TECHNOLOGIES TO REDUCE OIL and Grease Content of Well Treatment, Well Completion, and Workover Fluids for Overboard Disposal

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Regulatory and Scientific Affairs Department

API Publication Number 4702

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JULY 2000

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ABSTRACT

The flowback of non-produced fluids to surface de-oiling facilities on offshore platforms can create severe process upsets. Consequently, meeting oil and grease (O&G) effluent limits during flowback presents a serious challenge to the oil and gas industry. To meet this challenge, the industry is considering point source treatment options for non-produced fluids. In order to respond to industry's needs, the American Petroleum Institute (API) supported the present technology evaluation and development project. Promising technologies to reduce O&G concentrations in non-produced fluids were identified, reviewed, and investigated. The performances of selected technologies, including granular activated carbon adsorption, polymer-modified clay adsorption, iron-catalyzed hydrogen peroxide advanced oxidation, liquid-liquid extraction, electro-coagulation, and membrane filtration processes were assessed at laboratory scale. Based on laboratory scale process performance data, technology development was further pursued on granular activated carbon adsorption and polymer-modified clay adsorption at bench scale. The granular activated carbon process was shown effective in meeting O&G effluent limits. Treatment by polymer-modified clay adsorption did not meet O&G discharge objectives.

Sunders and a statements

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EXECUTIVE SUMMARY

The flowback of non-produced fluids (NPF) to surface de-oiling facilities on offshore platforms is a serious concern. These flowbacks create severe operational and performance problems for de-oiling water treatment processes such as gravity settling, flotation, hydrocycloning, and centrifugation. Meeting Environmental Protection Agency (EPA) oil and grease (O&G) effluent limits can be a serious challenge during flowback.

The American Petroleum Institute (API) initiated an independent study to identify effective technologies for the treatment of NPF. The study was structured into three phases: initial information collection; technology review and screening at laboratory scale; and bench scale technology development of the most promising technology.

To properly simulate NPF flowback, the first phase targeted the collection and review of chemical use procedures. A reduced-scale sand pack column simulated a downhole sandstone formation. Formulation and fluid preparation procedures were established for produced water, well stimulation solutions, and non-produced fluids. A nitrogen gas flotation process was used to simulate produced water de-oiling operations. Experimental protocols and O&G baseline data characterizing each fluid were rigorously established.

Treatability data confirmed the impact of non-produced fluids on water treatment processes designed for O&G removal from produced water. Even at a low volumetric blending ratio of five volumes of non-produced fluids to 100 volumes of produced water, the performance of the de-oiling flotation process was reduced by as much as 70%.

Next, O&G concentrations were determined for each of the four well stimulation fluids that comprise the composite non-produced fluids. O&G concentrations ranged from 1166 mg/L to 4252 mg/L. These high O&G concentrations were primarily attributed to the corrosion inhibitors, anti-sludge agents, and surfactants used. Other chemicals, such as iron and clay stabilizer chemicals, did not appear to contribute significantly to O&G.

The second phase consisted of a laboratory scale screening-level evaluation of treatment technologies that could either reduce the effect of NPF on O&G removal processes for "indirect" overboard discharge (controlled blending of treated NPF with produced water, followed by flotation treatment), or remove O&G from NPF for a "direct" overboard discharge of treated NPF in accordance with regulatory guidelines. The following processes were selected and screened at laboratory scale:

- Granular activated carbon adsorption;
- Polymer-modified clay adsorption;
- Iron-catalyzed hydrogen peroxide advanced oxidation;
- Liquid-liquid extraction;
- Electro-coagulation; and
- Membrane filtration.

Based on laboratory scale treatability data, two processes were initially retained: granular activated carbon (GAC) adsorption and iron-catalyzed hydrogen peroxide oxidation. Although both technologies demonstrated similar performance at laboratory scale, chemical oxidation was abandoned in favor of adsorption. This decision was based on technical and logistic scale-up considerations, safety requirements, process flexibility, process control needs, and capital costs.

Bench scale technology development activities were pursued on GAC adsorption. A polymermodified clay adsorbent (PCA) was also included in the bench scale experimental work since it has recently been introduced to offshore operations for the treatment of non-produced fluids from acidizing operations. The performance of PCA adsorption was evaluated both as an alternative to the GAC process and as a pretreatment step.

Two discharge options for the treated NPF were investigated: 1) direct overboard discharge, and 2) indirect overboard discharge entailing controlled blending of treated NPF with produced water prior to final de-oiling treatment by flotation. Adsorption performance was investigated on raw NPF (R-NPF), characterized by high dissolved O&G concentrations (300 mg/L – 400 mg/L) and no free/emulsified crude oil; and on produced water–spiked NPF (PW-NPF), characterized by high dissolved of mg/L – 400 mg/L) and moderate concentrations of emulsified CwG concentrations (300 mg/L – 400 mg/L) and moderate

Treatment of R-NPF and PW-NPF by GAC adsorption met the O&G discharge objective of 29 mg/L. High O&G reductions and high adsorbent capacities were measured when treating R-NPF or PW-NPF, in view of either direct or indirect discharge. This finding was expected, and correlates well with the isotherm data generated at laboratory scale. Treatment of R-NPF and PW-NPF by PCA adsorption never met the O&G discharge objective of 29 mg/L. Modest O&G reductions were measured. This finding was expected for the treatment of R-NPF, and correlates well with the isotherm data generated at laboratory scale.

Treatment of PW-NPF by GAC adsorption with PCA pretreatment met the O&G discharge objective of 29 mg/L. High O&G reductions and high adsorbent capacities were measured, in view of either direct or indirect discharge. The performance of this two-stage hybrid process, however, was very similar to that provided by the single-stage GAC adsorption process. This finding was somewhat unexpected. Although laboratory and bench scale data confirmed the low adsorptive performance of PCA for O&G contaminants in R-NPF, PCA adsorption was expected to be an effective pretreatment when used in conjunction with GAC in treating PW-NPF.

The performance of GAC and PCA, either separately or in tandem, was greater for direct discharge than for indirect discharge. The direct discharge option resulted in a net apparent increase in the performance and capacity of each adsorbent tested.

The treatability data clearly identified the feasibility of GAC adsorption, particularly in view of the direct discharge option.

Section 1 INTRODUCTION

Technologies for treating non-produced fluids from offshore production operations were identified and evaluated in this research work, and based on a review of treatability data from this study, the technologies most suited for handling non-produced fluids from offshore operations are recommended. Recommendations for future research on those technologies are also provided.

Environmental regulations placed on the disposal of treated produced water from offshore operations have become increasingly stringent. Environmental Protection Agency (EPA) specification of a 29 mg/L monthly average oil and grease effluent limit with a 42 mg/L daily maximum limit (Effluent limitation guidelines for the Oil and Gas Extraction Point Source Category, Best Available Technology, 40 CFR 435.13) has triggered the need for improved oil and grease removal prior to overboard discharge. A better understanding of the process upsets which contribute to poor disposal water quality is required (Bansal, 1993). One source of process upsets in de-oiling is flowback of non-produced fluids and their subsequent blending with main production streams.

Non-produced fluids include well stimulation, well completion, and workover fluids. This study focused on non-produced fluids originating from well stimulation operations relying on the use of chemical formulations. This focus excluded well treatment operations involving formation fracturing through the use of explosives or hydraulic pressure, and well completion and workover operations requiring cements and high solids drilling fluids. In production operations, water is generally produced with crude oil, resulting in the formation of emulsions that are stabilized to some extent by naturally occurring compounds present at the oil/water interface. These emulsions are routinely handled on the production platform. The total produced stream is first treated with chemicals to destabilize the emulsion. Heat is sometimes applied in three-phase separation vessels to facilitate separation of the phases. Produced water from these three-phase separators is further treated to remove dispersed oil prior to discharge.

The oil dispersed in produced water following the flowback of non-produced fluids is very different from that in the original production stream. Chemical constituents of non-produced fluids act to strongly stabilize the oil-in-water emulsions, rendering destabilization and phase separation difficult to achieve. These emulsions are responsible for increasing the oil and grease concentrations in discharged water. They also affect the quality of the dehydrated crude oil (Ali et al., 1997).

The high degree of stability of these oil-in-water emulsions can be attributed to several factors, such as (Bansal, 1993; Ali, 1997; Caudle, 1996):

- Acidizing additives, such as mutual solvents, surfactants, and corrosion inhibitors;
- Precipitates formed during acidizing, including colloidal ferric hydroxides;
- Iron (III) interactions with asphaltenes;
- Oil-wetted solids, including corrosion and scale compounds and formation fines; and
- Acidity of return non-produced fluids.

Although the industry is engineering well stimulation formulations and procedures for satisfactory formation acidizing while reducing the impact of fluid returns on de-oiling facilities, these measures alone are not capable of eliminating operational problems (Bansal, 1993; Ali and Hill, 1997; Hebert and Khatib, 1996). As part of the development of these integrated system approaches, effective point-source treatment processes, designed to selectively remove contaminants responsible for stabilizing emulsions and inducing process upsets, need to be developed.

Based on current industry needs, the American Petroleum Institute (API) initiated this independent study to identify effective technologies for the point-source treatment of non-produced fluids. The study was structured into four phases:

- Phase I consisted of collecting and reviewing current chemical use and procedures.
- Phase II targeted the laboratory simulation of produced water (PW), non-produced fluids (NPF), and a blend of PW and NPF (termed "combined fluids," CF). It also included the setup of a sand pack column simulating a sandstone formation, and the set-up of an induced gas flotation process for produced water de-oiling. Oil and grease (O&G) concentrations in all fluids prior to and following de-oiling treatment by flotation were determined.

- Phase III consisted of technology evaluation and development at laboratory and bench scale. Technologies identified in Phase II were first screened at laboratory scale. The most promising technology was retained for process development at bench scale.
- Phase IV consisted of data analysis. Recommendations were made for demonstrating the performance of the selected process on an offshore production platform.
- These study phases are discussed in the following sections of this report.

Section 2 WELL STIMULATION PROCEDURE REVIEW AND EXPERIMENTAL SET-UP AND PROTOCOL

Findings from the information review are presented in this section. Chemical use and procedures are summarized in the following two subsections. Baseline oil and grease (O&G) data for produced water (PW), well stimulation chemicals, non-produced fluids (NPF), and combined fluids (CF) are then presented.

WELL STIMULATION PROCEDURE

Well stimulation chemicals and injection procedures currently used on offshore production platforms in the Gulf of Mexico were identified. Although well stimulation fluid compositions and injected volumes are often site-specific, all procedures share some fundamental similarities. Also, it was assumed that well stimulation formulations provided by the main service companies shared similar chemistry.

The stimulation procedure for sandstone formations generally involves the injection of the following solutions, formulated with surfactants, sequestering agents, corrosion inhibitors, and/or mutual solvents:

- Solution of hydrochloric or acetic acid to displace connate water and dissolve any acidsoluble compounds, such as corrosion products, carbonates, and scales.
- Solution of hydrofluoric acid in conjunction with either hydrochloric or acetic acid to dissolve silicates.
- Solutions of ammonium chloride to flush the formation and avoid precipitate formation that could hamper ensuing oil production.

The acid and ammonium chloride solutions contain a variety of proprietary chemicals for the inhibition of corrosion, foaming, emulsification, etc.

A typical injection sequence, based on a single stage acidizing process for well stimulation with a 20-foot pay zone, is presented below. The chemical injection sequence is pursued over an eight-hour period, with flowback over three days. Total volume of solutions injected is 7,600 gal.

