

**ANALYSIS OF HYDROCARBON REMOVAL METHODS FOR THE
MANAGEMENT OF OILFIELD BRINES AND PRODUCED WATERS**

A Thesis

by

BRENDAN EUGENE FURROW

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2005

Major Subject: Petroleum Engineering

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Approved by:

Chair of Committee,	Maria Barrufet
Committee Members,	Ann Kenimer
	Richard Startzman
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ABSTRACT

Analysis of Hydrocarbon Removal Methods for the Management of Oilfield Brines and
Produced Waters. (August 2005)

Brendan Eugene Furrow, B.S., University of Cincinnati

Chair of Advisory Committee: Dr. Maria A. Barrufet

According to the Texas Railroad Commission (TRC), "...over 250 billion gallons of produced water is taken out of Texas Soil every year, and more than 35% of this water is not currently fit to use." Therefore, it can be assumed that domestically and globally, the petroleum industries challenge has been to develop a high-tech and cost effective method to purify the large volumes of oilfield brines and produced water. Currently, most of the produced water requires several pre- and post- treatment methods to aide in reducing fouling of membranes, separation of components, increasing influent and effluent quality, and preventing unwanted work stoppage during the desalination process. As a result, the pre- and post- treatment conditioning of the produced water affects the economics and scale-up (i.e. residence times, absorption capacity, etc...) of the varying processes parameters. Therefore, this research focuses on developing an economic analysis and determining the adsorption capacity of an organoclay system to remove oil.

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CHAPTER I

INTRODUCTION

Increasing consumption of oil and gas from industrialized nations along with newly enforced legislation on produced water quality has led to intensifying efforts to develop more efficient methods of hydrocarbon removal from water. It is known throughout the industry that proved oil reserves are declining and crude oil demand is increasing at an exponential rate. Therefore, tremendous pressure from government agencies has forced oil companies to investigate new technologies that both protect the environment and allow maximum hydrocarbon recovery.

Three fluids (gas, oil, and water) exist in a reservoir and are initially separated by gravity and capillary forces. As the formation fluids flow toward the wellbore, the dynamic flow causes the fluids to form an emulsion that must again be separated at the surface. Therefore, the produced water presents a problem from the moment that a well is placed on production. In fact, as indicated by past well data, the water cut continually increases throughout the life of an oilfield due to consequences of reservoir depletion, water influx from an adjoining reservoir, or through improved reservoir recovery processes.¹

This thesis follows the style of the *Journal of Petroleum Technology*.

It has been reported that the success of many oilfields depends upon the efficiency of the produced water disposal system.² The most widely used form of produced water disposal is re-injection into accepting formations. However, as the water cut increases, re-injection may not remain a feasible option for produced water treatment. Additionally, injectivity declines over time.

By definition, produced water is “the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.”³⁻⁶ Basically, produced water is a combination of formation water, injected water, dissolved organics, traces of heavy metals, dissolved minerals, suspended oil, solids, and production chemicals. However, the most harmful contaminants present in the produced water are benzene, toluene, ethyl benzene, and xylene (BTEX); polyaromatic hydrocarbons (PAH); alkylphenols; and heavy metals.

The ideal produced water treatment is one that is cost effective and that reduces the total amount of present contaminants below the EPA government specification of 30 ppm. However, many challenges such as concentration spikes and desorption accompany this objective. Nevertheless, if the produced water is left untreated or under-treated, then it can have potentially devastating irreversible impacts on the environment.

As the demand for oil and gas increases, and tighter government regulations are placed on produced water management, efforts have been focused on developing new hydrocarbon removal systems that are more effective and that minimize the operation costs incurred from effective disposal. A variety of products have been proposed with a range of complexities and applications. Some novel products are composed of absorbent medias while others are as simple as pumping into accepting formations. Surprisingly, no standard practice of produced water management has been developed. As a result, this study focuses on testing the efficiency of a platelet type product called Organoclay that is reported to, “completely remove free hydrocarbons from wastewaters and also remove dissolved hydrocarbons including BTEX.”^{4,6}

CHAPTER II

LITERATURE REVIEW

2.1 Present status of produced water treatments

Produced water management has been a major concern of the petroleum industry, and continues to affect drilling operations around the world. In the industry's infancy, oilfield brines were not well understood; however, the increasing water cut was almost always the leading factor for abandonment of the well. Engineers quickly began studying the phenomenon and developing preventive products. Perhaps the earliest produced water management technique was demulsification by gravitational forces.^{7,8} These treatment facilities consisted of static tanks that contained vast volumes of emulsion to be divided due to density differences. Some water management systems still incorporate gravitational separation to combat small quantities of produced water; however, some produced water management programs require more innovative techniques to effectively meet new government standards. Since the time of desperate measures to control the produced water, more technologically advanced fluid separation treatments have emerged that focus on rapid application and effectively minimizing environmental effects, therefore, minimizing production costs. Some of the hydrocarbon removal strategies include: hydrocyclones, centrifuges, coalescing media, downhole separation, and subsurface water shut off.^{9,10}

2.1.1 Hydrocyclone separation

A hydrocyclone is a geometrically engineered device that uses centrifugal separation and core reversal to remove oil from an oily water feed stream and produce two independent “pure” flow streams; one oil and one water. **Fig. 1** shows the design of the hydrocyclone system. With the centrifugal forces applied to the fluids, which may be 10,000 times the force of gravity, the water moves to the walls of the conical apparatus while the oil migrates to the center at the core of the hydrocyclone.^{1,11-13}

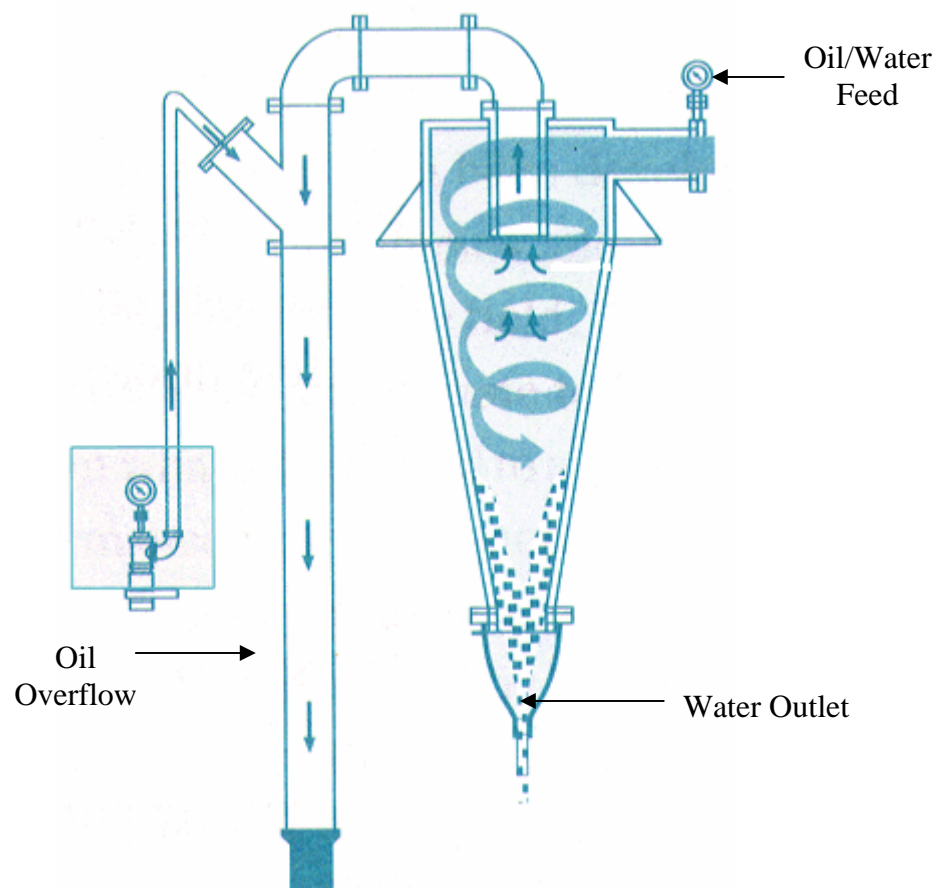


Fig. 1 — Schematic of hydrocyclone¹⁴.

In general, hydrocyclones have proven to be effective in high pressure situations; however, limitations are observed with low pressure flow. High pressure flow creates high fluid velocities, and thus, presents high centrifugal forces allowing the emulsion to dissociate efficiently. Low pressure flow, on the other hand, has the adverse affect. Additionally, small density differences between the water and oil present separation problems.

