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X-O-T TECHNOLOGY FOR THE TREATMENT OF CRUDE OIL EMULSIONS

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Abstract

SCOMI Energy in cooperation with PETRONAS Carigali Miri Crude Oil Terminal (MCOT) implemented a pilot project to demonstrate the effectiveness, technical and economical, of the emulsion treatment technology known as X-O-T for emulsion resolution and crude oil recovery.

A typical emulsion was drawn in batches from Emulsion Storage Tank into Scomi's system. This emulsion was processed on a continuous flow basis through a custom designed system in order to break "resolve" the emulsion and separate its constituents for further disposal or storage of the oil as "dry oil".

X-O-T is a proprietary process utilized to break emulsions of hydrocarbons/water/solids. The process is based on a series of chemical reactions that interact with other reagents releasing heat and neutralizing the non-covalent forces that form the bonds between the substrate and the wetting agents making it feasible to separate the components of an emulsified mixture of minerals, water and hydrocarbons.

A mechanical process for separating the emulsion constituents is needed.

The results of the processing of this emulsion were very promising. All solids contained in the initial emulsion were removed from the mixture; some of small particles in the colloidal size range were transferred directly to the recovered water.

The emulsion was resolved up to 92% to 98% leaving a small tough invert emulsion that contained no solids and a high concentration of heavy hydrocarbons. Recovered solids were "dry" and had hydrocarbon content around 15%. Recovered water was treated using ionic polymer. The result rendered clean water.

This technology can prove to be very economical not only for oil recovery, but also as preventative maintenance. The removal of all solids from this stream can strongly impact the tank farm operations budget by reducing downtime, increasing storage capacity and removing expenses such as tank cleaning and sludge processing.

Introduction

MCOT of Petronas Carigali is located by the ocean shore north of Miri City in the State of Sarawak (see Fig. 1). The terminal receives the daily production from off shore wells located on the great Sarawak basin (Fig. 2) which contains several tectono-stratigraphic provinces principally the Balingian, Luconia and the Baram Delta provinces. These are late Oligocene to mid Miocene deltaic strata formations. From early Miocene to present, these marine environments became more established with predominant deposition of mixed clastic facies and carbonates.

During offshore oil extraction in East Malaysia's South China Sea, a continuous flow of crude oil, water, and fine solids is extracted from the wells. Production in this area can reach 200,000 bbl/D with up to 50-60% free water content and 2-5% emulsion content. This mixture is sent to MCOT for further dehydrating, storing and export¹.

The formation of water in oil emulsions in the production oil has been well documented^{2 3 4}, as well as the problems associated with its handling, storage, transport and refining.

This interfacial emulsion forms upon cooling of the oil water mixture in combination by using a significant amount of agitation and pressure differentials from the formation to the oil Terminal. The chemicals contained in crude oil and water also intervene in the formation of emulsions. These chemicals in the oil can vary from long chain straight hydrocarbons (paraffinic) to complex hetero-atomic polycyclic and bi-polar molecules mostly carboxylic acids and naphthenic acids. Sandstone formations where the crude oil is extracted from provide an excellent base for emulsions. Fine silicon/oxygen (silicates) compounds form anionic crystallites which have a high affinity for water (through hydrogen bonding), oil tends to surround these structures forming an emulsion.

When the crude oil is being extracted, the pressure decreases, this leads to degassing of carbon dioxide from the formation water and, hence an increase in the pH. Dissolved metals and bicarbonate in the water intervene in the complexation of the carboxylic and naphthenic acids which become surface/interfacially active stabilizing colloidal structures.

