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Technologies to Reduce Oil and Grease Content of Well Treatment, Well Completion, and Workover Fluids for Overboard Disposal

Regulatory and Scientific Affairs Department

API Publication Number 4702

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FOREWORD

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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.

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TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

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

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 polymer-modified 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 and emulsified O&G concentrations (300 mg/L – 400 mg/L) and moderate concentrations of emulsified crude oil (200 mg/L).

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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

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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 acid-soluble 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

- 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

- 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.

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.

2-5

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

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

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

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

Table 4. Typical O&G Baseline Data for Simulated Combined Fluids.

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

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Table 5. Oil and Grease Sample Data.

	O&G Baseline Data						Treatability Data		
	O&G Conc. (mg/L)						Post-Flotation CF O&G Conc. (mg/L), Using NPF Pretreatment Technology:		
	Raw O&G Fluids Data			Post-Flotation O&G Data					
	PW	NPF	CF	PW	NPF	CF	I	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 mg/L to 230 mg/L).			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).		

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2-9

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

Well Stimulation and Non-Produced Fluids	Freon®-Extractables O&G Conc. (mg/L)
A	< 5
B	8
C	218
D	846
Composite Fluid (ABCD)	618
Non-Produced Fluids	263

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.

Table 9. Comparative O&G Data Measurements.

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

2-13

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 non-produced 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 mixer-settlers 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.

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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 μm glass micro-fiber filter.

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

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	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

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 µm glass micro-fiber filter.

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

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

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

Adsorbent ("m") (g/L)	O&G (mg/L)	O&G Removed ("x") (mg/L)	x/m (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") (g/L)	O&G (mg/L)	O&G Removed ("x") (mg/L)	x/m (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

Table 17. O&G Adsorption Data for PCA.

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:

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

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:

$$\log(x/m) = \log(k) + (1/n)\log(TOC_e) \qquad \text{(Equation 4-2)}$$

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.

Table 18. Adsorption Isotherm TOC Data Summary.

m (g/L)	(TOC$_e$) (mg/L)	Log(x/m) (-)	log(TOC$_e$) (-)
GAC 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
GAC 2			
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
CA			
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

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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.

4-8

Figure 10. GAC 1 O&G Performance Data.

Figure 11. GAC 2 O&G Performance Data.

Figure 12. CA O&G Performance Data.

