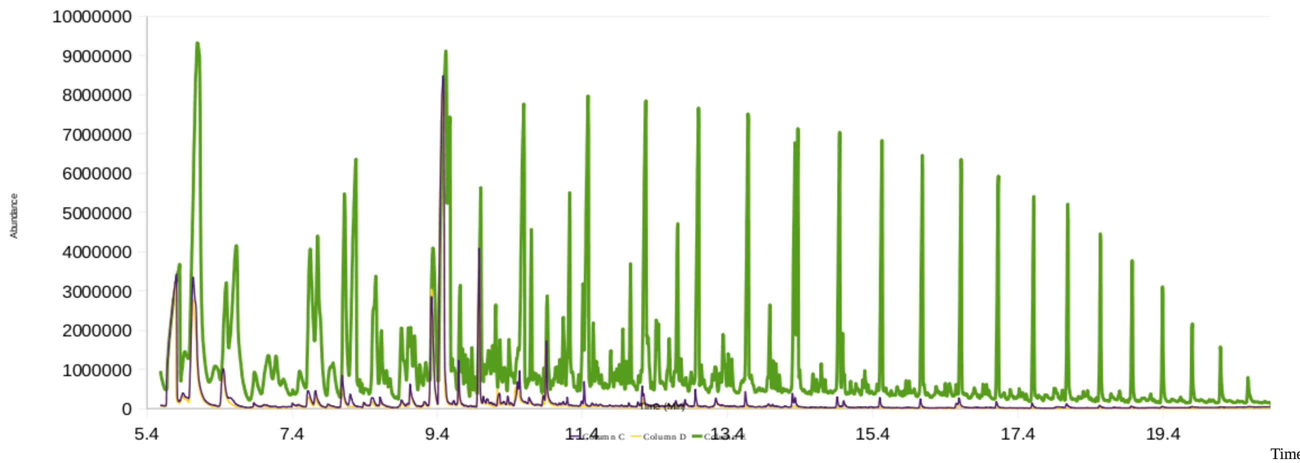

Figure 2. GC-MS chromatograms of produced water samples treated with Osorb for contact times of 30 seconds (blue), 60 seconds (yellow), and 120 seconds (green).

To gain a better understanding of the amount (% w/v) of Osorb required for remediation, 20 mL samples of Wyoming produced water were tested with 250 mg, 1 g, 1.5 g, and 3 g of Osorb, respectively. This testing was carried out with a contact time of 30 s. These extractions all yielded similar results (Table 2) to those obtained in the initial 2 g extraction test. The average extraction efficiency was 98.88%.

Table 2. Correspondence between amount of Osorb used and and the % extraction of the produced water. The contact time for all samples was 30 seconds.

Osorb (g)	Osorb (% w/v)	% Extraction
0.25	1.25%	99.54%
1.00	5.00%	98.93%
1.50	7.50%	98.54%
3.00	15.00%	98.22%

While this data indicates that 1.25 % w/v Osorb was effective at treating the Wyoming produced water, the results are not necessarily translatable to produced water samples from other locations. The amount of Osorb required to treat any contaminated water sample will depend on the identity and concentrations of the target species, as well as the formulation and quality of the Osorb.

To test the effectiveness of Osorb at decreased temperatures, a sample of Wyoming produced water was chilled to slightly above freezing (33.5 F). The standard 2 g of Osorb was used to treat 20mL of produced water with 30 seconds of contact time. The ISO 9377 method detailed earlier was used for extraction and analysis. The resulting spectra indicated an extraction efficiency of 99.18%, suggesting that cold temperatures do not inhibit the absorption of contaminants.

Alberta Produced Water Laboratory Tests

A sample of Alberta produced water was analyzed at the bench scale. A 20 mL sample of the water was treated with 3 g (15% w/v) Osorb for 30 seconds. The removal of organics was immediately observable after the addition of Osorb to the sample. The Osorb particles, initially clear and white, swelled and turned brown. At the same time, the treated produced water became a lighter brown and lost its odor. This physical observation indicates the transfer of organics from the water to the Osorb matrix.