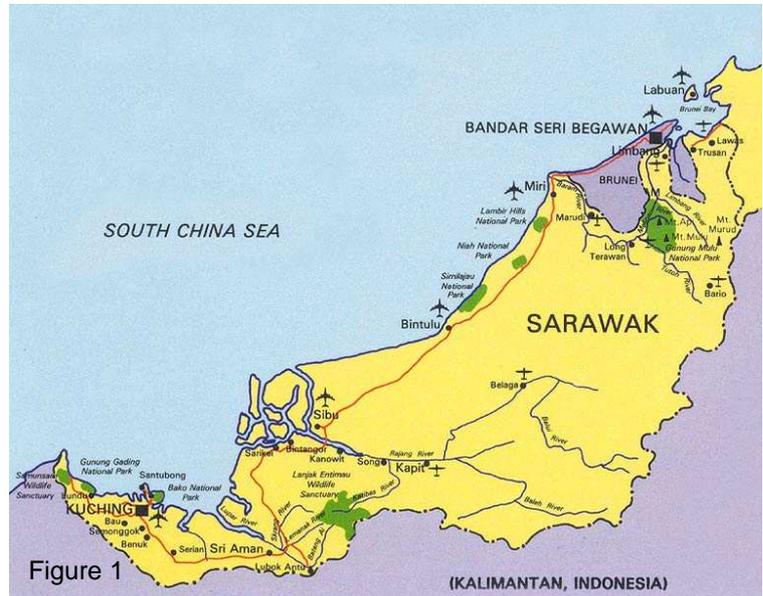


Figure 1

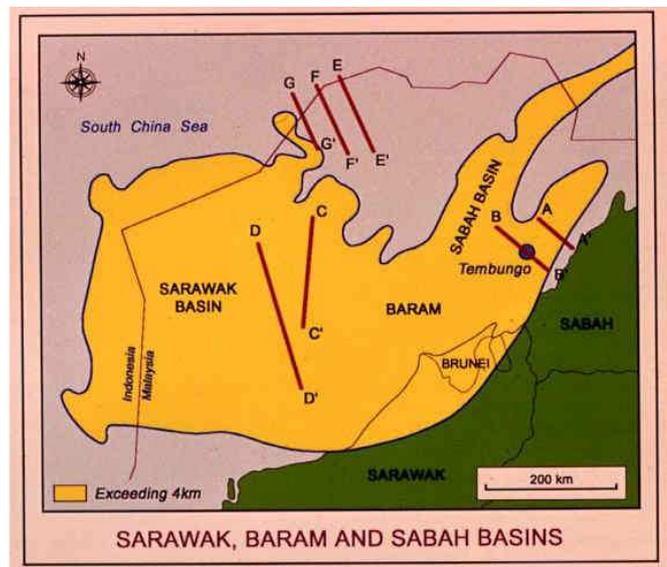


Figure 2

Typical values for this waxy emulsion are in the range of: ~40-70 wt% branched and straight hydrocarbons in the range of C_8 - C_{28} ; approximately ~8-18 wt% consists of C_{28} - C_{30} carboxylate salts, <5 wt% is inorganic minerals and the balance is water⁵.

Background

Current emulsion resolution practices include chemical treatment using acid based emulsion breakers and heat to promote viscosity reduction and separation. Electrostatic separation and mechanical methods like centrifugation have also been used with a certain degree of success. Though, a fraction of the emulsion remains unresolved generating problems associated with it, most likely sludge formation. The extensive use of furnaces in combination with heat exchangers is one of the most used techniques to break emulsions; furnaces pose a risk in a highly flammable environment and also generate large amounts of green house gases. The use of this technology can also bring extra benefits to the operator in the form of carbon credits for process substitution and the associated safety increase by removing open flames in such areas as the tank farms.

In Miri, (**Fig. 3**) the daily field production is sent to MCOT using underwater pipelines. The heavily water loaded fluid is sent to the Free Water Knock Out (FWKO) vessels (V-124, V-125 and V-126)¹, residence time here is approximately 24 min. After an initial separation, the fluid is then transferred to the Wet Crude Storage Tanks where it is enabled to settle under quiescent conditions permitting more of the free water to sink once again. Using decanting techniques the dry oil is sent to the Dry Crude Storage Tanks for further shipping.

The water collected through separation is sent to the Water Buffer Tank TK-68 and then it is processed throughout the effluent treatment plant and discharged back to the South China Sea.

The emulsion, which can reach up to 10,000 bbl/D is then sent to the emulsion storage tank T-41. The emulsion stored in T-41 is continuously pumped through the Emulsion and Wax Treatment Plant (EWTP) using 2 centrifugal pumps (P-100/P-101). Upstream of these pumps an inline dosing system adds an emulsion breaker. Heat is then applied to raise the temperature to ~70°C using furnaces and heat exchangers. After this process the fluid mixture is sent back to the wet tanks for decanting separation. The EWTP also uses electrostatic precipitators to help in the emulsion resolution; these are out of use because of the high water content¹. MCOT does not have specific provisions for solids removal; unless they can leave with the separated water. These solids accumulate in the system and a continuous maintenance plan for tank cleaning and sludge processing (using bio-remediation) has been implemented.

There is a fraction of this emulsion which is difficult to process and stays unresolved and the solids never leave the system until they form tank bottom sludge and tank cleaning takes place. Up to 1,000 bbl/D of unresolved emulsion can accumulate inside storage tanks at MCOT, with time the heavier fractions of the emulsion (rich in solids, water and heavy hydrocarbons) can settle down to form sludge in the storage tanks. The removed "tank bottoms" are sent to the slop farm for further treatment and disposal; these materials can contain up to 80% hydrocarbons which is not recovered under current practices.

Emulsion Characterization

A total of 180 bbl were treated during the Pilot Project. Two batches of 90bbl each were drawn from the T41 tank, processed at different flow rates to derive enough data for the optimization of the process. These two samples contained little or no free water and the emulsion breaker dosing pumps were stopped a few minutes before taking the samples to avoid chemical contamination. The emulsion looked as a brown greenish paste which settles right between the free water layer and the dry oil (**Fig. 3**).

Utilizing method API-13B-2 in the laboratory, the composition of the emulsion from the 1st batch was typified as follows:

- Crude oil	54%	48.60 bbl
- Water	42%	37.80 bbl
- Solids	4%	3.60 bbl

The composition of the emulsion from the 2nd batch was typified as follows:

- Crude Oil	60%	54.00 bbl
- Water	37%	33.30 bbl
- Solids	3%	2.70 bbl

A particle size analysis (utilizing Hydro2000 SM(A)) was performed on this emulsion. **Figure 4** shows the Particle Size Distribution for the raw emulsion before treatment.