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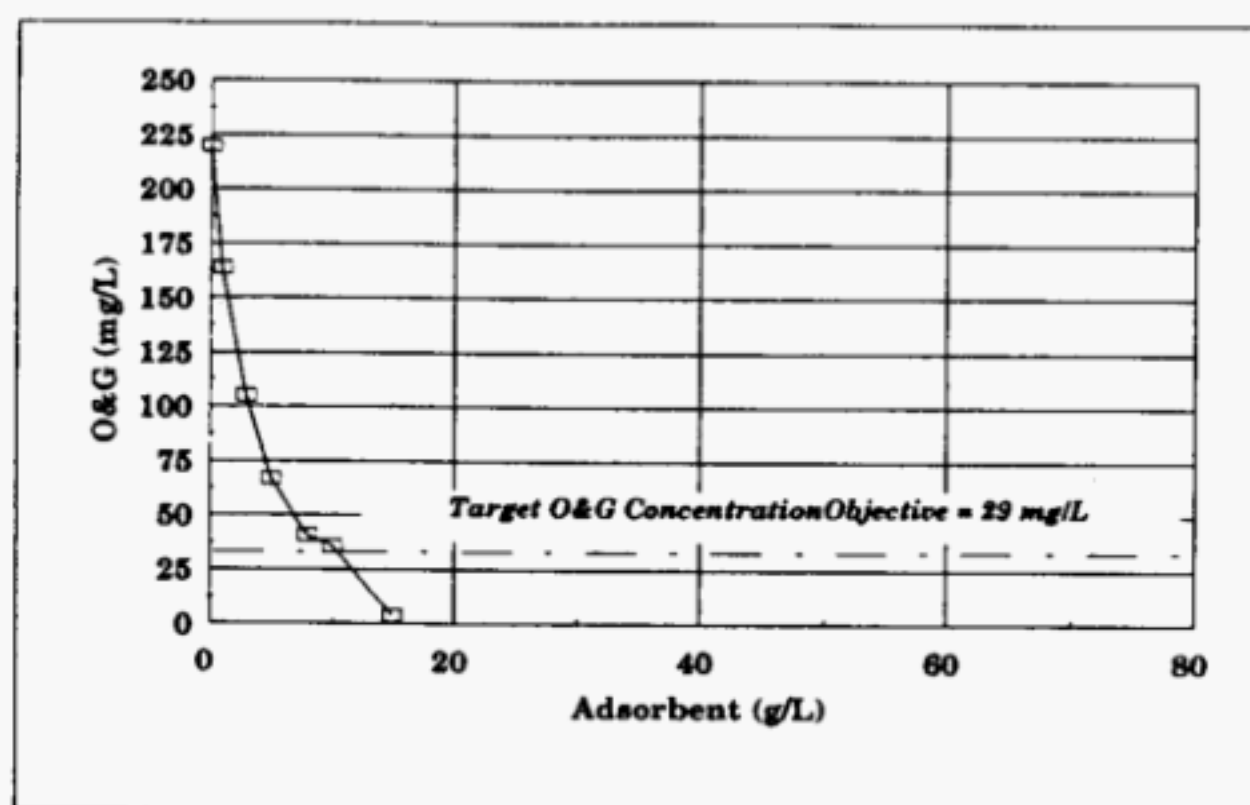
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