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Project Summary

Chemical Composition of Produced Water at Some Offshore Oil Platforms

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The effectiveness of produced water treatment was briefly studied in offshore oil and gas extraction operations in Cook Inlet, Alaska, and the Gulf of Mexico. Three offshore oil extraction facilities were examined in the Cook Inlet production field, and seven platforms were studied in the Gulf of Mexico. Overall treatment effectiveness, as well as effectiveness of individual process units, was determined in the Cook Inlet study. Final effluent quality was determined in the Gulf of Mexico study.

The chemical composition of process streams and final effluents was characterized in terms of total organic material balance. Determinations were made for suspended organic matter (the oil); dissolved, nonvolatile, organic matter; and volatile hydrocarbons.

State-of-the-art treatment was generally effective in reducing the free oil content (suspended organics) of produced water. Such treatment was less effective in reducing the aromatic hydrocarbon content of produced water; the average reduction in concentration was 30% to 50%. Benzene, toluene, and xylenes/ethylbenzene (BTX) were found at all stages of the processes and in all final effluents. The average BTX concentration in treated effluents from Cook Inlet operations was 9 milligrams per liter (mg/L). In Gulf of Mexico treated effluents, the BTX content averaged 2 mg/L.

High levels of dissolved nonvolatile organic matter, ranging from 60 to 600 milligrams carbon per liter (mg C/L), were found in treated effluents. Generally, the concentration of this fraction increased, rather than decreased, as a result of treatment. This increase might be due to addition of chemicals during the treatment and to oxidation of petroleum matter leading to the formation of water-soluble, oxygenated, organic compounds.

Four organic priority pollutants (benzene, toluene, ethylbenzene, and phenol) and two inorganic priority pollutants (chromium and lead) were found in all the treated effluents analyzed. Naphthalene, cadmium, nickel, zinc, silver, copper, and beryllium were intermittently present.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The gross fluid that is produced by all oil extraction operations usually contains a mixture of oil and water. The water content of gross fluids ranges from 0% for new oil wells to more than 90% for old oil wells. The subterranean water, or brine, that remains after the oil is separated and processed is called produced water. All produced waters are contaminated by petroleum matter and chemicals used in oil processing operations and in subsequent treatment of produced water. The produced water is usually treated before it is discharged into the receiving environment or reinjected. The treatment is performed either on the production platforms or on shore, and is usually conducted coincidentally with oil/water separation, which produces processed oil. Produced water treatment ranges from relatively simple gravity separation and flotation used on offshore platforms to complete oily wastewater treatment at land installations

The principal contaminants in produced water are water-soluble and water-insoluble petroleum compounds and the chemical compositions added as part of gross fluid processing and treatment of produced water. The water-soluble petroleum fraction is composed mainly of aromatic hydrocarbons (benzene, toluene, xylenes/ethylbenzene) and diaromatics (naphthalene and derivatives). Also present in this fraction are nonhydrocarbon compounds of petroleum origin, including phenolic and carboxylic acids, and other oxygen-, nitrogen-, and sulfur-containing compounds The water-insoluble fraction consists primarily of higher aliphatic hydrocarbons and other high molecular-weight, water-insoluble components of crude oil. The organic chemicals added to the process stream as part of processing or treatment may include a significant amount of proprietary formulations.

The produced water treatment technology is designed primarily for removal of water-insoluble petroleum and not for removal of the water-soluble organic fraction that might originate in crude oil or in chemical additives used as part of processing.

Experimental Design and Methodology

The principal objective of this study was to determine how effective state-of-the-art technology is in producing acceptable-quality effluents in produced water from offshore oil extraction operations. Additionally, an attempt was made to generate comprehensive information on the chemical composition of produced water and compositional changes in the process stream. The quality of the final effluent in terms of total organic content was established. This included determination of free oil; dissolved, nonvolatile, organic compounds; and volatile hydrocarbons. Special attention was given to aromatic hydrocarbons and their role and fate in the treatment process.

To obtain the necessary information, the organic composition of the process stream was established at various stages of treatment, and rates of reduction in concentrations of suspended oil, dissolved nonvolatile organics, and purgeable hydrocarbons were determined.

The analytical procedures for the determination of purgeable hydrocarbons and dissolved and suspended organic fractions were carried out as follows. Purgeable hydrocarbons, composed largely of benzene, toluene, xylenes, and ethylbenzene, were sparged by nitrogen and adsorbed in activated charcoal tubes. This was followed by desorption into carbon disulfide using reaction vessels equipped with Mininert* caps. The desorbed extract was analyzed by gas chromatograph for purgeable hydrocarbons. An 800- to 1000-fold concentration of hydrocarbons was realized using this procedure.