After treatment, the sample was analyzed using the same modified ISO9377 method as previously discussed. GC-MS indicates that ~94.15% of the organic species in the sample was successfully extracted. Figure 3, below, depicts the GC chromatograms of both the untreated sample and the sample treated with 15% w/v Osorb.

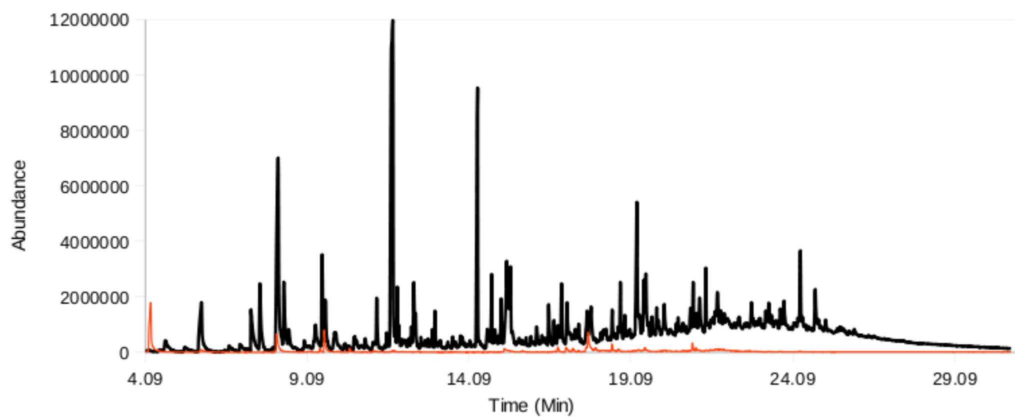

Figure 3. Gas chromatograph-mass spectrometry analysis of (black) untreated Alberta produced water and (red) water after a 30 seconds treatment with 3 g (15% w/v) Osorb.

Completed Clinton Produced Water Field Tests.

Produced water from the Clinton formation in Ohio was used to test PW Unit #1 at a well injection site near Wooster. A sample of untreated water and two samples of treated water were provided to the laboratory for testing. The untreated water was orange, cloudy, and smelled strongly of hydrocarbons. While the treated water was clear and had no odor, the samples did contain small amounts of fine, suspended solids, presumed to be fine Osorb. Therefore, the water samples were filtered through a 0.45 μm filter prior to GC analysis (ISO9377 method).

The analysis found that the untreated water contained 277 ppm hydrocarbons. The two water samples that had been treated with the PW1 system both contained only 0.1 ppm hydrocarbons, which is a 99.9% removal of contaminants. The GC chromatograms in Figure 4 depict this reduction in hydrocarbon concentrations.

