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Predictors of Water-soluble Organics (WS0s) in Produced Water— A Literature Review

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ABSTRACT

Discharge of treated produced water to offshore waters of the United States is regulated by NPDES permits. Current general permits for the discharge of produced water to Federal offshore waters of the Gulf of Mexico have total oil and grease limits of 42 mg/L (ppm) daily maximum and 29 mg/L monthly average. EPA requires oil and grease concentrations in produced water to be monitored by EPA Method 413.1 or 1664. Both methods are gravimetric. The methods tend to overestimate the concentration of petroleum hydrocarbons in produced water, due to interference from dissolved non-hydrocarbon chemicals. The objective of this report is to evaluate the chemical composition of produced water from oil and gas wells, and identify the water-soluble organic chemicals (WSOs) in produced water that interfere with gravimetric determination of oil and grease. An initial assessment is made of the physical and chemical properties of the produced water and the associated fossil fuel reservoir, in an effort to predict which produced waters will contain high concentrations of WSOs.

Produced water may contain up to 1,000 mg/L total organic carbon (TOC), most of it in solution. Most of the dissolved organic carbon in produced water is accounted for by C_2 through C_5 organic acid anions, such as acetate, propionate, and butyrate. Acetic acid usually is the most abundant organic acid in produced water. These organic acids are identical to volatile organic acids produced by marine organisms and are not toxic or persistent in the marine environment.

A small fraction (usually less than 20%) of the dissolved organic matter in produced water is comprised of low molecular weight alkanes and aromatic hydrocarbons. The most abundant dissolved hydrocarbons in most produced waters are the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX). BTEX concentrations usually are in the range of 0.07 to 500 mg/L. Benzene usually is the most abundant. Low concentrations of low molecular weight alkanes (C_5 to C_{20}) and traces of a few polycyclic aromatic hydrocarbons (PAHs) also may be present in produced water. The concentration of total PAHs usually is less than about 2 mg/L. Naphthalene and alkyl naphthalenes usually are the most abundant.

Phenols usually are present in produced water at concentrations lower than 20 mg/L. Phenol, C_{1}-, and C_{2}-phenols usually are the most abundant. Other dissolved hydrocarbon-like chemicals containing oxygen, sulfur, or nitrogen usually are present at trace concentrations.

Produced water contains in solution most of the non-metal inorganic and metal ions found in seawater. Many produced waters, including most of those from the U.S. Gulf of Mexico, have a salinity (total dissolved solids concentration) greater than that of sea water (≈ 35 g/kg). However, ionic ratios in produced water may be different from those in sea water. A few metals may be present in produced water from different sources at concentrations substantially higher (1,000-fold or more) than their concentrations in clean natural sea water. The metals most frequently present in produced water at elevated concentrations include barium, cadmium, chromium, copper, iron, lead, nickel, and zinc. Usually, only a few of these metals are present at elevated concentrations in a particular produced water sample. Produced water, particularly that from the Gulf of Mexico, contains radium isotopes (^{226}Ra plus ^{228}Ra) at concentrations up to about 2,800 pCi/L.

Organic acids are the quantitatively most important WSOs in produced water that interfere with the gravimetric methods for determination of total oil and grease. Although they are not extracted efficiently with the organic solvent used in the gravimetric methods (Freon® or hexane), their concentrations in most produced waters are high enough that they contribute substantially to the mass of organic matter extracted from produced water. Treatment of the extract with silica gel (an option in Method 1664) decreases the amount of interfering non-hydrocarbon WSOs in the extract.

Organic acids in petroleum or produced water are thought to form by thermal degradation of oxygenated organic matter in source rocks or by hydrous pyrolysis of hydrocarbons. Organic acid anions are more soluble in water than in oil and, so, partition into produced water from the oil in the reservoir. The optimum temperature for these processes appears to be in the range of 80°C to 120°C. At lower reservoir temperatures, microbial degradation of organic acids decreases their concentrations in the produced water. At higher reservoir temperatures, organic acids are unstable and undergo thermal decarboxylation, forming CO_2 and low molecular weight hydrocarbons (natural gas).

Because of these thermal processes, concentrations of total volatile organic acids in produced water tend to increase with increasing temperature below about 80°C, reach highest levels in reservoirs with temperatures between about 80°C and 120°C, and decline in reservoirs with higher temperatures. However, many secondary factors influence the concentration of organic acids in any given produced water. Thus, the relationship between temperature and organic acid concentration in produced water is only approximate. It is not possible to use reservoir temperature alone to predict the concentration of organic acids in produced water. The main secondary factors affecting organic acid concentrations in produced water include the nature and amount of organic matter in source rocks, the age of the reservoir, the geology and migration distance between source rocks and the reservoir, and the sources of connate water in the reservoir.

The following recommendations are based on the results of this review:

- The optional silica gel cleanup step in Method 1664 should be used to remove most of the polar organic chemicals that interfere with oil and grease measurement; and,
- Consistent correlations between organic acid concentrations in produced water and physical/chemical properties of the hydrocarbon-bearing formation, the crude oil or gas, and/or the produced water itself are needed, although the necessary composition and property data are rarely available. If such information can be obtained from operators, it may be possible to model the occurrence of organic acids and total WSOs in produced water.

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PREDICTORS OF WATER-SOLUBLE ORGANICS (WSOs) IN PRODUCED WATER—A LITERATURE REVIEW

1 Introduction

The U.S. Environmental Protection Agency (EPA) or a state agency designated by EPA issues region wide (general) or site-specific National Pollutant Discharge Elimination System (NPDES) permits to regulate discharges of treated produced water to State and Federal offshore waters of the United States. Produced water intended for ocean discharge is first treated in various oil/water separation devices to remove dispersed oil droplets. Current general permits for Federal offshore waters of the Gulf of Mexico have limits for total oil and grease in produced water of 42 mg/L (ppm) daily maximum and 29 mg/L monthly average.

EPA requires oil and grease concentrations in produced water to be monitored by EPA Method 413.1 or 1664 (EPA, 1983, 1995). Both methods are gravimetric. Nonpolar and slightly polar organic matter in produced water is extracted with Freon® (Method 413.1) or n-hexane (Method 1664). In Method 1664, the analyst has the option to treat the hexane extract with silica gel to remove polar interfering compounds. The extract is dried and weighed to derive a concentration of total extractable organic matter (total oil and grease).

Although the oil and grease methods are inexpensive and easy to perform, there are two technical problems that may have implications for the regulation of discharges of produced water to offshore marine waters. First, low-molecular-weight, volatile alkane and aromatic hydrocarbon (BTEX) analytes are lost by evaporation during sample processing. Second, many non-hydrocarbon organics, and possibly some metals, are extracted by the solvent and measured as part of the total oil and grease in produced water, even after extract cleanup with silica gel.

Loss of volatile hydrocarbons is not a concern, since these chemicals are not persistent in surface waters and so are unlikely to contribute to the toxicity of produced water plumes to marine animals (Neff, 1997). In a regulatory context, the second problem is more of an issue. The analytical methods may grossly overestimate the concentration of petroleum hydrocarbons in produced water if the concentration of non-hydrocarbon organic matter in the produced water is high (Brown et al., 1990, 1992; Otto and Arnold, 1996). Typical produced water from production platforms in U.S. Gulf of Mexico may contain 50 to more than 500 mg/L (ppm)[1] total organic carbon (TOC), of which approximately 8.5 to 16% is petroleum hydrocarbons (Neff et al., 1989). The remaining TOC is a mixture of non-hydrocarbon organics, including water-soluble production treatment chemicals, phenols, organic acids, alcohols, and ketones. These non-hydrocarbon organic fractions of produced water have not been well characterized. Some information is available about water-soluble production treatment chemicals, organic acids, and phenols (Neff, 1997).

If oil and grease concentrations in produced water from a platform exceed regulatory limits for oil and grease, the operator may be required to cease discharging produced water and upgrade the produced water treatment system on the platform. If most of the organic matter measured oil and grease is comprised of water-soluble organics and not true petroleum hydrocarbons, improvement of the efficiency of the oil/water separation system will not help to bring total oil and grease concentrations down below regulatory limits. Usually in such circumstances offshore compliance can only be accomplished by closing in the wells or reinjecting the produced water, both of which have substantial financial consequences, especially in a deep offshore environment. There are two approaches to resolving this problem:

- Develop and gain EPA approval of a new analytical method for total oil and grease that accurately measures the true concentration of produced water petroleum hydrocarbons, excluding non-hydrocarbon water soluble organics (WSOs); or,
- Develop and gain EPA acceptance of correlations or predictors of elevated concentrations of non-hydrocarbon WSOs in produced waters, so that these correlations might be used to adjust monitoring data in compliance determinations.

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[1] Concentration in parts per million should be expressed on a weight/weight basis as mg/kg; however, it often is expressed on a weight/volume basis as mg/L. The two values are essentially the same when the liquid is fresh water (specific gravity of 1.0 g/mL). However, many produced waters are concentrated brines with specific gravity of > 1.0. The error resulting from expressing ppm as mg/L is small and within the margin of error of the analytical method. For example, produced water with a salinity of 140 parts per thousand (specific gravity of 1.1009), containing 100 mg/L of a compound, actually contains 99 mg/kg of the chemical. In this document, concentrations in produced water will be expressed in mg/L, or µg/L, which are slightly greater than parts-per-million and parts-per-billion, respectively.

The ojectives of this study include:

- Defining the chemical composition and characteristics of WSOs in oil- and gas-well produced water, and identifying the WSOs that interfere with EPA standard methods for total oil and grease; and,
- Identifying reservoir geochemistry, and the physical and chemical characteristics of produced water and crude oil, that may be correlated with WSO concentrations or are indicative of the presence of WSOs in produced water.