2.1.2 Centrifuge separation

Centrifuges operate using the same concept applied in a hydrocyclone. The primary difference is that the centrifuge utilizes mechanical parts where the hydrocyclone imparts only fluid flowing pressures. **Fig. 2** shows the configuration of a centrifuge. Centrifuges operate efficiently in low pressure situations; however, high pressure flow presents some problems. In addition, oil/water streams that exhibit a high relative stability coupled with limited flowing capacity and high costs make centrifuges uneconomic in many cases.^{1,11-13}

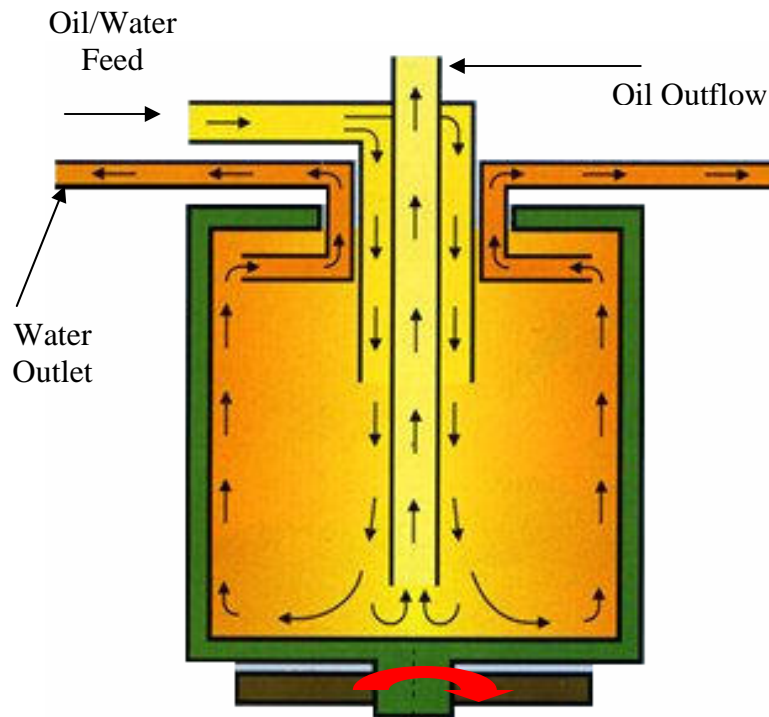


Fig. 2 — Schematic of a centrifuge¹⁵.

2.1.3 Coalescing

Coalescing is not a hydrocarbon removal technique; however, it does significantly aid in the extraction process. Essentially, coalescing is the consolidation of small oil beads into larger droplets. If coalescing is a chosen separation enhancement strategy, then the equipment is placed in line before the hydrocyclone or centrifuge.

Several methods including fiber medias, chemical injection, and mechanical agitation are used for improved oil/water separation. Fiber medias are very efficient in promoting coalescence into larger aggregates. However, the fiber medias are sensitive to abrasive elements. Chemical injection, also called coagulation or flocculation, and mechanical agitation are proven techniques for oil/water separation. Some of the main limitations are that the process of coagulation adds chemicals into the already polluted

emulsion, and that the further movement of the fluids subjects the fluids to additional shear therefore promoting remulsification.^{1,4,16-18}

2.1.4 Downhole separation

Conventional oil/water separation has always occurred at the surface using gravity separation techniques. In recent years, efforts have been made to place surface produced water management practices downhole to avoid some of the costs incurred from producing the underground water to the surface. It has been observed that “pure” streams of hydrocarbon production can be achieved using this technique. It has been reported that, “[downhole water separation] allows water to be divided in the wellbore and injected into a suitable injection zone downhole while oil with traces of water is produced to the surface.”^{1,5,19-21}

The basic design of Downhole Oil/Water Separators (DOWS) is to demulsify the emulsion near the wellhead, and reinject the water into a deeper formation while the hydrocarbons are produced to the surface. **Fig. 3** shows the design of one type of DOWS.

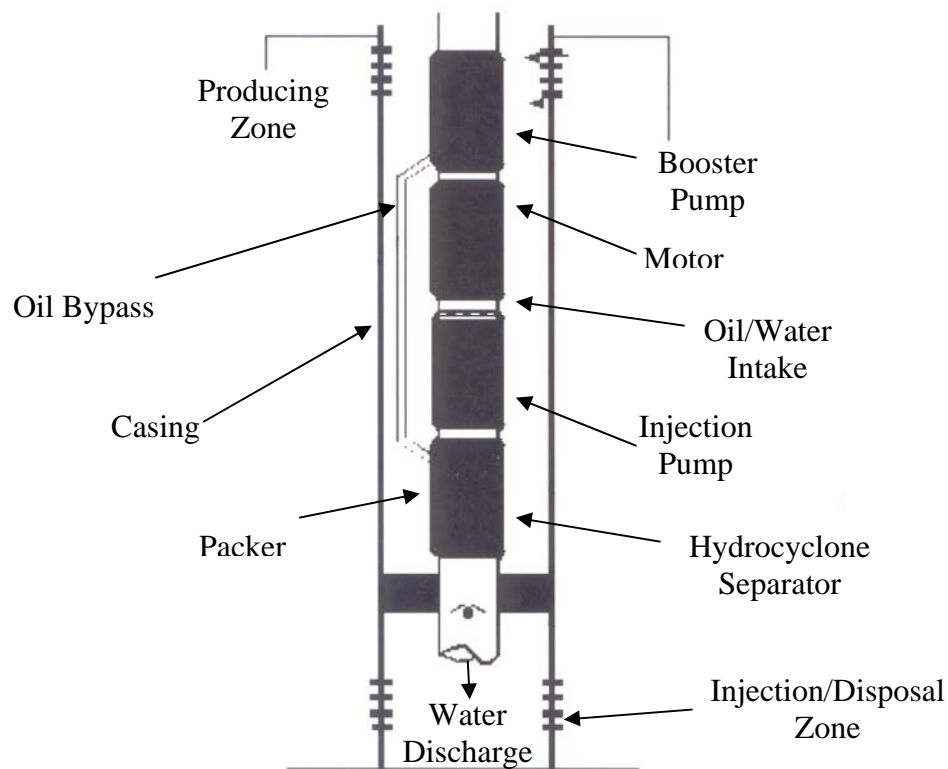


Fig. 3 — Schematic of a downhole oil/water separator¹.

One limitation associated with DOWS is that the separation equipment is placed downhole; therefore, maintenance is not favorable. However, the economics of DOWS makes them attractive for enhanced production techniques.

2.1.5 Subsurface water shutoff

Subsurface water shutoff refers to preventing water from being produced by consolidating the water producing zone. Two methods of water shutoff exist: mechanical and chemical. With mechanical shutoff, cement or mechanical devices plug or block the perforations of the water zone.

Chemical shutoff, on the other hand, utilizes chemical agents that increase the viscosity of the formation water to resist flow into the wellbore.

2.1.6 Advanced oil/water separation techniques

Despite the variety of produced water separation techniques that are available, there continues to be a need for a method that is more effective and predictable in its ability to remove hydrocarbons to a concentration below the satisfactory contamination limits. Therefore, impressive efforts have been geared toward developing produced water management techniques that provide an easy and effective solution that allows for further economic production of hydrocarbons, and that works uniformly in a wide range of applications. One of the earliest forms of demulsification utilized a filtration technique based on the size of screen mesh. Some of the forms of filtration are reverse osmosis, microfiltration, ultrafiltration, and nanofiltration. Each of these methods targets different size contaminants to be removed from the emulsion. Historically, the filtration methods have worked very well for desalination; however, uses for oil/water separation are limited.

Without a doubt, the most widely used oil/water separation techniques are those that combine individual strategies such as hydrocyclones and coalescing into complex produced water treatment plants.⁷⁻¹¹ A 2005 paper written by Saudi Aramco speaks of a six-year management strategy that includes extensive design in production optimization, rigless water shutoff jobs, and horizontal drilling.⁷ Another article by Saudi Aramco describes offshore oil/water separator plants.⁸ In addition, a publication by CETCO Oilfield Services in 2005 advertises a device called CrudeSep[®] that is able to “...replace conventional centrifuges, hydrocyclones, horizontal dissolved gas floatation devices, and degassers.”⁹ According to Bridson et al.¹¹ the CrudeSep[®] is capable of high removal efficiencies of solids as well as oil and grease in a very compact design.

Although complex produced water treatment plants appear to be the practical solution to meeting government regulations, other methods are continuously being developed in an effort to reduce costs and recover more hydrocarbons. It seems that the newest oil/water separation techniques utilize the mechanism of absorption. A 2001 publication by Neumann et al.²² describes a hydrocarbon adsorption product referred to as laponite that effectively removes oil from emulsions. A similar product proposed by Dalmazzone et al.²³ employs silicone as a demulsifying agent. Additionally, Kuwait Petroleum Corporation recommends a product known as CAPS for produced water purification.²⁴

It has been reported that the continuous and amorphous pore surfaces ceramic technology is very effective in eliminating numerous contaminants from emulsions and offers an economic alternative to produced water purification.^{24,25-29} Additionally, a product called Organoclay[®] appears to have the same characteristics as CAPS.⁴

Oil/water separation by adsorption seems to be the ultimate answer for a cost effective and environmentally friendly solution to produced water issues. However, problems do exist. According to Doyle and Brown⁴, all water/oil separators suffer from four limitations: (1) limited hydrocarbon removal, (2) efficiency in removing insoluble and dispersed hydrocarbons, (3) toleration of concentration spikes, and (4) desorption.

Since most recent advancements in produced water management technology seem to focus on oil/water separation by adsorption, then it seems that research efforts aimed at understanding the adsorption capacity capabilities are appropriate. Consequently, conducting experiments to simulate actual produced water management conditions with Organoclay[®] will be the main objective of this work.

CHAPTER III

OBJECTIVES AND PROCEDURES

3.1 Research objectives

The objectives of this research are as follows:

1. To design and implement a test matrix using laboratory data that will predict the adsorption capacity expressed as grams (oil) / grams (organoclay)
2. Examine the economics for a produced water and oilfield brine purification system.