The graph in **Figure 4** shows a considerable amount of solids in the range 10 to 100 micron, there is also a fraction of larger particles >100 micron and some in the smaller range <10 micron. Suspension size particles form the majority of the solids contained in the emulsion.

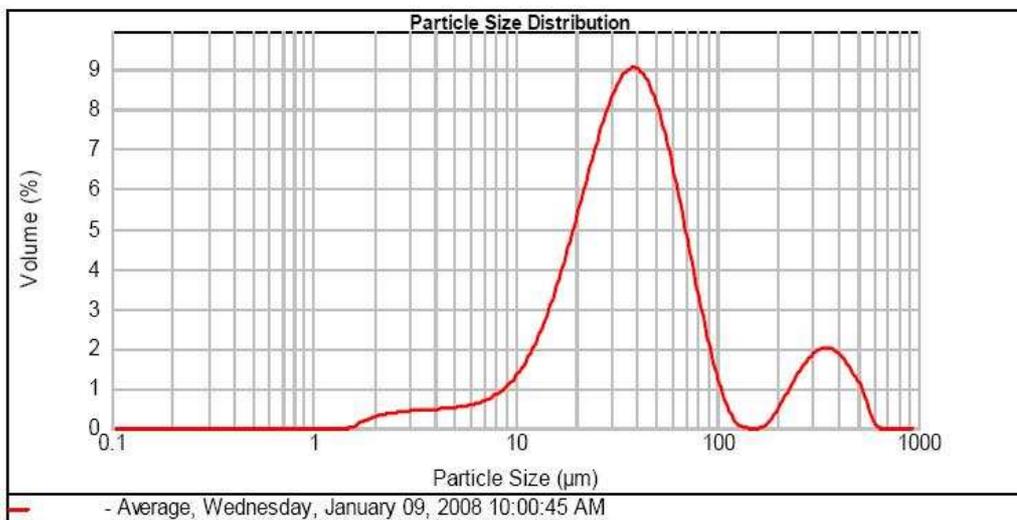


Figure 4



Figure 3

Laboratory bench tests were conducted to determine chemical dosage, and qualitative emulsion resolution using the XOT process to recover oil and separate the water and solids. The best results showed complete emulsion resolution with clean solids and water layers (**Fig. 5**). These tests also helped determine the scale up parameters (residence times, operating temperatures, agitation energy, etc) to design the basic Process and Instrumentation Diagram.

Technology Description

XOT is a proprietary process utilized for emulsion resolution. The process is based on a series of physical processes and chemical reactions involving amphiphilic surfactants (anionic and cationic) which interact as structural analogs disrupting the three layer surface of the emulsion micelles; the presence of other reactants which release heat and independently neutralize the Van der Waals ionic and induction of non-covalent forces including the dipole-dipole hydrogen bonds, the instantaneous dipole induction forces known as London forces and the long range induction forces known as Hamaker forces. These interactions form the bonds between the substrate and the wetting agents making the emulsion stable.

The exothermic reaction that evolves during the process does not change the chemical structure of the aliphatic hydrocarbons and is mainly a reaction among the specific reactants added. The byproducts of the reactions are inorganic salts, water and carbon dioxide that form tiny bubbles which promote oil flotation and solids separation. Solvation of the inorganic salts by the released water is also promoted while viscosity is reduced by means of the temperature increase resulting from the reaction. The reaction is not pH dependent and does not change the initial pH of the emulsion throughout the process. Once the emulsion is unstable, it is now possible to separate its constituents by specific gravity differential into minerals, water and hydrocarbons.

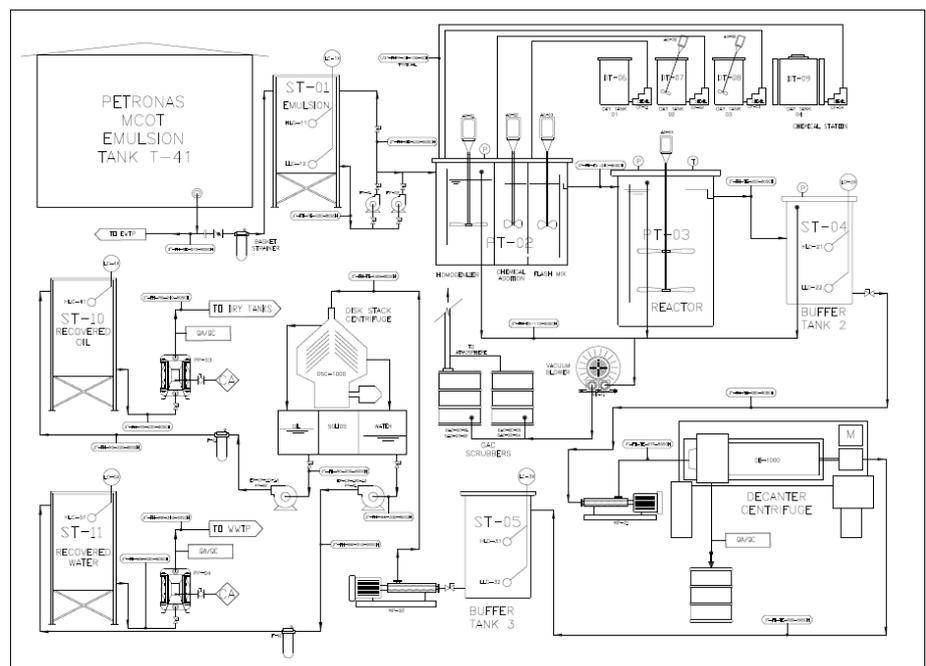


Figure 5

A mechanical process for separating the emulsion constituents is needed following the reaction; in this case the use of a centrifuge is essential to achieve a fast and accurate separation.

