ORNL/TM-2002/5

Ozone Treatment of Soluble Organics in Produced Water

Petroleum Environmental Research Forum Project 98-04

January 2002

Prepared by:
K. Thomas Klasson
Costas Tsouris
Sandie A. Jones
Michele. D. Dinsmore
Angela B. Walker
David W. DePaoli
Sotira Yiacoumi
Viriya Vithayaveroj
Robert M. Counce
Sharon M. Robinson

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge:

Web site: http://www.osti.gov/bridge

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-605-6000 (1-800-553-6847)
TDD: 703-487-4639
Fax: 703-605-6900
E-mail: info@ntis.fedworld.gov
Web site: http://www.ntis.gov/support/ordernowabout.htm

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone: 865-576-8401
Fax: 865-576-5728
E-mail: reports@adonis.osti.gov
Web site: http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-2002/5

OZONE TREATMENT OF SOLUBLE ORGANICS IN PRODUCED WATER
Petroleum Environmental Research Forum Project 98-04[1]

K. Thomas Klasson, Costas Tsouris, Sandie A. Jones, Michele. D. Dinsmore,
David W. DePaoli, Angela B. Walker, Sotira Yiacoumi, Viriya Vithayaveroj
Robert M. Counce, and Sharon M. Robinson

Date Published – January 2002

Prepared by
OAK RIDGE NATIONAL LABORATORY
P.O. Box 2008
Oak Ridge, Tennessee 37831-6285
managed by
UT-Battelle, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

---

[1] Funded by DOE Fossil Energy National Petroleum Technology Office in collaboration with Petroleum Environmental Research Forum.

CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

EXCUTIVE SUMMARY

This project was an extension of previous research to improve the applicability of ozonation and will help address the petroleum-industry problem of treating produced water containing soluble organics. The goal of this project was to maximize oxidation of hexane-extractable organics during a single-pass operation. The project investigated: (1) oxidant production by electrochemical and sonochemical methods, (2) increasing the mass transfer rate in the reactor by forming microbubbles during ozone injection into the produced water, and (3) using ultraviolet irradiation to enhance the reaction if needed.

Several types of methodologies for treatment of soluble organics in synthetic and actual produced waters have been performed. The technologies tested may be categorized as follows:

1. Destruction via sonochemical oxidation at different pH, salt concentration, ultraviolet irradiation, and ferrous iron concentrations.
2. Destruction via ozonation at different pH, salt concentration, hydrogen peroxide concentrations, ultraviolet irradiation, temperature, and reactor configurations.

Sonochemical oxidation can be effective in destroying some compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX); however, no destruction of a representative organic acid (hexanoic acid) was measured. The destruction efficiency was found to be a function of power input to the system, but the reaction times were long (approximately 1 h).

The combination of ozone and hydrogen peroxide did not improve the oxidation of organics to CO_2. This was true over a pH range of 3–11 in studies conducted with surrogate produced water.

The effect of ultraviolet irradiation by itself or in combination with ozone was studied with synthetic produced water. Based on the results of these experiments, it was concluded that UV light had a very minor effect on the ozonation of the extractable organics present in complex waters. UV light, when used in combination with ozone, did however improved the destruction of BTEX.

Results from experiments conducted with both synthetic and actual produced waters indicate that the content of extractable organics is highly variable making it difficult to run experiments on a small scale. Entrapment of solids and oil droplets in sub-samples of the produced water is the likely source of the variability. Filtration of produced water samples removed much of the extractable organics. Destruction of extractable organics in samples with or without particulates/droplets were nearly complete when exposed to ozone for 3 days, indicating that ozone is an effective oxidation agent.

The lower molecular-weight organic acids present in the company-supplied produced waters were not attacked and destroyed by ozone under normal operating conditions and were thus not considered ozone scavengers. The ozone scavenging effects of organic acids were pronounced at higher pH in experiments with model compounds. Organic acids do not contribute to water-soluble organics in the measurement technique used.

Rate experiments showed that the rate of disappearance of extractables was first-order with respect to the ozone and extractable concentrations. Rate data also suggested that there are several competing reactions demanding ozone and some of these reactions proceed at a faster rate. Some of these reactions do not initially occur but occur only after prolonged exposure to ozone. This fact contributes to the overall slow rate (in the order of hours) of destruction of extractable organics. It is speculated that, although some reactions between the organics and ozone may be fast (in the order of minutes), the conversion of extractable compounds to non-extractable compounds is slow. The extractable organics degradation rates

and ozone demands were significantly better at higher operating temperatures. Degradation rate constants were 0.04 min^{-1} at 80°C compared to 0.01 min^{-1} at 22°C (both at 40 mg ozone/L) and the ozone demand was approximately half at the higher temperature (22 mg O_3/mg extractables at 22°C compared to 11 mg O_3/mg at 80°C).

The products of ozonation proved to be an array of chemicals, many of which could not be verified with a 100% surety using gas chromatography mass spectroscopy. The partial identification suggested that several of the compounds were halogenated indicating activation of organic compounds by ozone-generated radials and the combination of these activated organics with salt water components such as chloride and bromide. The formation of CO_2 was monitored in many experiments. Even though CO_2 was formed in ozonation experiments, the quantity generated exceeded the amount predicted from the decrease in extractable organics. This indicates oxidation of organic carbon to CO_2 of an organics fraction that is not extractable under normal (acidic) conditions.

Formation of small bubbles (important for effective mass transfer) proved to be a function of the salt concentration. Bubbles were approximately 10 times as small in salt water than they were in fresh water. The use of electrostatic spraying as a methodology for creating very small bubbles were effective in fresh water but could not be used in salt water due to the increased electrical conductivity, which caused arcing and excessive power drain.