This report is a review of the scientific literature on the identity and physical/chemical characteristics of the water-soluble organics (WSOs) in produced water in relation to characteristics of fossil fuels and their reservoirs. The results of this review are the basis for recommendations about the feasibility of developing correlations between WSO concentrations in produced water and physical/chemical properties of the produced waters and/or their reservoirs.

2 Chemical Composition of Produced Water

2.1 ORIGINS OF PRODUCED WATER

During millions of years of geologic time, petroleum and natural gas may accumulate in porous sediments (e.g., sands) trapped between layers of impermeable rock deep within the earth (Collins, 1975). Water may be trapped during millions of years with the oil and gas. This water may be derived from ancient fresh or salt water (connate water) and often is as old as the fossil fuels in the reservoir. When the hydrocarbon reservoir is tapped by a well, the produced gases and fluids may contain connate water. Also, in some oil fields, fresh or salt water may be injected into the reservoir through injection wells to displace oil toward the production wells. Sometimes, this injection water channels through to the production well and is produced with the oil and gas. The water produced with oil and gas is called produced water, produced formation water, or oilfield brine (Neff, 1987, 1997; Black et al., 1994).

Before the crude oil can be refined or the gas processed, the water must be removed. During offshore operations, separation of the produced water from the oil and gas may take place on the production platform or the oil/gas/water mixture may be sent through a pipeline to a shore facility where the produced water is separated from the oil and gas. If not re-injected, the produced water is treated to meet regulatory limits for oil and grease so it may be discharged to the ocean from the platform or from an ocean outfall from a shore-based treatment facility. The current limit for total oil and grease in produced water destined for ocean disposal in U.S. Federal and Upper Cook Inlet, AK, waters is 42 mg/l (ppm) daily maximum and 29 mg/L monthly average (Otto and Arnold, 1996; Veil, 1997).

The oil/gas/water mixture may be processed through devices to separate the three phases from one another. On western Gulf of Mexico platforms, the types of equipment used to remove oil and grease from produced water include, in order of frequency of use, mechanical and hydraulic gas floatation units, skimmers, coalescers, hydrocyclones, and filters (Otto and Arnold, 1996). Chemicals may be added to the process stream to improve the efficiency of oil/gas/water separation. Even with the most advanced separation equipment, the oil/water separation is not 100% efficient. If the oil/water separation system is efficient, however, most of the chemicals remaining in the treated produced water are in solution or colloidal suspension in the water.

To prevent corrosion, foaming, scale formation, hydrogen sulfide formation, and bacterial growth, or to improve the efficiency and completeness of oil/water separation, small amounts of specialty chemicals may be added to the production stream at different steps in the production and treatment process (Hudgins, 1989, 1991, 1992). Most of these chemicals remain in the oil or gas phase; others are water-soluble, remain in the produced water, and are discharged. Approximately 19% of the offshore production chemicals used on platforms in the North Sea are discharged in treated produced water, including more than 50% of the emulsifiers, surfactants, oil removing agents, and scale inhibitors (van Hattum et al., 1992; Ynnesdal and Furuholt, 1994; Hudgins, 1994). Only small amounts (less than 20% of the amounts used) of corrosion inhibitors, oxygen scavengers, emulsion breakers, defoamers, and gas treatment agents are discharged with produced water.

Produced water represents the largest volume production waste stream on most offshore platforms (Stephenson, 1991). The amount of produced water discharged from a single platform usually is less than 9,400 barrels/day (bbl/d) (1.5 million liters/day), whereas discharges from large facilities that process produced water from several platforms may exceed 25 million liters/day (Menzie, 1982). Most discharges of produced water from individual oil/water separators or production platforms to Federal waters of the western Gulf of Mexico are less than about 500 bbl/d (80,000 liters/d) (Boesch and Rabalais, 1989). The total volume of produced water discharged to US State and Federal waters of the Gulf of Mexico in 1991 was approximately 3.45 million bbl/d (549 million liters/day) (Rabalais et al., 1991) (Table 1). A similar volume of produced water is discharge each day to the North Sea; smaller volumes are discharged to most other offshore oil production areas.

Table 1—Volumes of treated produced water discharged to the ocean from production platforms in several parts of the world. Volumes are liters/day.

Location	Discharge Rate
U.S. Gulf of Mexico	549,000,000
Offshore California	14,650,000
Cook Inlet, Alaska	22,065,000
North Sea	512,000,000
Australia	100,000,000
West Java Sea, Indonesia (3 Offshore Facilities)	192,000,000

Table 2—Concentration ranges of several classes of naturally-occurring organic compounds in produced water worldwide. Concentrations are in mg/L (parts per million). From Neff (1997).

Compound Class	Concentration Range[a]
Total Organic Carbon	≤ 0.1 – 11,314
Total Normal and Branched Alkanes	17 – 30
Total Benzene, Toluene, Ethylbenzene & Xylenes (BTEX)	0.068 – 578
Total Polycyclic Aromatic Hydrocarbons (PAH)	0.08 – 3.0
Steranes & Triterpanes (saturated)	0.14 – 0.175
Ketones	1.0 – 2.0
Phenols	0.6 – 21.5
Organic Acids	≤ 0.001 – 10,000

[a] Data from Kharaka et al. (1978), Armstrong et al. (1979), Brooks et al. (1980), Middleditch (1981, 1984), Sauer (1981), Lysyj (1982), Burns and Roe (1983), Hanor et al. (1986), Hanor and Workman (1986), Fisher, (1987), Grahl-Nielsen (1987), MacGowan and Surdam (1988), Boesch et al. (1989), Macpherson (1989), Neff et al. (1989), Means et al. (1989, 1990), Rabalais et al., (1991), Stueber and Walter (1991), Jacobs et al. (1992), Tibbetts et al. (1992), Stephenson (1992), van Hattum et al. (1992), Terrens and Tait (1993), and Stephenson et al. (1994).

2.2 ORGANIC CHEMICALS IN PRODUCED WATER

2.2.1 Total Organic Carbon

The concentration of total organic carbon (TOC) in produced water ranges from less than 0.1 to as high as 11,000 mg/L (Fisher, 1987) and is highly variable from one location to another (Table 2). Concentrations of TOC in produced water samples from the North Sea usually are in the range of 14 to more than 1,000 ppm (Tibbetts et al., 1992; Stephenson et al., 1994); produced water from the Bass Strait, Australia, contains 15 to 313 ppm TOC (Brand et al., 1989). Produced water from production wells in the U.S. Gulf of Mexico contain 68 to 540 ppm TOC (Neff, 1997).

Most of this organic matter is in solution or colloidal suspension in the produced water (Means et al., 1989). Therefore, dissolved organic carbon (DOC) concentration is almost equivalent to TOC concentration. Fisher (1987) and Neff (1997) reported DOC and organic acid concentrations in several produced waters from several basins throughout the world (Table 3). Concentrations of DOC varied widely in produced water from different formations and even within a particular basin. DOC concentrations ranged from 17 ppm to 11,314 ppm. Much of the DOC in the 144 samples of produced water analyzed by Fisher (1987) can be accounted for by volatile C_2 through C_5 organic acid anions. DOC tended to covary with total organic acid concentration. However, there was no clear relationship between DOC and organic acid concentrations on the one hand and age of the formation or its temperature on the other. Highest DOC concentrations were in produced waters from Pliocene formations. As discussed below, there is a tendency for highest DOC and organic acid concentrations to occur in produced waters from formations with temperatures of about 80°C to 120°C. At higher and lower temperatures, organic acid concentrations decrease.

2.2.2 Organic Acids

As shown in Table 3, much of the organic carbon in produced water consists of a mixture of low molecular weight carboxylic acids (organic acids), such as acetic acid and propionic acid (Somerville et al., 1987; Means and Hubbard, 1987; Barth, 1991). This can be seen clearly in the organic chemical composition of three produced waters from production facilities in the Norwegian Sector of the North Sea (Table 4). Volatile organic acids represent 60 to 98% of the total extractable organic matter in the three produced waters. Most of the remainder of the organic matter is saturated and aromatic hydrocarbons and phenols. Traces of higher molecular weight C8 through C17 fatty acids also are present.

The low molecular weight organic acids are identical to fatty acids synthesized by marine and freshwater bacteria, fungi, and plants and are common trace ingredients of clean marine sediments (Sansone, 1986; Brown et al., 1990; Albert and Martens, 1997). The most abundant organic acids in produced water are monofunctional acid anions, particularly acetic and propionic acids (Table 5). The difunctional acid anions, oxalic acid and malonic acid may also be abundant in some produced waters.

The relative and total concentrations of low molecular weight organic acids in produced waters vary widely, even in produced waters from the same geographic areas. Table 6 is a summary of organic acid concentrations in produced waters from two Gulf Coast locations and from the California coast (MacGowan and Surdam, 1988).

Table 3—Concentrations of total dissolved organic carbon (DOC) and total C_2 through C_5 organic acids in produced water from several geologic basins. Age and temperature of the formation are given. Concentrations of DOC and organic acids are mg/L. From Fisher (1987).