- 1. **Injection of Well Stimulation Fluid A** 8% ammonium chloride, spiked with 1% anti-sludge solution (mutual solvents/surfactants). Approximately 1,000 gal are injected, amounting to 13.2% of the total volume of injected fluids.
- 2. Injection of Well Stimulation Fluid B 10% hydrochloric acid or 10% acetic acid/5% ammonium chloride. Either acid solution is spiked with 0.1% corrosion inhibitor solution, 1.5% anti-sludge solution, and 0.3% iron stabilizer solution. Approximately 1,200 gal are injected, amounting to 15.8% of the total volume of injected fluids.
- 3. **Injection of Well Stimulation Fluid C** 13% hydrochloric acid and 1.5% hydrofluoric acid, spiked with 0.2% corrosion inhibitor solution, 1% anti-sludge solution, 0.3% iron stabilizer solution, and 3% acetic acid. Approximately 2,400 gal are injected, amounting to 31.6% of the total volume of injected fluids.
- 4. **Injection of Well Stimulation Fluid D** 8% ammonium chloride, spiked with 1% anti-sludge solution and 1% clay stabilizer solution. Approximately 3,000 gal are injected, amounting to 39.5% of the total volume of injected fluids.

These fluid formulations were used in all laboratory and bench scale technology development tests.

EXPERIMENTAL SET-UP AND PROTOCOL

The experimental design required accurate and reproducible simulations of the sandstone formation, produced water, non-produced fluids, and produced water de-oiling process. This design was accomplished as follows:

• A sand pack simulated the sandstone formation subjected to acidizing. The sand pack was prepared by blending bentonite (10% v/v), silica powder (10% v/v), and 100-mesh sand (80% v/v). The sand pack was packed to a bed depth of 18 inches in a 35 inch ID column. Assuming 35% porosity, each sand pack was designed to process 30 pore volumes (30 L or 1,818 cubic inches) of well stimulation fluids (A, B, C, and D) in the proportions given in the injection sequence presented previously.

- Field samples of well stimulation chemicals were used to simulate non-produced fluids. Well stimulation fluids A, B, C, and D were prepared, and each fluid was pumped through the sand pack in a downflow mode. The combined mixture was then pumped through the sand pack in an upflow mode, and spiked with a concentrated iron chloride solution to 1000 mg/L iron (as Fe). The resulting solution constituted the simulated non-produced fluids.
- The produced water was simulated by first dissolving sea salts in ultra-pure water, to a concentration of 35 g/L total dissolved solids. Sodium chloride was subsequently added, increasing the total dissolved solids content to 100 g/L. Finally, a field sample of light crude oil was used to prepare simulated produced water containing 1000 mg/L emulsified crude oil.
- A bench scale, induced nitrogen gas flotation process was used to simulate the performance of offshore de-oiling processes for produced water.

The experimental program evaluated the performance of selected technologies for pretreating non-produced fluids. The pretreatment performance evaluation method was as follows:

- Non-produced fluids were treated by the selected pretreatment process.
- Pretreated non-produced fluids were blended with produced water at a volumetric ratio of 5:100.
- These combined fluids were immediately subjected to de-oiling by flotation.
- The pretreatment technology evaluation focused on the effectiveness in reducing NPF impact on the flotation process. Pretreatment performance was assessed indirectly, by measuring the performance of the flotation process in reducing combined fluid O&G. This monitoring protocol was employed to accurately mimic performance and compliance monitoring practices used on offshore platforms (Bansal, 1995).

OIL AND GREASE BASELINE DATA

As a result of the on-going implementation of the Montréal Protocol, the O&G analytical method using Freon[®] as the extraction solvent, EPA Method 413.1, was abandoned in favor of the n-hexane extraction method, EPA Method 1664. Prior to the start of the treatability program, both Freon[®] and n-hexane gravimetric analytical methods were used to determine baseline O&G concentrations in well stimulation solutions, non-produced fluids, and produced water. An overview of the protocol for obtaining baseline O&G data is as follows:

• Preparation of the four well stimulation fluids and of the iron chloride solution.

- Preparation of the sand pack.
- Generation of a 30-L batch of simulated non-produced fluids.
- Set-up of the induced gas flotation process.
- Generation of a 4-L batch of simulated produced water.
- Generation of baseline (no pretreatment) O&G concentration data.
- Running the experimental program.

Baseline O&G data were generated for each experimental run to validate the characteristics of the fluids and the performance of the equipment used. The baseline data were carefully reviewed, and if data for any experimental run were considered questionable, all experimental results associated with that run were discarded, and the causes were investigated.

Beyond simple and direct O&G analytical measurements for raw and pretreated non-produced fluids, special attention was directed to ensure minimal variability in:

- Non-produced fluids simulation.
- Produced water simulation.
- Flotation process set-up and operation.
- O&G analysis.

Hexane-extractables O&G baseline concentration data for the following fluids were determined in the laboratory and were found to reflect typical field data:

- Non-produced fluids before and after flotation.
- Produced water before and after flotation.
- Combined fluids (at 5:100 v/v non-produced fluids to produced water) before and after flotation.

To validate the ensuing pretreatment performance data, baseline O&G data (six measurements) were consistently generated for every daily set of experiments. All process performance data presented in this report were validated as per this protocol. Figure 1 illustrates the experimental methodology.



Oil and Grease Baseline Data for Simulated Produced Water.



Oil and Grease Baseline Data for Simulated Non-Produced Fluids.



Oil and Grease Baseline Data for Simulated Combined Fluids.



Oil and Grease Treatability Data/Indirect Discharge of Pre-Treated Non-Produced Fluids.

Figure 1. Experimental Methodology.

Table 1 presents typical laboratory-simulated produced water emulsion profiles. The data quantify on-going gravity-induced phase disengagement of crude oil from the water phase, and reflect typical produced water emulsion destabilization.

Table 2 presents typical laboratory-simulated produced water O&G concentrations, prior to and following flotation treatment. The measured O&G reductions reflect typical de-oiling performance by flotation units.

Table 3 presents typical laboratory-simulated non-produced fluid O&G concentration data, following flotation treatment alone. As non-produced fluids do not contain free or emulsified oily liquids, the O&G concentration data reflect the presence of dissolved compounds extracted by the n-hexane solvent used in the O&G analytical method. The data reveal poor performance in removing these dissolved compounds by flotation.

Table 4 presents typical O&G concentration data for combined fluids, prior to and following flotation treatment. The data illustrate the impact of commingling non-produced fluids with produced water, at a low volumetric ratio of 5:100. A 56-72% decrease in the performance of the flotation unit was observed.

Simulated	Oil and Grease Concentration of Produced Water as a Function of Settling Time				
Produced	(mg/L)				
Water Batch:	1 min	20 min	60 min	180 min	1,440 min
Batch #1	224	195	176	148	33
Batch #2	311	259	218	199	75
Batch #3	263	241	235	236	48

 Table 1. Typical Emulsion Profiles for Simulated Produced Water.

Simulated	Oil and Grease Concentration of Produced Water			
Produced	(mg/L)			
Water Batch:	RawProduced Water After 20Produced Water After 20 r			
	Produced	min of Gravity-Settling	Treatment in the Flotation Cell	
	Water			
Batch #1	224	195	< 5	
Batch #2	311	259	< 5	
Batch #3	263	241	< 5	
Batch #4	300	278	< 5	

 Table 2. Typical O&G Baseline Data for Simulated Produced Water.

Table 3. Typical O&G Baseline Data for Simulated Non-Produced Fluids.

Simulated	Oil and Grease Concentration of Non-Produced Fluids			
Non-Produced	(mg/L)			
Fluids Batch:	Raw Non- Following One Day of Following 20 min Treatme			
	Produced Fluids	Gravity-Settling	the Flotation Process	
Batch #1	280	290	280	
Batch #2	300	280	275	
Batch #3	410	410	388	

Simulated	Oil and Grease Concentration of Combined Fluids			
Combined	(mg/L)			
Fluids Batch	Raw Combined	Following 20 min of	Following 20 min Treatment in	
	Fluids	Gravity-Induced Settling	the Flotation Process	
Batch #1	275	270	201	
Batch #2	250	259	143	
Batch #3	296	248	168	

Non-produced fluid pretreatment technology performance was monitored by comparing the performance of the de-oiling flotation process with and without NPF pretreatment. Table 5 illustrates a typical performance analysis:

- Beginning with O&G Baseline Data in Table 5, the Raw Produced Water (PW) and Non-Produced Fluids (NPF) O&G Concentrations were 250 mg/L and 300 mg/L, respectively. The Post-Flotation PW O&G Concentration was <5 mg/L, hence, O&G in PW was reduced from 250 mg/L to <5 mg/L by flotation treatment alone. The O&G concentration in NPF, on the other hand, was only reduced from 300 mg/L to 290 mg/L by flotation treatment alone. NPF was essentially unaffected by flotation.
- Again in Table 5, the Raw Combined Fluids (CF) O&G Concentration was 295 mg/L, and the Post-Flotation CF O&G Concentration was 230 mg/L, a decrease of only 22%. The CF was prepared by the addition of 5 parts of NPF to 100 parts of produced water. Since flotation was previously shown to completely remove O&G from produced water, it is important to note the impact a small NPF addition has on the de-oiling performance of the flotation process. This finding illustrates the need for NPF pretreatment.
- Turning to the Treatability Data presented in Table 5, the table presents Post-Flotation CF O&G Concentrations, with three different NPF pretreatment technologies (I, II, III) employed. By comparison with the Baseline Data for CF, Pretreatment Process I was not successful, as CF O&G was reduced by only 9%, from 230 mg/L (Baseline case) to 210 mg/L (with Pretreatment I). By a similar comparison, Pretreatment Process II was moderately successful, as CF O&G was reduced by 57%, from 230 mg/L to 100 mg/L. Pretreatment Process III, on the other hand, was quite successful, as CF O&G was reduced by 93%, from 230 mg/L to 15 mg/L.

It was by this technique of comparing post-flotation CF O&G concentrations with the baseline (no pretreatment) case, that the performance of the various NPF pretreatment technologies was evaluated.

	O&G Baseline Data					Treatability Data			
	O&G Conc. (mg/L)					Post-Flotation CF			
	Raw O&G Fluids Data			Post-Flotation O&G Data			O&G Conc. (mg/L), Using NPF Pretreatment Technology:		
	PW	NPF	CF	PW	NPF	CF	Ι	II	III
Oil&Grease Concentration (mg/L)	250	300	295	< 5	290	230	210	100	15
Observations	Typical and acceptable O&G analytical values for all three fluids. Acceptable visual characteristics also confirmed for all sample batches.		Typical and acceptable de-oiling performance data by the flotation process. Acceptable visual characteristics confirmed for all sample batches. Complete destabilization observed for PW (250 mg/L to <5 mg/L). Insignificant O&G reduction observed for NPF (300 mg/L to 290 mg/L). Slight O&G reduction observed for CF (295		Process I performance is poor. Process I had no impact on NPF: no change in O&G for CF (230 mg/L vs 210 mg/L). Process II performance is moderate but insufficient. Process II had a partial impact on NPF: partial reduction of O&G for CF (230 mg/L vs 100 mg/L). Process III performance is satisfactory. Process III allowed treatment objectives to be met (230 mg/L vs 15 mg/L).				

Table 5. Oil and Grease Sample Data.

ADDITIONAL OIL AND GREASE DATA

In addition to generating the O&G baseline data on PW, NPF, and CF, the following O&G measurements were made:

- Gravimetric Freon[®]-extractable O&G in each of the seven well stimulation chemical formulations at a 0.5% w/v concentration in a brine solution (100 g/L dissolved solids).
- Gravimetric Freon[®]-extractable O&G in each of the four well stimulation stock solutions (Solutions A, B, C, and D) prior to contacting the sand pack.
- Gravimetric Freon[®]-extractable O&G in each of the four well stimulation fluids following downflow contacting of the sand pack.
- Gravimetric Freon[®]-extractable O&G in the two composite well stimulation fluids, immediately following downflow and the subsequent upflow contacting of the sand pack.
- Gravimetric n-hexane and Freon[®] O&G in: 1) produced water, collected at different settling times over a wide concentration range; 2) produced water, following treatment in the flotation cell; 3) well stimulation solutions and fluids; and 4) non-produced fluids.