Fouling of process equipment was considered to be a potential operational issue. In our month-long studies, we found fouling to restrict the flow through the bubble diffusers. This fouling happened in a matter of minutes. The source of the fouling was not the formation of precipitated oxidized iron, but was the result of evaporative effects causing salt to be deposited in the diffusers. The fouling problem was solved by periodically introducing (either fresh or salt) water together with the gas in the diffuser. This quickly caused the salts to dissolve. Such a preventive maintenance approach would be easily implemented on any scale.

The results from this study were consistent with the data collected in an earlier Petroleum Environmental Research Forum project (PERF Project 93-23), although the reactor systems were quite different. Both studies show the degradation to be dependent on time, and the calculated first-order rate constants were similar in both studies, indicating that the degradation rate is slow. The same order-of-magnitude ozone requirements were found in both cases. This study resulted in identifying no rate improvement on the original study.

An economic evaluation indicated that a system for 75% conversion of extractable organics would have fixed capital costs in the range of $3.2 million, with annual operating costs of $1.1 million (or $7.31/1000 gal). The estimation was based on a produced water flow rate of 10,000 bbl/day (17,500 gal/hr), an initial content of 100 ppm of hexane-extractable organics, a liquid residence time of 30 minutes, and an ozone consumption of 10 g ozone/g extractable organics. It should be noted that treating this volume of produced water would require a very large contact vessel (36 feet tall). The fixed capital costs were strongly dependent on the contact time and ozone demand. The annual operating costs were less dependent on these variables. If a reduction of the contact time from 30 min to 10 min could be achieved, the capital cost would be reduced by approximately 10%, but the size of the vessel would be reduced by 67%.

1. PROJECT BACKGROUND

Oil production is shifting from “shallow” wells (0-650 ft. water depth) to off-shore, deep-water operations (>2,600 ft.). Production from these operations is now approaching 20% of U.S. production. By year 2007, it is projected that as much as 70% of the U.S. oil production will be from deep-water operations. The crude oil from these deep wells is more polar, thus increasing the amount of dissolved hydrocarbons in the produced water. Early data from Gulf of Mexico (GOM) wells indicate that the problem with soluble organics will increase significantly as deep-water production increases. Existing physical/chemical treatment technologies used to remove dispersed oil from produced water will not remove dissolved organics. Gulf of Mexico operations are rapidly moving toward design of high-capacity platforms that will require compact, low-cost, efficient treatment processes to comply with current and future water quality regulations.

This project was an extension of previous research to improve the applicability of ozonation and will help address the petroleum-industry problem of treating produced water containing soluble organics. The goal was to maximize oxidation of hexane-extractable organics during a single-pass operation. The project investigated: (1) oxidant production by electrochemical and sonochemical methods, (2) increasing the mass transfer rate in the reactor by forming microbubbles during ozone injection into the produced water, and (3) using ultraviolet irradiation to enhance the reaction if needed. The project was funded by U.S. Department of Energy Fossil Energy National Petroleum Technology Office in collaboration with several major petroleum companies through a joint project with the Petroleum Environmental Research Forum (PERF).

The research and demonstration program consisted of three phases:

1. Laboratory testing in batch reactors to compare effectiveness of the destruction of organics using corona discharge ozone generation methods with hydrogen peroxide (and hydroxyl radicals) generated sonochemically and to evaluate the enhancement of destruction by UV light and micro-bubble spraying.
2. Continuous-flow studies to determine the efficacy of various contactors, the dependency of organics destruction on process variables, and scale-up issues.
3. If the results were promising, field testing of a prototype system in close collaboration with an industrial partner would generate performance data suitable for scale-up and economic evaluation.

2. INTRODUCTION

The focus of this study is the use of ozone or hydroxyl radicals to decrease the concentration of hexane-extractable hydrocarbons in produced water from crude oil extraction. Crude oil may be characterized in terms of the following constituents:

- saturated hydrocarbons
  - normal and branched alkanes (paraffins)
  - cycloalkanes (naphthenes)
- aromatic hydrocarbons
  - pure aromatics
  - cycloalkanoaromatics (naphthenoaromatics)
  - cyclic sulfur compounds (usually benzothiophene derivatives)
- resins, and asphaltenes
  - polycyclic crude oils containing N, S or O compounds

Saturated hydrocarbons are usually the most important of these three main constituent groups (about 57% of normal crudes). Aromatic hydrocarbons are usually the second most important constituent group (about 29% of normal crudes). Resins and asphaltenes usually average about 14% of normal producible crudes. Resins and asphaltenes are closely related compounds. Resins are soluble in the crude oil whereas asphaltenes are dispersed colloidal asphaltenes;[1] another way of stating this is resins are similar but less aromatic than asphaltenes.

In general, solubility of crude oil constituents in water decreases with increased molecular weight and increases with increased temperature; solubilities of selected petroleum compounds are presented in Table 1. Aromatic hydrocarbons are among the most soluble, about two orders of magnitude higher than the corresponding saturated alkanes. The presence of hetero-atoms (N, S, and O) drastically increases the solubility of a compound; organic acids or alcohols are more soluble than hydrocarbons with the same carbon number. As asphaltenes are not extractable by hexane, the hydrocarbon constituents targeted for removal from produced water are likely to be the aromatic hydrocarbons and resins.

From the study by Bostick et al.,[2] the water soluble organic content in produced water from the Gulf of Mexico is in the range of 20 to 30 mg/L; approximately 80 to 90% of this material is present as polar compounds with the next largest fraction being aromatic materials. Data from Bostick et al. on fractional data for synthetic produced water are presented in Table 2; the water soluble organic content (total extractable material) was 21 mg/L; of this material, only 11 ± 5 mg/L is extractable with hexane (primarily the $C_{11} – C_{20}$ fraction).