After ultrasonation of the sample, the total nonvolatile organic content was determined by total organic carbon (TOC) analysis. Following this procedure, suspended oil was removed by Millipore® filtration (a 0.45-micron filter), and the filtrate was re-analyzed by the TOC analyzer. The difference between total nonvolatile and dissolved, nonvolatile, organic content corresponded to suspended organic matter. Quality assurance procedures included contamination checks; blank determinations; duplicate or triplicate analyses; and documentation of recoveries, accuracy, and precision of all methods used

Results

Cook Inlet, Alaska, Production Field

Trading Bay, Alaska, Production Facility

Four offshore platforms at this production facility supply gross fluid for onshore processing. The processing includes separation of oil from water in a battery of heater-treaters, and a multistage treatment process for produced water. The produced water treatment plant includes three gravity separators, two gas flotation units, and two water retention pits. The facility is capable of processing 131,000 barrels of gross fluid per day. Its typical production is 67,000 barrels of oil and 62,000 barrels of produced water per day. Additionally, 28,000 MCFPD (million cubic feet per day) of natural gas are produced.

To characterize the chemical composition of the process stream, the following four sampling stations were selected: Station 1, effluent from the heater-treater; Station 2, effluent from the gravity separator; Station 3, effluent from the gas flotation unit; and Station 4, effluent from the retention pit (final effluent)

Three sets of samples were collected at each sampling station at discrete time intervals and analyzed for suspended oil; dissolved, nonvolatile, organic matter; and volatile hydrocarbons. The results are reported in Table 1. The stepwise reduction of various organic fractions present in produced water is also depicted in Table 1.

The analysis of the reported data indicates that the treatment process is effective in reducing suspended oil and volatile aliphatic hydrocarbon concentrations. A 97% reduction in suspended organic matter resulted in a effluent containing 5 mg C/L of suspended organics. The concentration of volatile aliphatic hydrocarbons was reduced approximately 75%.

The process, however, was less effective in reducing purgeable aromatic hydrocarbons. A reduction of only 30% was realized, and treated effluent contained, on average, 6 mg C/L of purgeable aromatic hydrocarbons.

Very high concentrations of dissolved, nonvolatile, organic matter were observed at all stages of the treatment process. As a matter of fact, the dissolved organic content of the final effluent was significantly higher than that of untreated effluent from the heater-treater. The increase in concentration of dissolved, nonvolatile, organic matter, in all cases, took place in the initial stages of produced water treatment (between heater-treaters and gravity separators). Such an increase might be due, in part, to addition of organic chemicals used as part of the treatment. Oxidation of petroleum compounds might be an additional factor in the formation of water-soluble organic matter. When essentially anaerobic produced waters are exposed to an oxygen environment at relatively high temperatures (usually above 100°F), autocatalytic processes might lead to oxidation of some components of the organic matter present in produced water, resulting in the formation of water-soluble, oxygenated, organic compounds.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Table 1. Stepwise Reduction of Organic Content in Process Water by the Treatment Process, Trading Bay, Alaska, Production Facility, January 23, 1980

	Effluents (concentration in mg C/L)			
Organic Composition	Heater-Treater	Gravity Separator	Gas Flotator	Impound Basin (Final Effluent)
Suspended petroleum	148	38	33	5
Reduced by (%)		(74.3)	(77.8)	(96.6)
Dissolved organics	293	409	394	423
Reduced by (%)		(-)	(-)	(-)
Volatile hydrocardons	13.1	11.2	8.6	6.9
Reduced by (%)		(14.5)	(34.4)	(47.3)
• Aromatic	7.9	7.7	6.6	5.6
Reduced by (%)		(2.5)	(16.5)	(29.1)
• Aliphatic	5.0	3.6	2.0	1.3
Reduced by (%)		(28.0)	(60.0)	(74.0)

$\%Reduction = \frac{(C_o - C_n)}{C_o} \cdot 100$ where C_o is initial concentration in the effluent from the heater-treater and C_n is the concentration in effluents from various process units.

Kenai, Alaska, Production Facility

This production facility, located in North Kenai, Alaska, processes gross fluid from three offshore platforms with relatively new oil wells. The processing includes free water knockout, followed by additional separation of oil from water in heater-treaters. Produced water is treated in skim tanks (gravity separators) followed by dissolved air flotation with addition of flocculating agents. The retention time of produced water in the treatment plant is approximately 6 hours. The facility processes 21,000 barrels of gross fluid a day and typically generates 13,000 barrels of oil and 8,000 barrels of produced water.

The process stream was sampled at two points: Station 1, effluent from the water/oil separator, and Station 2, final effluent from the dissolved air flotation unit. Duplicate samples were collected at each station and analyzed for suspended organic matter, dissolved, nonvolatile, organic matter; and purgeable hydrocarbons. The treatment process effectively reduced the concentration of suspended oil from an average of 190 mg C/L to 14 mg C/L, or approximately 93%. Less effectively reduced were purgeable hydrocarbons (approximately 44%), and the treated effluent contained significant amounts of purgeable aromatic hydrocarbons. The BTX (benzene, toluene, xylenes) was present in the effluent at an average concentration level of 10 mg/L.

Dissolved nonvolatile organic matter **was present in the effluent from the oil/water separator at a concentration** of 336 mg C/L and at 269 mg C/L in the final treated effluent. It constituted approximately 92% of the total organic load discharged into the receiving environment.