3.2 Research procedures

To accomplish the goals of this research project, the following procedures were applied:

1. Conduct laboratory experiments using PS-12385 organoclay adsorbent provided by Polymer Ventures Incorporated.
2. Perform adsorption capacity experiments by analyzing organoclay via the Drying Analysis Method and Burning Analysis Method.
3. Verify the economics for a designated purification process incorporating organoclay.

CHAPTER IV

HYDROCARBON REMOVAL

4.1 Measurement of hydrocarbon content in water

Hydrocarbons are a common and natural occurrence in the environment and varying concentrations in produced water and oilfield brines are not unusual. Hydrocarbons in water can be found as free floating, emulsified, dissolved, or adsorbed to suspended solids. A hydrocarbon, by definition, is one of a group of chemical compounds composed only of hydrogen and carbon. Typically, hydrocarbons are broken down into three main classes; aliphatic, alicyclic, and aromatics.

There are a few different techniques available to determine hydrocarbon levels in water. Technologies that are restricted to laboratory use may provide the most valuable data, but are not favorable to field use where fast measuring times are critical for the management of an effective processing and effluent operation. For contamination purposes, the U.S. EPA determined that hydrocarbon extractables could provide a basis to the measurement ppm levels of hydrocarbons in water. Originally, freon was used to extract the hydrocarbons from the water. Once extracted these could be quantitatively analyzed to provide an indicator of the ppm of hydrocarbon in water. Atmospheric ozone depletion through the use of freons changed this method towards the use of n-hexane. Basically, this approach suggests that if a hydrocarbon can be extracted from water, it can, and should be, monitored. This technique provides data from a sample drawn at a specific time. It does not provide a continuous, real-time indication of the hydrocarbon

levels in a continuously operating process stream. **Fig. 4** shows the hydrocarbon monitor that was used in this experimentation. This apparatus uses fluorescence to evaluate each sample. The fluorescence technique uses an ultraviolet (UV) light source; however, the actual absorption is not measured only the fluorescing characteristics of the specific compounds are monitored. Fluorescence is a phenomenon whereby a portion of the absorbed wavelength in the targeted compound is re-emitted at a higher wavelength. When the water is excited at a specific wavelength of UV light, certain compounds, including hydrocarbons, will absorb energy. Even fewer compounds will re-emit this light at a higher wavelength. Hydrocarbon compounds will re-emit at a wavelength range that is unique to them. By measuring the fluorescence intensity at this wavelength, the ppm levels of hydrocarbons can be determined. This approach makes the instrument very selective to hydrocarbons. For bench-top units, an extraction of oil from the water can be used to provide accurate results to regulatory standards. Straight water samples can be inserted, making the unit an ideal screening tool to determine that hydrocarbons are present.

Hydrocarbon analysis or Total Organic Carbon (TOC) analysis of samples containing oil, help to evaluate the performance of the removal method in terms of efficiency and oil removal capacity. Paralleling a previous definition, TOC can also be expressed as the amount of hydrocarbons in a given sample that release carbon dioxide upon oxidation in an acidic solution. The value may differ from the solvent extraction process because it converts the total organic carbon into carbon dioxide versus only

extracting the aromatic parts of the sample, but this should be reconciled from proper calibration methods.

The calibration of the hydrocarbon analyzer is critical in making an accurate analysis of the given oil. By preparing oil samples with known concentrations a calibration curve can be formulated. A benefit for using the TD-500 analyzer is that allows the user to use a large sample size, which promotes more accurate measurements of the original solution.



Fig. 4 — Calibration apparatus TD-500 by Turner Designs Hydrocarbon Instruments³.

4.1.1 Oil in water analysis by TD-500 analyzer

The TD-500 Oil in Water Analyzer (OWA) measures the oil content of the oil/water solution using UV fluorescence. The device works with oilfield brines, produced water and any other application where oil components are mixed with water.

The TD-500 uses a highly accurate and reproducible solvent extraction process. The extraction method works with all non-polar solvents including n-Hexane, Vertrel, Freon and others.

4.1.2 Calibration and sample analysis method

1. Calibration method for the TD-500

First, determine the density of oil by measuring volume (via pycrometer) and mass (via gravimeter) of oil. Then determine the desired concentration of the oil/water solution along with the volume of concentration to prepare. The oil weight in grams is determined by multiplying the concentration in ppm by the volume in liters, and dividing by 1000. To arrive at oil volume in milliliters (ml), divide the oil weight in grams by oil density (g/ml). The prepared oil/water solution should be placed in an ice bath with agitation 30 minutes prior to adding oil volume. Add the oil volume. For a 1000 ppm solution, 3 grams of oil per 3 liters of water is necessary. Once the oil volume has been added cover the solution to lessen oil/water evaporation and agitate for 15 minutes. Prepare a 300 ml beaker to retrieve sample, along with 4 graduated cylinders (GC) and 4 separatory funnels (SF). Retrieve 300 ml of sample in the beaker. It is important to retrieve this sample all at the same time; otherwise calibration will be greatly influenced. Pour 90 ml of sample in GC 1, 67.5 ml in GC 2, 45 ml in GC 3 and 22.5 ml in GC 4. Fill the remaining volumes of GC 2 to GC 4 to 90 ml with pure water. GC 1 to GC 4 represents 1000 ppm, 750 ppm, 500 ppm, and 250 ppm respectively. Place each GC 1 to GC 4 into their separate SF. Proceed to add six drops of 32% Hydrochloric Acid to each solution and swirl gently. Add 10 ml of n-hexane to each sample. Shake each solution

gently for ten revolutions and then let the solution remain idle for 3 minutes while the oil/water separation takes place. The SF has an attached valve that is used to separate the bottom layer from the desired extracted layer (top layer). Place each sample into a separate beaker 1 to beaker 4. Turn on the TD-500 and press STD and key in the calibration value. For example, if the solution created was a 1000 ppm solution in water, key in 100. A background sample must be prepared by adding the dilution media (pure water) to a single cuvette and then placed into the sample reading position. It is important to always fill the cuvette half full or greater. Only handle the cuvette with tissue paper and refrain from using hands on bare glass. Finger smudges can lead to miscellaneous readings. Press CAL and then press Enter and it will ask for a reference sample, i.e. the background sample (pure water). Press Enter again and the TD-500 will store the fluorescence of the background sample. The TD-500 will then ask for a calibrated solution. The calibrated solution is the initial concentration created, i.e. the 1000 ppm solution which was placed in beaker 1. Place this solution into a cuvette and place into the sample reader and press Enter. The values being displayed during calibration must remain below 1000, if not, the solution is too concentrated and must be prepared again. The TD-500 will display STD TOO HIGH if this was the case. If calibration works, press Enter to continue. The next step is to check the fluorescence of the sample by pressing DIA. The %FS STD must be greater than 15%, if not, a larger cuvette size must be used. The larger cuvette size is an 8 mm cuvette and requires a different sample holder to be placed into the TD-500. The increase in size gives the sample more fluorescence for the TD-500 to evaluate. Place each remaining sample into

a clean cuvette and then into the sample reader for evaluation. The concentration of the remaining samples is evaluated by pressing READ. It is necessary to perform multiple readings of each sample to observe reproducibility. The values will be displayed will be between 0 to 100 millivolts (mV). The final step is to repeat the above steps for each oil to compare their calibration curves.

2. Sample analysis method

The sample size most commonly collected is 90 ml. The sample is collected via a graduated cylinder and then placed into a separatory funnel. The pH is brought below 2 by adding hydrochloric acid or sulfuric acid. N-hexane is added as 1 part in 9 parts of the sample per volume. The separatory funnel is gently swirled for 10 revolutions and allowed to rest for 3 minutes. The sample now contains two layers; the extract layer (top) and non-extract layer (bottom). The two layers are separated via the attached valve and the extract layer is placed in the appropriate flask. The amount of extracted phase should be from 2 to 3 milliliters. A clean pipette is used to collect the extract and place it into a clean minicell cuvette or 8 mm round cuvette. The general rule is to fill the cuvette half full. The cuvette is then placed into sample holder for analysis by the TD-500. The TD-500 will respond in 3 to 5 seconds with a digital reading in millivolts that is proportional to sample oil concentration in ppm.

Fig. 5 shows the calibration curve response of the TD-500 using crude oil/water emulsions. The oils chosen had American Petroleum Institute ($^{\circ}$ API) gravities of 38, 52 and 65 respectively. If the concentration of the solution created is above 1000 ppm, a

dilution step must be performed. The dilution step is performed after the extraction process and the dilution media used would be the n-Hexane.