Ozone or hydroxyl radicals attack high electron density centers in organic substrates.[3] Reactivity is enhanced by electron donating groups such as CH_3 and decreased by the presence of electron withdrawing groups such as C=O, COOH, Cl and NO_2. Ozone does not usually completely mineralize most organic compounds during treatment; this may be largely attributed to the low reactivity of common intermediates, acetic and oxalic acids. The rate constants of reaction of aqueous organics varies widely; examples at 25°C include phenol at $2\cdot10^{7}\ M^{-1}\cdot s^{-1}$, oxalic acid at $4\cdot10^{-2}\ M^{-1}\cdot s^{-1}$, and acetic acid at $3\cdot10^{-5}\ M^{-1}\cdot s^{-1}$.[4]

Ozone is sparingly soluble in water, and it has been speculated that the main limitation in some ozonation systems comes from the low mass-transfer rate of ozone from the gas phase to the liquid phase. The mass transfer efficiency of ozone from the gas phase to the liquid phase depends on the mixing characteristics of the gas-liquid contactor used, the kinetics of ozone reactions in the water, and the number and size of bubbles produced. The effectiveness of ozone as an oxidant can be increased by creating a higher surface-area-to-volume ratio for the contact of ozone with the solution through the generation of smaller bubbles. A smaller bubble size results in a higher surface-to-volume ratio. In addition, smaller bubbles have higher residence times in contactors, leading to higher gas volume fractions. These findings motivated the experimental work conducted in this project.

The chemistry of ozone in pure water is reported by Pontius.[5] Once ozone transfers into water, it becomes highly unstable and rapidly decomposes through a complex series of reactions. The following equations describe the various reactions that occur when ozone is dissolved in water:

$$OH^- + O_3 \rightarrow HO_2 + O_2^- \tag{1a}$$
$$HO_2 \leftrightarrow H^+ + O_2^- \tag{1b}$$
$$O_2^- + O_3 \rightarrow O_2 + O_3^- \tag{1c}$$
$$O_3^- + H^+ \rightarrow HO_3 \tag{1d}$$
$$HO_3 \rightarrow O_2 + OH\bullet \tag{1e}$$
$$O_3 + OH\bullet \rightarrow HO_2 + O_2 \tag{1f}$$

Table 1. Aqueous solubilities of selected petroleum compounds at 25°C.[6]

Hydrocarbon group	Compound	Concentration (mg/kg)
n-Paraffins	n-Pentane	39.5 ± 0.6
	n-Hexane	9.47 ± 0.20
	n-Heptane	2.24 ± 0.04
	n-Octane	0.431 ± 0.012
	n-nonane	0.122 ± 0.007
Isoparaffins	1,2-Dimethylbutane	19.1 ± 0.2
	2,2 Dimethylbutane	13.0 ± 0.2
	2,4 Dimethylpentane	4.41 ± 0.05
	2,3 Dimethylpentane	5.25 ± 0.02
	2,2,4 Trimethylpentane	1.14 ± 0.02
	Isobutane	48.0 ± 1.0
	2-Methylhexane	2.54 ± 0.02
Bicycloparaffin	Bicyclo[4,4,0]decane	0.889 ± 0.031
Napthoaromatic	Indan	88.9 ± 2.7
Cycloparaffins	Cyclopentane	160.0 ± 2.0
	Methylcyclopentane	41.8 ± 1.0
	n-Propylcyclopentane	2.04 ± 0.10
	1,1,3 Trimethylcyclopentane	3.73 ± 0.17
	Cyclohexane	66.5 ± 0.8
	Methylcyclohexane	16.0 ± 0.2
	1,trans-4-Dimethylcyclohexane	3.84 ± 0.17
	1,1,3-Trimethylcyclohexane	1.77 ± 0.05
Aromatics	Benzene	1740 ± 17
	Toluene	554 ± 15
	m-Xylene	134 ± 2
	o-Xylene	167 ± 4
	p-Xylene	157 ± 1
	1,2,4 Trimethylbenzene	51.9 ± 1.2
	Ethylbenzene	131.4 ± 1.4
	Isopropylbenzene	48.3 ± 1.2
	Isobutylbenzene	10.1 ± 0.4
Sulfur and nitrogen compounds	Thiophene	3015 ± 34
	2-Ethylthiophene	292 ± 7
	2,7 Dimethylquinoline	1795 ± 127
	Indole	3558 ± 171
	Indoline	10,800 ± 700

Table 2. Typical chemical fraction data for Gulf of Mexico crude contacted with synthetic seawater.[2]

	Approximate molecular size and concentration (mg/L)			
	$C_6 - C_{28}$	$C_6 - C_{10}$	$C_{11} - C_{20}$	$C_{21} - C_{28}$
Total extractable materials	21 ± 4	7 ± 0.4	13 ± 3	0.8 ± 1.3
Hexane extractable materials	11 ± 5	0.4 ± 0.4	10 ± 4	0.01 ± 0.01

These reactions apply to a system consisting of ozone and water, without influence from other substances. However, it has been demonstrated that the presence of other chemical additions can greatly influence these reactions.[7] From Eq. (1a), hydroxide ions (OH^-) initiate a chain of reactions when ozone is placed in water. The chain is prolonged by the formation of HO_2 in Eq. (1f), which can then initiate further reactions through Eq. (1b). The decomposition of ozone to its secondary oxidants in solution is very rapid, with OH• (the hydroxide radical) being the most important of these oxidants, especially at high pH levels.[8] It should be noted that ozone is a very selective oxidant that oxidizes only certain compounds, while the generated OH• radical is not selective and is a much more effective oxidant than ozone.

In order to enhance the ozonation efficiency, advanced oxidation processes have been developed to increase the rate of ozone dissociation in aqueous solutions. Such processes use UV light or H_2O_2, in addition to ozone, in order to accelerate the decomposition rate in water and thereby increase the production of the hydroxyl radical.