Field	Age	Temperature (°C)	DOC	Organic Acids
Poui Field, Trinidad	Pliocene	45 – 78	234 – 3777	0 – 3204
Samaan Field, Trinidad	Pliocene	58 – 80	321 – 4072	0 – 2428
Teak Field, Trinidad	Pliocene	48 – 88	425 – 11314	0 – 2795
McAllen Ranch Field, TX	Oligocene	156 – 174	124 – 272	27.4 – 54.6
Las Animas County, CO	Tertiary	32 – 52	115 – 378	211 – 595
San Juan County, NM	Cretaceous	49	1000 – 2185	1128 – 1774
La Plata County, CO	Cretaceous	46	553 – 745	60 – 888
Gunnison County, CO	Cretaceous	52	190 – 355	272 – 306
Summit County, UT	Triassic	102 – 117	47 – 172	56 – 128
Unita County, WY	Triassic	52 – 88	17 – 312	13 – 75
Summit County, WY	Triassic	96	323	110

Table 4—Mean concentrations of the main organic fractions in produced water from three offshore production facilities in the Norwegian Sector of the North Sea. BTEX (C_6 – C8 aromatics) are not included. Concentrations are mg/L. From Strømgren et al. (1995).

Chemical Class	Facility 1	Facility 2	Facility 3
Volatile Acids ($C_1 – C_{5+}$)	817	43	229
Fatty Acids ($C_8 – C_{17}$)	0.5	0.04	0.03
Phenols	7.8	0.8	2.8
Aliphatic Hydrocarbons ($C_{12} – C_{35}$)	4.6	25	14.3
Aromatic Hydrocarbons ($C_{10} – C_{35}$)	1.1	4.5	2.0
Total Extractable Organic Matter	831	73	248

Table 5—Maximum reported concentrations of several organic acids in produced waters. Concentrations are mg/L. From MacGowan and Surdam (1988).

Common Name	IUPAC Name	Formula	Max. Concentration
Formic acid	Methanoic acid	CHOOH	62.6
Acetic acid	Ethanoic acid	CH_3COOH	10,000
Propionic acid	Propanoic acid	CH_3CH_2COOH	4400
Butyric acid	Butanoic acid	$CH3(CH_2)_2COOH$	44.0
Valeric acid	Pentanoic acid	$CH_3(CH_2)_3COOH$	32.01
Oxalic acid	Ethanedioic acid	HOOCCOOH	494
Malonic acid	Propanedioic acid	$HOOCCH_2COOH$	2540
Succinic acid	Butanedioic acid	$HOOC(CH_2)_2COOH$	63
Pentanedioic acid	Pentanedioic acid	$HOOC(CH_2)_3COOH$	36

Table 6—Range of concentrations of several low molecular weight organic acids in produced water from three locations. Concentrations are mg/L. From MacGowan and Surdam (1988).

Organic Acid	Texas Coast	Louisiana Coast	Santa Maria Basin
Formic acid	ND – 3.8	ND – 67.6	4.2 – 40.1
Acetic acid	33.1 – 1030	50.1 – 2330	8.0 – 5735
Propionic acid	ND – 227	32.5 – 331	7.4 – 4400
Butyric acid	ND – 32.5	ND – 44.0	ND – 16.1
Valeric acid	ND – Tr	ND – 1.8	ND – 23.8
Oxalic acid	ND – 275	ND – 495	10.1 – 108
Malonic acid	ND – 195	ND – 405	ND – 1540
Total acids	98.6 – 1290	616 – 2740	724 – 7160

Small amounts of aromatic acids (e.g., benzoic acid) may also be present in produced water (Means et al., 1989, 1990; Brown et al., 1992). Rabalais et al. (1991) extracted with dichloromethane several acids and phenols from acidified produced water from coastal Louisiana. Concentrations of aliphatic acids (organic acids) in the samples ranged from 1.8 to 120 mg/L (Table 7). Concentrations of benzoic and alkylbenzoic acids were lower, in the range of 0.04 to 16 mg/L. In most cases, benzoic acid was more abundant than its alkyl homologues. Phenols were present in the produced waters at lower concentrations than benzoic acids. Produced water from oil and gas wells in the Sacramento Valley, CA, contains traces of hydroxybenzoic acids (Lundegard and Kharaka, 1994).

2.2.3 Phenols

Concentrations of total phenols in produced water usually range from 0.6 to 21.500 mg/L (Tables 2 and 7). Highest concentrations are in produced water samples from the North Sea (Grahl-Nielsen, 1987; Stephenson et al., 1994). Methylphenols (cresols) and dimethyl-phenols (xylenols) are more abundant than phenol in these samples. However, phenol and cresols are approximately equally abundant in several GOM produced waters analyzed by Rabalais et al. (1991).

Measured concentrations of total phenols in produced waters from Louisiana coastal waters range from 2.16 to 4.51 mg/L (Neff, 1997). The most complete analyses to date of phenols in produced water are those for three Indonesian produced waters (Neff and Foster, 1997). These produced waters contain 2.5 to 6.3 mg/L total phenols (Table 8). The most abundant phenols in the produced waters are phenol, methylphenols, and dimethylphenols. No phenols with alkyl side chains greater than C_5 were detected. However, 0.00056 mg/L 4-octylphenol, a known estrogen mimic compound, was detected in one produced water sample. Polyphenol ethoxylate surfactants, containing octylphenols and nonylphenols, sometimes are used in the production system to facilitate pumping viscous or waxy crude oils. If the surfactant degrades, some alkylphenols may be released into the produced water. Because of the toxicity of the more highly alkylated phenols as estrogen mimics, polyphenol ethoxylate surfactants are being replaced in applications where the surfactant or its degradation products may reach the environment in significant amounts (Getliff and James, 1996).

Table 7—Range of concentrations of organic acids, aliphatic acids, and phenols in produced water from Seven produced water treatment facilities in coastal Louisiana. Concentrations are mg/L. From Rabalais et al. (1991).

Chemical	Pass Furchon	Bayou Rigoud	5 Other Facilities
Aliphatic acids	8.5 – 120	1.8 – 78.0	7.9 – 75.0
Benzoic acid	0.92 – 15.0	0.13 – 16.0	1.2 – 13.0
C_1-Benzoic acid	1.6 – 11.0	0.089 – 14.0	1.6 – 16.0
C_2-Benzoic acid	0.42 – 2.3	0.043 – 2.7	0.29 – 3.8
Phenol	0.24 – 3.8	0.064 – 2.1	0.11 – 1.9
C_1-Phenols	0.23 – 2.4	0.047 – 3.4	0.23 – 2.4
C_2-Phenols	0.13 – 1.3	0.013 – 2.0	0.20 – 0.69
Total acid extractables	12.0 –160	2.2 – 120	13.0 – 110

Table 8—Concentrations of phenol and different alkylphenol groups in produced water from three production facilities in Indonesia. From Neff and Foster (1997). Concentrations are mg/L.

Compound	Widuri	Krisna	Cinta
Phenol	0.67	2.49	1.02
C_1-Phenols	0.77	1.69	0.85
C_2-Phenols	0.58	1.10	0.56
C_3-Phenols	0.30	0.59	0.28
C_4-Phenols	0.13	0.368	0.10
C_5-Phenols	0.040	0.089	0.030
C_6-Phenols	ND	ND	ND
C_7-Phenols	ND	ND	ND
C_8-Phenols	ND	ND	ND
C_9-Phenols	ND	ND	ND
Total Phenols	2.49	6.33	2.85

2.2.4 Petroleum Hydrocarbons

Petroleum hydrocarbons are the organic components of greatest environmental concern in produced water. Petroleum hydrocarbons (measured as oil and grease by infrared spectrometry) account for 25 to 65% of the TOC in produced water samples from Cook Inlet (Lysyj, 1982) and 8.5 to 16% of the TOC in produced water samples from the Gulf of Mexico analyzed by Neff et al. (1989). It should be pointed out that standard methods for analysis of oil and grease (e.g., EPA gravimetric Methods 413.1 and 1664 and infrared Method 418.1) are not specific for petroleum hydrocarbons and measure several other compounds in produced water (e.g., organic acids), in addition to petroleum hydrocarbons (Brown et al., 1992; Otto and Arnold, 1996).

The solubility of petroleum hydrocarbons in water decreases as their size (molecular weight) increases (McAuliffe, 1966; Eastcott et al., 1988). Because the oil/water separator equipment is efficient in removing oil droplets but not dissolved oil from the produced water, most of the petroleum hydrocarbons remaining in the produced water after treatment are low molecular weight aromatic and saturated hydrocarbons that are dissolved in the produced water.

Volatile Aromatic Hydrocarbons. The most abundant hydrocarbons in produced water are the one-ring aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes (the BTEX compounds) and low molecular weight saturated hydrocarbons. BTEX may be present in produced water from different sources at concentrations ranging from 0.068 to occasionally as high 600 mg/L (Table 2). In the North Sea, and probably elsewhere, produced water from gas wells usually contains higher concentrations of BTEX than produced water from oil wells (Stephenson et al., 1994). Produced waters from wells in the northwestern Gulf of Mexico contain 0.068 to 38 mg/L total BTEX (Neff, 1997). Benzene often is the most abundant BTEX compound in produced water, followed by toluene (Table 9). Ethylbenzene and the three xylene isomers usually are present at only a small fraction of the concentrations of benzene and toluene. Trimethyl- and tetramethyl-benzenes usually are present at much lower concentrations than BTEX.

Saturated Hydrocarbons. Saturated (aliphatic) hydrocarbons or alkanes with molecular weights in the range of those of BTEX usually are present at much lower concentrations (usually less than half) than the monoaromatic hydrocarbons in produced waters (Middleditch, 1981; Sauer, 1981; Neff et al., 1989). For example, two samples of produced water from coastal Louisiana analyzed by Neff et al. (1989) contained 1.09 to 2.14 mg/L C1 through C8 alkanes and 2.43 to 9.51 mg/L BTEX. This is due in large part to the much greater aqueous solubility of BTEX than of saturated hydrocarbons of similar molecular weight (McAuliffe, 1966).