Project Implementation

A Process and Instrumentation Diagram (Fig. 6) was developed for a nominal treatment facility of 500bbl/D. The equipment was sourced and shipped or fabricated in Miri. MCOT's Engineering personnel (Process / Mechanical / Electrical / HSE) inspected all the equipment before it's mobilization into MCOT and set up at the EWTP. A containment area had to be built for all the equipment which was set outside the existing bermed areas.



A complete list of the equipment used is shown on the equipment schedule chart below (**Table 1**):

MCOT 500bbi/D CONTINUOUS FLOW PROCESS EQUIPMENT SCHEDULE.

Item No.	Description	Additional Equip			
		ID		ID	Description
1	BUFFER TANK 1	ST-01	Pump	FP-01 & FP-02	Centrifugal Pump, open impeller
2	HOMOGENIZER TANK	PT-02	Agitator	AG-01	Direct drive Agitator
3	CHEMICAL ADDITION TANK	PT-02	Agitator	AG-02	Direct drive Agitator
4	FLASH MIX TANK	PT-02	Agitator	AG-03	Direct drive Agitator
5	REACTOR TANK	PT-03	Agitator	AG-04	Variable frequency drive
6	BUFFER TANK 2	ST-04	Level Controllers	LC-01, LC-02	
7	BUFFER TANK 3	ST-05	Level Controllers	LC-03, LC-04	
8	DECANTER DE 1000 CENTRIFUGE	DC-1000	Pump	MP-01	PROGRESSIVE CAVITY PUMP
9	DISK STACK CENTRIFUGE	DSC-1000	Pump	MP-02	PROGRESSIVE CAVITY PUMP
			Pump	PP-01, PP-02	Centrifugal Pumps
			Bag Filters	F-01, F-02	Bag Filter Housings ASME coded size # 2
10	WATER-SOLIDS TANK	ST-11	Pumps	PP-04	Pneumatic Pump
11	REC. OIL TANK	ST-10	Pump	PP-03	Pneumatic Pump
12	DAY TANK #01	DT-06	Pump	CP-01	Diaphragm metering pump, Max.Flow 24 GPH
13	DAY TANK #02	DT-07	Pump	CP-02	Diaphragm metering pump, Max.Flow 24 GPH
			Agitator	AG-05	Pneumatic Agitator
14	DAY TANK #03	DT-08	Pump	CP-03	Diaphragm metering pump, Max.Flow 24 GPH
			Agitator	AG-06	Pneumatic Agitator
15	DAY TANK #04	DT-09	Pump	CP-04	Diaphragm metering pump, Max.Flow 24 GPH

Table 1

The equipment was set inside the EWTP area close to pumps P-100 and P-101 (**Fig. 7**). A draw off line was flange attached to the sampling port line of the suction line from the outlet of T-41.