It has been shown that the ozonation of soluble organics is proportional to the gas-liquid interfacial area in the absence or presence of advanced oxidation processes, therefore, efforts are also focused on improving mass transfer conditions by increasing the contact surface area. The surface area is determined by the bubble size and gas volume fraction. A smaller bubble size results in a higher surface-to-volume ratio. An additional effect comes from the fact that smaller bubbles are associated with higher residence times and, therefore, higher gas volume fractions. A major focus of this work is to enhance ozonation rates by generating small bubbles containing ozone.

3. MATERIALS AND METHODS

3.1 SOURCES OF PRODUCED WATER IN EXPERIMENTS

Several synthetic and actual produced waters were used in the studies and may be characterized as follows:

1. Deionized water spiked with benzene (B), toluene (T), ethyl benzene (E), xylenes (X), and hexanoic (caproic) acid (H). This mixture of organics was referred to as BTEXH.
2. Salt water made with 65 g/L sodium chloride and 35 g/L sea salt (Aquarium Systems, Mentor, Ohio) and spiked with BTEXH.
3. Salt water made with 65 g/L sodium chloride and 35 g/L sea salt (Aquarium Systems, Mentor, Ohio) and spiked with 1 g/L oil (light Gulf of Mexico crude) and homogenized.
4. Salt water as described in ASTM D1141-90 (less trace metals) and mixed with oil (light crude from Gulf of Mexico) before separation using centrifugal separator equipment[9] and settling.
5. Produced water was provided by two oil companies (Company A and Company B). The original produced water from these companies came in 1-L bottles and was refrigerated. Visual inspection showed that at the top of each bottle there was a layer of organic and inorganic particles. Three stock solutions were made from the solution of each source. The first sample was labeled “clear” and was taken from the bottom of the bottles. Care was taken to avoid particles in the water. The second sample was termed “cloudy.” It was taken approximately 2 cm underneath the top layer of the bottle and included particles. The third sample was also taken from the cloudy area but was then filtered through a 0.2-µm-pore filter and was thus called the “filtered” sample.

3.2 ANALYTICAL METHODS AND PROCEDURES

The ozone generator was a Labozone L-100 (Ozonology, Northbrook, Ill.) rated at 10 g/h with oxygen feed and at 4.6 g/h with dry air feed. Low concentrations of ozone in gas (oxygen) were measured via direct ultra-violet absorption in a spectrophotometer (Model 8452A, Hewlett Packard, Avondale, Penn.) at 254 nm. The path length was 10 mm. For higher concentration of ozone in gas, a modified analytical method based on decolorization of indigo blue was used. In this method, known volumes (50 to 100 µL) of gas were injected with a gas-tight syringe (VICI Precision Sampling, Baton Rouge, La.) into a sealed (Teflon-lined septum and aluminum crimp-seal) 26 mL test tube containing 9 mL deionized water and 1 mL Indigo Reagent II solution [10 g NaH_2PO_4, 7.1 mL conc. H_3PO_4, 77 mg $C_{16}H_7N_2O_{11}S_2K_3$ (80% purity) per L].[10] The test tube was vigorously shaken for 2 minutes and then allowed to rest until entrapped air bubbles were liberated. The absorbance at a wavelength of 600 nm (ABS_{600}) of the liquid was directly read in the test tube using a Spectronic 21D spectrophotometer (Milton Roy, Rochester, New York) before and after the ozone-containing gas addition.

Carbon dioxide was analyzed by injecting 150 µL into a gas chromatograph (GC) using a gas-tight syringe. The GC was a Hewlett Packard Model 5890 Series II equipped with a thermal conductivity detector and a 30 m × 0.53 mm GS-Q capillary column (J&W Scientific, Folsom, Calif.). The injector, oven, and detector temperatures were 125, 50, and 150 degrees Celsius, respectively.

Concentrations of BTEXH were determined using a Hewlett-Packard (Avondale, Penn.) HP 3365 GC equipped with a flame ionization detector. The injector and detector temperatures were 200 and 250°C, respectively. The oven temperature was kept at 35°C for 4 min, followed by a 10°C/min increase to 240°C for a final hold time of 10 min. An example of the chromatogram is shown in Fig. 1. The HCl-acidified (<pH 2) samples were micro-extracted with hexane before injection of the organic phase.

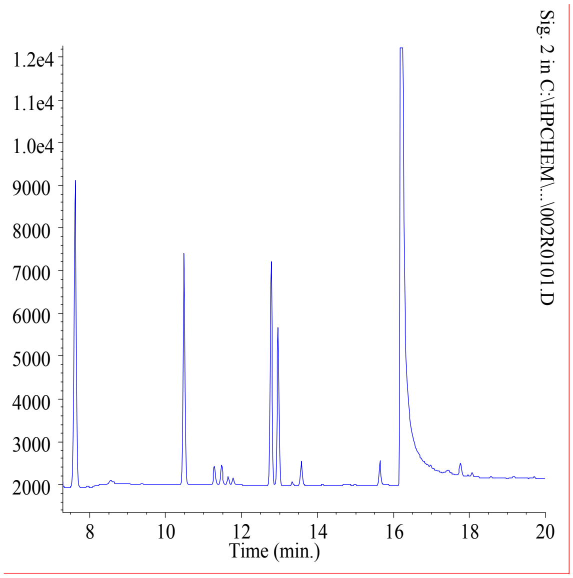


Fig. 1. An example GC chromatogram displaying the major peaks B, T, E, X, and H.

In early experiments, hexane extractable materials (HEM) were used as a method for determining extractable organics. HEM was measured using a Turner Design (Sunnyvale, Calif.) Model TD-700 hydrocarbon analyzer (Fluorometer). Extraction was carried out using 4 mL of HCl-acidified (< pH 2) sample and 4 mL hexane. This technique was later abandoned, as it only is capable of detecting organic compounds containing benzene rings. A new technique was developed based on absorbency of infrared radiation in samples extracted with perchloroethylene (PCE).