Table 6 presents Freon[®]-extractable O&G data for the 0.5% solutions of each well stimulation chemical formulation in a 100 g/L salt solution (35 g/L sea salt and 65 g/L sodium chloride). Table 6 illustrates that even at 0.5% concentration, high O&G concentrations (193-721 mg/L) were measured for the corrosion inhibitor, anti-sludge, and surfactant formulations. Significantly lower O&G concentrations (12–46 mg/L) were measured for the clay and iron stabilizer formulations.

Table 7 presents Freon[®]-extractable O&G data for each of the four well stimulation solutions prior to contacting the sand pack. High O&G concentrations (1166-4648 mg/L) were measured for each well stimulation stock solution. These high O&G concentrations primarily reflect the high concentrations of organic solvents and surfactants present in well stimulation formulations. These measurements were made on raw stock solutions prior to downflow contacting of the sand pack.

The stock solutions were pumped downflow through the sand pack. Each well stimulation fluid was collected in a separate container following downflow contacting. An aliquot of each fluid,

Chemical Formulation Type	Freon [®] -Extractables O&G Conc.	
(0.5% in 100 g/L brine solution)	(mg/L)	
Corrosion Inhibitor 1	193	
Corrosion Inhibitor 2	721	
Anti-Sludge Agent	516	
Surfactant	458	
Clay Stabilizer	46	
Iron Stabilizer 1	18	
Iron Stabilizer 2	12	

Table 6. O&G Data for Well Stimulation Chemical Formulations.

Table 7. O&G Data for Raw Stock Well Stimulation Solutions.

Well Stimulation Solution	Freon [®] -Extractables O&G Conc.	
	(mg/L)	
А	1166	
В	4648	
С	2397	
D	4252	

and one aliquot of blended composite fluid (ABCD), were analyzed for O&G. Care was taken to allow the sand pack to drain completely between the downflow pumping of each solution. As precautions were taken not to allow the sand pack to dry out, a minor amount of cross-contamination occurred.

The composite fluid (ABCD) was pumped upflow through the sand pack. The iron solution was then added, and the resulting fluid constituted the simulated non-produced fluids. Table 8 presents O&G data for the well stimulation and non-produced fluids.

Well Stimulation and Non-Produced Fluids	Freon [®] -Extractables O&G Conc.	
	(mg/L)	
А	< 5	
В	8	
С	218	
D	846	
Composite Fluid (ABCD)	618	
Non-Produced Fluids	263	

Table 8. O&G Data for Well Stimulation and Non-Produced Fluids.

O&G concentrations for well stimulation fluids A and B were extremely low (< 10 mg/L), in contrast to the high O&G concentrations observed for fluids C (218 mg/L) and D (846 mg/L). The O&G concentration for the composite sample of A (13% v/v), B (16% v/v), C (32% v/v) and D (40% v/v) was high (618 mg/L). The O&G concentration for the non-produced fluids was also high (263 mg/L), however significantly less than for the ABCD composite.

Based on the O&G data presented in Tables 6, 7, and 8, the following observations were noted:

- Well stimulation solutions are characterized by very high O&G concentrations. This observation is the direct result of high levels of extractable materials present in corrosion inhibitor, anti-sludge agent, and surfactant formulations.
- These extractables showed a strong affinity for the sand pack, and in all likelihood, to its bentonite clay constituent. O&G concentrations in all fluids were significantly reduced by the sand pack. Due to adsorption, O&G concentrations were reduced by 80-100% following a single-pass downflow pumping through the sand pack.
- A high O&G concentration was measured for the composite fluid ABCD (618 mg/L). Computing the expected O&G concentration for the composite fluid blend ABCD suggested a significantly lower composite O&G concentration of (13% x 0) + (16% x 8) + (32% x 218) + (40% x 846) = 338 mg/L. This finding illustrates the non-linear nature of O&G extraction. In addition to being a function of the solvent and extraction method and protocol, any changes in the chemical make-up of the fluid will impact analytical O&G results. As illustrated above, in this case, the blending of all four fluids resulted in an increase in the total quantity of solute partitioning into the solvent.

• O&G concentrations were further reduced by 57% following second-pass upflow pumping through the sand pack, suggesting that additional adsorption occurred in the sand pack. Nevertheless, even following a second pass through the sand pack column, a high O&G concentration was measured for the simulated non-produced fluids (263 mg/L).

Table 9 presents a comparison of n-hexane and Freon[®] O&G data. A good correlation was observed; in 13 out of 15 cases, the n-hexane O&G method gave slightly higher analytical results. The trend was noted for a wide range of concentrations (5-921 mg/L), and for all fluids/solutions studied. For the entire data set, n-hexane O&G concentrations were on average 15% above the Freon[®] O&G data, with a median value of + 6%. The high degree of correlation between both O&G data sets is attributed to the strict analytical protocol established and followed, and to the use of a single analyst for all O&G measurements throughout the project.

Fluid Type	Oil and Grease Concentration (mg/L)			
	Freon [®] –extractables	n-hexane –extractables		
	373	343		
	262	281		
	240	277		
Produced Water	220	251		
	225	236		
	104	139		
	56	40		
Produced Water				
Following Treatment	< 5	< 5		
In the Flotation Process				
	< 5	< 5		
	8	23		
Well Stimulation Fluids	218	255		
	846	921		
	618	439		
Non-Produced Fluids	263	280		
Treated Combined Fluids	72	76		

 Table 9. Comparative O&G Data Measurements.

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Section 3

REVIEW OF O&G REDUCTION TECHNOLOGIES

Following the review of chemical use and procedures, the experimental set-up at laboratory scale, and the generation of O&G baseline data, a review of applicable O&G reduction technologies was undertaken. The review focused on commercially available physical-chemical technologies. The following technologies were selected for study:

- Adsorption by selected grades of granular activated carbons, ion-exchange resins, zeolites, and polymer-modified clay-based adsorbents.
- Coagulation, including electrolytic-coagulation and chemical coagulant or flocculant addition.
- Liquid-liquid extraction, including extraction with synthetic and high-boiling solvents.
- Membrane filtration, including polymeric and inorganic-based micro-filtration, ultra-filtration, and nano-filtration membrane processes.
- Oxidation, including chemical-based advanced oxidation processes.

Technology suppliers were subsequently contacted to engage in detailed discussions on all aspects of the processes and materials considered, and to supplement in-house technical information.

ADSORPTION

Adsorption processes were considered for their ability to remove low-polarity solutes from nonproduced fluids. The following representative adsorbents were selected:

- Two selected grades of granular activated carbon (GAC) adsorbents;
- A polymer-modified clay-based adsorbent; and
- An unmodified clay adsorbent.

ELECTROLYTIC/CHEMICAL COAGULATION

Electro-coagulation and chemical treatment were considered for their ability to remove high molecular weight organics from non-produced fluids through coagulation, flocculation, or

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emulsion destabilization. These processes were considered as part of a hybrid system, in which a subsequent process would target lower molecular weight solutes.

LIQUID-LIQUID EXTRACTION

Liquid-liquid (solvent) extraction processes were considered for their ability to remove non-polar and high molecular weight polar solutes from non-produced fluids. Specific designs of mixersettlers and centrifugal separators were considered for this application. Two solvents were selected:

- Tri-alkyl phosphine oxide; and
- Decanol.

n-Hexane, the solvent used in O&G analyses, was used during experimentation to provide a basis of reference.

MEMBRANE FILTRATION

Membrane filtration processes were considered for their ability to remove intermediate to high molecular weight organics present in non-produced fluids. Membrane filtration processes were considered part of a hybrid system, in which another type of technology would target lower molecular weight solutes. Fourteen representative membrane filters were selected for treatability analysis.

OXIDATION

Oxidation processes were considered for their ability to preferentially oxidize unsaturated and cyclic hydrocarbons, including surfactants and mutual solvents, in non-produced fluids. An iron-catalysed hydrogen peroxide process was selected.

Ozonation and hydrogen peroxide/ozone coupling processes were also considered for the treatability study. However, these technologies were rejected due to the high anticipated cost of generating ozone on offshore platforms for this application. Photo-oxidation processes were rejected due to the anticipated high chemical oxidant demand and high opacity of non-produced fluids.
Section 4

LABORATORY SCALE TECHNOLOGY SCREENING

The technology review, presented in the previous section, identified five classes of technologies potentially applicable to the pre-treatment of non-produced fluids (NPF): adsorption, electrolytic coagulation, liquid-liquid extraction, membrane filtration, and oxidation. This section presents performance screening experimental data for these technologies at laboratory scale.

The experimental methodology relied on a comprehensive definition of all variables specific to each process and material considered. Each experimental variable (e.g., carbon dosage in GAC studies) was prioritized and assigned a number of levels (e.g., 1-80 g/L for carbon dosage). In certain cases, it was not deemed necessary to fully investigate the effects of certain experimental variables. For example, large solution pH changes for electro-coagulation or ozonation, or elevated driving pressure for nano-filtration, were not considered feasible options and were not investigated.

In all cases, laboratory scale experimentation was pursued in a batch mode on 0.1-8.0 L NPF per run. In the performance analysis of each pretreatment process, NPF was first pretreated by the technology under consideration. The pretreated NPF was then combined with produced water at a volumetric ratio of 5:100. This combined fluid (CF) was then subjected to de-oiling treatment by flotation.

At the completion of each set of runs, O&G concentrations in CF following flotation treatment were determined, as well as total organic carbon (TOC) concentrations in pretreated NPF. TOC monitoring was pursued to determine NPF organics removal. TOC measures all organics present in NPF, regardless of their contribution to O&G.

ADSORPTION

The pre-treatment studies evaluated the performance of four adsorbents in the removal of TOC from NPF and O&G from CF following treatment by flotation.

Two selected high-grade granular activated carbon (GAC) adsorbents, a clay adsorbent (CA) and a polymer-modified clay adsorbent (PCA) were retained for preliminary screening. Equilibrium isotherms were developed for all four adsorbents using a single homogeneous 30-L batch of NPF. Experiments were conducted at 20°C and at an unadjusted solution pH of 1.2.

A series of Pyrex[®] reaction vessels was filled with 0.1 L of NPF each. Each adsorbent was then added to its respective reaction vessel at dosages ranging from 1-80 g/L. The vessels were mechanically agitated for two hours, ensuring equilibrium conditions were reached. To remove carbon fines, each sample was subsequently gravity-filtered on a 1.2 μ m glass micro-fiber filter.

In addition to the routine monitoring of CF for O&G, TOC concentrations in raw and GACtreated NPF were also monitored. TOC was monitored to assess solute removal from nonproduced fluids and derive true adsorption isotherms. Tables 10-17 present TOC isotherm and O&G adsorption data.

Adsorbent ("m") (g/L)	Equilibrium TOC (mg/L)	TOC Removed ("x") (mg/L)	x/m (mg/g)
0	8520	0	0
1.0	8390	130	130
3.0	8250	270	90
5.0	7696	824	165
8.0	7520	1000	125
10.0	7280	1240	124
15.0	7046	1474	98

 Table 10. TOC Isotherm Data for GAC Adsorbent 1.

Adsorbent ("m") (g/L)	Equilibrium TOC (mg/L)	TOC Removed ("x") (mg/L)	x/m (mg/g)
0	8520	0	0
1.0	8500	20	20
3.0	8422	98	33
5.0	7680	840	168
8.0	7620	900	113
10.0	7358	1162	116
15.0	7220	1300	87

Table 11. TOC Isotherm Data for GAC Adsorbent 2.

 Table 12.
 TOC Isotherm Data for CA.

Adsorbent ("m") (g/L)	Equilibrium TOC (mg/L)	TOC Removed ("x") (mg/L)	x/m (mg/g)
0	8520	0	0
5.0	8450	70	14
10.0	8164	356	36
20.0	7112	408	20
40.0	7900	620	16
80.0	7820	700	9

Table 13. TOC Isotherm Data for PCA.