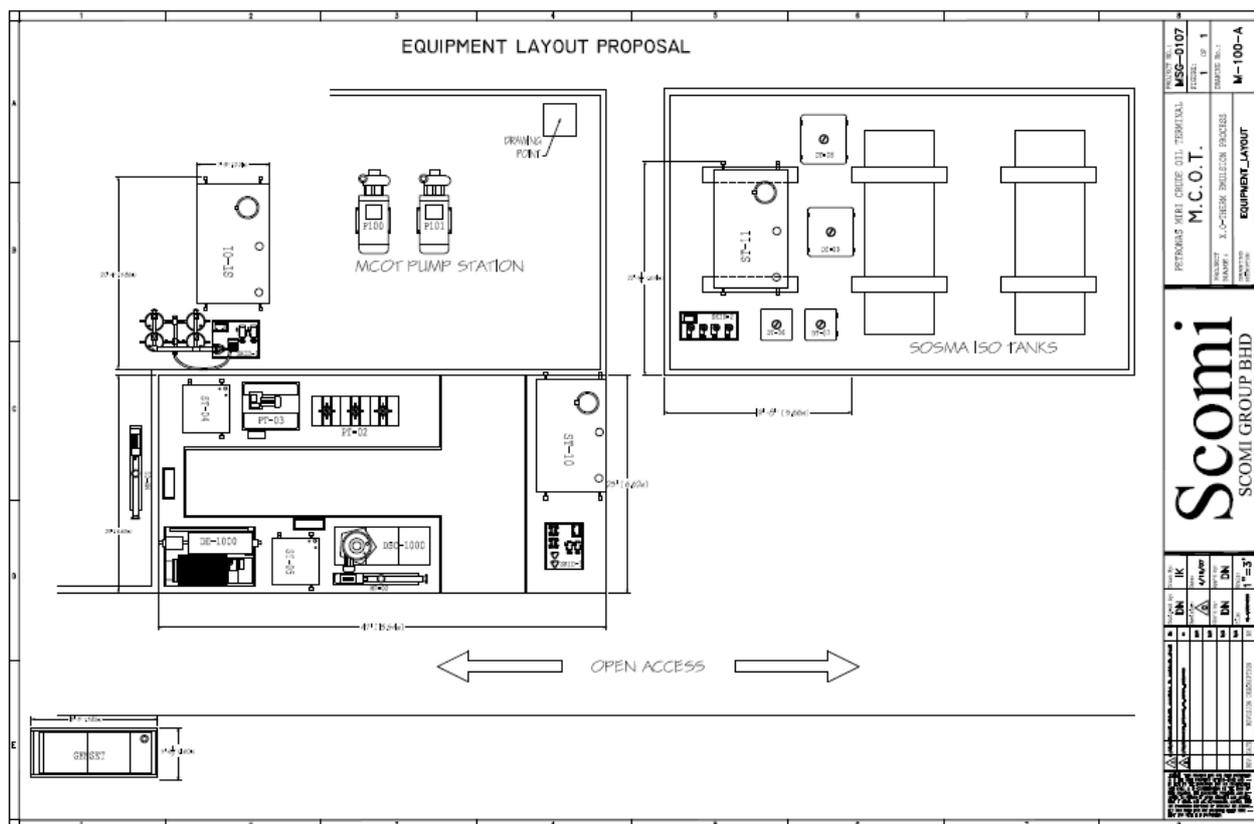


Figure 7

The emulsion was pumped from upstream of MCOT’s pumps P-100 and P-101 into tank ST-01 where batches were accounted for volume (two batches of 90bbl each) and quality, process speed (flow rate) was monitored by timing level sights. Initial temperature for the emulsion was 30-32°C. The emulsion was pumped into the homogenizer using a centrifugal pump with a fixed output (20l/min, 32l/min and 44l/min), the same pump was used for recirculation to keep the sample homogeneous; two chemicals were added in the homogenizer tank using chemical metering pumps with a variable output. Thorough mixing was kept in this tank where a series of baffles prevented the flow from short circuiting the tank. The flow moved into the Chemical Addition Tank in PT-02 where a catalyst is added and mixed. Finally inside the Flash mix tank the last chemical was added to start the exothermic reaction. Both tanks were also continuously agitated. The exothermic reaction took place inside the reactor PT-03, micro gas bubbles were released and the temperature increased see **Table 2** for residence times and operating temperature.

Operating Parameters:

FLOW RATE	REACTION RESIDENCE TIME	REACTION TEMPERATURE
20 l/min	118 min	50 °C
32 l/min	74 min	52 °C
44 l/min	53 min	54 °C

Table 2

All process tanks were covered and kept under negative pressure (~1.5 in H₂O) the recovered gases were directed into the scrubbing system and sent into the atmosphere through a discharge exhaust tower 8m

high. These gases were continuously monitored using 3M™ Multi-Gas Detector 740 Series. The gases monitored were:

- Carbon Monoxide CO. Alarm set 35ppm
- Hydrogen Sulfide H₂S Alarm set 10ppm
- Combustible Gases LEL Alarm set 10%
- Oxygen O₂ Alarm set 19.5% Low & 23.0% High

During all the trial tests none of the alarm conditions were reached.

The reacted mixture was then gravity fed into the Buffer Tank 2, ST-04 where the last of the gas bubbles surfaced and the mixture was now ready for phase separation. A couple of level sensors controlled the Progressive Cavity Pump which feed directly into the decanter centrifuge where separation of the large solids (>10micron) took place. These solids were collected at the bottom of the centrifuge and tested for hydrocarbon content.

The centrate of the centrifuge was then directed into Buffer Tank 3, ST-05 where level sensors controlled the activity of the Progressive Cavity Pump which fed the Disk Stack Centrifuge where a three phase separation took place.

The lighter phase (crude oil) was forced into the upper outlet and into the reservoir tank under the centrifuge. The water and colloidal solids were discharged into the second reservoir tank under the centrifuge. The solids were intermittently discharged into the collection tank under the centrifuge; these solids were processed again through the decanter centrifuge for drying.

The hydrocarbons were filtered using a centrifugal pump and bag filters to remove solids above 10 micron. The recovered oil was stored in ST-10 a Storage tank where samples were taken and analyzed. After quality assurance and quality control the hydrocarbons were sent back to the production Dry Tanks. The water containing ~ 5-8% colloidal and suspended solids was successfully tested for solids separation using coagulation / flocculation techniques by means of ionic polymers. The water was quality tested before and after this process.



Figure 8

The recovered water was sent to the Waste Water Treatment Plant. All collected solids were sent to the sludge farm after quality testing. The actual qualitative results of the whole process are shown on the following section.

Figure 8 shows the equipment disposition in the field.