A MIRAN-1A general purpose infrared analyzer (Model #063-0134, The Foxboro Co., East Bridgewater, Mass.) was used to measure PCE extractable materials (PEM) in the produced water. The wavelength was set to 3.4 µm, and the transmittance was calibrated with a blank to 100%. The blank consisted of a solution of acidified 100 g/L NaCl in distilled water. Samples (typically 2 mL) and blanks were acidified with 100 µL of 4 mol/L HCl and extracted with 3 mL PCE (IR Grade, Fluka Chemicals, Milwaukee, Wis.). The extractions were carried out in 8-mL glass vials with Teflon lined caps and shaken for approximately 2 minutes. The vials were allowed to sit overnight in order for the two phases to separate. The organic phase was removed with a disposable Pasteur glass pipette and placed into an infrared quartz cell with a path length of 10 mm. The transmittance was recorded and converted to concentration (PEM) using a light Gulf of Mexico crude oil as a standard.

For selected samples, the water phase in the extraction with PCE was analyzed for acids, as lower molecular-weight organic acids are not extracted into the PCE. The acids analyses were performed using a Dionex LC20 ion chromatograph (IC) (Dionex Corp., Sunnyvale, Calif.). A 50 µL sample loop was used with the Dionex IonPac ICE-AS6 column and the eluent was 20% (v/v) acetonitrile with 0.32 nM helptafluorobutyric acid at a flow rate of 2 mL/min. Pentanoic acid was used as an internal standard at 100 mg/L as it was not present in any of the samples.

The identification of organic compounds in produced water was performed before, during, and after ozonation using Gas Chromatography-Mass Spectroscopy (GC-MS). In the cases of the GC-MS, HPLC grade dichloromethane (99%, Aldrich Chemical Co., Mich.) was used as an extraction solvent instead of PCE. All of the gas samples were analyzed using a gas chromatograph (GC) (Hewlett Packard Model 6890) equipped with a capillary column (HP-5MS, 5% Phenyl Methyl Siloxane capillary column, 30 m × 0.25 mm × 0.25 µm, Hewlett Packard Co.) and a mass selective detector (Model 5973, Hewlett Packard Co.) with the HP Chemstation software (Hewlett Packard Co.). A 4-min solvent delay and scan range from m/z 15 to m/z 500 at 1.5 scan/s was used. The injector, ion source, and quadrupole detector temperatures were 250, 230, and 160°C, respectively. The oven temperature was set at 38°C for 4 minutes, then heated 10°C/min to 250°C and held there for 2 minutes. The NBS75K (National Bureau of Standards, Washington, D.C.) library was used for species identification as a supplement to mass spectral and retention time characteristics.

3.3 SONOCHEMICAL EXPERIMENTS TEST PROCEDURE

The generation of an ultrasonic wave in water for *in situ* creation of cavitation bubbles and hydrogen peroxide was carried out using a Sonochemist Model 300C (Ultrasonic Energy Systems, Panama City, Fla.) with an external test vessel (Fig. 2). The operating frequency was 660 kHz and the acoustic power output was controlled between 50 and 250 W.

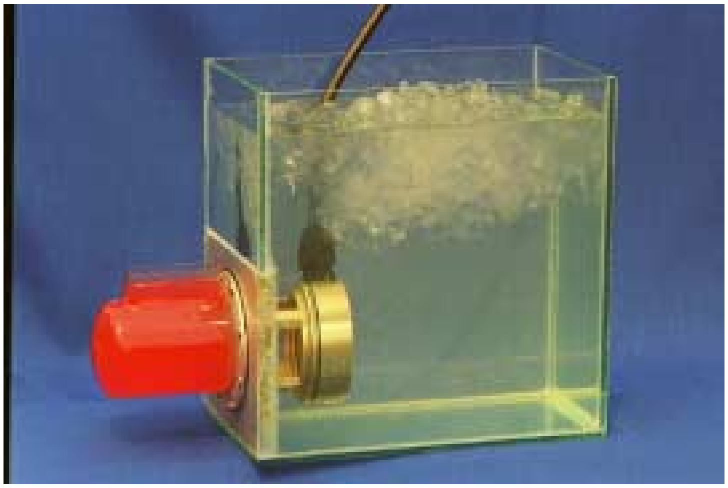


Fig. 2. Equipment used for sonochemical generation of hydrogen peroxide. The reaction chamber has been colored red for dramatization.

During sonochemical experiments, a 250-mL batch of solution was introduced into the sample vessel, the acoustic power was turned on, and samples of the solution were removed for analysis as a function of time.

3.4 OZONE REACTION VESSELS AND TEST PROCEDURES

Small batch reactors consisting of 60-mL or 160-mL bottles sealed with Teflon-lined caps were used in the initial ozone experiments. To perform experiments, ozone-containing oxygen or air was sparged into the bottle and sealed. Produced water was then added in various amounts ranging from 0.5 to 4 mL to the bottles using a syringe. The bottles were then allowed to sit for 2–3 days at room temperature to ensure complete reaction. Before analysis of CO_2 in the gas phase, 0.1–0.3 mL of 4 mol/L HCl was added to ensure that dissolved CO_2 was kept at a minimum. From each sample bottle, 150 µL was removed with a gas-tight syringe and injected into the GC to measure the CO_2 concentration. The sample bottles were then emptied into 8-mL sample vials and extracted with 3 mL PCE to measure extractable organics via infrared absorbance. In some cases, the water phase in the extraction was sampled for analysis of low molecular-weight organic acids.