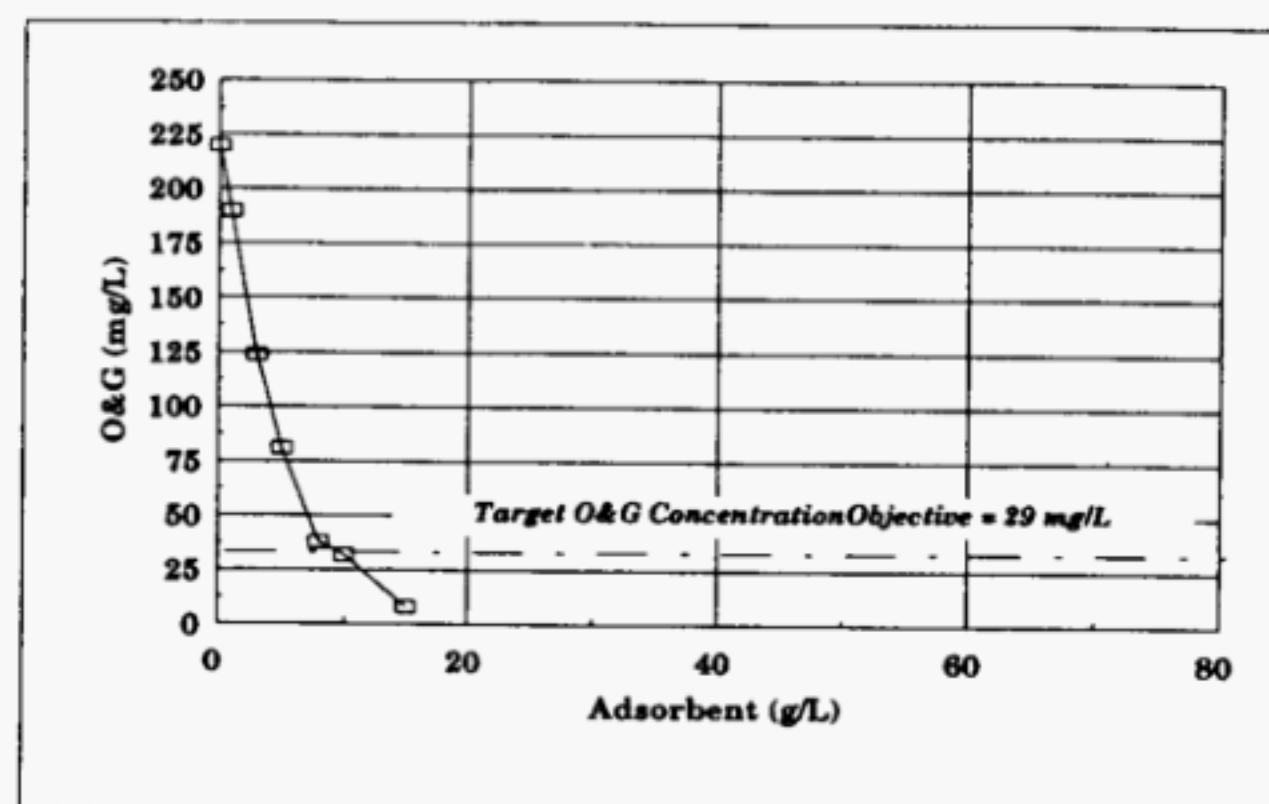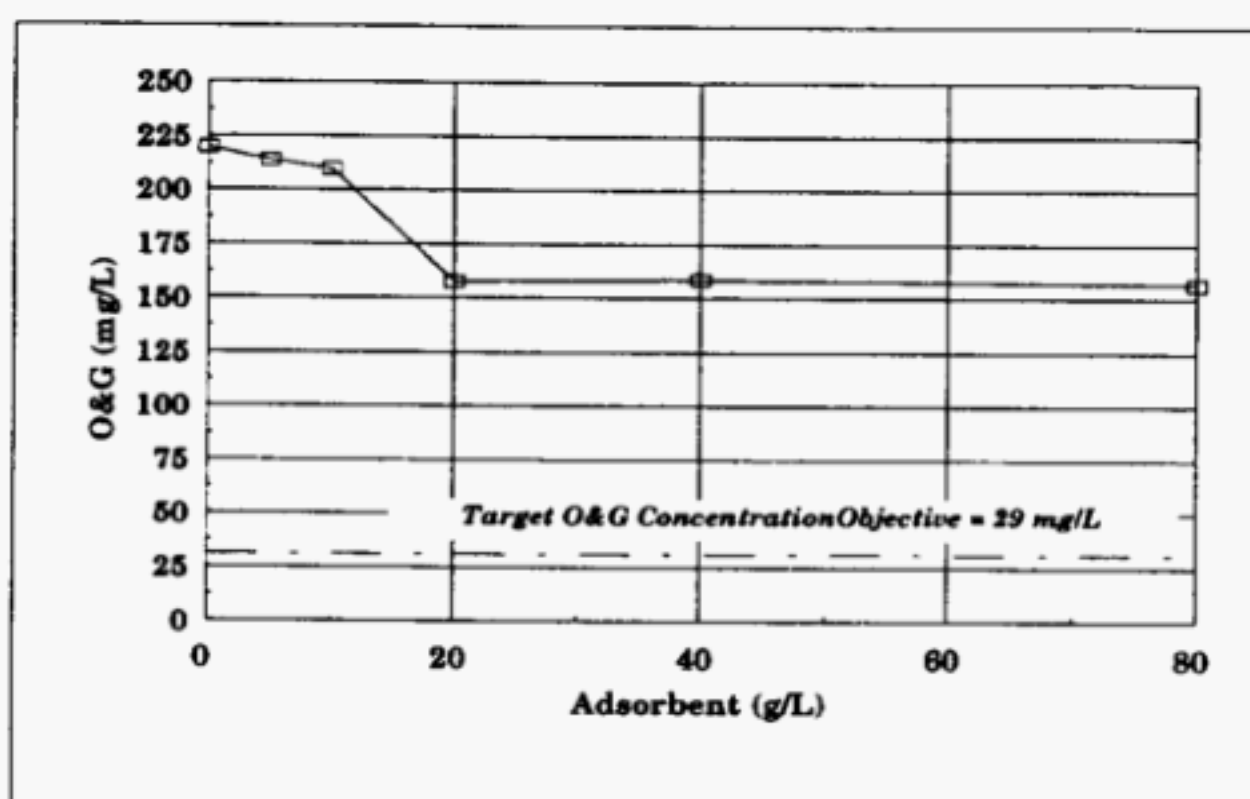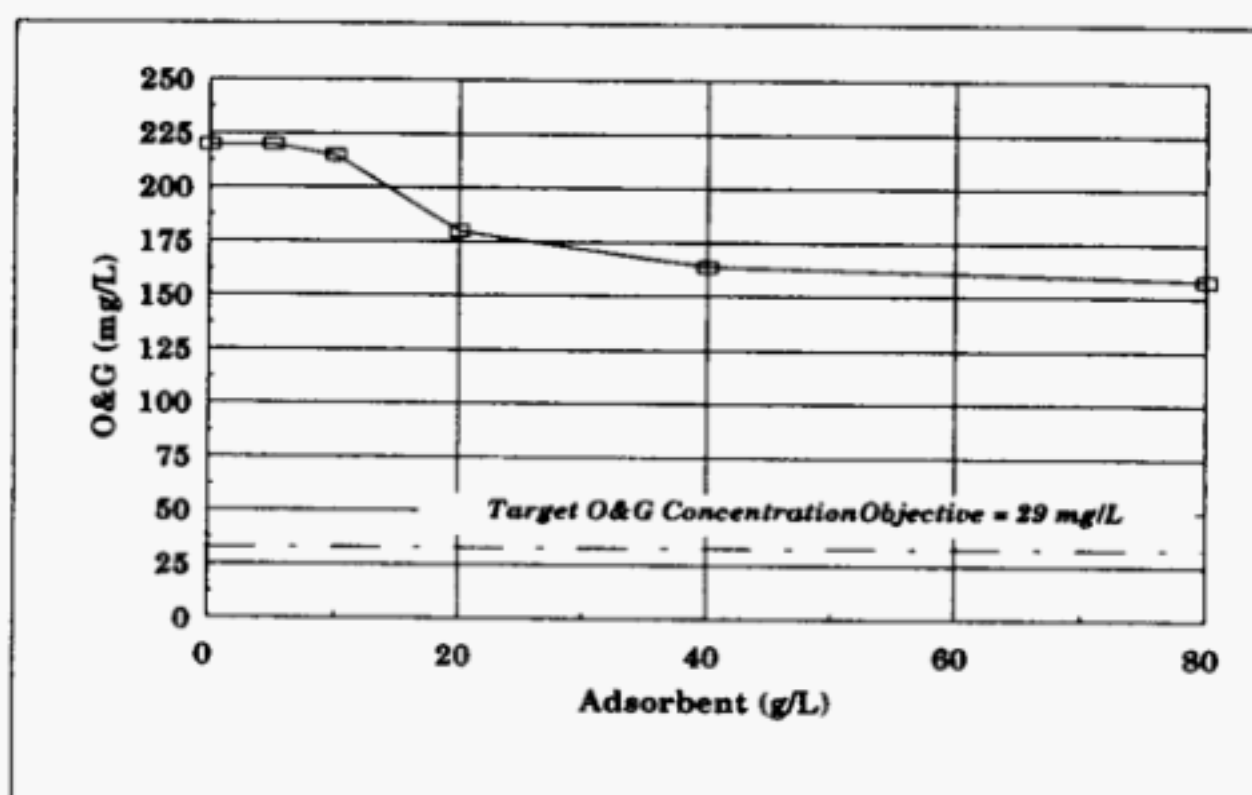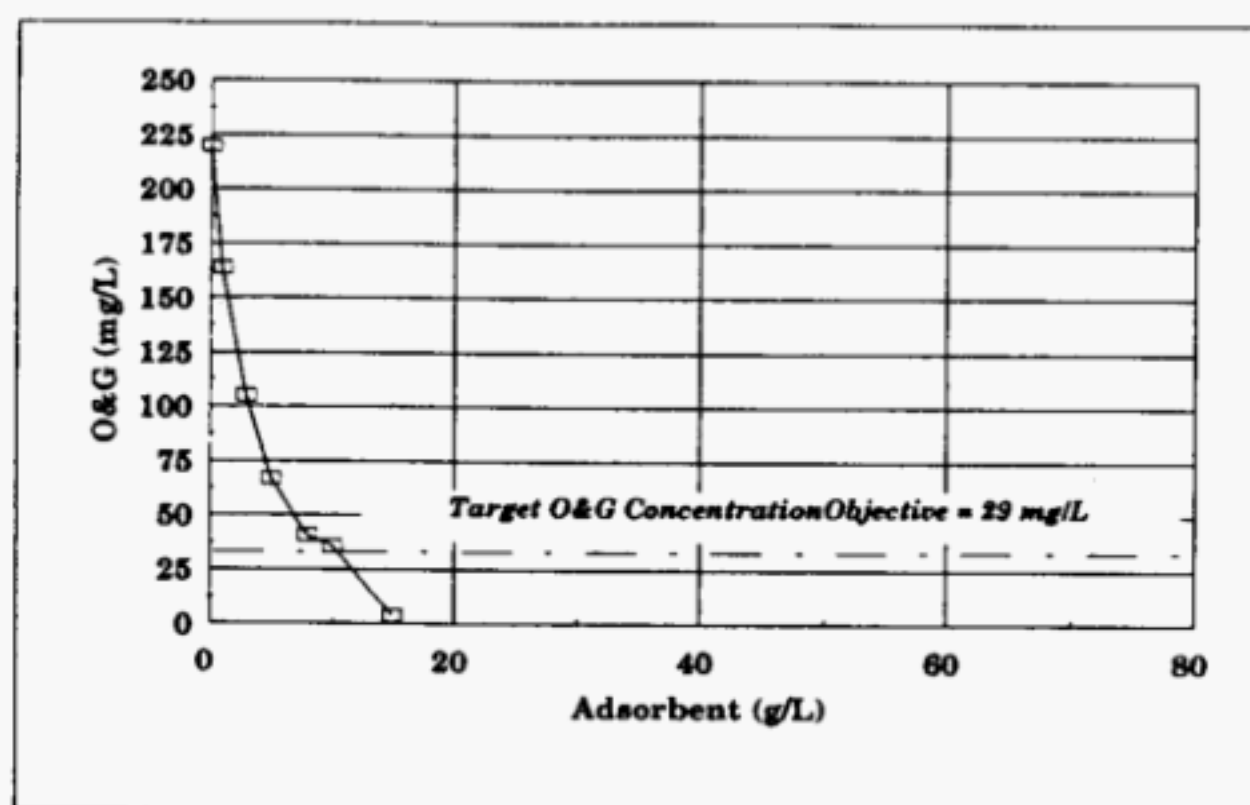