Results

The first 45 bbl were treated at a flow rate of 20 l/min. Then the second part of the first batch, a total of 45 bbl was treated at 32l/min. The process was followed by taking samples at the points of separation of the phases. The first point was the decanter centrifuge; here a sample of the solids was taken and analyzed in the laboratory for composition and particle size.

The retort showed a composition of:

- Oil 15%
- Water 40%
- Solids 45%

This is an important result; it shows that an actual volume reduction on the solids production can be achieved by removing the bulk oil and water from the solids particularly the long chain hydrocarbons. **Figure 9** shows the sample fractions after the retort.



Figure 9

The particle size analysis for the recovered solids from the decanter centrifuge is shown on **Figure 10**.

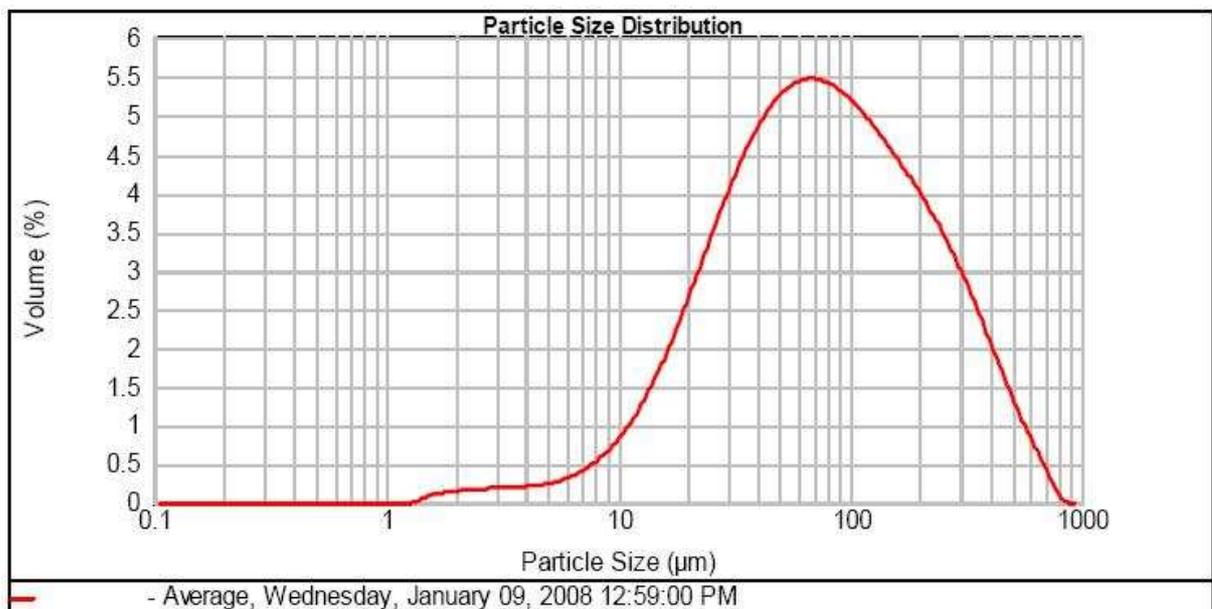


Figure 10

As expected, the decanter centrifuge is capable of removing the solids larger than 10 micron.

From the decanter centrifuge the fluid was pumped into the disk stack centrifuge, three streams were collected here: Oil, water and solids. Several adjustments were needed to control the cutting point of the interface oil/water to achieve a good separation. The sample had to be “polished” to remove the water to minimum levels (~0.3%).

Solids were completely removed to 0% (see **Fig. 11**).



Figure 11

Without polishing, a light yellowish interface composed mostly by heavy hydrocarbons (paraffinic) and water was clearly observed. **Figure 12** shows a typical result of the BS&W test of the recovered oil from the disk stack centrifuge



Figure 12



Figure 13

without polishing. This interface will vary from 2% to 4%. To separate this yellowish interface, samples were cooled to 4.4°C where the interface solidified (see **Fig. 13**), with the oil still liquid it was easy to decant it.

This fraction was also analyzed using the retort and a Varian Gas Chromatograph to determine the hydrocarbon distribution.

The results of the retort showed:

- Oil 86%
- Water 14%
- Solids 0%

Figure 14 shows the retort distillates (paraffin hangs from the walls of the graduated tube).

It is important to remark that complete emulsion resolution was achieved only by polishing the recovered oil.

The yellowish fraction still contains water in the form of an invert emulsion with ~14% water, remarkably, there are no solids **in this emulsion which can have a great impact on the overall production.**



Figure 15 shows the hydrocarbon distribution in this sample, as expected; long chained hydrocarbons (C16-C36) constitute the bulk of it. Calculating back from the oil content in this paraffinic emulsion to the overall BS&W it turns out to be around 0.56% of the whole sample.