Normal paraffins from n-C_{10} to n-C_{34} are generally much less abundant than BTEX in produced water (Table 10). Often, the most abundant normal alkane is in the C_{13} to C_{16} range and abundance decreases with increasing molecular weight. This is due to the volatility of the low molecular weight alkanes and the extremely low aqueous solubility of alkanes with more than about 16 carbons (Coates et al., 1985). In a typical crude oil, the concentration of n-paraffins decreases with increasing molecular weight and this trend is reflected in the relative concentrations of alkanes in produced water.

Alkanes have much lower aqueous solubilities than aromatic hydrocarbons of similar molecular weight. Therefore, some of the alkanes in produced water, particularly the higher molecular weight ones, may be associated with dispersed oil droplets in the produced water. For example, the solubility of n-alkanes decreases with increasing molecular weight from 1 µg/L for tridecane (n-C_{13}) to less than 0.0000006 µg/L for tetracosane (n-C_{24}). These solubilities are lower than concentrations of

Table 9—Concentrations of BTEX and other selected monocyclic aromatic hydrocarbons in produced water from four platforms in the U.S. Gulf of Mexico (OOC, 1997; DOE, 1997) and from three offshore production facilities in Indonesia (Neff and Foster, 1997). Concentrations are mg/L.

Compound	7 Gulf of Mexico Produced Waters	3 Indonesian Produced Waters
Benzene	0.44 – 2.80	0.084 – 2.30
Toluene	0.34 – 1.70	0.089 – 0.80
Ethylbenzene	0.026 – 0.11	0.026 – 0.056
Xylenes (3 isomers)	0.16 – 0.72	0.013 – 0.48
Total BTEX	0.96 – 5.33	0.33 – 3.64
Propylbenzenes (2 isomers)	NA	ND – 0.01
Methylethylbenzenes (3 isomers)	NA	0.031 – 0.051
Trimethylbenzenes (3 isomers)	NA	0.056 – 0.10
Total C_3-Benzenes	0.012 – 0.30	0.066 – 0.16
Methylpropylbenzenes (5 isomers)	NA	ND – 0.006
Diethylbenzenes (3 isomers)	NA	ND
Dimethylethylbenzenes (6 isomers)	NA	ND – 0.033
Total C_4-Benzenes	ND – 0.12	ND – 0.068

Note: NA: Not analyzed. ND: Not detected.

these alkanes in many produced waters (Table 10), indicating that the higher molecular weight alkanes are not in solution in the produced water. The oil/water separator system is designed to efficiently remove oil droplets from the produced water; therefore, there is a strong inverse correlation between the efficiency of oil/water separation and the concentration of n-alkanes in produced water.

Polycyclic Aromatic Hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons (PAHs: also called polynuclear aromatic hydrocarbons), defined as hydrocarbons containing two or more fused aromatic rings, are the petroleum hydrocarbons of greatest environmental concern in produced water, because of their toxicity and persistence in the marine environment (Neff, 1987). Concentrations of total PAHs in produced water typically range from about 0.08 to 3.0 mg/L (Table 2). Naphthalene and occasionally phenanthrene and their alkyl homologues are the only PAHs that are sometimes present at higher than trace concentrations (Table 11). These lower molecular weight PAHs often are present at higher concentrations in produced water from gas wells than in produced water from oil wells (Stephenson et al., 1994).

Individual higher molecular weight PAHs, such as benzo(a)pyrene, rarely are present in produced water at concentrations greater than about 0.0001 mg/L. The aqueous solubility of benzo(a)pyrene is so low (≈ 0.0038 mg/L) and its affinity for the oil phase so high (log K_{ow} 6.04) that it would not be expected to be present in solution in produced water. Crude oils rarely contain more than about 1 ppm benzo(a)pyrene (Neff, 1979). Thus, high molecular weight PAHs, such as benzo(a)pyrene, are not expected in produced water, unless the produced water contains a high concentration of dispersed oil droplets.

Measured concentrations of total PAHs in Gulf of Mexico produced water are in the range of 0.08 to 1.86 mg/L (Neff, 1997). Concentrations of individual PAH from naphthalene to chrysene in produced waters from different sources nearly always are in the range of a few thousandths to about 0.2 mg/L (Table 11); concentrations decrease as molecular weight increases. In most cases, except for naphthalene, the alkyl homologues are more abundant than the parent PAHs. Naphthalene, because of its high aqueous solubility (≈ 22 mg/Lin sea water: Whitehouse, 1984), partitions from the oil phase into the produced water. Naphthalene and alkylnaphthalenes are the most abundant PAHs in most produced waters.

If the oil/water treatment system is operating efficiently, most of the hydrocarbons in produced water are present at concentrations well below their single-phase aqueous solubilities. The amount of a hydrocarbon that dissolves from the oil phase into produced water depends on the concentration of the hydrocarbon in the oil and the oil/water partition coefficient for the hydrocarbon (Lee et al., 1992a; Neff and Sauer, 1995a). For example, a No. 2 fuel oil containing 4,000 mg/kg naphthalene produced a water-soluble fraction (similar to a produced water) containing 0.84 mg/L naphthalene (Anderson et al., 1974). This concentration is about 4% of the saturation concentration of naphthalene in seawater.

Other Organic Components of Produced Water. There is little information about the concentrations of cyclic alkanes (naphthenes) and sulfur-, nitrogen-, and oxygen-substituted saturated and aromatic (heterocyclic) organic compounds in produced water. These chemicals usually are more water-soluble than normal or branched alkanes or unsubstituted hydrocarbons of similar molecular weight (McAuliffe, 1966). Three produced waters from Indonesia contain

Table 10—Concentrations of n-alkanes in produced water from two platforms in coastal Louisiana and two platforms in Thailand. Concentrations are mg/L. From Neff et al. (1989) and Battelle (1994).

Chemical	Louisiana	Thailand
Decane (n-C_{10})	0.014 – 0.019	0.169 – 1.01
Undecane (n-C_{11})	0.030 – 0.093	0.307 – 1.11
Dodecane (n-C_{12})	0.044 – 0.193	0.383 – 1.08
Tridecane (n-C_{13})	0.055 – 0.272	0.456 – 1.03
Tetradecane (n-C_{14})	0.056 – 0.308	0.545 – 0.957
Pentadecane (n-C_{15})	0.057 – 0.266	0.483 – 0.830
Hexadecane (n-C_{16})	0.055 – 0.177	0.336 – 0.629
Heptadecane (n-C_{17})	0.056 – 0.142	0.367 – 0.705
Octadecane (n-C_{18})	0.033 – 0.215	0.205 – 0.384
Nonadecane (n-C_{19})	0.038 – 0.180	0.140 – 0.338
Eicosane (n-C_{20})	0.036 – 0.171	0.096 – 0.277
Heneicosane (n-C_{21})	0.030 – 0.123	0.071 – 0.219
Docosane (n-C_{22})	0.025 – 0.107	0.052 – 0.172
Tricosane (n-C_{23})	0.022 – 0.085	0.040 – 0.144
Tetracosane (n-C_{24})	0.020 – 0.069	0.030 – 0.105
Pentacosane (n-C_{25})	0.018 – 0.057	0.025 – 0.087
Hexacosane (n-C_{26})	0.016 – 0.050	0.017 – 0.065
Heptacosane (n-C_{27})	0.012 – 0.040	0.017 – 0.056
Octacosane (n-C_{28})	0.010 – 0.030	0.098 – 0.043
Nonacosane (n-C_{29})	0.008 – 0.026	0.008 – 0.036
Triacontane (n-C_{30})	0.006 – 0.019	0.008 – 0.028
Hentriacosane (n-C_{31})	0.007 – 0.018	0.006 – 0.024
Dotriacontane (n-C_{32})	0.004 – 0.011	ND – 0.016
Tritriacosane (n-C_{33})	NA	ND – 0.013
Tetratriacosane (n-C_{34})	0.002 – 0.007	ND – 0.007
Total n-Alkanes	0.606 – 2.68	3.90 – 7.83

ND. Not detected. NA. Not analyzed.

traces of decalins (decahydronaphthalenes), dibenzofuran, benzothiophene, and dibenzothiophene (Table 12). Decalin is a typical cyclic alkane, composed of two conjugated, saturated six-member carbon rings. Benzothiophene and dibenzothiophene usually are the most abundant sulfur heterocyclic compounds in produced water. Concentrations of these compounds in crude oils and the produced waters associated with them usually vary directly with the concentration of sulfur in the oils. Dibenzofuran is a typical oxygen-substituted heterocyclic compound, and usually is present at low concentrations in produced water. There is no information about the concentrations of nitrogen heterocyclics in produced water. Some of the lower molecular weight N-heterocyclics, such as acridine and carbazole, probably are present in some produced waters at low concentrations.

Several other soluble organic chemicals have been indentified in produced water (Lundegard and Kharaka, 1994). These include cyclohexanone, serine, glycine, alanine, aspartic acid, citric acid, and quinoline. Barth (1987) identified lactic acid in two samples of Norwegian produced water.

2.3 INORGANIC CHEMICALS IN PRODUCED WATER

2.3.1 Salinity and Inorganic Ions

The salt concentration (salinity) of produced water may range from a few parts per thousand (‰) to that of a saturated brine (≈ 300‰) (Rittenhouse et al., 1969; Large, 1990). Some produced waters have so little salt that the salinity is in the range of drinking water salinity. However, most produced waters have salinities greater than that of seawater (≈ 35‰) (Collins, 1975). Produced waters from production facilities in the Central Valley of California, the North Slope of Alaska, coastal Texas, and central Mississippi, U.S.A., have salinities of 18 to 320‰ (Kharaka et al., 1995).