Adsorbent ("m") (g/L)	Equilibrium TOC (mg/L)	TOC Removed ("x") (mg/L)	x/m (mg/g)
0	8520	0	0
5.0	8480	40	8
10.0	8346	174	17
20.0	8216	304	15
40.0	7930	590	15
80.0	7850	670	8

Adsorbent ("m") (g/L)	O&G (mg/L)	O&G Removed ("x") (mg/L)	x/m (mg/g)
0	220	0	0
1.0	164	56	56
3.0	105	115	38
5.0	67	153	31
8.0	41	179	22
10.0	36	184	18
15.0	4	216	14

 Table 14. O&G Adsorption Data for GAC Adsorbent 1.

 Table 15. O&G Adsorption Data for GAC Adsorbent 2.

Adsorbent ("m")	O&G	O&G Removed ("x")	x/m
(g/L)	(mg/L)	(mg/L)	(mg/g)
0	220	0	0
1.0	190	30	30
3.0	124	96	32
5.0	81	139	28
8.0	38	182	23
10.0	32	188	19
15.0	8	212	14

Table 16. O&G Adsorption Data for CA.

Adsorbent ("m")	O&G	O&G Removed ("x")	x/m
(g/L)	(mg/L)	(mg/L)	(mg/g)
0	220	0	0
5.0	214	6	1
10.0	210	10	1
20.0	158	62	3
40.0	159	61	2
80.0	157	63	1

Adsorbent ("m") (g/L)	O&G (mg/L)	O&G Removed ("x") (mg/L)	x/m (mg/g)
0	220	0	0
5.0	220	0	0
10.0	215	5	1
20.0	180	40	2
40.0	164	56	1
80.0	158	62	1



The adsorption isotherm data were matched to the Freundlich equation:

 $x/m = k(TOC_e)^{1/n}$ (Equation 4-1)

with x = mass of adsorbate (TOC) removed. m = mass of adsorbent (per fixed volume). $(TOC_e)=$ concentration of TOC in solution after adsorption. k, n = constants.

In linear-logarithmic form, Equation 4-1 becomes:

$$log(x/m) = log(k) + (1/n)log(TOC_e)$$
(Equation 4-2)

Table 18 presents the transformed TOC isotherm data for all adsorbents. Figures 2 to 5 illustrate the TOC isotherm data for each adsorbent. Table 19 presents the transformed O&G adsorption data for all adsorbents. Figures 6 to 9 illustrate the O&G adsorption data for each adsorbent.

Figures 10 to 13 present equilibrium O&G data as a function of carbon dosage. The target O&G concentration was 29 mg/L. Equilibrium isotherm data present the ultimate capacity and performance of each adsorbent tested. Actual batch or column performance will be lower and limited by a number of factors, including adsorption kinetics.

\mathbf{m}	(TOC _e) (mg/L)	Log(x/m) (-)	log(TOC _e)		
	GA	AC 1			
1.0	8390	2.114	3.924		
3.0	8250	1.954	3.916		
5.0	7696	2.217	3.886		
8.0	7520	2.097	3.876		
10.0	7280	2.093	3.862		
15.0	7046	1.991	3.848		
	GA	AC 2	1		
1.0	8500	1.301	3.929		
3.0	8422	1.519	3.925		
5.0	7680	2.225	3.885		
8.0	7620	2.053	3.882		
10.0	7358	2.064	3.867		
15.0	7220	1.940	3.859		
	(ĊA	1		
5.0	8450	1.146	3.927		
10.0	8164	1.556	3.912		
20.0	7112	1.301	3.909		
40.0	7900	1.204	3.898		
80.0	7820	0.954	3.893		
PCA					
5.0	8480	0.903	3.928		
10.0	8346	1.230	3.921		
20.0	8216	1.176	3.915		
40.0	7930	1.176	3.899		
80.0	7850	0.903	3.895		

Table 18. Adsorption Isotherm TOC Data Summary.



Figure 2. GAC 1 Isotherm TOC Data.



Figure 4. CA Isotherm TOC Data.



Figure 6. GAC 1 O&G Adsorption Data.



Figure 8. CA O&G Adsorption Data.



Figure 3. GAC 2 Isotherm TOC Data.



Figure 5. PCA Isotherm TOC Data.



Figure 7. GAC 2 O&G Adsorption Data.



Figure 9. PCA O&G Adsorption Data.



Figure 10. GAC 1 O&G Performance Data.



Figure 11. GAC 2 O&G Performance Data.



Figure 12. CA O&G Performance Data.



Figure 13. PCA O&G Performance Data.

m (g/L)	(O&G) (mg/L)	Log(x/m) (-)	log(O&G) (-)			
	GAC 1					
1.0	164	1.748	2.215			
3.0	105	1.580	2.021			
5.0	67	1.491	1.826			
8.0	41	1.342	1.613			
10.0	36	1.255	1.556			
15.0	4	1.146	0.602			
	G	AC 2	1			
1.0	190	1.477	2.279			
3.0	124	1.505	2.093			
5.0	81	1.447	1.908			
8.0	38	1.362	1.580			
10.0	32	1.279	1.505			
15.0	8	1.146	0.903			
		CA				
5.0	214	0.000	2.330			
10.0	210	0.000	2.322			
20.0	158	0.477	2.199			
40.0	159	0.301	2.201			
80.0	157	0.000	2.196			
PCA						
5.0	220	0.000	2.342			
10.0	215	0.000	2.332			
20.0	180	0.301	2.255			
40.0	164	0.000	2.215			
80.0	158	0.000	2.199			

Table 19. Adsorption O&G Data Summary.

For all four adsorbents studied, a good correlation was observed between the TOC isotherm and the corresponding O&G adsorption data (Figures 2-5 versus Figures 6-9). The adsorbed contaminant mass increased with the applied mass of adsorbent. This increase was not linear, however; the sudden changes in the slope of the isotherm curves clearly identify the presence of a number of different adsorbed compounds with different loading capacities onto each adsorbent. As a consequence, solution TOC concentration could not be readily correlated with adsorbed TOC concentration. The anticipated adsorptive capacity of each adsorbent could not be readily calculated from the isotherm TOC data.

Although the adsorption performances of the GAC adsorbents appear comparable over the entire TOC or O&G concentration range studied, a lower adsorptive performance was noted for GAC adsorbent 2 at the very high TOC concentration range. This lower adsorption capacity performance was also observed in the O&G data set, although to a lesser extent.

Although the isotherm and adsorption curves for both GAC adsorbents are at a high level, only slight slopes characterize both sets of curves. This indicates that adsorption is relatively large over the entire concentration range studied. It should be noted that the slope of the O&G adsorption curve for GAC adsorbent 1 is steeper than that of GAC adsorbent 2, suggesting a greater efficiency for this adsorbent in countercurrent column operation.

For both GAC adsorbents, the feasibility of meeting the O&G target of 29 mg/L is well illustrated in Figures 10 and 11. Based on the adsorption data sets, it is estimated that the O&G objective of 29 mg/L can be met with 11 g of GAC adsorbent 1 per liter of NPF. Contaminant loading on the adsorbent is expected to be very high, and is estimated at 1.3 g per 11 g of adsorbent, a 12 % mass loading.

The adsorption capacities of the two GAC adsorbents over the concentration ranges studied were significantly higher than that provided by either CA or PCA.

PCA performance was very similar to CA performance. TOC and O&G adsorption was low, as can be seen from Figures 4, 5, 8, and 9. The adsorption data indicate targeted adsorbates

removed by low GAC dosages were not removed by very high dosages of CA or PCA. Figures 12 and 13 further illustrate this point. Based on the isotherm data, it was determined that neither CA nor PCA could meet the 29 mg/L O&G discharge objective.

Based on the TOC isotherm and O&G adsorption data, the following conclusions were drawn:

- Both GAC adsorbents were found very effective in removing the target contaminants responsible for high O&G concentrations in these fluids.
- Neither CA nor PCA could meet the targeted O&G discharge objective, even at an excessive sorbent dosage (80 g/L).
- The adsorption performance of GAC adsorbent 1 was superior to that of GAC adsorbent 2, particularly at higher TOC concentrations. It was recommended to retain GAC adsorbent 1 for the ensuing adsorption column studies.
- PCA performance was very similar to CA performance.
- Although the adsorption performance of either PCA or CA was not comparable to that provided by either GAC adsorbent, PCA was retained for treatability testing in the ensuing column adsorption studies. This decision was based in part on the offshore use of a PCA-based process to treat non-produced fluids from acidizing operations, and thus an anticipated high level of interest in PCA performance data.

ELECTROLYTIC COAGULATION

The performance of laboratory scale electro-coagulation in removing TOC and O&G from NPF and CF was assessed. The electro-coagulation unit consisted of an 8 L electrode chamber with iron electrodes placed in two rows of multi-rectangular sheets (10 cm x 8 cm). Care was taken to thoroughly remove all corrosion products in the chamber and clean the iron electrodes immediately prior to filling the chamber with 8 L of NPF to initiate experimentation.

Commercial electro-coagulation processes operated under the following conditions destabilize micro-emulsions and remove high molecular weight dissolved complexes:

- Voltage of 6 volts,
- pH range of 5 to 10, and
- Retention time of 1 to 5 minutes.

In accordance with commercial operating procedures, the laboratory scale process was operated at 6 V, for reaction times ranging from 1 to 180 minutes, at an unadjusted pH value of about 1.2.

Samples of raw and electro-coagulated fluids were analyzed for TOC and O&G. In addition to routine monitoring of CF O&G concentrations, raw and electro-coagulated NPF were analyzed for TOC. Iron concentrations in NPF were also monitored to indirectly assess the extent of the electrolytic reaction. Oxidation reduction potential (ORP), solution pH and temperature were monitored as well. Table 20 presents the treatability data.

Reaction Time	pH/T/ORP	TOC	O&G	Total Iron Conc.
	(-7C/mV)	(g/L)	(IIIg/L)	(g/L)
0 (control)	1.2 / 20 / 350	9.2	219	1.0
2	1.3 / 20 / 338	9.2	185	7.8
5	1.3 / 20 / 327	9.2	170	7.7
30	1.3 / 25 / 321	9.1	158	7.7
180	3.0 / 38 / 121	9.1	65	22.7

 Table 20.
 Electro-Coagulation Treatability Data.

Process performance was clearly poor. TOC remained unchanged throughout the run. Although a significant reduction in O&G concentrations in CF could be achieved, the discharge objective of 29 mg/L could not be met even after a reaction time of 180 minutes. Moreover, in order to reduce O&G from 219 mg/L to 65 mg/L, a significant iron mass came into solution from the electrodes; the NPF iron concentration increased from 1 g/L to 23 g/L. Such high iron concentrations would require precipitation treatment, necessitating costly sludge disposal.

Thus, the treatability study results strongly suggested that electro-coagulation and chemical coagulation were not viable and did not need to be considered further.

LIQUID-LIQUID EXTRACTION

The performance of two solvents - TAPO, a tri-alkyl phosphine oxide (alkyl chains of six and eight carbons), and decanol (a ten-carbon straight chain aliphatic alcohol) – in removing TOC

and O&G from NPF and CF was assessed. To provide a basis for comparison, the performance of n-hexane (the solvent used in the analytical determination of O&G) was also assessed. These solvents were selected on the basis of the partitioning properties of the target contaminants. The solvents are characterized by low aqueous solubility, low vapour pressure under ambient conditions, a moderate degree of polarity, and high molecular weight.

Batch extractions were conducted in a one-liter Pyrex[®] mixing vessel. In order to ensure adequate contacting, the experiments were conducted at high stirring speed and shear, over a 10-minute mixing time. A 5:100 volumetric ratio of solvent to NPF was selected for all extraction runs. Additional exploratory runs were pursued at different solvent-to-water ratios and at lower mixing energies, to visually assess phase mixing and disengagement. Actual working volumes exceeded 0.5 L. The NPF phase was allowed to disengage overnight at room temperature, and was subsequently micro-filtered to remove finely emulsified solvent droplets. In addition to the routine monitoring of O&G concentrations in CF, TOC concentrations in raw and extracted NPF were also monitored.