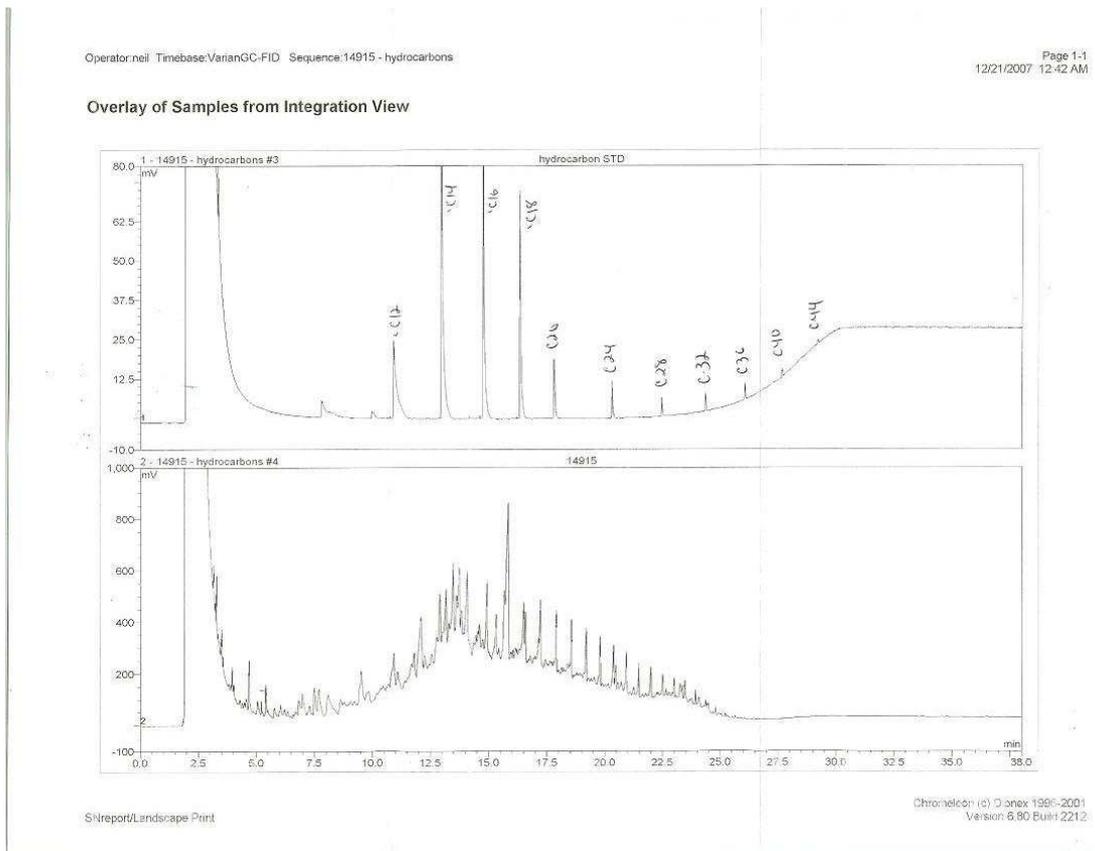


Figure 15

The recovered solids from the disk stack centrifuge were analyzed for particle size distribution (see **Fig. 16**).

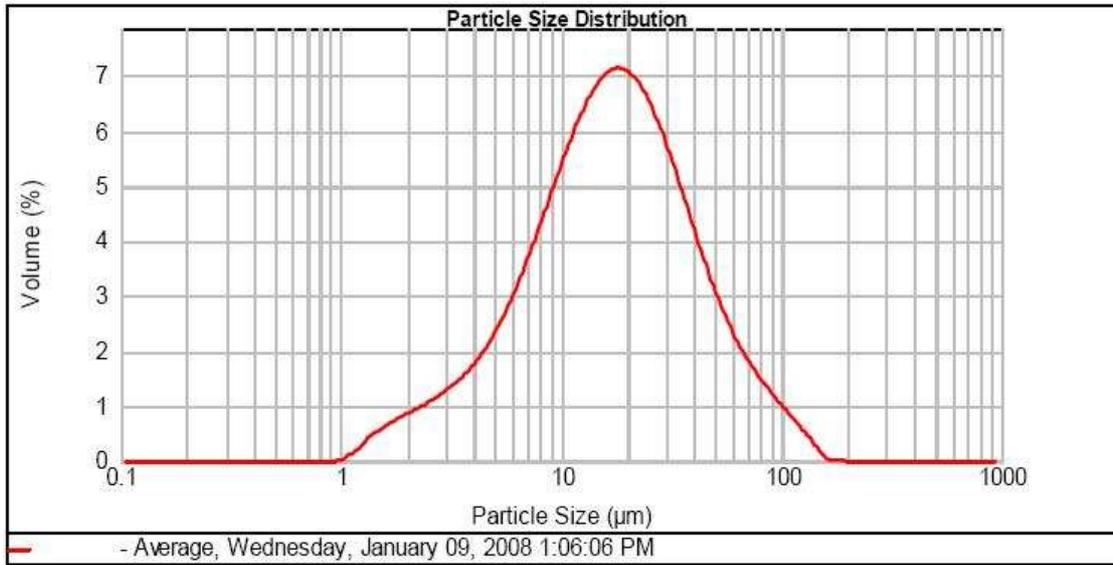


Figure 16

The results on **Figure 16** show that the disk stack centrifuge is capable of removing the small solids (>1 micron) leaving the water and the oil almost solids free.