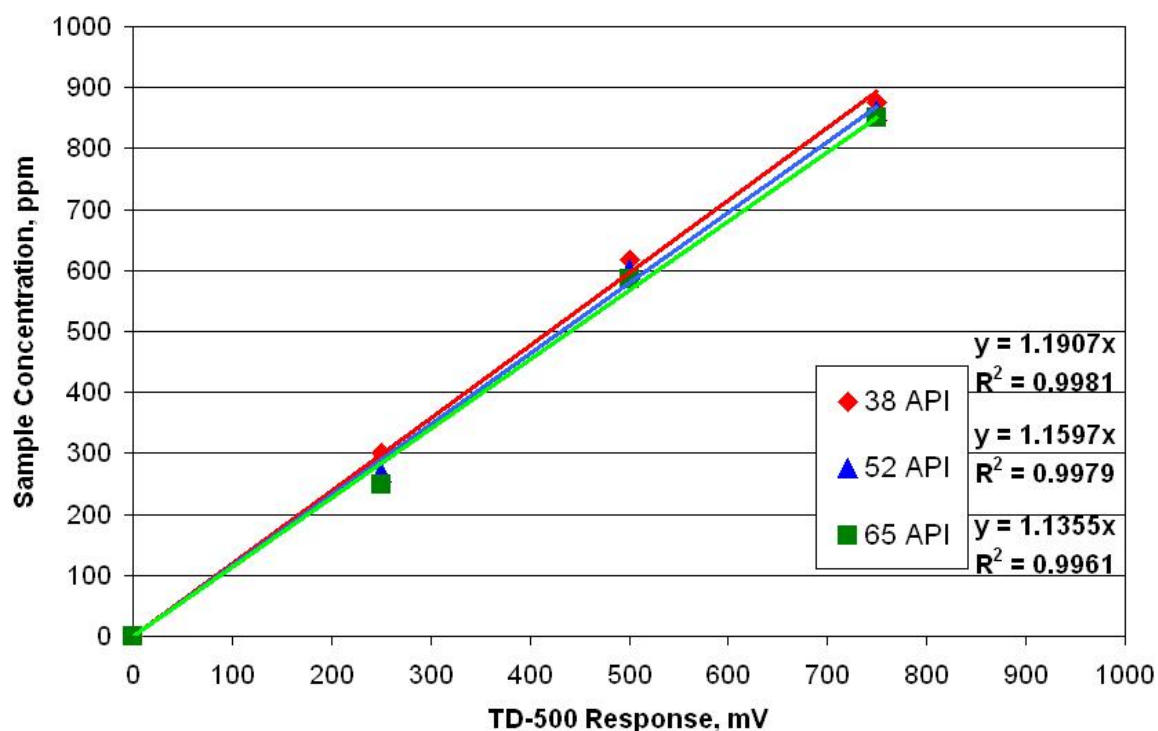


Fig. 5 — Calibration curve for TD-500 analyzer that analyzes oil present in water.

Upon completion of the calibration procedure the standard procedure is followed to analyze each sample. Routine calibration is necessary to ensure that correct sample readings are being performed. According to Patel³, calibration can be monitored through the use of the CheckPOINT solid calibration check standard for easy field calibration checks and system diagnosis. The CheckPOINT is an adjustable adapter that fits into the sample reader after calibration has been performed. The solid check point contains a small screw that can be adjusted to reflect the original fluorescence given by the

calibrated solution. The solid check point makes it possible to verify if the calibration settings are still in memory because the TD-500 will eventually require another calibration to be performed.

4.2 Adsorption capacity experiments

Experiments were performed with low concentrated crude oil-water emulsions (1500 ppm). Three different oils were chosen to test the adsorption capacity of the PS-12385 organoclay. Loading capacity or adsorption capacity is defined as the highest amount of solute present in the liquid phase that can be adsorbed by the organoclay. Generically, it is defined as gm of oil or solute adsorbed per gm of adsorbent.

4.2.1 Methodology and procedure

Table 1 shows several properties for the PS-12385 organoclay. The dry organoclay was sifted with a 710 micron mesh sieve plate to eliminate organoclay dust and non-uniform particles. The desired amount of sifted organoclay was then soaked in water for 24-hours before the experimentation began. **Fig. 6** shows the schematic for the bench-top setup of the adsorption capacity experiments.

Table 1 — Properties of PS-12385 organoclay.

Appearance	Gray to Tan Granules
Bulk Density	42 – 46 lbm/ft ³
Granule Size	16/50 U.S. Sieve Size

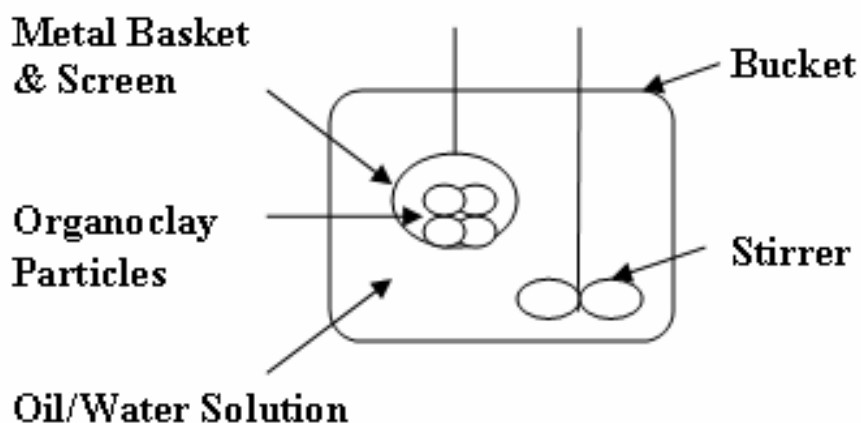


Fig. 6 — Schematic of the adsorption capacity experiments.

To analyze the adsorption capacity of the organoclay, it was necessary to encapsulate the organoclay with the metal screen that was placed in the perforated metal basket as seen in **Fig. 7**. The purpose for this was to provide contact between the organoclay and the oily solution, along with keeping the organoclay from freely floating in the bucket. The data collected from the bucket portion of the experiment was the initial and final concentration of the bucket. This was achieved by following the sample analysis method described in Section 4.1.2.



Fig. 7 — Perforated metal basket (left) and the metal basket plus metal screen (right).

4.3 Experimental setup

The standard experimental procedure consisted of five stand-alone systems as in **Fig. 8 and Fig. 9**. Each experimental system was covered to lessen oil/water evaporation. Each metal basket contained approximately 8 grams of organoclay. The 8 grams represents the maximum amount of organoclay that can successfully fit into the metal basket system. The initial concentration of each bucket was 1500 ppm. The reason for choosing this concentration was because it represented a value that upon introduction of the organoclay, the TD-500 would be able to detect a change from the initial to final concentration. Since the calibration was performed from 0 to 1000 ppm, the final concentration of the system should lie between those values. A reference sample was also setup to compare the behavior of organoclay without hydrocarbons. This system was setup exactly as the other systems, except it only contained a water solution.



Fig. 8 — Experimental setup for adsorption experiment.



Fig. 9 — Single bucket adsorption experiment view.

4.4 Data acquisition and presentation

In each experiment the following were held constant; organoclay amount, theoretical bucket concentration, time of experiment and solution agitation. The organoclay amount was not varied because the oil adsorption is determined as grams of oil per grams of organoclay which is an intensive property. Intensive properties do not depend on the sample size used. For each experiment the initial and final bucket concentration were analyzed by the TD-500 analyzer. Material balance was used to trace the hydrocarbon content from the initial bucket concentration to the final step of characterization. Adsorption capacity was characterized via two methods; drying analysis method and burning analysis method. **Table 2** shows the list of data acquired when performing the adsorption experiments.

Table 2 — A list of parameters to be acquired in each adsorption experiment.

Bucket Volume, B_{volume}
Oil Specific Volume, ρ_{gravity}
Oil Volume Added, O_{volume}
TOC in Bucket, B_{conc}
Initial TOC content of the bucket, $\text{TOC}_{\text{initial}}$
Final TOC content of the bucket, $\text{TOC}_{\text{final}}$
Initial Metal Basket Weight (includes organoclay, metal basket, metal screen, and string), $\text{MB}_{\text{initial}}$
Final Metal Basket Weight (includes organoclay, water, oil, metal basket, metal screen, and string), MB_{final}
Initial Drying Weight, $\text{IDW}_{\text{initial}}$
Final Drying Weight, $\text{FDW}_{\text{final}}$
Initial Burning Weight, $\text{IBW}_{\text{initial}}$
Final Buring Weight, $\text{FBW}_{\text{final}}$

Each adsorption system was in contact with the oil/water solution for approximately 8-hours. The amount of time chosen was predetermined from previous experiments where the organoclay was in contact with the oil/water solution for a 24-hour period. Those experiments showed that after an 8-hour period the incremental oil adsorption was negligible.

4.5 Organoclay characterization

Each metal basket system was removed from the oil/water solution and weighed. The organoclay was then removed from the metal basket and placed onto a tarred aluminum foil sheet. The amount of organoclay, including water and oil, was weighed for each metal basket system. The five samples were then numbered and their individual weights recorded. The reference sample was prepared in the same manner.

4.5.1 Drying analysis

The first step to characterize the organoclay was performed through a drying analysis method. All five samples, plus reference sample, were placed into an oven at 105°C for one hour and thirty minutes. The oven removed all the water that was present on each sample and the amount of time chosen was sufficient to successfully perform this step to consistent weight. This led to evaluating the amount of water the organoclay contained and an estimate of TOC. To perform the material balance based on the drying analysis, it was assumed that only water evaporated in the oven and no oil evaporate from the surface of the organoclay. The assumption should be valid since the boiling points of all the oils exceeded the temperature in the oven.

4.5.2 Burning analysis

The final step to characterize the organoclay was performed through a burning analysis method. The dried organoclay from the drying analysis step was used to perform this step. Each dried sample was divided into 2 gram samples. The importance of dividing the samples was two fold:

- increase the amount of organoclay that would be in contact with the flame
- provide more control of the combustion reaction

One sample at a time was placed into a tarred metal, mesh basket and placed over a Bunsen burner. All the samples were combusted (**Fig. 10** and **Fig. 11**) in the fume-hood and each sample was initially in contact with the flame for 10 minutes. The samples were removed and weighed and placed into the flame for an additional 5 minutes. The samples were removed and weighed and then placed back into the flame for an additional 2 minutes and the weight measured once again. If the sample weight did not change appreciably, the final weight recorded was used as the final burned weight. **Table 3** contains a sample calculation for the drying and burning analysis methods.