The equilibrium partition coefficient (ratio of equilibrium contaminant concentration in the organic phase to that in the aqueous phase) was calculated. Table 21 presents the data.

Extractant	тос	O&G	Partition	Partition
	(g/L)	Concentration (mg/L)	(TOC-based)	(O&G-based)
- (control)	8.7	296	-	-
ТАРО	6.7	62	6	75
Decanol	8.1	59	2	80
Hexane	8.3	277	1	1

 Table 21. Liquid Extraction Treatability Data.

Process performance was poor. TOC remained relatively unchanged for each solvent tested. Although it might appear that a significant reduction in CF O&G was achieved, process performance was not satisfactory. With n-hexane, a TOC reduction of 0.4 g/L was observed, indicating the majority of organics in non-produced fluids do not readily partition to n-hexane. Thus, the experimental data strongly suggested that liquid extraction was not viable and should not be considered further.

MEMBRANE FILTRATION

The performance of fourteen filtration membranes in removing TOC and O&G from NPF and CF was assessed. Raw and filtered (permeate) fluids were analyzed for O&G and TOC. In addition to routine monitoring of CF O&G, NPF TOC was also directly monitored. The experimental work was pursued as follows:

- 1. Membrane material compatibility was first assessed. Membrane coupons were immersed in NPF, at room temperature, for a (relatively short) period of 72 hours. This conservative test was conducted to rapidly screen out incompatible membrane materials. A visual assessment was sufficient in most cases to document structural changes and reject incompatible membranes.
- 2. Preliminary performance data were subsequently generated for the membranes that had passed the compatibility assessment. A six-cell coupon process, operated at 150 psi, was used.

Table 22 presents the material compatibility results. The material compatibility assessment study effectively screened out eight membranes that suffered from moderate to severe structural changes from short time exposure to NPF. Four membranes passed the preliminary compatibility test with no noticeable changes, while three others appeared to have suffered minimal changes.

The following six membranes were retained for the treatability study:

- Membrane 1
- Membrane 3
- Membrane 6
- Membrane 8
- Membrane 9
- Membrane 13

Table 23 presents the preliminary performance assessment. Pure water fluxes were initially measured for the virgin membranes (initial PWP) and were subsequently measured immediately following the completion of the test run (final PWP).

4-14

Membrane Supplier	Membrane	Membrane Type (UF=Ultrafiltration NF=Nanofiltration)	Compatibility
	1	UF	YES
А	2	NF	NO
В	3	UF	YES
С	4	NF	NO
C	5	NF	NO
	6	NF	
D	7	NF	Some Change
	8	NF	Observed
Е	9	NF	YES
	10	NF	NO
	11	NF	NO
F	12	NF	NO
	13	NF	YES
	14	NF	NO

Table 22. Membrane Compatibility Assessment.

 Table 23. Membrane Filtration Treatability Data.

		Performance Data							
Membrane		Perm	ieate Fli	ux (L/m	r ² h) at t	ime =		тос	0&C
Туре	PWP _{initial}	10	30	60	90	120	PWP _{final}	(g/L)	(mg/L)
		min	min	min	min	min		(g/L)	(ing/L)
Control	-	-	-	-	-	-	-	8.35	230
1	279	33	30	28	27	26	130	7.05	45
3	54	59	59	65	71	73	105	7.05	24
6	21	2	2	2	2	2	19	2.78	n.a.
8	21	20	16	16	16	15	42	6.90	48
9	42	0	0	1	1	1	38	1.62	n.a.
13	42	0	0	0	0	0	21	n.a.	n.a.

n.a.: data not available, due to insufficient volume of permeate collected.

.....

With the exceptions of Membrane 6 and Membrane 9, all membranes showed early signs of membrane fouling and/or degradation. Membrane degradation was especially apparent for Membrane 3 and Membrane 8, for which pure water fluxes increased following the two-hour test run.

Product fluxes across all membranes were unsatisfactorily low under the conditions tested. The experimental data collected strongly suggested that membrane filtration was not viable. Membrane filtration data provided some insight, however, into the nature and characteristics of NPF:

- The majority of the organics responsible for high O&G concentrations are dissolved macromolecules with molecular weights of tens to hundreds of thousands of grams per mole. These compounds amount to approximately 15% of TOC in NPF.
- Approximately 1.3 g of TOC (in the micro- to ultra–filtration range) appear to be primarily responsible for high O&G concentrations.
- TOC data appear to correlate with adsorption TOC and O&G data, where approximately the same concentration of TOC was responsible for high O&G concentrations.
- Membrane filtration data confirm that NPF organics are dissolved and that an oil-in-water micro-emulsion is not present. The latter point further substantiates the poor process performance of the electro-coagulation process. The membrane filtration data explain the very high loadings of targeted contaminants (of very high molecular weight) onto GAC.
- The bulk of the remaining organics (65% of TOC) are characterized by molecular weights of a few hundred grams per mole, with the balance (20%) being characterized by molecular weights less than a couple of hundred grams per mole. These low molecular weight organics (85% of TOC) appear to have a smaller impact on O&G concentrations.
- The membrane filtration, adsorption, and liquid extraction NPF treatability data suggest that NPF is an elaborate mixture of organics and inorganics, in which complex chemical interactions have formed very high molecular weight compounds. The very high solvating properties provided by low molecular weight polar solvents explain the poor performance observed during the liquid extraction treatability.

OXIDATION

The performance of chemical oxidation in removing TOC and O&G from NPF and CF was assessed. An iron-catalyzed hydrogen peroxide process was selected as the most feasible

advanced oxidation process for this application, given the nature and concentration of organic contaminants in NPF, low intrinsic solution pH, and high intrinsic iron concentration.

In addition to the routine monitoring of O&G concentrations in CF, both TOC and residual (unreacted) hydrogen peroxide concentrations in NPF were monitored. Batch experiments were performed in open-top Pyrex[®] reaction vessels, and were initiated at room temperature. Three process variables were studied:

- Initial solution pH: 0.8 (raw); 1.5; 2.5; and 3.5. Solution pH was adjusted by the addition of a concentrated sodium hydroxide solution.
- Hydrogen peroxide concentration: 0 (control); 1 g/L; 3 g/L; 4 g/L; 5 g/L; and 6 g/L.
- Iron (II) concentration: 0 (control); 0.1 g/L; and 1.0 g/L. Although iron (III) was present in NPF at a concentration of 1 g/L and is a known reaction initiator, process performance was also investigated when iron (II) was added to NPF as a second reaction initiator.

Table 24 presents process performance data as a function of initial solution pH. Hydrogen peroxide and iron (II) were added at 5 g/L and 1 g/L, respectively. Under these conditions, hydrogen peroxide and iron (II) were present at sufficiently high concentrations to not limit oxidation reaction kinetics, leaving the initial solution pH as the primary rate-limiting factor. Reaction time was set at 24 hours. Initial solution temperature was 25°C.

Initial Solution	pH	ORP (- at time =	/ mV) =	TOC Conc. (g/L)	O&G Conc.	Hydrogen Peroxide	Observations
рН	• •	<i>(</i>) .	241		(mg/L)	Conc.	
	0 min	60 min	24 hours			(g/L)	
Control		0.8 / 42	6	6.8	250	-	-
0.8	0.8/426	0.9/677	0.6/684	5.4	< 10	2.1	slow initiation
1.5	1.5/411	1.4/650	1.1/658	4.7	< 10	1.3	slow initiation
2.5	2.5/326	2.0/613	1.5/616	4.8	< 10	< 0.5	acceptable
							kinetics
3.5	3.5/220	2.5/559	2.2/571	4.6	< 10	< 0.5	acceptable
							kinetics

 Table 24. Chemical Oxidation Process Performance Data.

Process performance was satisfactory under all four experimental conditions. Even at the unadjusted initial pH value of 0.8, discharge O&G objectives were met at a hydrogen peroxide dose of 5 g/L, iron (II) concentration of 1 g/L, and a reaction time of 24 hours. O&G concentrations were reduced from 250 mg/L to <10 mg/L. In meeting the O&G objective, a TOC reduction of 1.4 g/L was observed.

A marked difference in oxidation reaction rate was observed, and was further reflected by solution pH after 60 minutes. Initial solution pHs of 0.8 and 1.5 resulted in very slow initiation of the oxidation reaction. pH remained essentially constant during the first hour, with a marked decrease over the ensuing 23-hour period. Initial solution pHs of 2.5 and 3.5, on the other hand, promoted fast reaction initiation. A marked decrease in solution pH was measured at a reaction time of one hour.

The preliminary process data confirmed the feasibility of the proposed chemical oxidation process. Preliminary process optimization was subsequently initiated. To further investigate the performance of this technology, a hydrogen peroxide consumption profile was developed. Experiments were conducted at an adjusted initial pH of 2.5, and hydrogen peroxide and iron (II) concentrations of 6 g/L and 1 g/L, respectively. Table 25 presents the hydrogen peroxide consumption profile.

Reaction Time (min)	pH / T / ORP (- / C / mV)	Hydrogen Peroxide Conc. (g/L)	Hydrogen Peroxide Consumption (%)
0 (control)	2.5 / 25 / 352	6.0	-
15	-	3.6	40
27	2.0 / 30 / 585	3.3	45
40	2.0 / 28 / 584	3.0	50
50	-	3.0	50
60	1.9 / 25 / 581	2.6	57
75	-	2.6	57
90	1.9 / 23 / 586	2.4	60
120	1.8 / 23 / 586	2.3	62
180	1.8 / 22 / 585	1.9	68
18 hours	1.8 / 22 / 582	0.6	90

Table 25. Hydrogen Peroxide Consumption Profile.

Figure 14 illustrates the hydrogen peroxide decomposition profile. The plot illustrates fast reaction initiation, with close to half of the hydrogen peroxide concentration being consumed within a 30-minute reaction time.

Preliminary process optimization studies were then conducted. Shorter reaction times and lower hydrogen peroxide and iron (II) concentrations were evaluated at an initial solution pH of 2.5 \pm 0.1 and an initial temperature of 22°C. Table 26 presents the performance data, and Figure 15 illustrates the results at an initial concentration of 1 g/L iron (II). The O&G objective was met in all runs at initial hydrogen peroxide concentrations of 1-6 g/L, at a reaction time of 24 hours.

At an initial hydrogen peroxide concentration of 6 g/L and for a reaction time of 24 hours, O&G concentrations ranged from 11 mg/L to 23 mg/L. The addition of 1 g/L of iron (II) significantly increased the rate of oxidation: the O&G objective was met within a three-hour reaction time. Duplicate and triplicate runs (3d and 3t) were undertaken to confirm process data: minimal variability was observed with O&G concentrations ranging from 11 mg/L to 14 mg/L.

At an initial hydrogen peroxide concentration of 4 g/L and for a reaction time of 24 hours, O&G concentrations varied from 16 mg/L to 25 mg/L. The addition of 1 g/L of iron (II) significantly increased the rate of oxidation. The O&G objective was met within a three-hour reaction time. At an initial hydrogen peroxide concentration of 3 g/L and an iron (II) concentration of 1 g/L, the O&G discharge objective was also met within a 30-minute reaction time. The data were supplemented with an additional sampling time of 3 hours, during which time the O&G concentration remained relatively unchanged at 10 mg/L.

Even at a low initial hydrogen peroxide concentration of 1 g/L and for an iron (II) concentration of 1 g/L, the O&G discharge objective was met within 3 hours reaction time. However, at this low initial hydrogen peroxide concentration, a reaction time of 30 minutes was insufficient to meet the objective.



Figure 14. Hydrogen Peroxide Consumption Profile.



Figure 15. Chemical Oxidation Process Performance.