The large-scale batch reactor consisting of a 4.5-L Erlenmeyer flask equipped with 3 sample ports that could be sealed with Teflon-lined caps was used in later ozone experiments. The upper sample port was used for gas venting during water addition and for gas sampling during the experiment. The lower sample port was used for water sampling. A Teflon tube with an open/close stopcock was fitted through the middle sample port to allow for produced water addition using large glass syringes. A magnetic stirrer bar was used to insure good contact between the produced water and the gas phase containing ozone. For a typical experiment, the dry reactor was sparged with ozone-containing gas for at least one hour and sealed. An initial gas sample was taken from the reactor and analyzed for ozone and CO_2. Produced water was then added via 50-mL glass syringes at a total volume of 200 mL. Ten milliliters of 4 mol/L HCL was added immediately following the addition of produced water. Samples were taken at varying intervals from 0 to approximately 1600 minutes, adjusting sampling events depending upon the disappearance of ozone in the gas phase. Gas samples consisted of 70–100 µL for the indigo blue method to test for ozone and 150 µL for CO_2 analysis on the GC. A 2-mL water sample was taken at the same time with each gas sample and extracted with 3 mL PCE to measure extractable organics (PEM). The GC or IC was also used for analysis of formic, acetic, propionic, and butyric acids in the water phase.

Several experiments were conducted to study the ozonation kinetics of soluble organics using electrostatic spraying of ozone-containing gas into water in continuous flow experiments. The reactor consisted of a 31.5-cm high quartz column with a diameter of 2.5-cm enclosed in an UV unit (Aquafine, Ultraviolet Water Sterilizer, Valencia, Calif.). The volume of solution used per experiment was 130 mL. To ensure representative sampling, a PTFE diaphragm pump head was installed in the system to continuously recycle the liquid. The gas-liquid flow was countercurrent in the reactor and a metal capillary tube assembly was used to introduce gas into the aqueous phase. A glass T fitted with Teflon-lined septa was installed in the line to allow aqueous samples to be collected from the sampling port to measure the concentration of the BTEX components with time. An illustration of gas dispersal using the metal capillary is shown to the left in Fig. 3. The ozone/UV system was also used with a small-pore bubble diffuser for introduction of ozone-containing gas. While a metal capillary tube was used in the electrostatic spraying experiments, the bubble-diffuser experiments incorporated a small-pore glass bubble diffuser (4–8 µm) for gas delivery. The right picture in Fig. 3 shows a magnified view of gas bubbles leaving the surface of the bubble diffuser and entering the aqueous phase.

When UV irradiation was not desired a continuous-flow column reactor with a 25.4-mm internal diameter and jacketed wall for temperature control was used for some of the experiments. The feed solution was pumped from the bottom of the source vessel to the top of the column reactor. A gas mixture containing either pure oxygen, oxygen and ozone, air and ozone, or air was introduced through a porous glass injector at the bottom of the reactor and removed at the top. Due to the high ionic strength of the solution, the porous material formed small bubbles on the order of 100 µm. The exit gas was directed through a flow meter and to a spectrophotometer for ozone concentration measurements. Gas and liquid samples were taken every 30 minutes for measurements of carbon dioxide using the GC and PEM infrared spectroscopy, respectively. Typical conditions used in these experiments were: 200 mL of synthetic produced water in the reactor, 20 mL/min liquid flow rate (10-min residence time), pH 8, room temperature, and 90–1000 mL/min gas flow rate.

Fig. 3. Gas injection in the UV-ozonation reactor. Left: using a sparger (without electrostatic spraying); right: using a fine bubble diffuser.

Month-long experiments of microbubble formation and fouling were conducted using synthetic saltwater containing ferrous chloride. The iron became oxidized, forming a precipitate phase. In these tests, several size columns and bubble diffusers were tested to develop a robust approach for continuous, long-term formation of large contact area for ozone transfer from bubbles to the solution. These columns were 105 to 230 mm in diameter and 500 to 990 mm in length. The diffusers' pore sizes were 10–16 µm. The gas flow rate ranged between 4.5 and 21 L/min.

Each of these different experimental systems was employed to address the effect of different variables. More details of the variables studied may be found in Table 3 and some of the systems are depicted in Fig. 4–6.

Table 3. Experimental systems used in experimental studies.

System	Description	Variables studied or type of experiments
Batch reactors	Sealed glass bottles (60 and 160 mL) with Teflon-lined caps. Large-scale bottles (4.5 L were also used when multiple samples of liquid was desired (see Fig. 4).	These bottles are charged with water samples, ozone (O_3) or oxygen (O_2), and kept at a constant temperature. Acid is injected, and the gas phase is sampled for CO_2. The liquid phase is extracted with perchloroethylene (PCE). The extractable organics are determined via infrared absorption at a wavelength of 3.4 µm. The water-phase is injected into a GC or IC for analysis of formic, acetic, propionic, and butyric acids. Variables Studied: O_3–produced water ratio O_3 versus O_2 treatment pH Produced water variability Effect of hydrogen peroxide (H_2O_2) addition Reaction rate
Small columns	Continuous-flow counter-current column reactors. One with a 25.4-mm internal diameter. Gas (O_3 or O_2) was supplied through bubble diffusers at the bottom of column. Synthetic produced water was fed from the top of the column (see Fig. 6). Typical working volume was 200–350 mL liquid in columns.	The gas feed and gas effluent were continuously monitored for ozone concentration. Periodically, the effluent gas was collected in gas sample bags and analyzed for CO_2. The feed and effluent liquid streams were sampled and the samples were analyzed for total extractable organics via PCE-IR or hexane-fluorometry. Variables Studied: UV enhancements Fouling Removal via flotation O_3/O_2 versus O_3/air mixtures for oxidation Gas-liquid flow ratio pH
Large columns	Continuous gas-flow column with 105- to 230-mm internal diameter. Air was supplied from the bottom through bubble diffusers. Equipped with automatic cleaning mechanisms for the gas diffusers to correct fouling problems (see Fig. 5). Typical working volumes were 4.2 to 30 L.	Long term studies to demonstrate a technique for automatic cleaning of gas diffusers. Variables Studied: Flow rate Diffuser flushing with fresh or salt water. Bubble-size measurement

Fig. 4. Photo of the type of reactor used in large batch experiments (4.5 L).