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Figure 12. CA O&G Performance Data.

Figure 13. PCA O&G Performance Data.

4-8

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.

Table 20. Electro-Coagulation Treatability Data.

Reaction Time (min)	pH/T/ORP (- / C / mV)	TOC (g/L)	O&G (mg/L)	Total Iron Conc. (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

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

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.

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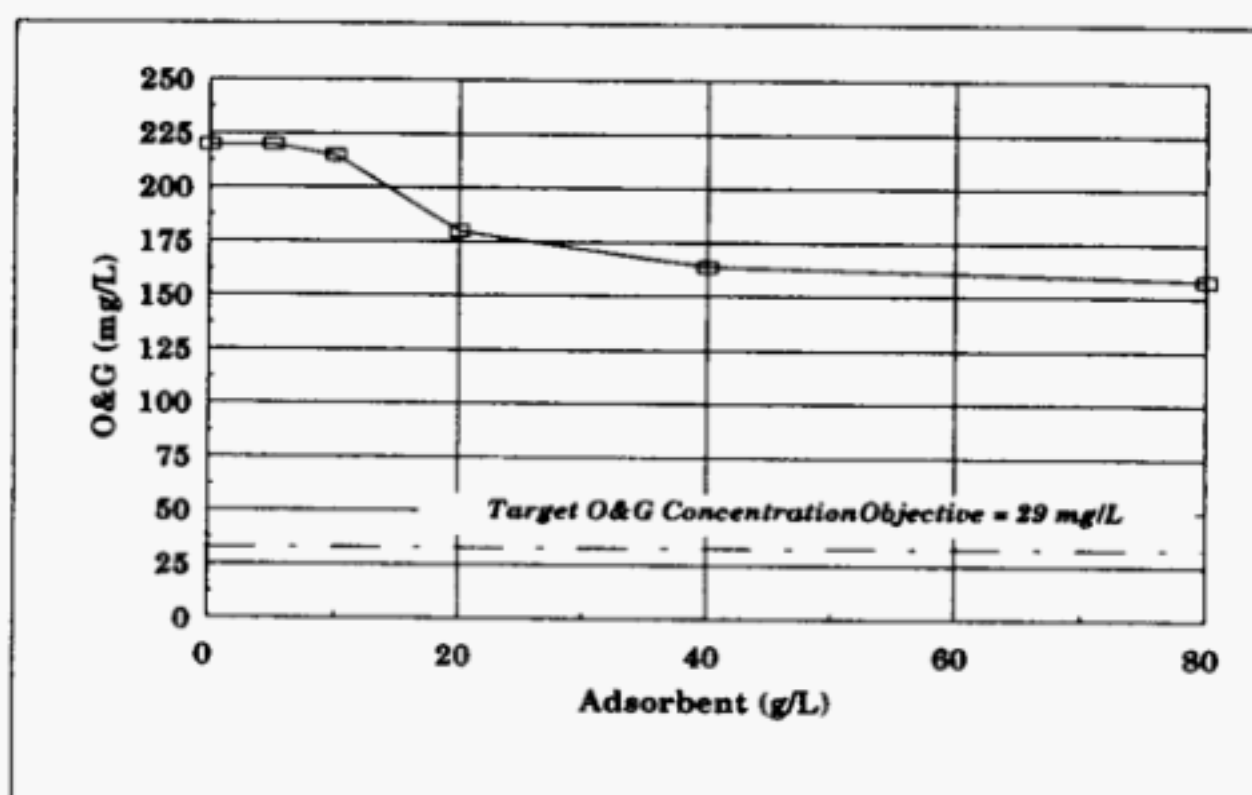
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With the exceptions of Membrane 6 and Membrane 9, all membranes showed early signs of membrane fouling and/or degradation. Membrane degradation was especially apparent for Membrane 3 and Membrane 8, for which pure water fluxes increased following the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

4-16

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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

4-16

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.

Table 25. 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

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 ± 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.

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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.

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.

5-5

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:

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- 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.

5-5

- 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.

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

Operating Conditions:		O&G Concentration (mg/L):	
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	-

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

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

Operating Conditions:		O&G Concentration (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

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

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

| Operating Conditions: | | O&G Concentration (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

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

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

Operating Conditions:		O&G Concentration (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

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

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

Operating Conditions:		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	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

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

Table 32. PW-NPF GAC 1 Adsorption Data – Direct Discharge.

Operating Conditions:		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

R-NPF O&G Concentration = 346 mg/L
PW O&G Concentration = 300 mg/L
PW-NPF O&G Concentration = 345 mg/L

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

Operating Conditions:		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	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

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

Table 32. PW-NPF GAC 1 Adsorption Data – Direct Discharge.

Operating Conditions:		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

R-NPF O&G Concentration = 346 mg/L
PW O&G Concentration = 300 mg/L
PW-NPF O&G Concentration = 345 mg/L

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

Operating Conditions:		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	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

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

Table 32. PW-NPF GAC 1 Adsorption Data – Direct Discharge.

Operating Conditions:		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

R-NPF O&G Concentration = 346 mg/L
PW O&G Concentration = 300 mg/L
PW-NPF O&G Concentration = 345 mg/L

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

Operating Conditions:		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	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

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

Table 32. PW-NPF GAC 1 Adsorption Data – Direct Discharge.