Run	Initial Hydrogen Peroxide	Initial Fe (II) Conc.		pH / T / ORP (- / C / mV) at time =				O&G Concentration (mg/L) at time =			Hydrogen Peroxide Conc. (g/L) at time =		
	Conc.	(g/L)	1	30	3	24	30	3	24	10	30	3	24
	(g/L)		min	min	hours	hours	min	hours	hours	min	min	hours	hours
1		0	2.7/29/557		2.2/21/564	1.9/24/573		57	17	5.2		4.2	
2		0.1	2.5/30/574		2.2/20/570	1.9/24/585		52	23	5.3		4.2	
3	6.0			-			-	18	13	4.9	- 1	3.1	1.1
3d		1.0	2.6/34/576		2.0/20/580	1.8/24/583			11				
3t								-	14	-		-	-
4		0	3.0/28/553		2.2/21/567	1.9/24/570		64	16	3.7		2.7	1.3
5	4.0	0.1	2.6/33/560	-	2.0/21/569	1.8/24/580	_	76	25	3.7	-	2.5	1.1
6		1.0	2.6/34/565		2.1/20/570	1.9/24/516	9	18	19	3.1]	1.3	0.3
7	3.0	1.0	2.8/28/589	2.4 / 22 / 585	2.1/22/503	-	12	10		2.7	1.9	0.3	
8	1.0	1.0	2.8/28/534	3.0 / 24 / 419	2.9/22/395	_	59	22	-	0.6	0.3	0.2	-

 Table 26. Chemical Oxidation Process Performance Data.

An initial temperature increase was noted for all runs. This initial temperature rise was especially apparent when iron (II) was added as a reaction initiator. The rapid onset of the oxidation reaction was confirmed by a correspondingly rapid decrease in solution pH. Solution pH values consistently followed this profile for all runs: a decrease of varying magnitude was observed within the first three hours, with pH values leveling off over the ensuing 21 hours.

The hydrogen peroxide consumption profile correlated well with the other process data presented above. The hydrogen peroxide demand was small. When iron (II) was added to NPF at 1 g/L, a net hydrogen peroxide demand of approximately 0.8 g/L to 1.1 g/L was required to meet the discharge O&G objective. Where hydrogen peroxide was dosed in excess (~ 200%), a reaction time equal to or less than thirty minutes was sufficient. Where hydrogen peroxide was added in roughly stoichiometric amounts, a reaction time equal to or less than three hours was required. Figure 15 highlights the findings. When hydrogen peroxide and iron (II) were added to NPF at dosages \geq 3 g/L and 1 g/L, respectively, the discharge O&G objective was readily met within a 30-minute reaction time.

Visual observations indicate that at the end of the reaction time (up to 24 hours), iron is in an oxidized state (Fe⁺³) and remains either in solution or as very fine colloidal matter. If iron hydroxide precipitates were present, these did not settle. Moreover, micron-size filtration (0.45 μ m cellulose acetate paper) did not capture any iron flocs. Given the 1 g/L iron concentration and the acidic nature of the fluids after oxidation (pH ~ 2), it is suggested that iron (III) remained in solution due to the presence of sequestrants in the NPF. These sequestrants do not appear to have been affected by the chemical oxidation process.

The following conclusions were drawn:

- 1. The iron-catalysed hydrogen peroxide process was found effective in removing the targeted contaminants responsible for high O&G concentrations in NPF.
- 2. This advanced oxidation process was effective even on raw NPF (no pH adjustment). However, long reaction times (up to 24 hours) would be required.
- 3. When iron (II) was retained as a process catalyst, at 1 g/L, the discharge objective was readily met within a 30-minute reaction time, at an initial hydrogen peroxide concentration of 3 g/L. Under these conditions, 1.1 g/L of hydrogen peroxide were consumed in the reaction.

- 4. When the initial hydrogen peroxide concentration was only 1 g/L, and 1 g/L iron (II) was used as the process catalyst, the discharge O&G objective was still met for a reaction time of three hours. It should be noted, however, that the discharge O&G objective could not be met with a 30-minute reaction time at such low hydrogen peroxide dosing.
- 5. The oxidation reaction was observed to be highly exothermic. The 10°C increase in solution temperature at laboratory scale implies significant temperature increases in full-scale reactors. A controlled addition of hydrogen peroxide would be required. In addition, quick process-control loops and the need for reactor cooling would require serious consideration. Based on the aforementioned considerations, oxidation was not judged a practical technology for field use.

SUMMARY OF LABORATORY SCALE FINDINGS

In summary, the following technologies were selected for preliminary laboratory scale screening

on NPF:

- Adsorption (activated carbon, clay adsorbent, and polymer-modified clay adsorbent).
- Chemical oxidation (iron-catalysed hydrogen peroxide).
- Micro-filtration and ultra-filtration.
- Liquid-liquid extraction.
- Electro-coagulation.

Of these technologies, process feasibility was demonstrated for:

- Granular activated carbon adsorption.
- Iron-catalysed hydrogen peroxide oxidation.

Performance data for these processes appeared comparable, and equivalent material and chemical costs were projected; however, because of the following anticipated full-scale design and operating constraints of the oxidation process, granular activated carbon adsorption alone was selected for further evaluation at bench scale:

- More stringent safety requirements would be necessary with the use of an advanced chemical oxidation process;
- Adsorption would provide greater process flexibility; and
- Due to more demanding instrumentation, process control, and cooling requirements, chemical oxidation would have a higher capital cost.

In the following section, bench scale evaluation of the adsorption technology is discussed.

Section 5

BENCH SCALE TECHNOLOGY DEVELOPMENT

After evaluation of available technologies for processing non-produced fluids for removal of components affecting oil and grease processing or contributing to oil and grease concentrations, adsorption technology was chosen for detailed evaluation. Process development studies were conducted at bench scale using a granular activated carbon (GAC 1) and a polymer-modified clay-based adsorbent (PCA). Although PCA alone could not meet treatment objectives during the laboratory scale screening studies, the technology was retained for the bench scale column adsorption studies, as a PCA-based process is currently used offshore to treat non-produced fluids from acidizing operations, and its impact on such operations needed evaluation. Three process options were evaluated:

- GAC 1 as the sole adsorbent.
- PCA as the sole adsorbent.
- PCA preceding GAC 1, as a two-stage adsorption process.

EXPERIMENTAL PROCEDURES

Experimental procedures are presented in Section 2 as a part of the process screening studies. Pertinent details on the column studies are presented below.

- 1. Adsorbent performance and capacity were determined for pre-determined adsorbent bed depth, column configuration and empty bed contact times for each bed. These operating conditions were based on previous experimental work, a sequence of exploratory runs, and discussions with suppliers of the GAC 1 and PCA adsorbents. Selected operating conditions for the column studies were:
 - PCA adsorber bed depth of 0.057 m;
 - PCA adsorber internal column diameter of 0.057 m;
 - GAC 1 adsorber bed depth of 0.30 m;
 - GAC 1 adsorber internal column diameter of 0.025 m;
 - Empty bed contact time of 7.5 min for each adsorber;
 - Downflow operation;

- Room temperature (~ 25 C);
- Closed-vessel atmospheric pressure (1.0 1.2 atm); and
- Preparation and blending of three 30-L batches of non-produced fluids (permitting evaluation of the performance of each single process option as a function of the direct/indirect discharge option).

Although different vessel configurations were retained for each adsorbent, each adsorber was operated at the same empty bed contact time of 7.5 min. These different vessel configurations were selected to optimize the use and performance of each adsorbent.

- 2. Column adsorption studies were conducted on two fluids, namely:
 - Raw non-produced fluid (R-NPF), characterized by high (300-400 mg/L) O&G concentrations and the absence of free or emulsified crude oil; and
 - Produced-water-spiked non-produced fluid (PW-NPF), characterized by high (300-400 mg/L) O&G concentrations and moderate (200 mg/L) emulsified crude oil concentrations. For these studies, produced water was blended with non-produced fluids to achieve the desired emulsified oil content. Produced-water-spiked NPF (PW-NPF) was prepared by blending four (4) parts of NPF with one (1) part of produced water (PW). These studies were designed to determine the impact on adsorption performance of emulsified oil in non-produced fluids.
- 3. Direct and indirect discharge options were evaluated for R-NPF and PW-NPF. Figures 16 and 17 present conceptual process schematics for R-NPF and PW-NPF, respectively.
- 4. In the indirect discharge option, R-NPF or PW-NPF was first subjected to the adsorption process, then combined with produced water (10% pretreated non-produced fluids or PW-NPF and 90% produced water) prior to de-oiling treatment in a flotation process. Consequently, O&G concentration data for the indirect discharge option represent analytical measurements taken on combined fluids following treatment by flotation.
- 5. In the direct discharge option, experiments evaluated the performance of selected adsorbents for removing O&G-contributing components from NPF or PW-NPF to meet regulatory overboard O&G limits.
- 6. Adsorption process performance was monitored by measuring hexane-extractable O&G concentrations.
- 7. Samples of NPF or PW-NPF were taken prior to and after the adsorption process at selected time intervals, the latter being expressed as the number of bed volumes treated. These samples were either sent as is for O&G analyses (direct discharge), or were first blended with produced water and thereafter subjected to treatment by flotation prior to analysis for O&G (indirect discharge).



Figure 16. Process Schematics Overview: Raw NPF



Figure 17. Process Schematics Overview: Produced Water Spiked NPF

RESULTS AND DATA ANALYSIS

Tables 27 to 32 present the bench scale adsorption column data. Each respective data set is illustrated in Figures 18 to 23. The raw non-produced fluids (R-NPF) adsorption column data are tabulated first:

- Indirect discharge data for the PCA process and for the PCA/GAC 1 process are presented in Table 27 and Figure 18; and
- Direct discharge data for the PCA process and for the PCA/GAC 1 process are presented in Table 28 and Figure 19.

Direct and indirect discharge data for the GAC 1 process were not developed and are not provided. The produced-water-spiked NPF (PW-NPF) adsorption column data are subsequently tabulated:

- Indirect discharge data for the PCA process and for the PCA/GAC 1 process are presented in Table 29 and Figure 20;
- Direct discharge data for the PCA process and for the PCA/GAC 1 process are presented in Table 30 and Figure 21;
- Indirect discharge data for the GAC 1 process are presented in Table 31 and Figure 22; and
- Direct discharge data for the GAC 1 process are presented in Table 32 and Figure 23.

Raw NPF-Indirect Discharge

Table 27 presents adsorption performance data for PCA and for PCA/GAC 1. The data are illustrated in Figure 18. The O&G concentration for R-NPF was 410 mg/L. Significant findings are summarized below:

- The R-NPF O&G concentration following treatment by flotation alone was 288 mg/L, representing a modest 30% decrease. The O&G objective of 29 mg/L was not achieved by flotation alone.
- O&G concentrations ranged from 198 mg/L, at 11 bed volumes treated, to 300 mg/L, at 272 bed volumes treated, following PCA treatment. PCA never met the O&G objective of 29 mg/L. High O&G concentrations were immediately observed at the start of experiment, and O&G concentrations increased steadily thereafter. Bed exhaustion was observed at 219 bed volumes: At this point, the PCA effluent O&G concentration was comparable to the R-NPF O&G concentration following flotation treatment. PCA had a minimal impact on O&G removal from R-NPF.



Figure 18. Breakthrough Curves for R-NPF: Indirect Discharge.



Figure 20. Breakthrough Curves for PW-NPF: Indirect Discharge.



Figure 22. Breakthrough Curve for PW-NPF: Indirect Discharge.



Figure 19. Breakthrough Curves for R-NPF: Direct Discharge.



Figure 21. Breakthrough Curves for PW-NPF: Direct Discharge



Figure 23. Breakthrough Curve for PW-NPF: Direct Discharge.