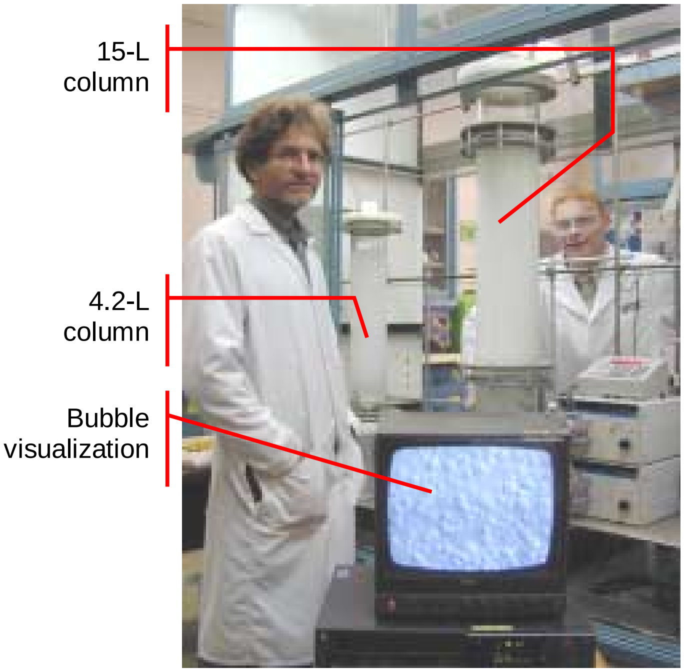


Fig. 5. Photo of the type of reactors used in large-scale column experiments.

Fig. 6. Photo of the type of reactor used in small column, continuous-flow experiments (350 mL).

4. RESULTS

4.1 SONOCHEMICAL OXIDATION

The results of a typical experiment for destruction of organics using sonochemistry principles may be seen in Fig. 7. As is noted the BTEX compounds were destroyed within the treatment time of 60 min, but the hexanoic acid (H) proved to be recalcitrant.

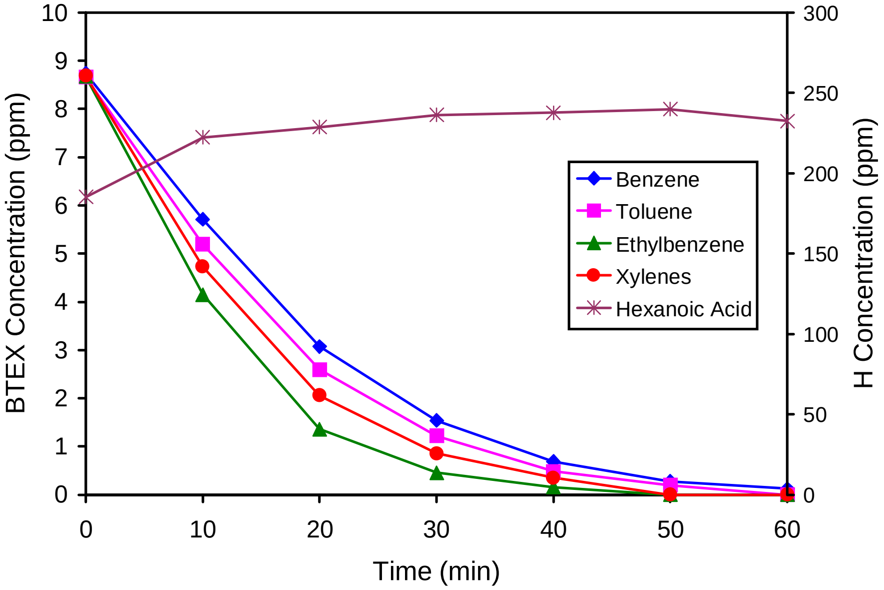


Fig. 7. Destruction of organics using deionized water and BTEXH. The acoustic output was 250W.

The decrease of BTEX contaminants followed a first-order rate expression according to Eq. (2).

$$C = C_0 \times e^{-kt} \tag{2}$$

where C, C_0, k, and t refer to the concentration at time t, the initial contaminant concentration, the reaction rate constant, and time of treatment, respectively. The values of k for the four compounds are listed in Table 4. A higher value of k indicates a faster destruction rate. Using ultraviolet light in order to enhance the destruction rate was not beneficial when done in an external water recycling loop attached to the reaction chamber (see Fig. 2 for reaction chamber).

Table 4. First-order reaction rate constants for the disappearance of BTEX. Data taken from Fig. 7.

Compound	k (min^{-1})
Benzene (B)	0.072
Toluene (T)	0.076
Ethyl benzene (E)	0.10
Xylenes (X)	0.081

The effect of acoustic power input may be seen in Fig. 8. An almost linear relationship was found between the power output and the *k* values. In all experiments ethyl benzene was degraded fastest, followed by xylenes, toluene, and benzene.