Operating Conditions:		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

R-NPF O&G Concentration = 346 mg/L
PW O&G Concentration = 300 mg/L
PW-NPF O&G Concentration = 345 mg/L

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:
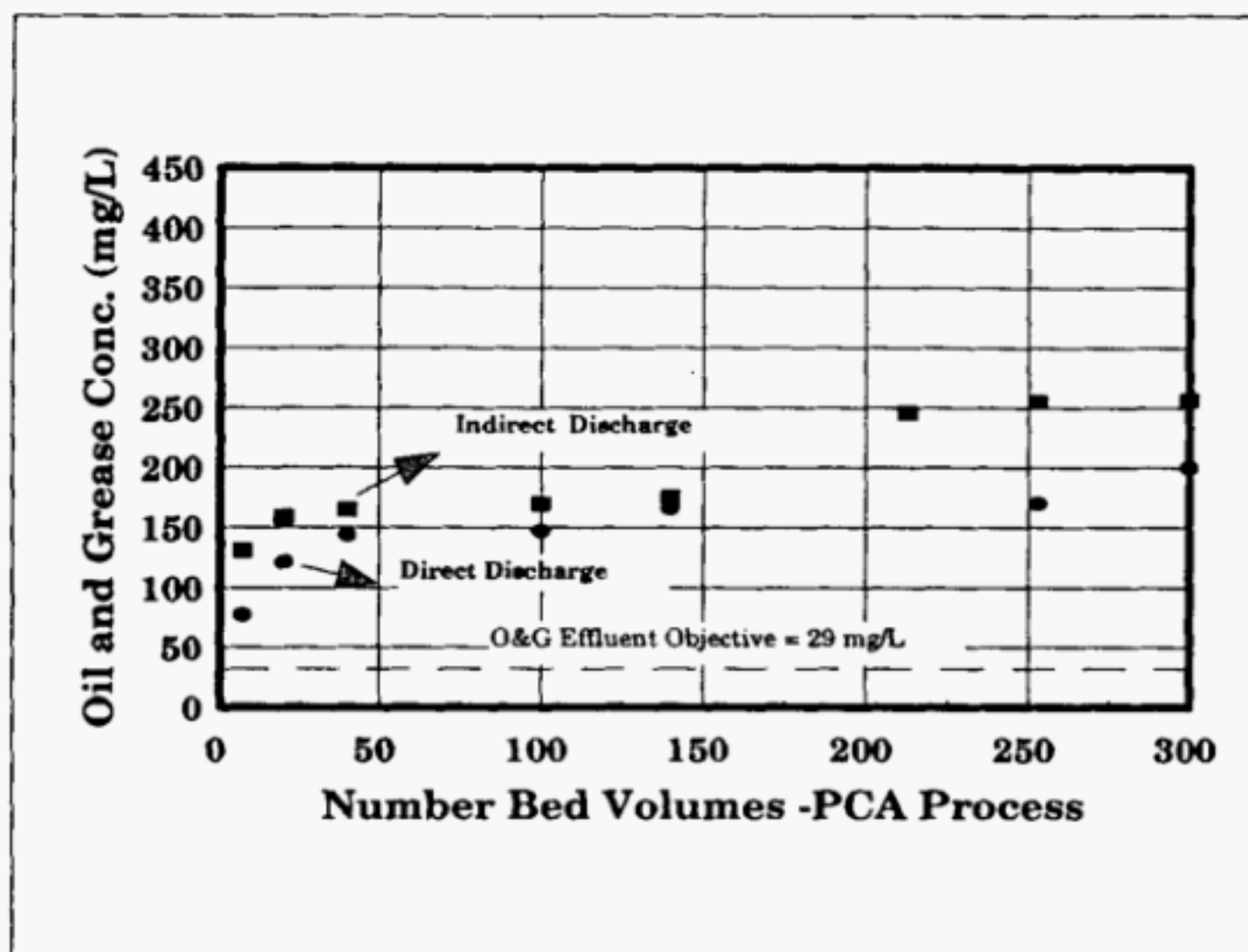
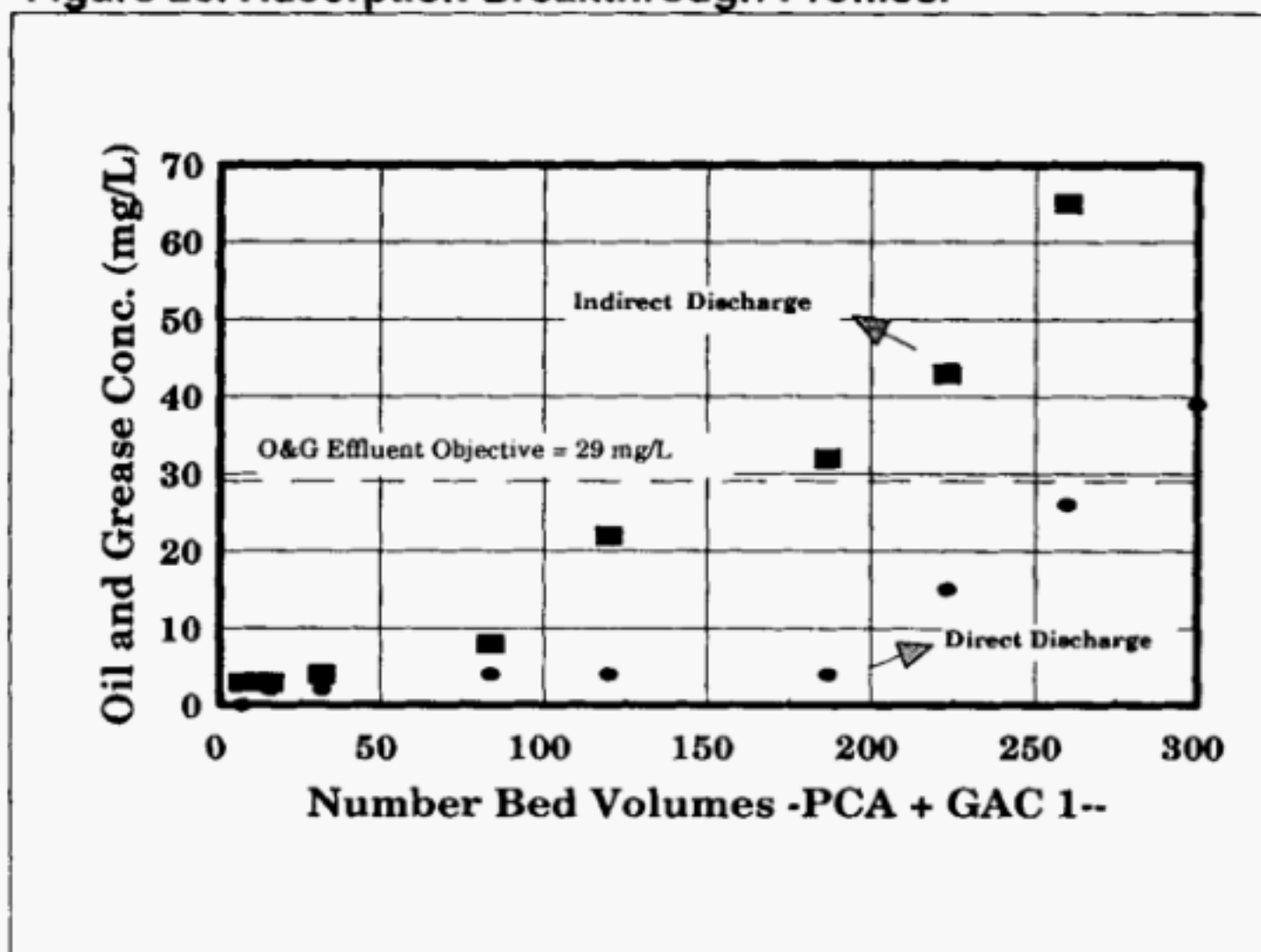5-15