Fig. 10 — Combustion of organoclay for the burning analysis method.



Fig. 11 — Combustion of organoclay and effects.

Table 3 — Sample calculation for drying and burning analysis.

Drying Analysis									
Step 1	Step 2	Step 3	Step 4	Step 5					
	Initial Sample Amount (grams)	After Drying to Constant Weight (grams)	Water Removed (grams)	Apparent Water (%)					
Sample Formula			= 8.00-6.05	= (1.95/5.45)*100					
Sample 1	8.00	6.05	1.95	35.78					
Reference Formula			= 8.00-5.45	= (2.55/5.45)*100					
Reference Sample	8.00	5.45	2.55	46.79					
Burning Analysis									
Step 6	Step 7	Step 8	Step 9	Step 10	Step 11	Step 12	Step 13	Step 15	Step 16
Sample (#)	Initial Weight (grams)	Weight Reduction from Burning (%)	After Burning Weight (grams)	Oil (grams)	Oil Burned (%)	Oil Adsorbed (%)	Oil Adsorbed in Original Burning Sample (grams)	Adsorption Capacity Using After Burning Weight (%)	Adsorption Capacity Using Before Burning Weight (%)
Sample Formula			= 6.05-(41.30%*6.05)	= 6.05-3.55	= 2.5/6.05*100	= 41.30 - 26.00	= 15.3*6.05/100	= 0.93/3.55*100	= 0.93/6.05*100
Sample 1	6.05	41.30%	3.55	2.50	41.30	15.30	0.93	26.20	15.37
Reference Formula			= 5.45-(26.00%*5.45)	= 5.45-4.03	= 1.42/6.05*100				
Reference Sample	5.45	26.00%	4.03	1.42	26.00				

CHAPTER V

PRODUCED WATER ECONOMICS

5.1 The impact of economics

Historically, produced water has just been considered a by-product of oil production.^{5,30-32} Typically, it is contaminated with many constituents that hinder its reuse. Siddiqui⁵ noted that the most important constituents include; the amount of suspended and dissolved hydrocarbons present, and the amount of suspended and dissolved salts present in the produced water. Siddiqui⁵ also noted that the cost of treating the produced water is based in part on the total recovery desired. As the total recovery of the system is increased the total cost of the system also increases. The goal is to find a balance between the parameters that leads to high recovery and high economic efficiency.

In this chapter presents the water treatment costs for produced water containing 15,000 ppm total dissolved solids (TDS) and approximately 200 ppm TOC. **Fig. 12** shows the schematic for the proposal system. Each system was modeled using SuperPro Designer (SPD). The software provided most of the economic values that will be presented. The following two scenarios were chosen:

- 1) The first scenario is a large mobile produced water unit with maximum feed flow capacity of 14,000 gallons per day with 50% recovery, which leads to 7,000 gallons per day permeate/treated water rate

2) The second scenario is small mobile produced water unit with maximum feed flow capacity of 6,000 gallons per day with 50% recovery, which leads to 3,000 gallons per day permeate/treated water

Further subdivision was necessary for modeling purposes. The two systems presented are after the first step of pretreatment, but before the water is passed through the organoclay canister. The TOC inlet to the organoclay canister for Scenario 1 and Scenario 2 has been reduced to 30 ppm TOC and 80 ppm TOC respectively. The total water treatment cost consists of two items:

- 1) capital cost per gallon of permeate (treated produced water)
- 2) operating cost per gallon of permeate (treated produced water)

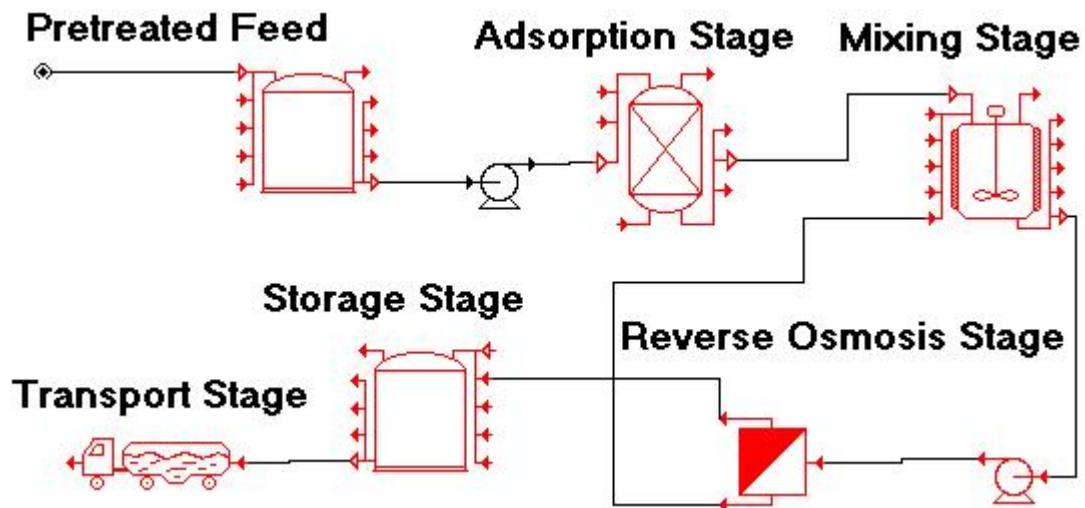


Fig. 12 — Schematic of proposed produced water system.

5.2 Capital costs

The costs of these units were provided by the SPD software. The software contains a built-in-model to provide economic output. **Table 4** breaks down the capital costs involved in assembling the produced water treatment units based on the produced water rates mentioned earlier.

The primary oil/water separation equipment is represented by traditional equipment that is being used in the oil field today. The traditional equipment might be a plate separator, hydrocyclone, centrifuge, or any of the equipment mentioned in the literature review. The organoclay equipment includes a column of activated carbon for the removal of any final remaining BTEX compounds that may be present in the produced water. It should be noted that the capital costs do not include any adsorbent materials that are used in the separation processes, only the equipment that houses those materials.

Table 4 — Capital investment costs for produced water treatment units.

	14,000 gpd (9.7 gpm)	6,000 gpd (4.2 gpm)
Produced Water Flow Rate		
Capital Investment		
Primary Oil/Water Separation Equipment	\$20,000	\$13,000
Membrane Unit R/O	\$60,000	\$50,000
Instrumentation & Control	\$11,000	\$11,000
Organoclay+Activated Carbon Equipment	\$8,000	\$6,000
Total Capital Investment	\$99,000	\$80,000

The desalination capital investment is based on using membranes mentioned in **Table 5**.

Table 5 — Membrane specifications for each unit.

	14,000 gpd	6,000 gpd
Produced Water Flow Rate	(9.7 gpm)	(4.2 gpm)
Membrane Unit R/O		
Size, inch	4x40	2.5x40
Surface Area, ft ²	70	40
Type	Spiral	Spiral

The instrumentation and control of the system refers to all the equipment necessary for automation and accurate data collection. The transporting of the treated water from the mobile unit to an area within close proximity was assumed.

The capital costs for both the 14,000 gpd and 6,000 gpd units have been calculated, as seen in **Table 6**. The capital costs were amortized over 3, 5, 7 and 10 year periods. Straight-line amortization schedule was used to calculate the costs for the differing time periods.

Table 6 — Capital cost per volume of treated water assuming straight line amortization.

Produced Water Flow Rate	14000 gpd (9.7gpm)				6000 gpd (4.2 gpm)			
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)				3000 gpd (2.1 gpm)			
Total Capital Investment	\$99,000				\$80,000			
Unit Life (years)								
(Straight Line Depreciation)	3	5	7	10	3	5	7	10
Capital Cost (\$/year)	33,000	19,800	14,143	9,900	26,667	16,000	11,429	8,000
Capital Cost (\$/gal permeate)	0.013	0.008	0.006	0.004	0.024	0.015	0.010	0.007
Capital Cost (\$/bbl permeate)	0.542	0.325	0.232	0.163	1.023	0.614	0.438	0.307

5.3 Operating Costs

5.3.1 Operating cost for primary oil/water separation (pretreatment)

Table 7 gives operating costs for the primary removal of suspended hydrocarbons before the produced water is passed through the organoclay. The assumption is that the primary oil/water separation will be done using one of the traditional oil/water separation techniques discussed in previous chapters. The traditional equipment might be a plate separator, hydrocyclone, centrifuge, etc.

The primary hydrocarbon content of the feed into the initial oil removal equipment is 200 ppm TOC, and the output concentration of the produced water from the pretreatment stage is 30 and 80 ppm TOC. The 30 ppm TOC and 80 ppm TOC are two scenarios for what would enter the organoclay canister.

Table 7 — Operating costs for primary oil/water separation pretreatment.