The ions contributing most to the salinity of produced water are sodium and chloride (Table 13.). Calcium, magnesium, and potassium concentrations usually are higher than would be expected if the produced water were merely a concentrate of

Table 11—Concentrations of individual PAHs in seven produced waters from the U.S. Gulf of Mexico (DOE, 1997; OOC, 1997), three produced waters from Indonesia (Neff and Foster, 1997), and one produced water from Thailand (Battelle, 1994). Concentrations are µg/L.

Compound	Gulf of Mexico	Indonesia	Thailand
Naphthalene	5.3 – 90.2	45.6 – 156	395
C1-Naphthalene	4.2 – 73.2	63.5 – 100	207
C2-Naphthalene	4.4 – 88.2	43.4 – 126	166
C3-Naphthalene	2.8 – 82.6	19.3 – 81.3	71.1
C4-Naphthalene	1.0 – 52.4	6.4 – 36.2	21.0
Acenaphthylene	ND – 1.1	ND	ND
Acenaphthene	ND – 0.10	ND – 1.3	ND
Biphenyl	0.36 – 10.6	2.3 – 6.9	NA
Fluorene	0.06 – 2.8	3.4 – 5.5	2.13
C_1-Fluorenes	0.09 – 8.7	3.3 – 9.2	3.55
C_2-Fluorenes	0.20 – 15.5	2.2 – 13.3	4.03
C_3-Fluorenes	0.27 – 17.6	1.9 – 15.6	2.24
Anthracene	ND – 0.45	0.17 – 0.63	ND
Phenanthrene	0.11 – 8.8	9.3 – 29.5	3.12
C_1-Phenanthrenes	0.24 – 25.1	4.2 – 29.5	4.06
C_2-Phenanthrenes	0.25 – 31.2	3.8 – 31.5	3.43
C_3-Phenanthrenes	ND – 22.5	3.0 – 25.4	1.91
C_4-Phenanthrenes	ND – 11.3	1.3 – 11.9	ND
Fluoranthene	ND – 0.12	0.13 – 0.24	ND
Pyrene	0.01 – 0.29	0.12 – 0.49	ND
C_1-Fluoranthenes/Pyrenes	ND – 2.4	1.0 – 4.3	0.34
C_2-Fluoranthenes/Pyrenes	ND – 4.4	0.93 – 7.3	NA
Benz(a)anthracene	ND – 0.20	0.06 – 0.43	ND
Chrysene	ND – 0.85	0.10 – 1.4	ND
C_1-Chrysenes	ND – 2.4	0.41 – 5.6	0.16
C_2-Chrysenes	ND – 3.5	0.69 – 8.8	ND
C_3-Chrysenes	ND – 3.3	0.52 – 6.4	ND
C_4-Chrysenes	ND – 2.6	ND – 2.4	ND
Benzo(b)fluoranthene	ND – 0.03	ND – 0.31	ND
Benzo(k)fluoranthene	ND – 0.07	ND	ND
Benzo(e)pyrene	ND – 0.10	0.05 – 0.81	ND
Benzo(a)pyrene	ND – 0.09	ND	ND
Perylene	0.04 – 2.0	ND – 0.09	ND
Indeno(1,2,3-cd)pyrene	ND – 0.01	ND	ND
Dibenz(a,h)anthracene	ND – 0.02	ND	ND
Benzo(ghi)perylene	ND – 0.03	ND	ND
Total PAHs	40 – 600	230 – 745	888

Note: ND. Not detected. NA. Not analyzed.

modern seawater. However, the ratios of different ions in produced water vary widely, depending in large part on the geologic age of the formation from which it was produced. Sulfate concentration usually is low, allowing barium and some other elements that form insoluble sulfates and sulfides to be present in solution at high concentrations. Ammonium ion may be present at elevated concentrations in some produced waters. It probably is derived from biodegradation or hydrolysis of nitrogen-containing organic compounds in the oil or gas.

2.3.2 Metals

Produced water may contain several metals in solution. The metals present and their concentrations in produced waters from different sources are extremely variable, depending on the age and geology of the formations from which the oil and gas are produced (Collins, 1975). A few metals may be present in produced waters from different sources at concentrations substantially higher (1,000-fold or more) than their concentrations in clean natural seawater. The metals most frequently

Table 12—Concentration ranges of selected cyclic alkanes and heterocyclic compounds in produced water from three production treatment facilities in Indonesia. Concentrations are µg/L. From Neff and Foster (1997).

Compound	Widuri	Krisna	Cinta
Decalin	1.0	16.8	3.4
C_1-Decalins	1.94	38.9	7.3
C_2-Decalins	2.53	35.6	7.9
C_3-Decalins	ND	33.3	4.3
C_4-Decalins	ND	35.0	6.6
Benzothiophene	0.4	ND	0.4
C_1-Benzothiophenes	2.6	2.3	1.7
C_2-Benzothiophenes	8.2	4.9	4.2
C_3-Benzothiophenes	4.0	3.5	2.8
C_4-Benzothiophenes	1.5	1.2	ND
Dibenzothiophene	0.47	3.8	1.3
C_1-Dibenzothiophenes	1.0	4.1	2.0
C_2-Dibenzothiophenes	1.0	4.2	1.7
C_3-Dibenzothiophenes	ND	3.1	1.0
C_4-Dibenzothiophenes	ND	ND	ND
Dibenzofuran	6.8	7.2	2.2

Note: ND: Not detected.

present in produced water at elevated concentrations include barium, cadmium, chromium, copper, iron, lead, nickel, and zinc (Neff et al., 1987) (Table 14). Usually only a few of these metals are present at elevated concentrations in a particular produced water sample. For example, Neff et al (1989, 1992) reported that only barium, lead, and zinc are present at elevated concentrations in produced water from 2 platforms off Louisiana.

If water flooding with seawater is used to enhance hydrocarbon production, the metal concentrations in produced water often change gradually over time to more closely resemble the metal concentrations in modern seawater (Stephenson et al., 1994). For most metals, this is a decrease in concentration. Some chemicals such as barium and radium may precipitate with the sulfate if seawater (high in sulfate) is used for water flooding (Neff and Sauer, 1995b). Therefore, although the volume of produced water usually increases with the age of the well, total mass loadings of metals discharged in produced water may not increase; mass loadings of some metals may actually decrease. Produced waters from wells in the northwestern Gulf of Mexico generally contain metals at concentrations comparable to concentrations in produced waters from other locations (Table 14). The highest concentrations of arsenic and barium have been recorded for Gulf of Mexico produced waters, probably because these elements usually are not analyzed in produced water from other sources. Barium may be present at high concentrations in produced waters that contain very low concentrations of sulfate (Neff and Sauer, 1995b).

Water-flooding with sea water may increase the concentration of sulfate (present in sea water at a concentration of about 900 mg/L) in the formation water, causing barium precipitation as barite, lowering the concentration of barium in the produced water (Stephenson et al., 1994). In the absence of sulfate, barium is soluble in hot, geopressured, high ionic strength connate water in the hydrocarbon-bearing formation. The concentrations of barium and other elements in produced water probably are in equilibrium with elements in the feldspars, plagioclase, biotite, and sandstones in the formation (Bloch and Key, 1981; Macpherson, 1989). Barium concentrations as high as 650 mg/L have been reported in produced water from the Gulf of Mexico (Neff, 1997).

Produced water from platforms in the northwest Gulf of Mexico, analyzed by modern analytical methods, sometimes contains elevated concentrations of barium, iron, manganese, lead, and zinc, and in a few cases arsenic, compared to concentrations in sea water (Table 14). Produced water from natural gas platforms in the Gulf of Thailand often contains elevated concentrations of mercury (1.41 to 14.3 µg/L) (Battelle, 1994). The mercury is from cinnabar deposits in the formation and is produced as a vapor (elemental mercury) with the natural gas. Generally, produced water from gas wells contains more mercury than produced water from oil wells.

Table 13—Concentrations of several elements and inorganic ions in produced waters from different geologic ages. Concentrations are mg/kg (ppm). From Collins (1975).

Element/Ion	Highest Concentration (Age[1])	Range of Mean Concentrations
Sodium	120,000 (J)	23,000 – 57300
Chloride	270,000 (P)	46,100 – 141,000
Calcium	205,000 (P)	2530 – 25,800
Magnesium	26,000 (D)	530 – 4300
Potassium	11,600 (D)	130 – 3100
Sulfate	8400 (T)	210 – 1170
Bromide	6000 (J)	46 – 1200
Strontium	4500 (P)	7 – 1000
Ammonium	3300 (P)	23 – 300
Bicarbonate	3600 (T)	77 – 560
Iodide	1410 (P)	3 – 210
Barium	670 (C)	5 – 60
Boron	450 (T)	8 – 40
Carbonate	450 (M)	30 – 450
Lithium	400 (J)	3 – 50
Manganese	200 (D)	12 – 175
Rubidium	11 (D)	0.1 – 4.0
Cesium	8.5 (P)	0.1 – 0.6
Copper	3 (M)	0.6 – 3.0

[1] C, Cretaceous; D, Devonian; J, Jurassic; M, Mississippian; P, Pennsylvanian; T, Tertiary.

Table 14—Concentration ranges of several metals in produced water from seven platforms in the northwestern Gulf of Mexico. From DOE (1997) and OOC (1997). Concentrations are mg/L.