Figure 26. Adsorption Breakthrough Profiles.

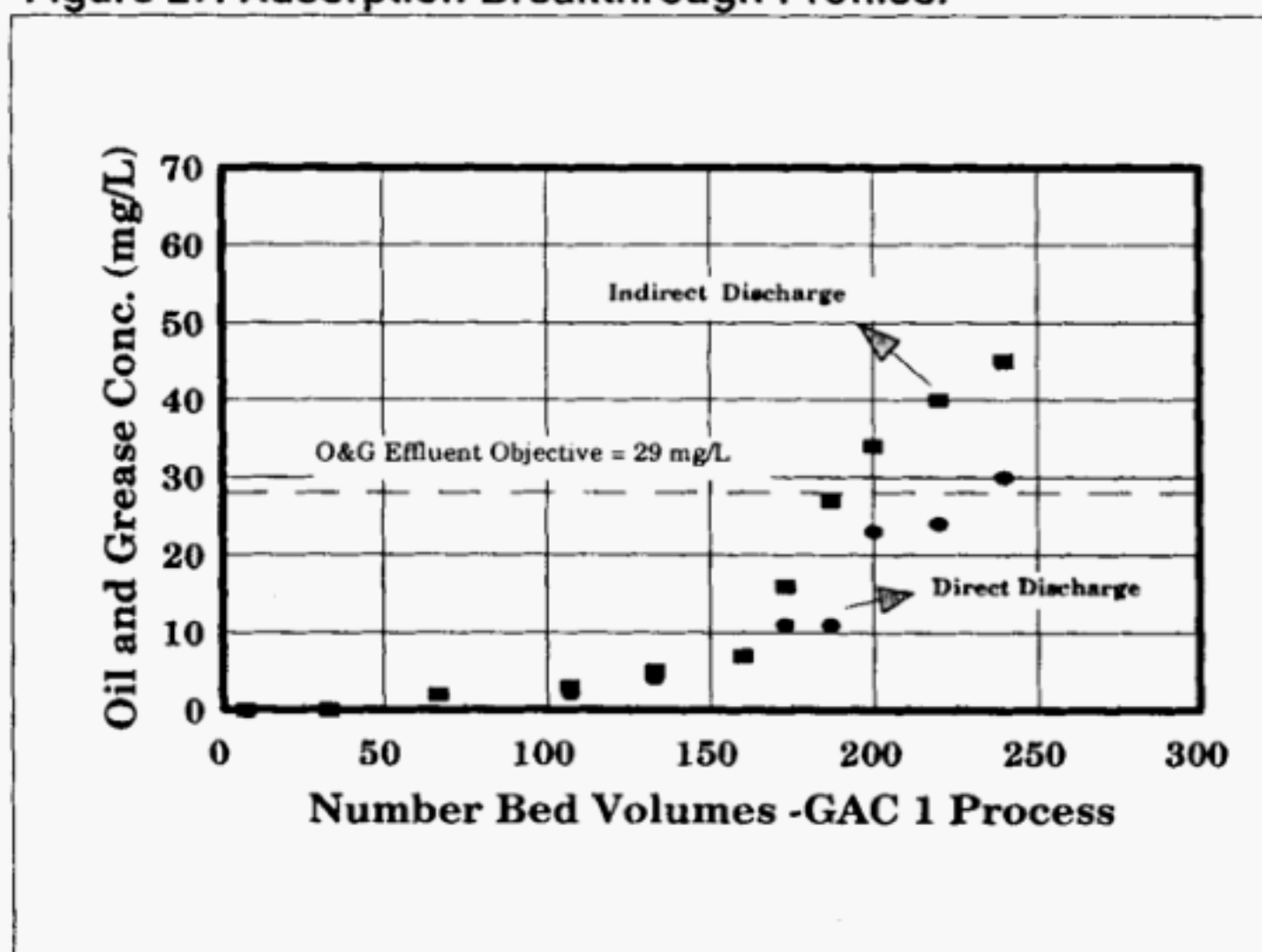**Figure 27. Adsorption Breakthrough Profiles.**