The recovered water showed a dark black color and high turbidity, this water was filtered using a 10 micron bag and still retained the same color. Samples were taken and analyzed for particle size, **Figure 17** shows the distribution. A lab centrifuge was used to see if it was possible to clean it; the results were negative. Both tests consistently show that the suspended solids were colloidal or near colloidal in nature.

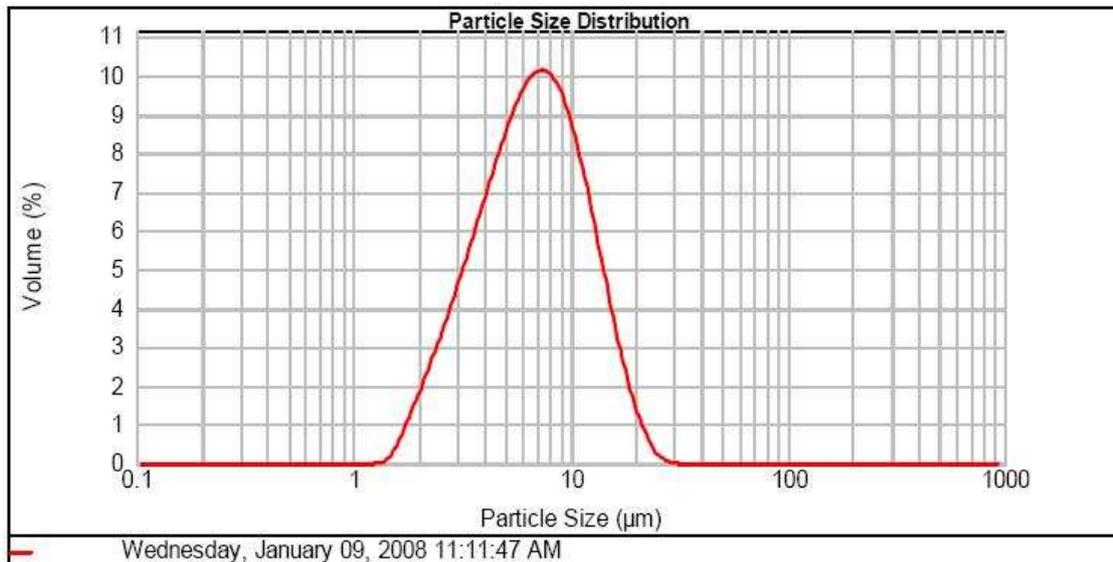


Figure 17

A coagulation/flocculation technique using ionic polymers was implemented with excellent results. **Figure 18** shows a sample of the recovered water from ST-11 and the same sample after coagulation, flocculation and sedimentation using a centrifuge at 700 g's.

Analytical results from the treated sample performed by MCOT's laboratory personnel showed:

- COD	196 mg/l
- TSS	0.0093 mg/l
- pH	8.1
- Oil / Grease	20.9 mg/l

All these parameters are less than the limits for water discharge.

The results of the processing of this emulsion can be summarized as:

- Oil	102.58 bbl with a BS&W of 0.0 to 0.4
- Water	71.00 bbl
- Solids	6.47 bbl



Figure 18

Conclusions

The main objectives contemplated at the beginning of the pilot test were achieved. Though complete emulsion resolution was not achieved at 100% in the first pass, the results from the production point of view are excellent. The minimum content of water in oil emulsion left would not in any way impact the quality needed for exporting the crude.

The solids were completely removed from the emulsion and the volume and mass reduced drastically; furthermore, the concentrations of oil and water in these solids show them as an excellent candidate for rapid photodecomposition and biodegradation.

Water was removed above 98% of the emulsion and the recovered water can be easily treated for safe disposal. These results can be summarized as:

1. All solids contained in the initial emulsion were removed from the mixture (this includes particulate as small as 1 micron) some of these small particles in the colloidal or suspended size range were transferred directly to the recovered water.
2. The emulsion was resolved up to 92%-98% leaving a small tough invert emulsion which contained no solids and a high concentration of heavy hydrocarbons (C_{14} - C_{36}) well in the range of the paraffinic hydrocarbons. This small percentage of unresolved emulsion was later resolved in the laboratory, these results show a good potential for economic scale up and field implementation.
3. The recovered solids were minimized and had hydrocarbon content around 15%.
4. The recovered water was treated using an ionic polymer to promote flocculation followed by coagulation. The result rendered a clean water with the following parameters:

- COD	196 mg/l
- TSS	0.0093 mg/l
- pH	8.1
- Oil/Grease	20.9mg/l

These results also show that scaling up of the process is just a matter of proper equipment sizing and, that the equipment footprint would not impact actual facilities space.

At a time when crude oil prices have reached historical highs this technique can prove to be very economical not only for oil recovery, but also as preventative maintenance. The main benefits of utilizing this process can be listed as:

1. Bottom line production increase.
2. Complete solids removal from the system.
3. Increased storage capacity.
4. Reduction of the water stored in tanks.
5. Minimization of tank cleaning and sludge processing.
6. The substitution of heat sources (furnaces and boilers) that burn fossil fuels by this technology can also bring to the operator the upside addition of carbon credits improving the overall environmental impact of the industry.

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