Metal	Concentration Range
Arsenic (As)	0.0005 – 0.031
Barium (Ba)	81 – 342
Cadmium (Cd)	< 0.00005 – 0.001
Chromium (Cr)	< 0.0001 – 0.0014
Copper (Cu)	<0.0002
Iron (Fe)	10 – 37
Mercury (Hg)	< 0.00001 – 0.0002
Manganese (Mn)	1.0 – 7.0
Molybdenum (Mo)	0.0003 – 0022
Nickel (Ni)	< 0.001 – 0.007
Lead (Pb)	< 0.0.001 – 0.028
Vanadium (V)	< 0.0012
Zinc	0.01 – 3.60

Table 15— Activities of natural ^{226}radium and ^{228}radium in produced water from the U.S. Gulf of Mexico. Activities are pCi/L. 1 picocurie (pCi) = 0.037 bequerels (BQ). From Neff (1997).

Radionuclide	Concentration Range
^{226}Radium	< 1 – 1565
^{228}Radium	< 1 – 1509
Total Radium	< 1 – 2,805

Nearly all the iron is particulate and probably is metallic iron or precipitated iron oxide. Formation water is anoxic and iron may be present in solution at high concentration. However, when the formation water is brought to the surface and is exposed to the atmosphere, the iron precipitates as iron oxides. Manganese behaves like iron. Several other metals in produced water co-precipitate with iron and manganese oxides. Zinc and possibly lead could be derived in part from galvanized steel structures in contact with the produced water or with other waste streams that may be treated in the oil/water separator system.

Gulf of Mexico produced waters, recently analyzed by advanced methods, contained < 0.00005 to 0.001 mg/L cadmium (Table 14). Chromium, copper, molybdenum, nickel, and vanadium concentrations usually are low relative to expected concentrations in the environment. Arsenic concentrations usually are low, but some produced waters from coastal Louisiana contain concentrations higher than those in clean seawater.

2.3.3 Radioisotopes

The natural radioactive elements, radium-226 and radium-228 (^{226}Ra and ^{228}Ra) may occur at trace concentrations in produced water. The radium is derived from the radioactive decay of uranium and thorium associated with certain rocks and clays in the hydrocarbon reservoir (Reid, 1983; Kraemer and Reid, 1984; Michel, 1990). ^{226}Ra (half-life 1,601 years) is an α-emitting daughter of uranium-238 and uranium-234; ^{228}Ra (half-life 5.7 years) is a β-emitting daughter of thorium-232. The concentration of radium isotopes in produced water tends to increase as the salinity of the produced water increases. Concentrations of both ^{226}Ra and ^{228}Ra increase with salinity in oil and gas well produced waters from coastal Louisiana. However, the correlation between the salinity and concentrations of ^{226}Ra, ^{228}Ra, and total radium in produced water is not good; many produced waters of all salinities contain little or no radium and some low-salinity produced waters contain significant amounts of radium.

Concentrations of total ^{226}Ra plus ^{228}Ra in produced water from oil, gas, and geothermal wells along the Gulf of Mexico coast range from less than 0.2 picocuries/liter (pCi/L) to 13,808 pCi/L (Kraemer and Reid, 1984; Neff et al., 1989). A picocurie of ^{226}Ra is equivalent to 1 picogram (pg) of radium; a pCi of ^{228}Ra is equivalent to 0.0037 pg of radium (Santschi and Honeyman, 1989). Concentrations of ^{226}Ra and ^{228}Ra range from below the detection limit to 1565 pCi/L and 1509 pCi/L, respectively (Table 15), equivalent to 1.56 ng/L (parts per trillion) ^{226}Ra and 0.006 ng/L ^{228}Ra. There is no correlation between the concentrations of the two radium isotopes in produced water because of their different origins in the geologic formation.

The average concentrations of ^{226}Ra and ^{228}Ra in produced water from the North Sea are 44.8 pCi/L and 105 pCi/L, respectively (Stephenson et al., 1994). Produced water from Cook Inlet, Alaska, contains less than <0.4 to 9.7 pCi/L total radium isotopes (Neff, 1991). By comparison, the concentration of ^{226}Ra and ^{228}Ra in surface waters of the ocean is 0.027 to 0.040 pCi/L and about 0.005 pCi/L, respectively (Santschi and Honeyman, 1989; Nozaki, 1991). Radium concentrations often are much higher in coastal and estuarine waters; a typical background concentration of total radium isotopes in nearshore Gulf of Mexico seawater is 1.0 pCi/L (Reid, 1983).

2.4 PRODUCTION CHEMICALS IN PRODUCED WATER

Large numbers of specialty additives are available for use in the production system of a well to aid in recovery and pumping of hydrocarbons, protect the production system from corrosion, and facilitate separation of oil, gas, and water (Table 16). The difference between the mass of a chemical used and the amount discharged or injected in Table 16 is approximately equivalent to the mass that remains with the produced oil and gas streams. Many of these chemicals are more soluble in the oil than in produced water and remain in the oil phase. Others are water-soluble and concentrate in the produced water and are disposed of with it. The point in the production stream where the chemical is added influences the amount that may be discharged in the produced water. The number of additives used in a particular production system usually is low, and depends on the particular production problems encountered in the well.

Biocides usually are added to the water treatment system for produced water intended for re-injection. Biocides used for this purpose include hypochlorite and glutaraldehyde (Hudgins, 1991). The hypochlorite is destroyed rapidly by the oxygen scavenger. Gluteraldehyde usually is destroyed by reaction with organic matter in the produced water.

Corrosion inhibitors may be water-soluble or oil-soluble. Most corrosion inhibitors used on platforms in the North Sea are oil-soluble. Only small amounts remain in the treated produced water. Corrosion inhibitors are complex mixtures of medium to high molecular weight nitrogen-containing fatty acids, based on rosin acids (from plants).

Table 16—Amounts of production chemicals used on production platforms in the North Sea and amounts discharged with produced water to the ocean or injected into a well. Masses are metric tons/year. Table From Hudgins (1994).

Chemical	Used	Discharged	Injected
Biocides	2584	81	2446
Corrosion Inhibitors	2471	216	0
Oxygen Scavengers	1277	22	1241
Scale Inhibitors	1727	1143	515
Demulsifiers	444	9	21
Coagulant/De-Oiler	222	189	17
Antifoam Agent	144	0	39
Flocculant (Injection)	203	108	4
Dispersants	NR	NR	NR
Thinners	NR	NR	NR
Fluid-Loss Control	103	15	NR
Viscosifiers	24	24	NR
Emulsifiers	NR	NR	NR
Surfactants/Detergents	24	24	NR
Detergents/Cleaning	92	87	0
Gas Treatment	9307	2846	2800
Paraffin Control	202	NR	NR
Other	1219	1184	NR
Total Additives	30,038	5936	7078

Note: NR Not reported.

Scale inhibitors are water-soluble and tend to remain in the produced water fraction of the production stream. Scale inhibitors inhibit formation of barium or calcium scale on the inside of production pipe and usually are nitrogen-containing phosphate esters, such as phosphatidal ethanolamine, or organic phosphonates (Hudgins, 1991). Large amounts of gas-treating chemicals are used to treat gas production streams and about one-third of the amount used is discharged in the produced water. These chemicals include methanol, ethylene glycol, and triethylene glycol. Methanol and ethylene glycol are used to prevent gas hydrate formation; they remain associated with the water phase. Triethylene glycol is used in a closed loop system to dehydrate the gas. It is recycled and little enters the produced water stream. Di- or tetra-ethylene glycol may be used instead of triethylene glycol for gas dehydration at some production facilities. If the produced gas is sour (contains high concentrations of H_2S and CO_2), it may be sweetened in a closed loop system containing polyethylene glycol dimethyl ether, which acts as an absorbent for the sour gases. Little of the polyethylene glycol gets into the produced water stream and is discharged with it.

3 Nature of the Water-soluble Organic Matter in Produced Water

3.1 WSOS IN PRODUCED WATER

As discussed above, there are several types of water-soluble organic chemicals (WSOs) in produced water. Short-chain organic acids (C_2 through C_5) account for most of the total or dissolved organic carbon (TOC and DOC) in produced water. Second in relative abundance are low molecular weight saturated and aromatic hydrocarbons. Volatile aromatic hydrocarbons are most abundant. Organic acids and hydrocarbons combined represent more than 90% of the TOC in all produced waters analyzed to date. Small amounts of phenols and heterocyclic compounds also are present. Some cationic metals, such as barium, may form stable complexes with organic acids, particularly dicarboxylic acids, and be included in the WSO phase. It also is possible that some produced waters contain high molecular weight organic matter (e.g., fulvic and humic acids) in colloidal suspension. These high molecular WSOs probably would not be extracted efficiently with the Freon® or hexane solvent used in the gravimetric method for total oil and grease.

The low molecular weight organic acids are very soluble in water and only slightly soluble in oil. Although crude oils contain these acids, most partition from the oil phase into the connate water associated with the oil in the reservoir (Barth and Bjørlykke, 1993; Borgund and Barth, 1993; Jaffé and Gallardo, 1993). They are thought to have been formed by hydrous pyrolysis of low molecular weight hydrocarbons in the formation (Barth et al., 1989; Kharaka et al., 1993;

Borgund and Barth, 1994). Hydrous pyrolysis occurs in the formation in the presence of crude oil, water, and a suitable mineral phase. The rate of organic acid formation is limited by the availability of a suitable oxidation agent. The rate of organic acid formation increases with increasing formation temperature. However, at high temperatures, the organic acids are thermally decarboxylated to produce carbon dioxide and hydrocarbon (Borgund and Barth, 1994). This may be an important source of natural gas formation (Carothers and Kharaka, 1978; Kharaka et al., 1983). The proposed reaction for acetate is:

$$CH_3COO^- \rightarrow CH_4 + HCO_3^-$$

Hydrocarbon solubility in water decreases with increasing molecular weight. Low molecular weight saturated and aromatic hydrocarbons are sufficiently water-soluble that they readily partition from the oil phase into produced water. Aqueous solubilities and octanol/water partition coefficients for several low molecular weight "soluble" hydrocarbons are summarized in Table 17.