Produced Water Flow Rate	14000 gpd (9.7 gpm)	6000 gpd (4.2 gpm)
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)	3000 gpd (2.1 gpm)
Electricity Cost	\$0.1 /kilowatt-hr	\$0.1 /kilowatt-hr
Pretreatment Power Requirements	1.05 horsepower	1.05 horsepower
	0.78 kilowatt	0.78 kilowatt
Electricity Cost	0.03 ¢/gal permeate	0.06 ¢/gal permeate
	1.12 ¢/bbl permeate	2.55 ¢/bbl permeate
Total Operating Costs – Primary Oil/Water Separation	0.013 ¢/gal permeate	0.031 ¢/gal permeate
	0.56 ¢/bbl permeate	1.31 ¢/bbl permeate

5.3.2 Operating cost for treating produced water with organoclay

Table 8 details the calculation for the treating of the produced water with organoclay. The calculations are based on using two containers of organoclay with residence times of 6 minutes. As previously mentioned, the pretreatment for these two scenarios has been performed, but not included in the modeling scheme. The assumption

is that the amount hydrocarbons present in the produced water as it exits the pretreatment step is reduced to either 30 ppm TOC or 80 ppm TOC. Both conditions have been considered in calculating the operating costs for both produced water flow rates. The final assumption is that the removal capability of organoclay is 90% of the hydrocarbons present in the inlet. For example, if 30 ppm of TOC entered the organoclay canister, only 3 ppm of TOC would be seen on the outlet. The price used in the calculations for the organoclay was \$2 /lb and the density of the organoclay was 46 lb/ft³.

5.3.3 Operating cost for membranes

Table 9 lists the operating cost for the membranes used in each produced water flow rate. The operating pressure chosen was 700 psi and the recovery factor is 50% (defined as gallons of permeate per gallons of feed). The inlet TDS is 15,000 ppm while the outlet (permeate) TDS is less than 500 ppm.

Table 8 — Operating costs for produced water treatment with organoclay.

Produced Water Flow Rate	14000 gpd (9.7 gpm)		6000 gpd (4.2 gpm)	
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)		3000 gpd (2.1 gpm)	
Electricity Cost	0.1 \$/kilowatt-hr		0.1 \$/kilowatt-hr	
TOC in Produced Water (pretreated)	30 ppmC	80 ppmC	30 ppmC	80 ppmC
TOC removed at 90% efficiency	27 ppmC	77 ppmC	27 ppmC	77 ppmC
TOC removed, lb/gal	0.000225	lb/gal	0.0006	lb/gal
TOC removed, lb/bbl	0.0094	lb/bbl	0.027	lb/bbl
Final TOC removed, lb/day	3.15	lb/day	8.98	lb/day
Canister Volume (assuming 28% porosity)	373	gal	373	gal
Fluid Volume in Canister	82	gal	82	gal
Weight of Organoclay	1793.6	lb	1793.6	lb
Weight of Hydrocarbons held by Organoclay, 70% Loading Capacity	896.8	lb	896.8	lb
Change out Time for Organoclay	285	days	100	days
Replacing organoclay frequency	1.28	per year	3.65	per year
Cost of Organoclay, \$/day	\$12.60		\$35.92	
Organoclay Power	0.079	horsepower	0.079	horsepower
	0.059	kilowatt	0.059	kilowatt
Electricity Cost – Organoclay	0.002	¢/gal permeate	0.002	¢/gal permeate
	0.085	¢/bbl permeate	0.085	¢/bbl permeate
Organoclay Cost	0.09	¢/gal permeate	0.26	¢/gal permeate
	3.78	¢/bbl permeate	10.78	¢/bbl permeate
Total Operating Cost – Organoclay	0.18	¢/gal permeate	0.51	¢/gal permeate
	7.65	¢/bbl permeate	21.64	¢/bbl permeate
	0.18	¢/gal permeate	0.18	¢/gal permeate
	7.65	¢/bbl permeate	7.65	¢/bbl permeate
	0.18	¢/gal permeate	0.18	¢/gal permeate
	7.65	¢/bbl permeate	7.65	¢/bbl permeate
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	7.65	¢/bbl permeate	7.65	¢/bbl permeate
	0.18	¢/gal permeate	0.18	¢/gal permeate
	7.65	¢/bbl permeate	7.65	¢/bbl permeate
	0.18	¢/gal permeate	0.18	¢/gal permeate
	7.65	¢/bbl permeate	7.65	¢/bbl permeate

Table 9 — Operating costs for the membranes.

Produced Water Flow Rate	14000 gpd (9.7 gpm)	6000 gpd (4.2 gpm)
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)	3000 gpd (2.1 gpm)
Membrane Operating Pressure	700 psi	700 psi
Electricity Cost	\$0.1 /kilowatt-hr	\$0.1 /kilowatt-hr
Membrane life	1 year	1 year
Membrane cost	\$8,000	\$8,000
Cost of Chemicals	0.001 \$/gallons	0.001 \$/gallons
Pump Power	6 hp	3 hp
Membrane Cost	\$21.92 /day	\$21.92 /day
	0.31 ¢/gal permeate	0.73 ¢/gal permeate
	13.15 ¢/bbl permeate	30.68 ¢/bbl permeate
Water Chemical Costs	\$14.00 /day	\$6.00 /day
	0.20 ¢/gal perm	0.20 ¢/gal perm
	8.40 ¢/bbl perm	8.40 ¢/bbl perm
Membrane Power	6 hp	3 hp
	4.48 kilowatt	2.24 kilowatt
Electricity Cost	0.15 ¢/gal perm	0.17 ¢/gal perm
	6.44 ¢/bbl perm	7.52 ¢/bbl perm
Total Operating Cost – Membrane	0.66 ¢/gal perm	1.1 ¢/gal perm
	27.72 ¢/bbl perm	46.20 ¢/bbl perm

5.3.4 Total operating costs for produced water treatment

Table 10 gives the total operating cost for the production of irrigation quality water from produced water. The produced water contained 15,000 ppm TDS and 200 ppm TOC. According to Siddiqui⁵, class 1 irrigation quality water is considered to be water with less than 500 ppm TDS. The costs are further broken down to examine two types of incoming TOC to the organoclay, 30 ppm TOC and 80 ppm TOC.

The range for the total operating cost for treating the produced water varies between 0.85¢/gal permeate (35.93 ¢/bbl permeate) and 1.64 ¢/gal perm (69.15 ¢/bbl permeate). The operating costs can be reduced further by recovering more treated water (permeate) from the overall system.

Table 10 — Summary of operating costs for the production of irrigation quality water.

Flow rate (Produced Water)	14000 gpd (9.7 gpm)		6000 gpd (4.2 gpm)	
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)		3000 gpd (2.1 gpm)	
Electricity Cost	0.1 \$/kilowatt-hr		0.1 \$/kilowatt-hr	
TOC in Produced Water (pre-treated)	30 ppm	80 ppm	30 ppm	80 ppm
	c/gal		c/gal	c/gal
Primary Oil/Water Separation	0.01 permeate	0.01 c/gal permeate	0.03 permeate	0.03 c/gal permeate
	c/bbl		c/bbl	c/bbl
Operating Costs	0.56 permeate	0.56 c/bbl permeate	1.31 permeate	1.31 c/bbl permeate
	c/gal		c/gal	c/gal
	0.18 permeate	0.51 c/gal permeate	0.18 permeate	0.51 c/gal permeate
	c/bbl		c/bbl	c/bbl
Operating Costs Organoclay	7.65 permeate	21.64 c/bbl permeate	7.65 permeate	21.64 c/bbl permeate
	c/gal		c/gal	c/gal
	0.66 permeate	0.66 c/gal permeate	1.10 permeate	1.10 c/gal permeate
	c/bbl		c/bbl	c/bbl
Membrane Operating Cost	27.72 permeate	27.72 c/bbl permeate	46.20 permeate	46.20 c/bbl permeate
	c/gal		c/gal	c/gal
	0.85 permeate	1.18 c/gal permeate	1.31 c/gal perm	1.64 c/gal permeate
	c/bbl	c/bbl		c/bbl
Total Operating Cost	35.93 permeate	49.92 permeate	55.16 c/gal perm	69.15 permeate

5.4 Total water treatment costs

Table 11 gives the total cost for treating 15,000 ppm TDS produced water to primary irrigation quality water. It is noticed that when examining the amortization schedule, the 3 years life cycle is not feasible. It provides the highest cost in each case and is not a fiscally responsible option. It can be expected the mobile unit would at least follow a 5 year amortization schedule, but 10 years is more likely.

For a 5 year life-time, the cheapest water treatment cost per gallon permeate obtained is 1.62 ¢/gal permeate (\$0.71 /bbl permeate) for the 14,000 gpd water treatment unit and 30 ppm TOC hydrocarbon content at the organoclay inlet. For the 6,000 gpd mobile unit, the water treatment cost is 2.08 ¢/gal permeate (\$0.87 /bbl permeate) for 30 ppm TOC hydrocarbon content at the inlet of the organoclay.

For a 10 year life-time, the cheapest water treatment cost per gallon permeate obtained is 1.24 ¢/gal permeate (\$0.55 /bbl permeate) for the 14,000 gpd water treatment unit and 30 ppm TOC hydrocarbon content at the organoclay inlet. For the 6,000 gpd mobile unit, the water treatment cost is 1.70 ¢/gal permeate (\$0.71 /bbl permeate) for 30 ppm TOC hydrocarbon content at the inlet of the organoclay.