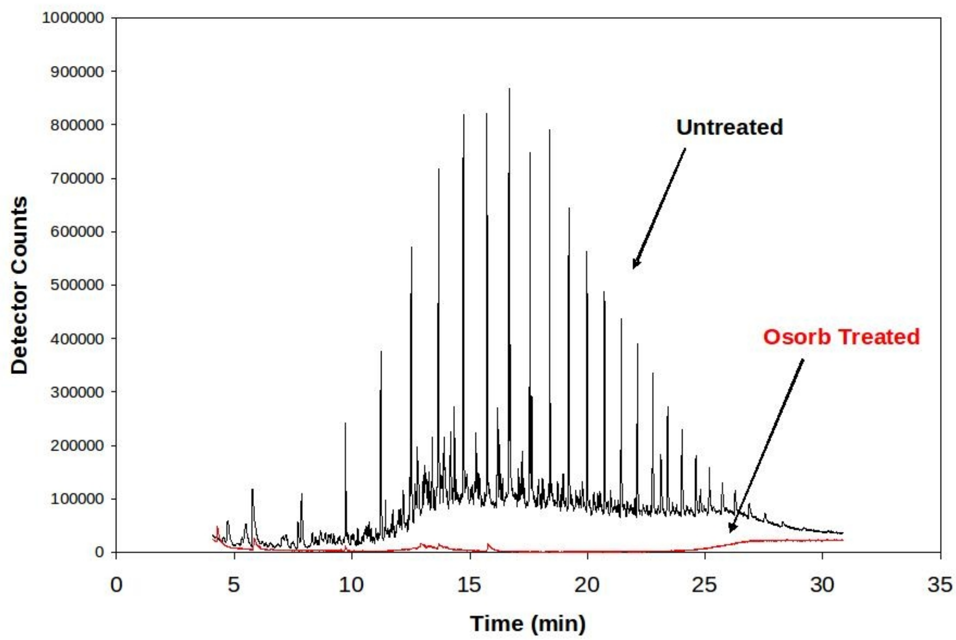

Figure 4. GC chromatograms of Clinton produced water before and after treatment by the PW Unit #1.

PW Unit #1 Development

PW Unit #1 has been extended from 1 trailer to 2 trailers: one for contaminant capture, and one for Osorb regeneration. The contaminant capture trailer includes extensive modifications and upgrades and is designed to treat contaminated water at a rate of 1.5 bbl/min. A high capacity, automatic media filtration system is being added to remove any sand and silt from the incoming water. Following this pre-filtration stage, the water will be pumped through an in-line mixing eductor. Osorb will be added into the top of this mixing eductor via a volumetric feeder, allowing the continuous addition of Osorb into the contaminated water stream. This feed system will allow our team to optimize the amount of Osorb to use as little as needed to meet client requirements. After the addition of Osorb, the water will be pumped into the mixing vessels through tank mixing eductors. These mixing eductors create the necessary turbulence that will result in sufficient contact between the Osorb and the organic species in the water. Following the contaminant capture inside the mixing vessel, the Osorb and clean water will be passed over a vibratory separator to collect the laden Osorb from the clean water discharge. Figure 5 depicts the preparation of the capture trailer during the Clinton produced water field pilot, prior to many of these aforementioned modifications.

Figure 5. Preparation of PW Unit #1 to treat Clinton gas-field produced water.

The complete Osorb regeneration trailer will include a double cone vacuum dryer, complete with thermal fluid system, vacuum pump, heat exchanger, and solvent collector. This system will allow for more rapid thermal regeneration of the Osorb, preparing the glass for reuse in the contaminant capture system.

Skid Unit #1 Development and Pilot Tests

A fixed bed, capture-only treatment system, Skid Unit #1, was developed to treat produced water at flow rates of 1-4 gpm. This system consists of two fixed beds of Osorb, which are contained in filter bags within two stainless steel vessels. The development of a fixed bed system for produced water treatment was important for comparison of fixed bed and fluidized bed (PW Unit #1) systems. Skid Unit #1, shown below in Figure 6, does not include an Osorb regeneration system.