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O&G concentrations ranged from 2 mg/L, at 5 bed volumes treated, to 66 mg/L, at 229 bed volumes treated, following adsorptive treatment by the PCA/GAC 1 process. The O&G objective of 29 mg/L was met by the GAC 1 adsorbent. Breakpoint O&G concentration of 29 mg/L was observed at approximately 190 bed volumes. Bed exhaustion was not observed during experimentation. As illustrated in Figure 18, discharge O&G concentrations were very low for the first 150 – 200 bed volumes treated, thereafter increasing markedly. No O&G measurements were pursued beyond 229 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA treatment, GAC 1 treatment was effective in removing O&G from R-NPF.

Operating	Conditions:	nditions: O&G Concentration (n		
Throughput (L)	Bed Volumes	Following PCA	Following PCA-GAC 1	
0.8	5	-	2	
1.6	11	198	-	
4.0	27	-	3	
4.8	32	192	-	
6.4	43	-	3	
8.0	53	202	-	
8.8	59	-	3	
11.2	75	210	-	
12.0	80	-	4	
16.0	107	222	5	
21.6	144	260	-	
22.4	149	-	19	
25.4	169	270	-	
26.4	176	-	25	
30.4	203	282	37	
32.0	213	-	56	
32.8	219	290	-	
34.4	229	-	66	
35.2	235	294	-	
40.8	272	300	-	

Table 27. R-NPF PCA and PCA/GAC 1 Adsorption Data – Indirect Discharge.

R-NPF O&G Concentration = 410 mg/L

PW O&G Concentration = 300 mg/L

Post-Flotation O&G Concentration for R-NPF = 288 mg/L

Post-Flotation O&G Concentration for PW = 0 mg/L

Operating	Conditions:	O&G Conc	entration (mg/L):
Throughput (L)	Bed Volumes	PCA Process	Following PCA/GAC 1
0.8	5	-	0
1.6	11	116	-
4.0	27	-	3
4.8	32	126	-
6.4	43	-	3
8.0	53	136	-
8.8	59	-	2
11.2	75	152	-
12.0	80	-	4
16.0	107	188	5
21.6	144	180	-
22.4	149	-	4
25.4	169	180	-
26.4	176	-	15
30.4	203	236	15
32.0	213	-	24
32.8	219	255	-
34.4	229	-	28
35.2	235	324	-
40.8	272	358	34

Table 28. R-NPF PCA and GAC 1 Adsorption Data – Direct Discharge.

R-NPF O&G Concentration = 410 mg/L

Operating	Conditions:	O&G Conce	entration (mg/L):
Throughput (L)	Bed Volumes	Following PCA	Following PCA/GAC 1
1.0	7	131	3
2.4	16	-	3
3.0	20	159	-
4.8	32	-	4
6.0	40	165	-
12.6	84	-	8
15.0	100	170	-
18.0	120	-	22
21.0	140	176	-
28.0	187	-	32
32.0	213	246	-
33.4	223	-	43
38.0	253	255	-
39.0	260	-	65
45.0	300	256	-

Table 29. PW-NPF PCA and PCA/GAC 1 Adsorption Data – Indirect Discharge.

R-NPF O&G Concentration = 377 mg/L PW O&G Concentration = 300 mg/L

PW-NPF O&G Concentration = 355 mg/L

Post-Flotation O&G Concentration for PW-NPF = 261 mg/L

Operating	Conditions:	O&G Conce	ntration (mg/L):
Throughput (L)	Bed Volumes	Following PCA	Following PCA/GAC 1
1.0	7	77	0
2.4	16	-	2
3.0	20	121	-
4.8	32	-	2
6.0	40	144	-
12.6	84	-	4
15.0	100	147	-
18.0	120	-	4
21.0	140	166	-
28.0	187	-	4
32.0	213	192	-
		(probable outlier)	
33.4	223	-	15
38.0	253	170	-
39.0	260	-	26
45.0	300	200	39

Table 30. PW-NPF PCA and PCA/GAC 1 Adsorption Data – Direct Discharge.

R-NPF O&G Concentration = 377 mg/L PW O&G Concentration = 300 mg/L PW-NPF O&G Concentration = 355 mg/L

Operating	Operating Conditions:		
Throughput (L)	Bed Volumes	Following GAC 1	
1.0	7	0	
5.0	33	0	
10.0	67	2	
16.0	107	3	
20.0	133	5	
24.0	160	7	
26.0	173	16	
28.0	187	27	
30.0	200	34	
33.0	220	40	
36.0	240	45	

Table 31. PW-NPF GAC 1 Adsorption Data – Indirect Discharge.

R-NPF O&G Concentration = 346 mg/L

PW O&G Concentration = 300 mg/L

PW-NPF O&G Concentration = 345 mg/L

Post-Flotation O&G Concentration for PW-NPF = 261 mg/L

Post-Flotation O&G Concentration for PW = 0 mg/L

Operating	O&G Concentration (mg/L):	
Throughput (L)	Bed Volumes	Following GAC 1
1.0	7	0
5.0	33	0
10.0	67	2
16.0	107	2
20.0	133	4
24.0	160	7
26.0	173	11
28.0	187	11
30.0	200	23
33.0	220	24
36.0	240	30

Table 32.	PW-NPF	GAC 1	Adsorption	Data -	Direct Disc	harge.
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R-NPF O&G Concentration = 346 mg/L PW O&G Concentration = 300 mg/L

PW-NPF O&G Concentration = 345 mg/L

Raw NPF-Direct Discharge

Table 28 and Figure 19 present adsorption performance data for the PCA and for PCA/GAC 1 direct discharge configuration. Significant findings are summarized below:

- O&G concentrations ranged from 116 mg/L at 11 bed volumes treated, to 358 mg/L at 272 bed volumes treated, following PCA adsorption alone. The O&G objective of 29 mg/L was never met by PCA adsorption. High O&G concentrations were immediately observed at the start of the experiment, and O&G concentrations increased steadily thereafter. Bed exhaustion was not observed. As illustrated in Figure 19, a small and steady increase in O&G concentrations was observed until 169 bed volumes had been treated. Thereafter, O&G concentrations markedly increased. No O&G measurements were made beyond 272 bed volumes treated, and hence bed exhaustion could not be determined. PCA adsorption had a small impact on O&G removal from R-NPF.
- O&G concentrations ranged from 0 mg/L at 5 bed volumes treated, to 34 mg/L at 272 bed volumes treated, following the PCA/GAC 1 adsorption treatment train. The O&G objective of 29 mg/L was met following PCA/GAC 1 adsorption. Breakpoint O&G concentration of 29 mg/L was observed at approximately 235 bed volumes. Bed exhaustion was not observed during the experiment. As illustrated in Figure 19, discharge O&G concentrations were very low for the first 175 bed volumes treated, thereafter increasing steadily. No O&G measurements were made beyond 272 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA treatment alone, the PCA/GAC 1 treatment train was effective in removing O&G from R-NPF.

Raw NPF Performance Data Comparison: Direct and Indirect Discharge Options

Results using the direct and indirect discharge options were compared. Figure 24 illustrates the performance of PCA adsorption for the indirect and direct discharge options. Figure 25 illustrates the performance of the PCA/GAC 1 process for the indirect and direct discharge options. Significant findings are summarized below:

- The data generated clearly indicate that treatment of R-NPF by flotation alone is inadequate in meeting the 29 mg/L discharge objective. The data further show that the GAC 1 adsorption treatment is required to meet this objective, either for a direct or an indirect discharge option. The PCA adsorption treatment was never able, on its own, to meet the 29 mg/L O&G objective, either for a direct or an indirect discharge option.
- A significant difference in the performance of the process options tested was observed when the direct discharge option was considered instead of the indirect discharge alternative. A direct discharge option resulted in a net apparent increase in the performance and capacity of each adsorbent tested. The PCA/GAC 1 process met the O&G discharge objective of 29 mg/L for 190 bed volumes (indirect discharge) and 230 bed volumes (direct discharge).


Figure 24. Adsorption Breakthrough Profiles.



Figure 25. Adsorption Breakthrough Profiles.

Produced Water-Spiked NPF-Indirect Discharge

Table 29 presents adsorption performance data for PCA adsorption alone, and for PCA adsorption preceding GAC 1 adsorption. The data are illustrated in Figure 20. Significant findings are summarized below:

- PW-NPF O&G following treatment by flotation alone was 261 mg/L. A modest 26% decrease in O&G concentration was achieved by flotation. The O&G objective of 29 mg/L was not achieved.
- O&G concentrations ranged from 131 mg/L at 7 bed volumes treated, to 256 mg/L at 300 bed volumes treated, following PCA adsorption. The O&G objective of 29 mg/L was never met. High O&G concentrations were immediately observed at the start of experiment, and O&G concentrations increased steadily thereafter. Bed exhaustion was observed at approximately 213 bed volumes, at which point the PCA-treated O&G concentration was comparable to the O&G concentration achieved by flotation alone.
- O&G concentrations ranged from 3 mg/L at 7 bed volumes treated, to 65 mg/L at 260 bed volumes treated, following the PCA/GAC 1 adsorption treatment train. The O&G objective of 29 mg/L was met following PCA/GAC 1 adsorption. The breakpoint O&G concentration of 29 mg/L was observed at approximately 175 bed volumes. Bed exhaustion was not observed during the experiment. As illustrated in Figure 20, discharge O&G concentrations were very low for the first 100 bed volumes treated, thereafter increasing steadily. No O&G measurements were made beyond 260 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA adsorption alone, the treatment train was effective in removing O&G from PW-NPF.

Table 31 presents adsorption performance data for GAC 1 adsorption, and the data are illustrated in Figure 22. Data analysis shows that:

- PW-NPF O&G was 261 mg/L following flotation treatment alone. A modest 24% decrease in O&G concentration was achieved by flotation. The O&G objective of 29 mg/L was never achieved.
- O&G concentrations ranged from 0 mg/L at 7 bed volumes treated, to 45 mg/L at 240 bed volumes treated, following GAC 1 adsorption. The O&G objective of 29 mg/L was met. The breakpoint O&G concentration of 29 mg/L was observed at approximately 190 bed volumes. Bed exhaustion was not observed during experiment. As illustrated in Figure 22, discharge O&G concentrations were very low for the first 160 bed volumes treated, thereafter increasing steadily. No O&G measurements were made beyond 240 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA adsorption, GAC 1 adsorption was effective in removing O&G from PW-NPF.

Produced Water-Spiked NPF-Direct Discharge

Table 30 presents PCA and PCA/GAC 1 adsorption data. The data are illustrated in Figure 21. Data analysis shows that:

- O&G concentrations ranged from 77 mg/L at 7 bed volumes treated, to 200 mg/L at 300 bed volumes treated, following PCA adsorption. The O&G objective of 29 mg/L was never met. High O&G concentrations were immediately observed at the start of the experiment, and O&G concentrations increased steadily thereafter. Bed exhaustion was not observed during the experiment. As illustrated in Figure 21, a small and steady increase in O&G concentration was observed throughout the run. No O&G measurements were made beyond 300 bed volumes, and hence bed exhaustion could not be determined.
- O&G concentrations ranged from 0 mg/L at 7 bed volumes treated, to 39 mg/L at 300 bed volumes treated, following PCA/GAC 1 adsorption. The O&G objective of 29 mg/L was met, as a breakpoint O&G concentration of 29 mg/L was observed at approximately 270 bed volumes. Bed exhaustion was not observed during the experiment. As illustrated in Figure 21, discharge O&G concentrations were very low for the first 200 bed volumes treated, thereafter increasing steadily. No O&G measurements were pursued beyond 300 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA adsorption, PCA/GAC 1 adsorption was effective in removing O&G from PW-NPF.