Concentrations of hydrocarbons in solution in produced water in equilibrium with a crude oil phase can not reach the single phase solubility of the hydrocarbons as listed in Table 17. The concentration of each hydrocarbon in produced water in equilibrium with the crude oil phase is proportional to the mole fraction of the chemical in the oil phase, in agreement with Raoult's law (Shiu et al., 1990; Lee et al., 1992a,b; Lane and Loehr, 1995). The distribution of hydrocarbons between the oil and water phases can be expressed as the oil/water partition coefficient (K_{oil}). For middle weight crude oils, Koil is close to the octanol/water partition coefficient (K_{ow}), for which extensive published values are available. For example, Shiu et al., (1990) estimated oil/water partition coefficients for several aromatic hydrocarbons in three crude oils. The estimated log Koil for naphthalene in the crude oils ranged from 3.28 to 3.32. These values are slightly lower than the log K_{ow} for naphthalene (3.37). Thus, K_{ow} can be used to estimate the maximum concentration of a hydrocarbon in solution in produced water. For example, North Slope (Alaskan) crude oil contains 622 mg/kg naphthalene. Naphthalene has a log K_{ow} of 3.37 (K_{ow} 2344). Thus, the maximum concentration of naphthalene in produced water in equilibrium with North Slope crude oil is 0.27 mg/L, which is within the range of naphthalene concentrations in the produced waters in Table 11. Thus, produced water, even after extensive treatment to remove dispersed oil contains significant concentrations of low molecular weight hydrocarbons.

3.2 INTERFERENCE OF WSOS WITH OIL & GREASE ANALYSIS

EPA Methods 413.1 and 1664 for analysis of total recoverable oil and grease involve extraction of an acidified water sample with a nonpolar organic solvent, evaporating the solvent at 70°C to 85°C, and weighing the resulting residue EPA, 1983, 1995). Method 1664 includes an optional silica gel cleanup step to remove interfering polar compounds from the extract.

Table 17—Aqueous solubilities and values for log K_{ow} for several low molecular weight petroleum hydrocarbons. Concentrations are mg/L. From TPH Criteria Working Group (1997).

Chemical	Solubility @ 25°C	Log K_{ow}
	Aliphatic Hydrocarbons	
Cyclopentane	156	3.00
Pentane	38.5	3.45
Cyclohexane	55	3.44
n-Hexane	9.5	4.11
Heptane	2.93	5.00
Octane	0.66	5.15
	Aromatic Hydrocarbons	
Benzene	1770	2.13
Toluene	530	2.69
p-Xylene	180	3.18
Naphthalene	31	3.37
Biphenyl	7.2	3.69
Fluorene	1.9	3.97
Phenanthrene	1.1	4.36

The methods will measure as total oil and grease all chemicals that are extracted from the water sample with the solvent. Method 413.1 used Freon® (fluorocarbon-113: 1,1,2-trichloro-1,2,2-trifluoroethane) as a solvent. Fluorocarbon use has been phased out and Method 413.1 has been replaced by method 1664, in which n-hexane is the extracting solvent.

Several WSOs and possibly some forms of the inorganic ions and metals may be extracted from produced water with Freon® and hexane. Hydrocarbons in solution in the produced water will be extracted almost quantitatively. However, the lower molecular weigh volatile hydrocarbons, such as BTEX, will be lost during the evaporation step. Some heavy residual materials (e.g., resins, waxes, and asphaltenes) that may be present in colloidal suspension in the produced water, probably will not be extracted efficiently.

Stephenson (1991) reported that low molecular weight organic acids in acidified produced water are not very soluble in Freon®. He estimated that between 1.9 and 20.8% of 6 organic acids in a North Sea produced water sample were extracted into Freon®. Extraction efficiency increases with increasing molecular weight of the organic acids. However, because organic acid concentrations in some produced waters are very high, even a poor extraction efficiency of 10% or less is sufficient to substantially increase the concentration of organic matter in the extract. The organic acids have low enough volatilities (the boiling point of acetate is 118°C) that they will not be lost completely from the extract during drying. Thus, it is highly likely that organic acids are the major contributors to higher than expected concentrations of total oil and grease measured gravimetrically.

Brown et al. (1990, 1992) characterized the organic compounds in Freon® extracts of produced water from the Gulf of Mexico. Between 79 and 98% of the material extracted from produced water was polar (i.e, removed by silica gel chromatography). The composition of organic compounds with five or more carbons in the polar fraction determined by gas chromatography/mass spectrometry was highly variable from one produced water sample to another. However, most extracts contained a complex mixture of straight-chained, branched, unsaturated and cyclic fatty acids as well as smaller amounts of aromatic acids and phenols. Thus, dissolved organic acids probably are major contributors to high measured "oil and grease" concentrations in produced water. Brown et al. (1992) concluded that method 413.1 is unsuitable for measuring total oil and grease in produced water.

The geochemistry of these organic acids will be reviewed in the next section in an attempt to identify correlations between concentrations of organic acids in produced water and characteristics of the produced water or hydrocarbon reservoir.

4 Geochemistry Of Organic Acids In Produced Water

Numerous field, laboratory, and computer modeling studies have been performed in attempts to better understand the origin, occurrence, and effects of organic acids in crude oil and produced water (e.g., Fisher, 1987; Means and Hubbard, 1987; Shock, 1988; Barth et al., 1989; Lundegard and Kharaka, 1990, 1994; Barth, 1991; Harrison and Thyne, 1992). Much of the research conducted on organic acids in produced water stems from their possible role in clastic diagenesis and formation porosity enhancement (Lundegard and Land, 1986; MacGowan and Surdam, 1988; Helgeson et al., 1993). This research has shown that many biological, geological and geochemical factors may affect the concentration of organic acids in produced water. Temperature usually is considered to be a primary factor affecting the concentration of organic acids in produced water. Temperature further influences, or is further influenced by, many secondary factors that confound the use of temperature alone to predict organic acid concentration. These factors are summarized in Table 18 and discussed further in the following paragraphs.

The primary relationship between subsurface temperature and the concentration of organic acids in produced water is fairly well established (Carothers and Kharaka, 1978). Below approximately 80°C, the organic acid concentration usually is low because of organic acid degradation by microorganisms that utilize the available acids as an energy source. Microbial degradation is consistent with the usually low concentrations of organic acids in produced water from reservoirs containing biodegraded oil (Fisher, 1987; Barth and Riis, 1992). Above about 80°C, however, microbial activity is inhibited and the concentration of organic acids in produced water increases sharply. The source of the organic acids above 80°C is believed to be from the thermal breakdown of sedimentary organic matter or hydrous pyrolysis. (These processes are described further later.) The concentration of total organic acids in produced water usually reaches a maximum in the 80°C to 120°C temperature range (Carothers and Kharaka, 1978; MacGowan and Surdam, 1988). Above about 120°C, organic acids are unstable and undergo thermal decarboxylation, forming CO_2 and low molecular weight hydrocarbons (Kharaka et al., 1983). For example, thermal decarboxylation of acetate (usually the most abundant organic acid in produced water) will yield CO_2 and methane (Kharaka et al., 1983). Total organic acid concentrations in produced water gradually decrease with increasing temperature until the concentration drops below about 1 mg/L at about 200°C (Carothers and Kharaka, 1978).

However, the rate at which thermal decarboxylation occurs (acid concentration decreases) with increasing temperature may vary due to secondary factors (e.g., catalytic phenomena).

Depth of the hydrocarbon reservoir below the surface can be used as a surrogate for subsurface temperature to predict organic acid concentrations in produced water. Temperature in the subsurface is largely a function of the geothermal gradient of the basin or area. A typical vertical geothermal gradient in oil-bearing basins is about 30°C/km. Higher geothermal gradients are expected to increase the rate of organic acid generation from sedimentary organic matter (see below) whereas lower geothermal gradients are expected to produce higher organic acid concentrations (Lundegard and Kharaka, 1994). The geothermal gradient in the Gulf of Mexico (GOM) region ranges from 22°C/km to 24°C/km off the Louisiana Gulf Coast, to 29°C/km to 33°C/km off the Texas Gulf Coast (Tissot and Welte, 1984). Given these constraints and the temperature/organic acid concentration relationship described above (assuming a seafloor temperature of 5°C), the predicted maximum organic acid concentration in produced water should occur at reservoir depths of about 3.2 to 4.1 km along the Louisiana Gulf Coast and 2.4 to 3.0 km along the Texas Gulf Coast. The lower geothermal gradient along the Louisiana Gulf Coast might be expected to produce higher concentrations of organic acids (but at a lower rate). This approach for predicting organic acid concentrations in produced water ignores other factors and hence is an oversimplification.

Unfortunately, the multi-basin data-set assembled by Fisher (1987) and Lundegard and Kharaka (1994) demonstrate considerable “scatter” in the temperature/organic acid concentration relationship described above. The data show that while the maximum concentration of organic acids in produced water might be predicted grossly by reservoir temperature, the actual concentration of organic acids cannot be. In other words, many reservoirs with temperatures in the 80 – 120°C range contain produced water with low concentrations of organic acids; some produced waters from cooler or warmer reservoirs contain high concentrations of organic acids (Fisher, 1987; Lundegard and Land, 1993). For example, Fisher (1987) reported high (nearly 5000 mg/L) concentrations of organic acids in the produced water in many reservoirs with temperatures less than 80°C. Thus, it is clear that predicting the actual concentration or organic acids in produced water cannot be done based on reservoir temperature alone. Secondary factors (Table 18) clearly influence the concentration of organic acids.