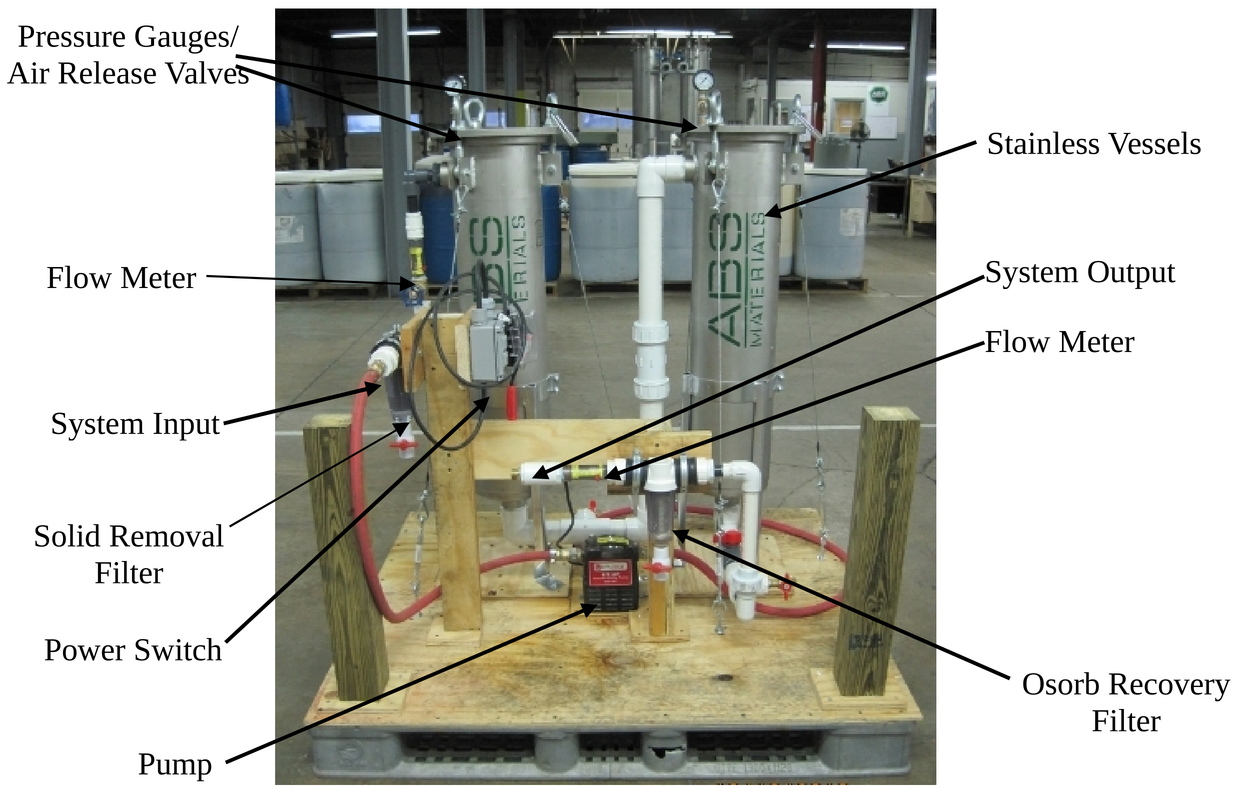

Figure 6. Skid Unit #1 is a capture only, fixed bed treatment systems designed to treat produced water at 1-4 gpm. The glass is regenerated using a separate system.

A pilot test of Skid Unit #1 was carried out in collaboration with the Global Petroleum Research Institute (GPRI) at Texas A&M University. During testing, 100 gal produced water was treated at a rate of 2 gpm. The results from this test are shown in Table 3. Most notably, the fixed bed system reduced Benzene concentrations from 4.24 ppm to 0.206 ppm and oil and grease from 11.5 ppm to no detect. This corresponds with reduction efficiencies of 95.14% and ~100.00%, respectively.

Table 3. Analytical data collected during pilot testing of Skid Unit #1 in collaboration with GPRI.

Analyte	Untreated Water (ppm)	25 gal (ppm)	50 gal (ppm)	75 gal (ppm)	100 gal (ppm)	% Reduction
Benzene	4.24	0.114	0.139	0.194	0.206	95.14%
Ethylbenzene	0.094	0.0016	0.0022	0.0025	0.0027	97.12%
Toluene	0.244	0.046	0.55	0.088	0.094	61.47%
1,2,4-Trimethylbenzene	0.01	0.0011	0.0014	0.0019	0.0019	61.47%
Total Xylenes	0.062	0.011	0.015	0.018	0.019	69.35%
Oil&Grease	11.5				0	100.00%

While the Osorb in the system was able to significantly reduce the concentrations of oil and grease and BTEX compounds in the produced water, analysis of the system indicated that the original design of the fixed bed columns (Figure 7a) could be improved. Due to the low density of Osorb, ~0.55 g/mL, it was determined that the Osorb was likely floating to the top of the filter bag once the columns were completely filled with water. This would have resulted in the formation of preferred paths for the water passing through the column (Figure 7b), reducing the contact time between the Osorb and the species in the water. In order to prevent the formation of these preferred paths, a porous filter disc and layer of sand pebbles were added to the column on top of the Osorb (Figure 7c). The sand pebbles and filter disc exert a downward force on the bed of Osorb, keeping the Osorb in a compact layer.