Table 32 presents performance data for GAC 1 adsorption. The data are illustrated in Figure 23. Significant findings are summarized below:

• O&G concentrations ranged from 0 mg/L at 7 bed volumes treated, to 30 mg/L at 240 bed volumes treated, following GAC 1 adsorption. The O&G objective of 29 mg/L was met, as a breakpoint O&G concentration of 29 mg/L was observed at approximately 235 bed volumes. Bed exhaustion was not observed during experiment. As illustrated in Figure 23, discharge O&G concentrations were very low for the first 190 bed volumes treated, thereafter increasing steadily. No O&G measurements were made beyond 240 bed volumes, and hence bed exhaustion could not be determined. Unlike PCA adsorption, GAC 1 adsorption was effective in removing O&G from PW-NPF.

Produced Water-Spiked NPF Performance Data Comparison: Direct and Indirect Discharge Options

Results using the direct and indirect discharge options were compared. Figure 26 illustrates the performance of PCA adsorption for indirect and direct discharge. Figure 27 illustrates the performance of the PCA/GAC 1 treatment train for indirect and direct discharge. Figure 28 illustrates the performance of GAC 1 adsorption alone. Significant findings are summarized below:







Figure 27. Adsorption Breakthrough Profiles.



Figure 28. Adsorption Breakthrough Profiles.

- PW-NPF treatment by flotation alone is inadequate in meeting the 29 mg/L discharge objective.
- GAC 1 adsorption is required to meet 29 mg/l discharge objective, whether for direct or indirect discharge. PCA adsorption alone never met the 29 mg/L O&G objective, either for direct or indirect discharge.
- The O&G removal performance of the PCA/GAC 1 treatment train was similar to that provided by GAC 1 adsorption alone. The hybrid, two-stage process met the O&G discharge objective at 175 bed volumes (indirect discharge) and 270 bed volumes (direct discharge). Yet, single stage GAC 1 adsorption alone met the O&G discharge objective at 190 bed volumes (indirect discharge) and 235 bed volumes (direct discharge).
- Table 33 illustrates the significant difference in process performance when the direct discharge option is compared to the indirect discharge option. The direct discharge option resulted in a net apparent increase in the performance and capacity of each adsorbent tested.

	Number of Bed Volumes* Meeting O&G 29 mg/L Objective for:				
O&G Reduction Process	Indirect Discharge	Direct Discharge			
R-NPF					
Flotation	Not Applicable	Not Applicable			
PCA	0	0			
PCA/GAC 1	190	235			
PW-NPF					
Flotation	Not Applicable	Not Applicable			
PCA	0	0			
PCA/GAC 1	175	270			
GAC 1	190	235			

Table 33.	Adsorption	Performance	Data	Summary.
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*rounded to the nearest 5 bed volumes.

DISCUSSION

Bench scale column adsorption studies were conducted to assess the performance and capacity of GAC 1, PCA, and two-stage PCA/GAC 1 in removing O&G from raw and produced-water-spiked non-produced fluids. The raw non-produced fluids were characterized by high dissolved O&G concentrations (300-400 mg/L), and the produced water-spiked non-produced fluids by high dissolved and emulsified O&G concentrations (300-400 mg/L). O&G concentrations were

determined following adsorption (direct discharge), and following controlled dilution with produced water and de-oiling by flotation (indirect discharge).

Table 33 summarizes the adsorption data for each adsorption process, fluid, and discharge option. Significant findings were as follows:

- The 29 mg/L O&G objective was not met by treating either R-NPF or PW-NPF by the flotation process. A modest O&G reduction of 24% to 30% was observed. This finding was expected for R-NPF, based on the preliminary baseline data presented in Section 2 and on the laboratory scale technology screening data presented in Section 4.
- The 29 mg/L O&G objective was not met by treating either R-NPF or PW-NPF by PCA adsorption. Modest O&G reductions were observed. This finding was expected for treatment of R-NPF, and correlates well with the isotherm data generated at laboratory scale.
- The 29 mg/L O&G objective was met by treating either R-NPF or PW-NPF by GAC 1 adsorption. High O&G reductions and high adsorbent capacities were observed. This finding was expected for treatment of R-NPF, and correlates well with the isotherm data generated at laboratory scale.
- The 29 mg/L O&G objective was met by treating PW-NPF by two-stage PCA/GAC 1 adsorption. High O&G reductions and high adsorbent capacities were observed.

The performance of two-stage PCA/GAC 1 adsorption was very similar to the performance of GAC 1 adsorption alone. This finding was somewhat unexpected. Although laboratory and bench scale data confirmed the poor performance of PCA adsorption in removing O&G from R-NPF, PCA adsorption was expected to be an effective PW-NPF pretreatment prior to GAC 1 adsorption.

Given these findings, the following further observations were observed:

- In the indirect discharge configuration, GAC 1 and two-stage PCA/GAC 1 adsorption treated 190 and 175 bed volumes of PW-NPF, respectively. The difference was attributed to a slightly lower untreated PW-NPF O&G concentration for GAC 1 adsorption (345 mg/L vs. 355 mg/L). The performance of the two treatment options can be considered essentially equivalent—PCA pretreatment did not improve the performance of GAC 1 adsorption.
- In the direct discharge configuration, GAC 1 and two-stage PCA/GAC 1 adsorption treated 235 and 270 bed volumes of PW-NPF, respectively. The volume and mass of adsorbent used

in the two-stage PCA/GAC 1 process were double and triple, respectively, than used in GAC 1 adsorption alone. In comparing GAC 1 adsorption with PCA/GAC 1 adsorption performance, however, PCA was observed to increase by only 15% the number of bed volumes treated. This small increase does not justify the increased cost associated with installing and operating PCA pretreatment.

A significant difference in the performance of the adsorbents was observed as a function of the discharge configuration. The performance and capacity of each adsorbent tested were higher for the direct discharge option. This finding suggests that both adsorbents studied are more effective at removing O&G from non-produced fluids than at removing those constituents of non-produced fluids that hinder O&G removal from produced water. Hence, although GAC 1 adsorption in either configuration met the 29 mg/L O&G discharge objective, the process was more effective in the direct discharge configuration.

PRELIMINARY COST ESTIMATES FOR GAC 1

In order to bridge the technical findings of this study with process economics, some preliminary cost data for GAC 1 adsorption are presented. The cost data do not include costs for chemicals, equipment, manpower, spent carbon disposal, etc. These costs are likely to be significant, and must be properly quantified for an accurate assessment of total treatment cost.

The GAC 1 cost data provided below are based on:

- A typical acidizing injection sequence requiring 7600 gallons (181 barrels) of acidizing chemicals pumped down-hole over an eight hour period, and flowing back over a seventy-two hour period at a similar flow rate, i.e., 3.6 m³/h (22.64 barrels/hr);
- Produced fluids, following acidizing, may or may not be treated with a demulsifier to break water-in-oil emulsion. These fluids are then processed in a conventional 3-phase separator (upstream of the GAC 1 process) to remove from non-produced fluids all free oil and grossly emulsified crude oil. The oil phase from this 3-phase separator is diverted for further processing at the platform;
- The aqueous phase from the 3-phase separator contains 200 to 2000 ppm dispersed oil in water. This aqueous phase may or may not be treated by a reverse emulsion breaker to reduce the dispersed oil concentration to around 500 ppm. The treated fluids may be processed (in a skim tank or with a centrifuge type equipment upstream of the GAC 1 process) to remove separated oil and/or oil wet floc;

- The aqueous phase from the above process is treated by GAC 1 adsorption;
- Oxygen introduction into the non-produced fluids is kept to a minimum, and the process equipment is sized to rapidly process the non-produced fluids; and
- Process demand is highest in the early stages of flowback from the well. It is in the early stages of flowback that the maximum O&G concentration in the non-produced fluids is observed. It is also in these early stages that the maximum emulsified crude oil content is observed. Process demand presented below does not take into consideration variability in fluids characteristics, and assumes a worst-case scenario. It assumes that over the 72-hour flowback period, the high O&G and emulsified crude oil contents remain constant and are treated by GAC 1 adsorption.

The cost estimates are for a single-stage GAC 1 adsorption process. This assumption means that once the GAC 1 adsorbent is not able to meet the 29 mg/L O&G objective, it is considered spent and is disposed. Under field operating conditions, it is likely that this partially spent adsorbent would be retained and used to its full adsorption capacity. A field adsorption system would likely use two rotating vessels: the first vessel as a sacrificial adsorber with partially spent adsorbent, and the second vessel as a polishing adsorber with virgin adsorbent.

The GAC 1 adsorption process could require as little as 0.8 barrels of GAC 1 (65 kg), at an estimated material cost of \$200, to treat the 181 barrels of non-produced fluids flowing back. This estimate assumes that the acidizing chemicals pumped down-hole would flow back as an ideal slug. It is unlikely that ideal plug flow would be observed. On the other hand, the worst-case scenario would be that non-produced fluid O&G disperses evenly in the flowbacks over the entire 72-hour flow back period. In this case, a significant percentage of the adsorbent capacity would be spent removing low levels (200 mg/L) of emulsified crude oil, in addition to diminishing levels of non-produced fluid O&G. In this example, the GAC 1 adsorption process could require as much as 7.2 barrels of GAC 1 (575 kg), at an estimated material cost of \$1700, to treat 1630 barrels of acid flowbacks composed of 10% non-produced fluid O&G and 90% formation water. It should be noted that the material cost may be a small fraction of the total overall cost of handling and treating non-produced fluids.

Section 6

CONCLUSIONS AND RECOMMENDATIONS

A number of technologies for reducing the impact of NPF on offshore oil removal processes were evaluated in treatability studies:

- Adsorption (granular activated carbon, clay adsorbent, polymer-modified clay adsorbent);
- Chemical oxidation (iron-catalysed hydrogen peroxide);
- Membrane filtration (micro- and ultra-filtration);
- Liquid-liquid extraction; and
- Electro-coagulation.

Process feasibility was demonstrated for adsorption and iron-catalyzed hydrogen peroxide oxidation. Performance data for the two processes were comparable; however, peroxide oxidation was rejected based on logistic scale-up considerations, including safety requirements, process flexibility, process control needs, and capital costs. Bench scale performance studies were conducted on adsorption by granular activated carbon (GAC 1) and a polymer-modified clay adsorbent (PCA). PCA adsorption performance was evaluated both as an alternative to, and as a pretreatment prior to, GAC 1 adsorption. Two discharge configurations were investigated: 1) direct discharge of treated NPF, and 2) controlled blending of treated NPF with produced water for final de-oiling treatment by flotation (indirect discharge). Adsorption performance was investigated on raw NPF (R-NPF), characterized by high dissolved O&G concentrations with no free/emulsified crude oil, and produced water–spiked NPF (PW-NPF), characterized by high dissolved and emulsified O&G concentrations.

The O&G discharge objective of 29 mg/L was met by GAC 1 adsorption treatment of R-NPF and PW-NPF, for both direct and indirect discharge. High O&G reductions and high adsorbent capacities were observed. The O&G objective was also met by two-stage PCA/GAC 1 adsorption treatment of PW-NPF, for both direct and indirect discharge. Conversely, the O&G objective could not be met by PCA adsorption treatment of either fluid.

The direct and indirect discharge configurations differed markedly in technology performance. Adsorption performance and capacity were higher for the direct discharge option, regardless of the adsorbent tested. Lower O&G concentrations were attained and higher absorption capacities were consistently observed. The two-stage PCA/GAC 1 process with direct discharge treated 270 bed volumes before exceeding the O&G objective, whereas with indirect discharge, only 175 bed volumes could be treated. GAC 1 adsorption with direct discharge treated 235 bed volumes, and with indirect discharge, only 190 were treated.

The treatability data demonstrated the feasibility of GAC 1 adsorption. On the other hand, PCA adsorption was not demonstrated to be effective as an alternative adsorption treatment to GAC 1 adsorption, and as a pretreatment step to GAC 1 was only marginally effective at increasing GAC 1 bed capacity (~15% increase). This small increase does not justify the increased cost associated with installing and operating PCA adsorption as a pretreatment technology.

An offshore field evaluation of GAC 1 adsorption is recommended, to evaluate its performance in treating actual, rather than simulated, non-produced fluids under dynamic and variable conditions.

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