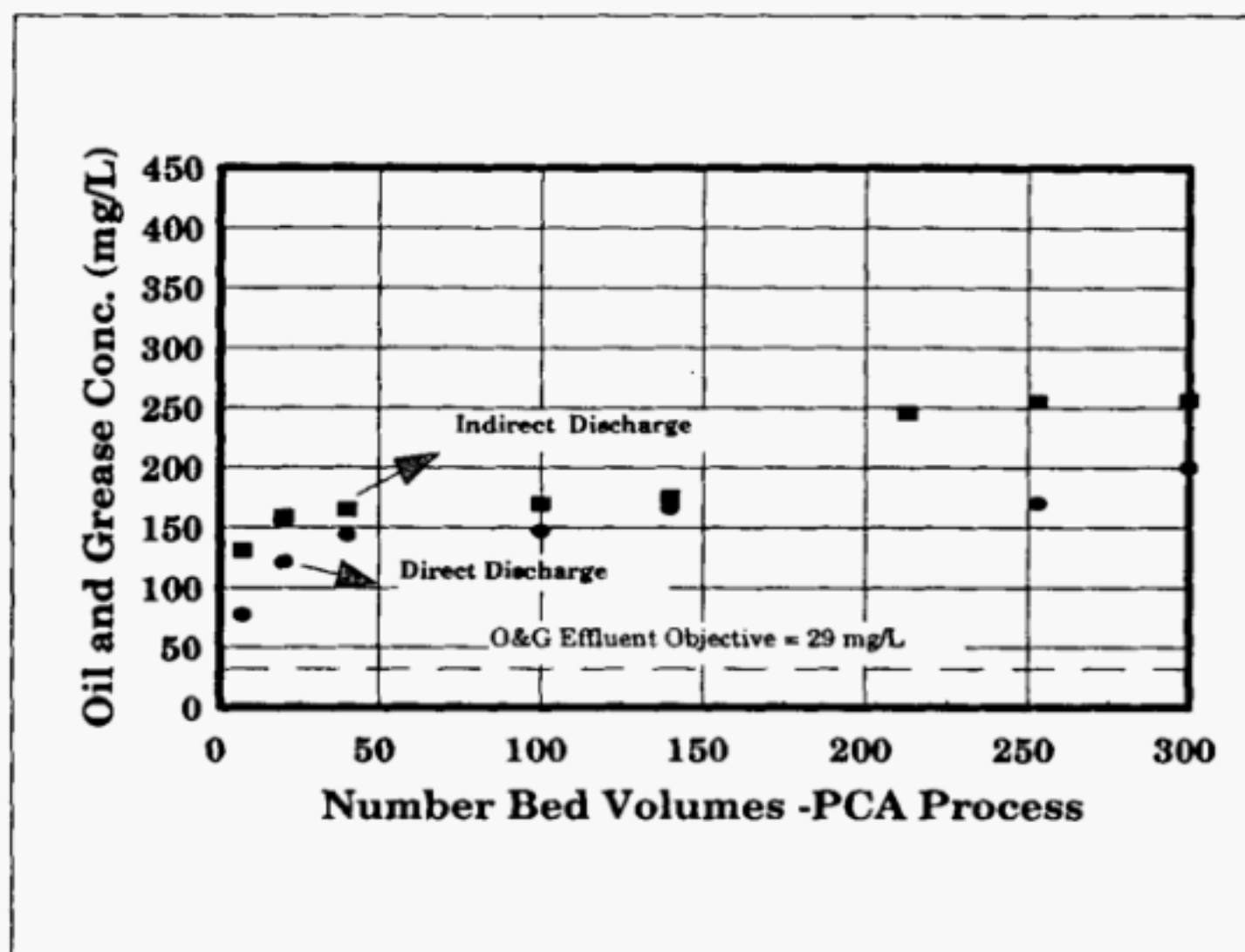**Figure 28. Adsorption Breakthrough Profiles.**

Figure 26. Adsorption Breakthrough Profiles.
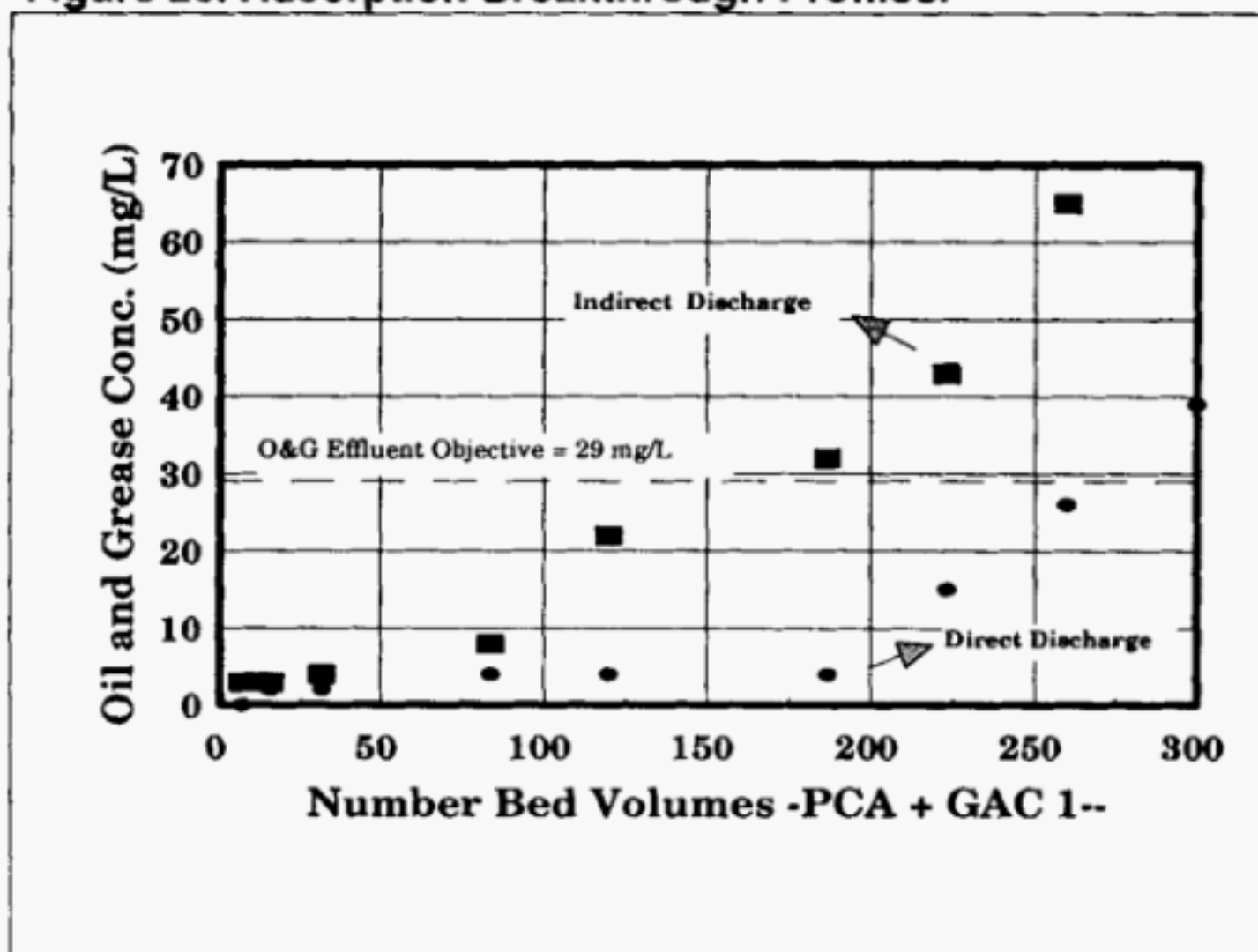