The feasible of this data shows that where produced water can be produced between \$0.55/bbl to \$1.71/bbl, that this method can be competitive and applicable as indicated in **Table 12**. The category of *Typical Costs for Disposal of Produced Water* was provided by Patel³ and refers to the maximum amount that could seen in the treatment of produced water, based on transportation arrangements and initial water quality.

Table 11 — Total water treatment costs for both produced water treatment units.

Produced Water Flow Rate	14000 gpd (9.7 gpm)										6000 gpd (4.2 gpm)									
Treated Water (Permeate) Flow Rate	7000 gpd (4.9 gpm)										3000 gpd (2.1 gpm)									
Total Capital Investment	\$99,000										\$80,000									
TOC prior to Organoclay	30 ppmC					80 ppmC					30 ppmC					80 ppmC				
Unit Life, years	3	5	7	10	3	5	7	10	3	5	7	10	3	5	7	10	3	5	7	10
Capital Cost, \$/year	33,000	19,800	14,143	9,900	33,000	19,800	14,143	9,900	26,667	16,000	11,429	8,000	26,667	16,000	11,429	8,000	26,667	16,000	11,429	8,000
Capital Cost, \$/gal permeate	1.29	0.77	0.55	0.39	2.43	1.46	1.04	0.73	1.29	0.77	0.55	0.39	2.43	1.46	1.04	0.73	1.29	0.77	0.55	0.39
Operation Cost, \$/gal permeate	0.85					1.18					1.31					1.64				
Total Water Cost, \$/gal permeate	2.14	1.62	1.40	1.24	3.61	2.64	2.22	1.91	2.60	2.08	1.86	1.70	4.07	3.10	2.68	2.37	4.07	3.10	2.68	2.37
Capital Cost, \$/bbl permeate	0.54	0.32	0.23	0.16	1.02	0.61	0.44	0.31	0.54	0.32	0.23	0.16	1.02	0.61	0.44	0.31	1.02	0.61	0.44	0.31
Operation Cost, \$/bbl permeate	0.39					0.49					0.55					0.69				
Total Water Cost, \$/bbl permeate	0.93	0.71	0.62	0.55	1.51	1.10	0.93	0.80	1.09	0.87	0.78	0.71	1.71	1.30	1.13	1.00	1.71	1.30	1.13	1.00

Table 12 gives some comparisons of treated produced water with other commonly used items. The importance of this information can be seen if we examine the price of treated produced water in the recent decade. A downward trend has been seen in the recent decade in the cost of treating the produced water. The economic benefit of treating produced water in the aforementioned manner is becoming more applicable as technology and competition continue to thrive.

Table 12 — Price comparison of common products.

Product	Price
Treated Produced Water	\$ 0.55 - 1.71 /bbl
Typical Costs for Disposal of Produced Water	\$ 2.00 - 4.00 /bbl
Filtered Water at Grocery Store	\$ 40.00 - 42.00 /bbl
Crude Oil	\$ 47.00 - 55.00/bbl
Bottled Water	\$ 71.00 - 75.60 /bbl
Dr. Pepper, Coke, etc...	\$ 94.24 - 96.00/bbl
Milk	\$ 147.00 - 150.00/bbl

CHAPTER VI

RESULTS AND DISCUSSION

6.1 Varying oil type to test adsorption capacity

The study of the adsorption capacity of the organoclay was accomplished by analyzing the drying and burning analysis methods. Patel³ noted that adsorption is a two step process.

Step I: The diffusion of the solute from the bulk fluid solution to the surface of adsorbent. The mechanism that drives this reaction is molecular diffusion.

Step II: The adsorption of the solute within the pore structure of the adsorbent. The mechanisms that drive this reaction are pore diffusion and/or surface diffusion.

Previous work by Patel³ showed the rate of adsorption is affected by adsorbent particle size and adsorbent surface area. The research provided here is to show the effect of oil type on oil adsorption by organoclay. **Table 13** shows several of the properties that were held constant in each oil type experiment. The 38 °API oil is a Remington Light Crude and has a density of 0.83 g/ml. The 52 °API oil is 99% Hexadecane and has a density of 0.773 g/ml. The 65 °API oil is Golden West Superior motor oil with a density of 0.72 g/ml.

Table 13 — Experimental parameters held constant.

Oil Type, °API	38	52	65
Bucket Volume, liters	3.00	3.00	3.00
Bucket Concentration, ppm	1500	1500	1500
Particle size, U.S. Sieve Size	0.32	0.32	0.32
Weight of organoclay, grams	8.00	8.00	8.00
Loading Capacity, %	50	50	50

6.1.1 Effect of oil type

As the °API gravity of the oil in the feed solution increased, an increased amount of oil was adsorbed within the pore structure of the organoclay. **Table 14** indicates that for the 38 °API oil, the final adsorption capacity was 15%. **Table 15** indicates that for the 52 °API oil, the final adsorption capacity was 24%. **Table 16** indicates that for the 65 °API oil, the final adsorption capacity was 34%. Overall, this indicates that for the burning and drying analysis experiments, when the °API gravity of the oil increased by approximately 14 °API units the adsorption capacity increased by approximately 10%. The higher API gravity oils appear to provide a higher adsorption capacity, and the reasoning for this might be two fold:

1. The higher gravity oils contain more aromatics, which provide higher fluorescents in the TD-500 apparatus.
2. Organoclay particles are more receptive to refined oils compared to unrefined oils.

A final observation is that the organoclay must contain structural oil because the dry organoclay combusted, reducing its initial weight by approximately 26%. The importance of this observation is that it reduces the final TOC values for each of the

Table 15 — Drying and burning analysis data for 52 °API oil.

52 API Oil										
Drying Analysis										
			Sample (#)	Initial Sample Amount (grams)	After Drying to Constant weight (grams)	Water Removed (grams)	Apparent Water (%)			
			11	8.00	6.67	1.33	23.84			
			12	8.00	6.59	1.41	25.27			
			13	8.00	6.70	1.30	23.30			
			14	8.00	6.72	1.28	22.94			
			15	8.00	6.68	1.32	23.66			
			Reference	8.00	5.58	2.42	43.37			
Burning Analysis										
Sample (#)	Initial Weight (grams)	Weight Reduction from Burning (%)	After Burning Weight (grams)	Oil (grams)	Oil Burned (%)	Oil Adsorbed (%)	Oil Adsorbed in Original Burning Sample (grams)	Total Oil Desorbed in Burning (grams)	Adsorption Capacity Using After Burning Weight (%)	Adsorption Capacity Using Before Burning Weight (%)
16	6.67	51.10%	3.26	3.41	51.10	25.10	1.67	1.67	51.33	25.10
17	6.59	49.43%	3.33	3.26	49.43	23.43	1.54	1.54	46.33	23.43
18	6.70	51.32%	3.26	3.44	51.32	25.32	1.70	1.70	52.01	25.32
19	6.72	51.98%	3.23	3.49	51.98	25.98	1.75	1.75	54.10	25.98
20	6.68	49.76%	3.36	3.32	49.76	23.76	1.59	1.59	47.29	23.76
Reference	5.58	26.00%	4.13	1.45	26.00	0.00	0.00	0.00	0.00	0.00
								Average	24.72%	
								Standard Deviation	1.08	

Table 16 — Drying and burning analysis data for 65 °API oil.

65 API Oil										
Drying Analysis										
			Sample (#)	Initial Sample Amount (grams)	After Drying to Constant weight (grams)	Water Removed (grams)	Apparent Water (%)			
			21	8.00	7.21	0.79	14.23			
			22	8.00	7.20	0.80	14.41			
			23	8.00	7.18	0.82	14.77			
			24	8.00	7.13	0.87	15.68			
			25	8.00	7.16	0.84	15.14			
			Reference	8.00	5.55	2.45	44.14			
Burning Analysis										
Sample (#)	Initial Weight (grams)	Weight Reduction from Burning (%)	After Burning Weight (grams)	Oil (grams)	Oil Burned (%)	Oil Adsorbed (%)	Oil Adsorbed in Original Burning Sample (grams)	Total Oil Desorbed in Burning (grams)	Adsorption Capacity Using After Burning Weight (%)	Adsorption Capacity Using Before Burning Weight (%)
26	7.21	61.20%	2.80	4.41	61.20	35.20	2.54	2.54	90.72	35.20
27	7.20	60.59%	2.84	4.36	60.59	34.59	2.49	2.49	87.77	34.59
28	7.18	61.21%	2.79	4.39	61.21	35.21	2.53	2.53	90.77	35.21
29	7.13	59.76%	2.87	4.26	59.76	33.76	2.41	2.41	83.90	33.76
30	7.16	61.01%	2.79	4.37	61.01	35.01	2.51	2.51	89.79	35.01
Reference	5.55	26.00%	4.11	1.44	26.00	0.00	0.00	0.00	0.00	0.00
								Average	34.75%	
								Standard Deviation	0.61	

6.1.2 TOC material balance

The final step to characterize the adsorption capacity experiments is to provide a material balance of each system. For this research, the hydrocarbons could be found in four locations; adsorbed to the organoclay, lost to evaporation, left in the bucket and unaccounted. **Table 17** contains the material balance for the performed experiments. The data is based on accounting for mass (grams) of TOC in the system and converting to their respective volumes (ml).

