

TECHNOLOGIES TO REDUCE OIL AND GREASE CONTENT OF WELL TREATMENT, WELL COMPLETION, AND WORKOVER FLUIDS FOR OVERBOARD DISPOSAL

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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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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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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 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).

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.

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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 set-up 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.

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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 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.

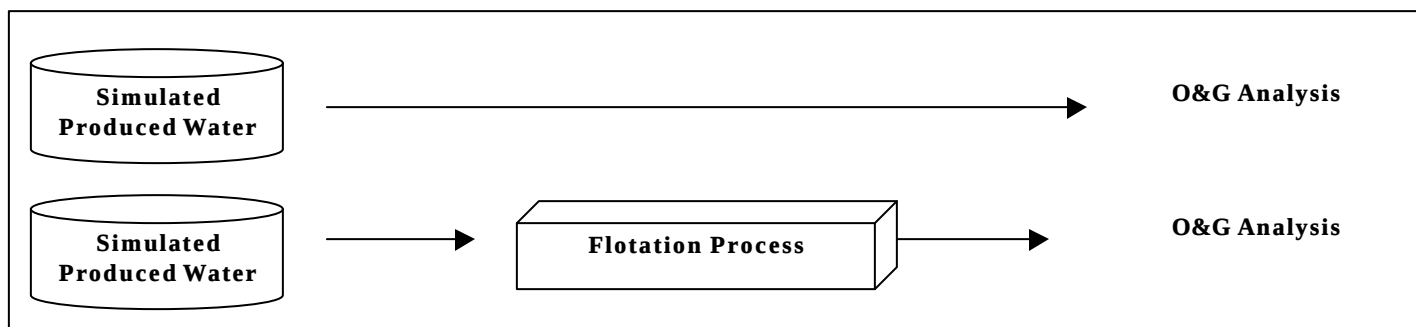
Beyond simple and direct O&G analytical measurements for raw and pretreated non-produced fluids, special attention was directed to ensure minimal variability in:

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

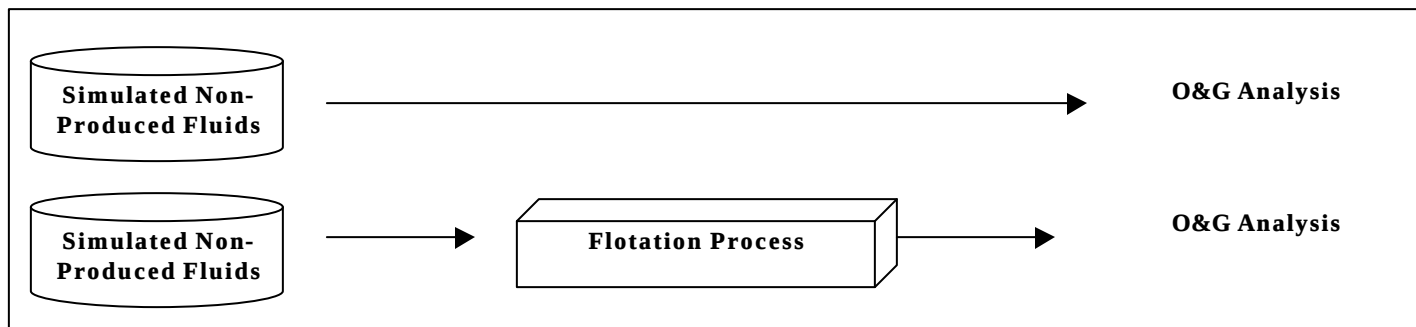
Hexane-extractables O&G baseline concentration data for the following fluids were determined in the laboratory and were found to reflect typical field data:

- 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.

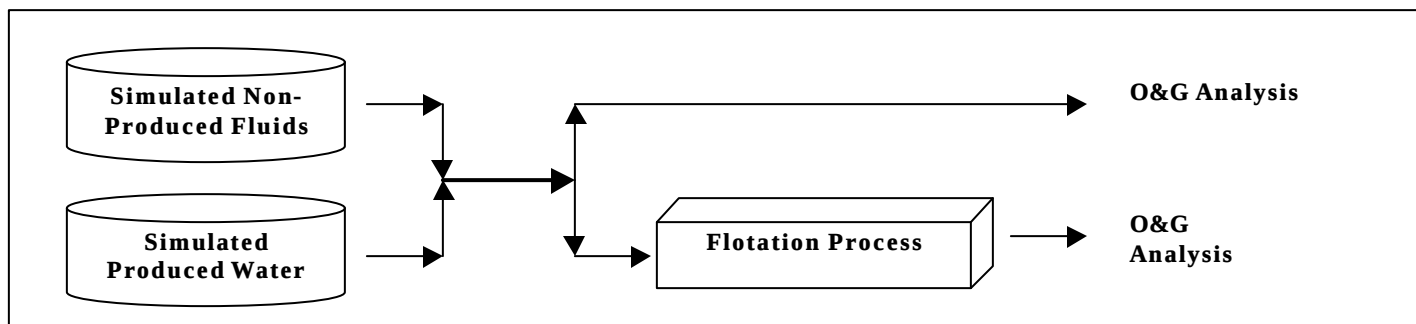
To validate the ensuing pretreatment performance data, baseline O&G data (six measurements) were consistently generated for every daily set of experiments. All process performance data presented in this report were validated as per this protocol. Figure 1 illustrates the experimental methodology.



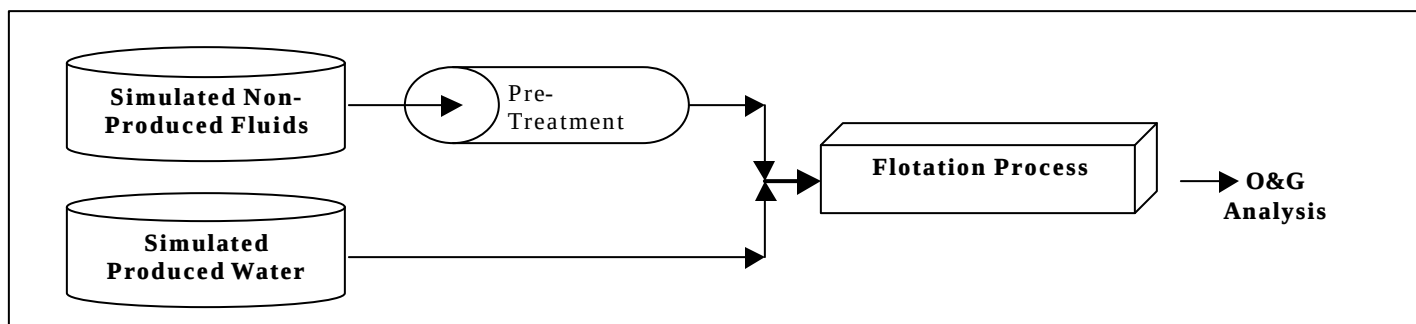
Oil and Grease Baseline Data for Simulated Produced Water.



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.

Table 1. Typical Emulsion Profiles for Simulated Produced Water.

Simulated Produced Water Batch:	Oil and Grease Concentration of Produced Water as a Function of Settling Time (mg/L)				
	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