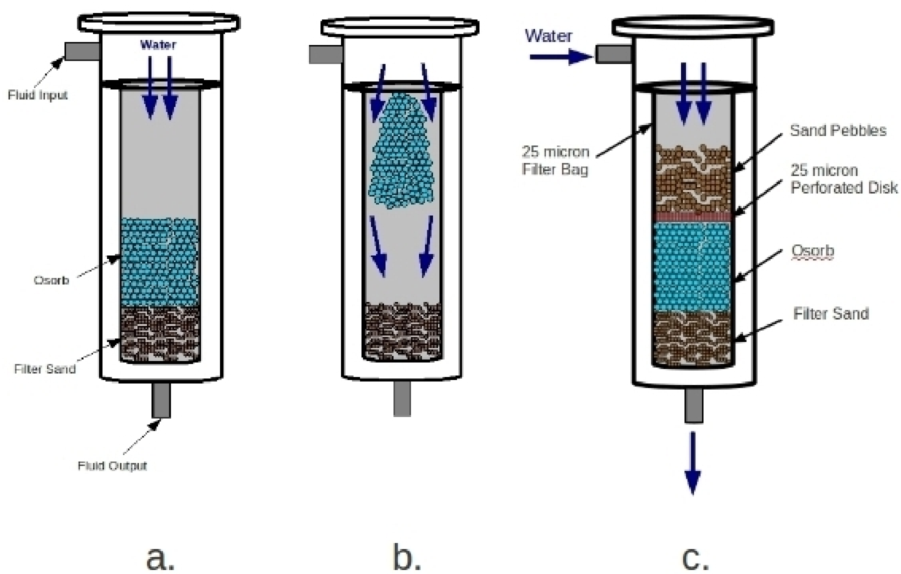

Figure 7. (a) The first generation fixed bed column design. (b) The preferred paths created during operation of the Skid Unit #1 when the columns are full of water. (c) The second generation fixed bed column design.

After modifying the design of the fixed bed columns, Skid Unit #1 completed a pilot treatment of 50 gal of Clinton produced water at 2 gpm. The data collected from this test is shown below in Table 4. The data indicates a reduction efficiency of >93% for BTEX compounds and >99% for oil and grease.

Table 4. Analytical data collected during the treatment of Clinton produced water with Skid Unit #1.

Analyte	Untreated Water (ppm)	50 gal (ppm)	% Reduction
Benzene	1.28	0	100.00%
Toluene	1.4	0.08	94.20%
p-Xylene	2.83	0.18	93.80%
Oil and Grease	290	2.48	99.10%

Conclusions and Future Work

At the bench scale, Osorb is working effectively on all produced water samples provided. ISO9377 appears to be an accurate method for assessing hydrocarbon content, but other analytical techniques such as TOC are also being explored. The PW Unit #1 pilot scale unit has proven effective at using Osorb to treat Clinton produced water. Upcoming field tests in Wamsutter, WY will be useful to further study the ability of Osorb to remove BTEX, oil and grease, and other organic species from produced waters at 1.5 bbl/min. These tests will provide more quantitative data regarding the reduction in contaminant concentrations in produced water from over 11 locations. The unit will continue to be refined as a continuous process system, working towards a system capable of operating at 5 bbl/min. Skid Unit #1 has provided valuable data regarding the performance of Osorb in a fixed bed system, and its upcoming field pilots in south Texas and the Marcellus will provide additional quantitative data.