The 65 °API oil provided the best accountability for the hydrocarbons in the system. On average, 3.45 ml was adsorbed to the organoclay, 0.65 ml lost to evaporation and 1.96 ml left in the bucket. The 52 °API oil provided the second best accountability for the hydrocarbons in the system. On average, 2.13 ml was adsorbed to the organoclay, 0.96 ml lost to evaporation and 2.38 ml left in the bucket. The 38 °API oil provided the final place in the accountability of hydrocarbons. On average, 1.12 ml was adsorbed to the organoclay, 1.99 ml lost to evaporation and 1.92 ml left in the bucket.

The material balance required performing experiments to evaluate evaporation effects. For this analysis, a 1500 ppm solution was created using each oil and agitated for a 24-hour period. **Fig. 13** shows the concentration of the bucket was monitored over time. The value achieved after 8-hours was roughly the same as the value achieved after a 24-hour period. The resulting value after 8-hours was recorded to provide a constant evaporation concentration for the differing oils.

The unaccounted portion that was found in the 38, 52 and 65 °API were approximately 7%, 6% and 3% respectively. The percentages are so small that it could be possible that this amount was lost during the drying analysis step.

Table 17 — TOC material balance for 38, 52 and 65 °API oils.

TOC Material Balance										
Sample (#)	Oil Type	Total Oil Added (ml)	Total Oil Desorbed in Drying & Burning (ml)	Oil Lost to Evaporation (ml)	Oil Left in Bucket (ml)	Total Oil Accounted (ml)	Total Oil Unaccounted (ml)	Total Oil Accounted (%)	Total Oil Unaccounted (%)	Total Oil (%)
6	38 API	5.42	1.12	1.99	1.98	5.08	0.34	93.68	6.32	100
7		5.42	1.19	1.99	2.01	5.19	0.23	95.68	4.32	100
8		5.42	1.02	1.99	2.02	5.04	0.39	92.88	7.12	100
9		5.42	1.24	1.99	1.75	4.97	0.45	91.68	8.32	100
10		5.42	1.03	1.99	1.86	4.88	0.55	89.94	10.06	100
	Average		1.12	1.99	1.92	5.03	0.39	92.77	7.23	
16	52 API	5.82	2.17	0.96	2.42	5.54	0.28	95.20	4.80	100
17		5.82	2.00	0.96	2.34	5.30	0.53	90.98	9.02	100
18		5.82	2.19	0.96	2.38	5.53	0.29	95.03	4.97	100
19		5.82	2.26	0.96	2.35	5.57	0.25	95.69	4.31	100
20		5.82	2.05	0.96	2.39	5.40	0.42	92.83	7.17	100
	Average		2.13	0.96	2.38	5.47	0.35	93.95	6.05	
26	65 API	6.25	3.52	0.65	1.99	6.16	0.09	98.62	1.38	100
27		6.25	3.46	0.65	1.96	6.07	0.18	97.12	2.88	100
28		6.25	3.51	0.65	1.85	6.01	0.24	96.18	3.82	100
29		6.25	3.34	0.65	2.10	6.09	0.16	97.49	2.51	100
30		6.25	3.48	0.65	1.93	6.06	0.19	97.04	2.96	100
	Average		3.46	0.65	1.96	6.08	0.17	97.29	2.71	

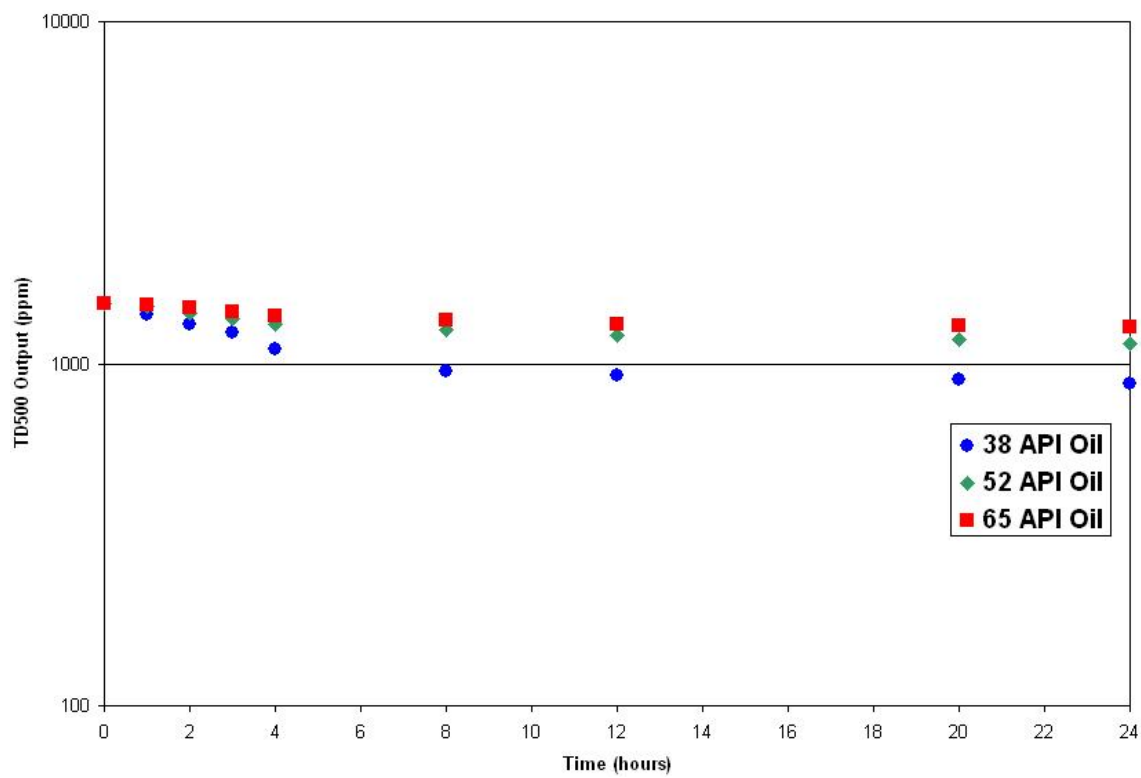


Fig. 13 — Evaporation data for the differing oils.

6.1.3 Comparison to conventional column

Table 18 shows the data provided by Patel's PWSim Software³. The table shows that after 8-hours of operation the conventional column only adsorbs, on average, 17%. If we examine the 65 °API oil system performed in the bucket experiments, the average adsorption capacity was 35%. So to achieve a similar adsorption capacity to the bucket experiments, the column experiments would have to run nearly twice as long to achieve the same adsorption values. Therefore, the bucket experiments provide for higher adsorption in a shorter amount of time. Consequently, the conventional column requires 3 times as much fluid to achieve the same adsorption capacity as the bucket experiments.

Table 18 — Output from PWSim software.

EBCT (minutes)	Time (hours)	Oil Adsorption (%)	Time (hours)	Oil Adsorption (%)
4	8	21%	18	39.8%
5	8	17%	22	39.0%
6	8	14%	23	37.7%

6.2 Economic evaluation

The data shows that it is feasible to treat produced water economically beyond methods currently accepted. The economic analysis predicted the water treatment costs for treating produced water with 15,000 ppm TDS and 200 ppm TOC. The two units used were a 14,000 gpd and a 6,000 gpd produced water feed rate.

The assumed recovery was 50%, which yielded 7,000 gpd and 3,000 gpd of permeate respectively. The two hydrocarbon scenarios were with 30 ppm and 80 ppm hydrocarbon concentration at the organoclay inlet.

The capital investment items used in the produced water system were amortized considering schedules of 3, 5, 7 and 10 years. The predicted cost for treating water over a five year life could range from \$0.71 /bbl treated water to \$1.30/bbl treated water for both the 14,000 gpd and 6,000 gpd units. The predicted cost for treating water over a ten year life could range from \$0.55/bbl treated water to \$1.00/bbl treated water for both the 14,000 gpd and 6,000 gpd units. An important factor is the value the purified water will have in the community/oil field operations and the resulting revenue that can be generated from this new source. However, it is important to realize that an individual analysis must be conducted to ascertain the profitability for each organization. In this it can be assured that the options being considered are the correct path for the company and communities.

CHAPTER VII

CONCLUSIONS AND FUTURE WORK RECOMMENDATIONS

7.1 Conclusions

The continued characterization of organoclay PS-12385 will enable future produced water and oilfield brine systems to operate more efficiency and more effectively. The following conclusions can be drawn from this study;

1. The conversion of produced water and oilfield brines into agriculture or fresh water is feasible given today's technologies.
2. Adsorption capacity of organoclay PS-12385 by the Drying Analysis Method must be used in conjunction with the Burning Analysis Method.
3. The purification of produced water via an organoclay and reverse osmosis system can prove an economically viable process given the correct parameters. The advancement of technology and stricter environmental standards will promote this option more frequently in the future.
4. The produced water treatment system provided economic values ranging from \$0.55/bbl of treated water to \$1.71/bbl of treated water.
5. For the adsorption capacity experiments, the bucket experiments prove to be more effective in adsorbing hydrocarbons versus conventional adsorption capacity experiments performed in a column. In an 8-hour period, a bucket experiment can adsorb 35% of the oil versus 17% of the oil for a conventional column experiment.

7.2 Future Work Recommendations

The following recommendations can be made on the basis of the results and conclusions.

1. Detailed experimentation of organoclay adsorption with oilfield brines as a feed solution is required.
2. Detailed experimentation involving a fixed bed system that will achieve breakthrough to test adsorption kinetics.
3. Examining other separation techniques beyond RO and adsorption experiments to evaluate the most economical process available.

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