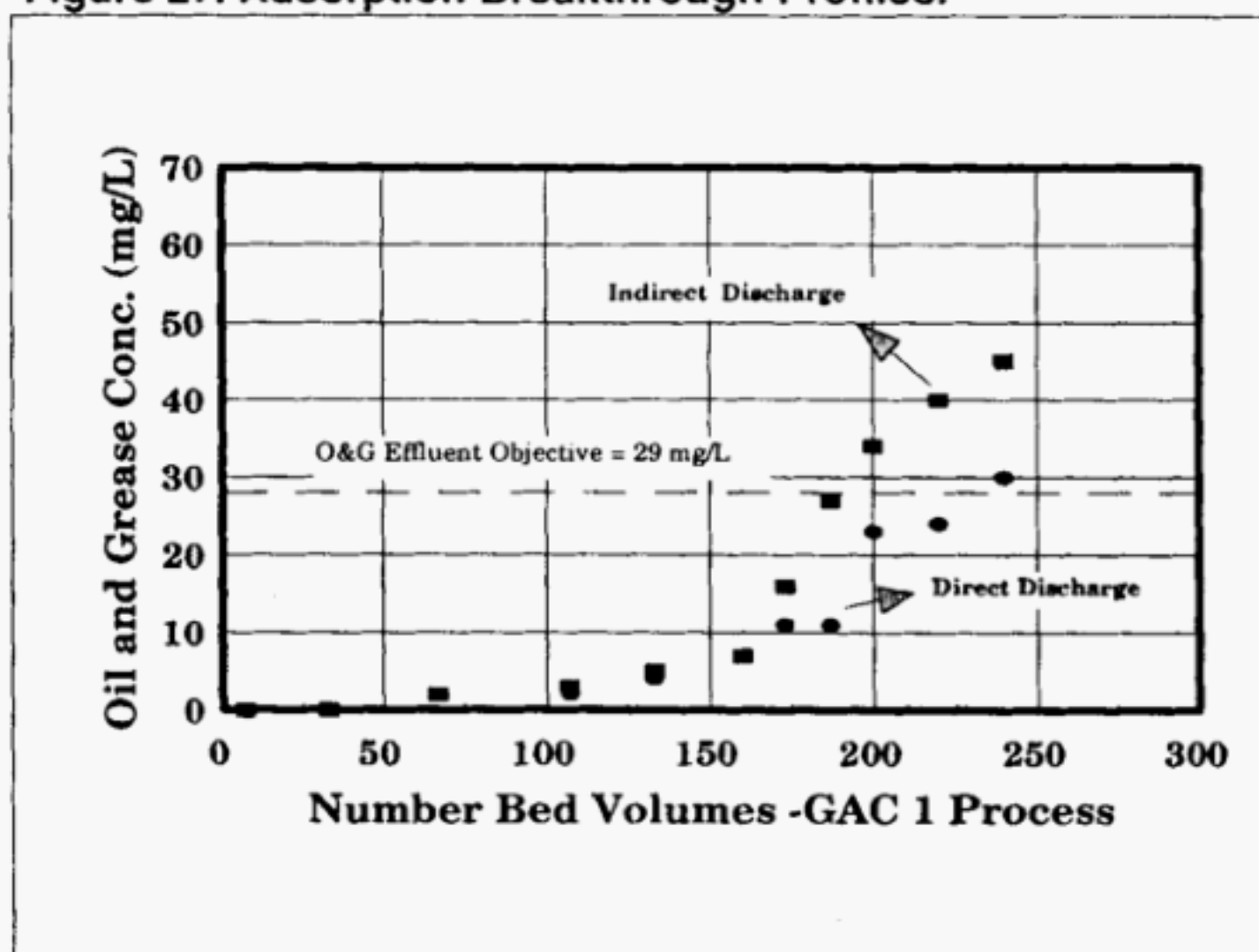**Figure 27. Adsorption Breakthrough Profiles.**

Figure 28. Adsorption Breakthrough Profiles.

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

5-18

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 m^3/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;

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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 m^3/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;

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.

6-2

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