Offshore Platform, Cook Inlet, Alaska

This platform is one of the older ones in Cook Inlet. The gross fluid is processed on the platform, and produced water is threated on-site and discharged into inlet waters. The platform typically processes 13,000 barrels of gross fluid per day and generates 2000 barrels of oil and 11,000 barrels of produced water. Extracted gross fluid contains approximately 85% water. The treatment process consists of a free-water knockout unit (no heater-treaters), and the produced water is treated in one step by a gravity separator.

Two sampling points were selected on this platform: Station 1, the effluent from the water knockout unit, and Station 2, final effluent. Triplicate samples were collected at each station and analyzed for suspended oil; dissolved, nonvolatile, organic matter; and purgeable hydrocarbons. The suspended oil content was reduced from 405 mg C/L to 36 mg C/L, or approximately 91%. The concentration of volatile aromatic hydrocarbons present in the final effluent was 11 mg/L, the highest level observed in this study. The dissolved, nonvolatile, organic compounds were present in significantly high levels, both in the effluent from the water knockout unit (129 mg C/L) and in the final effluent (141 mg C/L). Such compounds constitute approximately 75% of the total organic load in the effluent.

Gulf of Mexico Offshore Production Platforms

Seven production platforms were examined in the Gulf of Mexico All produced water was treated offshore using gravity separation and gas flotation methods. The final effluents were analyzed for suspended organic matter; dissolved, nonvolatile, organic compounds; and volatile hydrocarbons to ascertain the organic material balance. Additionally, analyses were performed for the following types of priority pollutants· purgeables, acid-neutral, base-neutral, pesticides, and metals.

It was found that between 9 and 46 mg C/L of suspended organic matter (free oil) was present in treated effluent. The average for the six platforms tested was 26 mg C/L.

High levels of dissolved, nonvolatile, organic matter were also found in the effluent from offshore gas and oil extraction in the Gulf of Mexico. The concentration range of this fraction was found to be 57 to 624 mg C/L with an average value of 376 mg C/L. The *dissolved nonvolatile organic fraction* constituted up to 90% of all organic matter discharged from the platforms.

It is possible that this organic matter originates from at least three different sources. Some of it can be present in extracted brine; chemicals added during the treatment might contribute additional quantities of dissolved organics; and finally, compositional changes induced by the processing of gross fluid might result in the formation of water-soluble petroleum derivatives such as carboxylic acids, alcohols, ketones, and aldehydes. Chemical additives to the process stream can account for approximately 10% of the dissolved nonvolatiles. The remaining 90% originates in the produced brine or is produced during processing of gross fluid. The relative contribution of each of these two sources is unknown at this time.

The volatile hydrocarbon fraction of the treated effluent consisted largely of benzene, toluene, and xylenes/ethylbenzene. The total aromatic hydrocarbon content was found to average 2 mg/L. This value was considerably lower than the value for aromatic hydrocarbons observed in Cook Inlet's production field. The concentration of individual hydrocarbons was as follows: benzene,

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1.1 mg/L; toluene, 0.8 mg/L; and xylenes/ethylbenzene, 0.3 mg/L.

Treated effluents from six offshore oil-producing platforms in the Gulf of Mexico were also examined for priority pollutants. Sampling, preservation, and transport of samples were carried out in accordance with EPA procedures as reported in the Federal Register (December 3 and 18, 1979). Collected samples were analyzed for purgeables, acid-neutral, base-neutral, and metallic priority pollutants.

Consistently present in all treated effluents were three priority pollutants in the purgeable group (benzene, toluene, and ethylbenzene), and one priority pollutant in the acid-neutral group (phenol). Lower concentrations of naphthalene (base-neutral group) were found intermittently. No pesticides were found in the effluent.

Average concentrations of organic priority pollutants found consistently in effluents discharged from offshore operations in the Gulf of Mexico were as follows:

Pollutant	*Concentration, µg/L*
Benzene	*836*
Toluene	*2074*
Ethylbenzene	*101*
Phenol	*480*

Treated effluents were examined for 13 priority pollutant metals: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). Chromium (Cr) and lead (Pb) were found in the effluent from every platform examined. Lead was found in the greatest concentration, averaging 597 µg/L. Chromium averaged 260 µg/L. Nickel, zinc, copper, silver, cadmium, and beryllium were found intermittently. Nickel was present in concentrations ranging from 68 to 1674 µg/L, copper in the concentration range of <25 to 137 µg/L, and silver in a concentration range of <1 to 152 µg/L. Cadmium was present in a concentration range of <25 to 56 µg/L; the concentration range for beryllium was <1 to 4 µg/L, and zinc was found in a concentration range of <25 to 640 µg/L. Concentrations of antimony, arsenic, mercury, selenium and thallium were generally below the limit detection limits of the methods used.

The generated data indicate that significant amounts of priority pollutant metals are discharged from offshore oil extraction platforms. Four metals (lead, chromium, nickel, and zinc) are the most widely distributed inorganic priority pollutants in treated effluent and, together with four organic priority pollutants (benzene, toluene, ethylbenzene, and phenol) constitute the principal contribution of toxicants discharged from offshore oil producing platforms.

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The complete report, entitled "Chemical Composition of Produced Water at Some Offshore Oil Platforms," (Order No. PB 82-227 489; Cost: $9.00, subject to change) will be available only from:
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