Geothermal gradient, alone, does not determine the rate of organic acid generation and degradation reactions occurring in the subsurface, because time is not considered. Thus, many basins are described in terms of their heating rate (°C/million years). Heating rates range from less than 1°C/My (East Shetland Basin, North Sea) to 15°C/My (Pannonian Basin, Hungary) (Tissot and Welte, 1984). Most petroliferous basins, including those in the GOM, have heating rates of about 5 to 10°C/My. Variations in heating rate may contribute to the ‘scatter’ observed in the temperature/organic acid concentration relationship.

Geologic age of the reservoir has been suggested to correlate with organic acid concentration in produced water (Lundegard and Land, 1986). This relationship, however, may simply be a secondary phenomenon related to reservoir temperature, since older reservoirs usually are deeper and hotter. Nonetheless, this relationship has been used to calculate *psuedo*-half-lives of organic acid anions in produced water from hydrocarbon reservoirs in the GOM (Lundegard and Kharaka, 1994). The use of reservoir age in predicting organic acid concentration is difficult to justify except perhaps in the absence of reservoir temperature data.

Table 18—Factors potentially influencing the concentration of organic acids in produced water.

Primary
Subsurface/reservoir temperature
Secondary
Biodegradation
Heating/burial rate
Organic matter type and amount
Geologic age of reservoir
Reservoir and petroleum system lithology and mineralogy
Uplift of reservoir
Temperature of the source rock area
Migration distance (horizontal and vertical)
Influx of acid-depleted meteoric water (rainwater, snow, hail, sleet) into shallow reservoirs
Influx of deeper water to shallow reservoirs
Oil cracking *in situ*

An important secondary factor that confounds a clear relationship between reservoir temperature and organic acid concentration in produced water is the type and amount of organic matter present within the hydrocarbon reservoir system. As discussed above, the increase in concentration of organic acids in produced water at reservoir temperatures above 80°C is believed to be due to a combination of inhibition of microbial activity and increased thermal degradation of sedimentary organic matter. Sedimentary organic matter occurs in several ‘types’ and several studies have identified the organic matter type within the reservoir or through which the fossil fuels migrate as an important factor in the formation and concentration of organic acids in the petroleum and associated produced water (e.g., Lundegard and Land, 1986). The organic matter type present in GOM source rocks varies regionally and stratigraphically. Two main categories of petroleum source rocks are recognized, Jurassic shales and Tertiary shales/coaly shales. Jurassic shales are enriched in marine (algal or Type II) organic matter, whereas the Tertiary shales/coals are enriched in mixed marine and terrestrial organic matter (Type II/III). The extent of mixing of organic matter type varies with depositional environment, a parameter that can sometimes be predicted with a sequence stratigraphic method (e.g., transgressional sequences are enriched in marine, Type II, while regressional sequences are enriched in terrestrial, Type III). Though some exceptions undoubtedly exist, both laboratory experiments (hydrous pyrolysis; e.g., Lundegard and Kharaka, 1990; Borgund and Barth, 1994) and field observations have demonstrated that Type III organic matter exceeds Type II organic matter in the concentration of oxygen that becomes depleted with increasing thermal maturity. The higher concentration of oxygen-containing moieties (e.g., carboxyl groups) in the Type III organic matter within the Tertiary petroleum system in the GOM, particularly sequences containing abundant coaly shales, would be expected to yield higher concentrations of organic acids during maturation. Characterizing organic matter type and amount in source rocks and hydrocarbon reservoirs, which can vary on very small scales, would be extremely difficult in the complex depositional sequences in the GOM. Any attempt would necessarily rely on gross generalizations.

The migration distance between the source rock strata containing the sedimentary organic matter and the reservoir may also affect the concentration of organic acid in produced water. This factor was recognized in the data from Alberta Basin (Connelly et al., 1990) where the concentration of organic acids in formation water correlated most highly with the proximity of the produced water to the source rock strata (rather than temperature, depth, or geologic age). Water recovered from the deeper, mature source rock area contained a higher concentration of organic acids than water recovered from the immature reservoir area.

Mineralogy of the producing reservoir(s) and its associated strata may also play a role. For example, mineral oxidants (e.g., ferric iron) in associated clastic shales may play a role in the oxidation of organic carbon and thus, in turn, the formation of organic acids (Surdam et al., 1984). Unfortunately, little or no data exist concerning the iron content of shales or its oxidation state. The relative abundance of carbonate minerals in strata may also play a role in organic acid formation because carbonate tends to neutralize organic acids in formation water.

In some produced waters, there is an inverse relationship between concentrations of inorganic ions and organic acids. Produced waters containing high concentrations of organic acids have a higher alkalinity and pH than those with low concentrations of organic acids (Lundegard and Kharaka, 1994). However, some produced waters have high inorganic alkalinity due to the presence of high concentrations of bicarbonate. In Cenozoic formations, organic alkalinity (from organic acid anions) usually exceeds bicarbonate alkalinity in the temperature range 80°C to 140°C (Lundegard and Kharaka, 1994). At lower and higher temperatures, bicarbonate alkalinity usually is greater than organic alkalinity.

The mineralogy of the source strata and carrier beds from and through which reservoir fluids migrated may also play a role in determining the concentration of organic acids in produced water. This may be particularly important in areas where deeper water can migrate vertically along normal faults, which are common in the GOM (Lundegard and Land, 1986). The upward migration of deep water containing organic acids was recognized along the flanks of salt domes in the Tertiary formations of southern Louisiana (Hanor and Workman, 1986). Mixing of connate water from a deeper source with connate or meteoric water from a shallower source will confound the reservoir temperature/organic acid concentration relationship described above. In other words, the relationship of temperature-to-organic acid concentration may be related more to the temperature of the strata through which the water has migrated than to the temperature of the reservoir. Given the temperature considerations described above, however, rising water originating from depths where formation temperatures exceeds about 140°C would not be expected to be enriched in organic acids.

Opposite to the influx of deeper water is the influx of acid-poor, gravity-driven meteoric water into some shallow reservoirs. This phenomenon has been hypothesized as the reason for lower than expected concentrations of organic acids in produced waters from formations in some areas of the Louisiana Gulf Coast (Kharaka et al., 1986 in Lundegard and Kharaka, 1990).

Production from strata that have been uplifted may contribute to a change in the relationship between temperature and organic acid concentration. For example, an uplifted reservoir's current temperature would not be its maximum temperature and, thus, water from this horizon may be depleted in organic acids compared to a non-uplifted reservoir at the same depth in the same basin. Given the relative tectonic quiescence in the GOM, this factor probably is unimportant there.

From hydrous pyrolysis experiments, some evidence exists for the formation of organic acids by thermal cracking of oil in the reservoir (Lundegard et al., 1992; Borgund and Barth, 1994). The yield of organic acids is dependent upon the composition of the crude oil, particularly oxygen concentration. The oxygen concentration is much lower in petroleum than in sedimentary organic matter. However, biodegraded oils (in which oxygen has become enriched by bacterial removal of hydrocarbons or by formation of oxidized compounds; Jaffe and Gallardo, 1993) may, upon continued burial, release significant quantities of organic acids into associated water. Some investigators have even suggested that formation of organic acids in situ from cracked oil may be the dominant source of organic acids in produced water (Barth and Bjørlykke, 1993). This argument is of particular interest if the migration distance between source rock and reservoir rock is large. There is no driving mechanism forcing the migration of water containing organic acids toward the reservoir, whereas oil is driven by buoyancy forces (Barth and Bjørlykke, 1993). Thus, organic acids formed from source rocks may not migrate to and accumulate in the hydrocarbon reservoir. The organic acids in reservoir fluids may be derived in situ from hydrous pyrolysis of petroleum. Because of the high aqueous solubility of low molecular weight organic acid anions, they will tend to partition from the oil and accumulate in the produced water phase in equilibrium with the oil. Thus, the potential for in situ hydrous pyrolysis to enrich the organic acid concentration in produced water warrants further consideration.

As described above, most investigators still contend that organic acids are generated primarily from the degradation of oxygen-containing moieties in sedimentary organic matter. The loss of oxygen functional groups from sedimentary organic matter generally precedes the main phase of oil generation (Tissot and Welte, 1978). However, some sedimentary organic matter, for example that enriched in sulfur, can liberate significant amounts of hydrocarbons earlier than other types, leading to the formation of ‘immature’ oils. Immature oils (oils generated very early in the oil generation window) may be associated with higher concentrations of organic acids than more ‘mature’ oils. Many geochemical parameters relating to various isomerization reactions (e.g., of biomarkers) are used to recognize ‘immature’ oils.

The literature available indicates that the concentrations of total and individual organic acids in produced waters are not strongly correlated with any physical or chemical parameters of the produced water or the geologic formation from which it was produced. The existing data demonstrate clearly that the maximum concentration of organic acids in produced water is largely a function of the reservoir temperature. However, the actual concentration of organic acids in any given produced water can be highly variable due to numerous secondary factors. As a result, prediction of organic acid concentrations in produced water, if possible, will require integration of reservoir temperature with the numerous secondary factors.

5 RECOMMENDATIONS

The optional silica gel sorption in EPA's oil and grease analytical method, Method 1664, should be consistently used to remove most of the polar organic chemicals that interfere with the oil and grease measurement. Efforts should continue to develop consistent correlations between organic acid concentrations in produced water and the physical/chemical properties of the hydrocarbon-bearing formation, crude oil or gas, and the produced water itself. The main difficulty is that complete data rarely are available for a given produced water, co-produced oil or gas, and formation geochemistry. If this information can be obtained from operators, it may be possible to model the occurrence of organic acids and total WSOs in produced water.

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