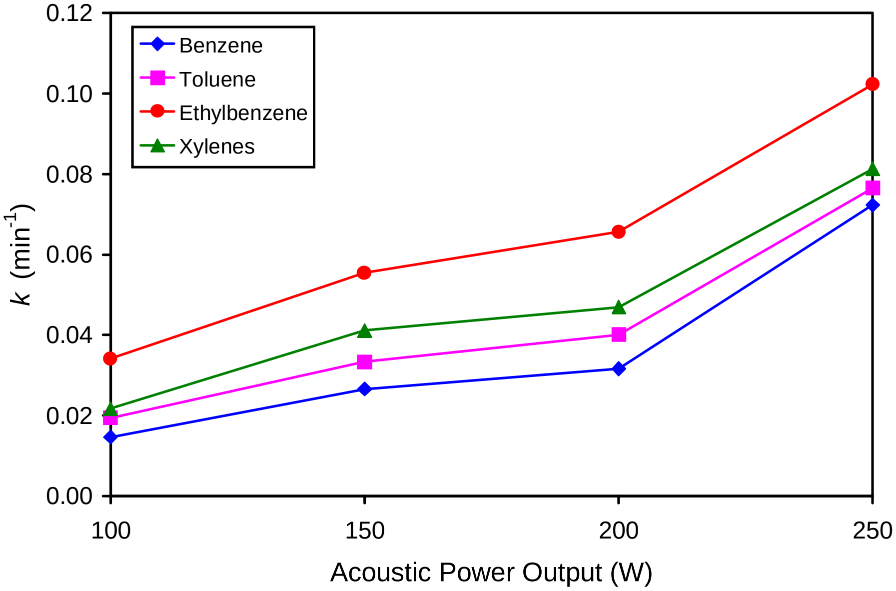


Fig. 8. Effect of acoustic power output on the rate of destruction of BTEX.

The destruction of the contaminants was not very sensitive to other parameters as is noted in Fig. 9, where the rate constant has been plotted for different environments. The baseline condition was 10 mg/L of each contaminant in deionized water and 150 W of acoustic power. Reducing the pH to 4, adding ferrous sulfate (0.25 g/L $FeSO_4 \cdot 7H_2O$), irradiation of the reactor content with ultraviolet light did not improve the reaction rate. The only positive effect was noted when the contaminants were dissolved in salt water (100 g/L salt).

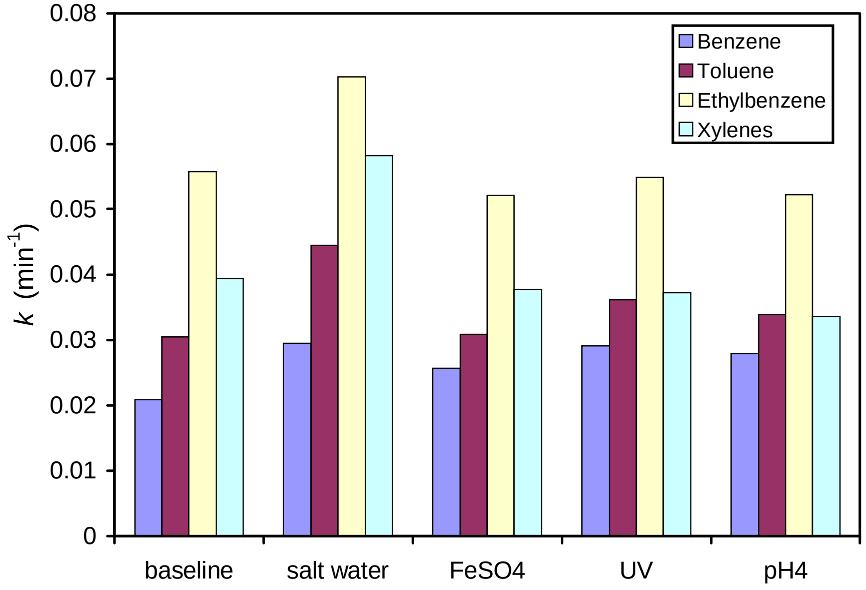


Fig. 9. Effect of various parameters on the rate constant in sonochemical experiments.

4.2 ELECTROSTATIC SPRAYING OF OZONE GAS MIXTURES

Initial experiments in this work utilized electrostatic spraying[11] as a means of creating microbubbles to increase mass transfer rates of ozone into the aqueous phase and thereby enhance the ozonation rate. Results obtained with spiked deionized water were promising for destruction of dissolved organics (BTEX). In addition, it was determined that oxidizing agents could be generated in situ by electrostatic spraying of oxygen into water under electrical discharge conditions. However, microbubble production was not possible in high-conductivity solutions, such as salt water, since difficulties such as electrical arcing and significant electrolysis were encountered. Therefore, further testing of electrostatic spraying was not conducted. It was determined that similar-sized microbubbles (80-µm range) could be produced in high-ionic-strength solutions by simply using a small pore bubble diffuser (4–8 µm).[12] Therefore, future experiments were focused on this technique for gas dispersal into the aqueous phase.

4.3 OZONATION OF BTEX SOLUTIONS

Several parameters were studied using the UV-ozonation reactor (see Fig. 3 for reactor type). Variables, including gas flow rate, ozone concentration of the feed gas, application of UV, and salt concentration were varied and the destruction of BTEX monitored. The results are summarized below:

Effect of UV: The application of UV enhanced BTEX removal. This is shown graphically in Fig. 10 for a gas flow rate of 32 mL/min.

Effect of ozone concentration: Fig. 11 shows that, as expected, increasing ozone concentration yields greater removal of BTEX.

Effect of flow rate: A higher gas flow rate results in more BTEX removal. Fig. 12 shows a comparison for 22 mL/min and 32 mL/min in salt solution.

Effect of salt concentration: Salt concentration was observed to negatively affect the rate of BTEX removal. Fig. 13 shows a comparison for several solutions ranging in salt concentration from 0–100 g/L. For the first few minutes of the experiments, the removal rate is lower for increasing salt concentration; at later times, the removal rates are similar.

Effect of bubble size: Paired experiments were conducted to illustrate the effect of bubble size on ozonation efficiency. The experiments directly compared BTEX removal for gas injection using a bubble diffuser and a capillary (simulating a sparger). Photographs of the two gas dispersal methods were shown in Fig. 3. Fig. 14 shows that the removal rate is higher using the bubble diffusers when all other conditions are the same.

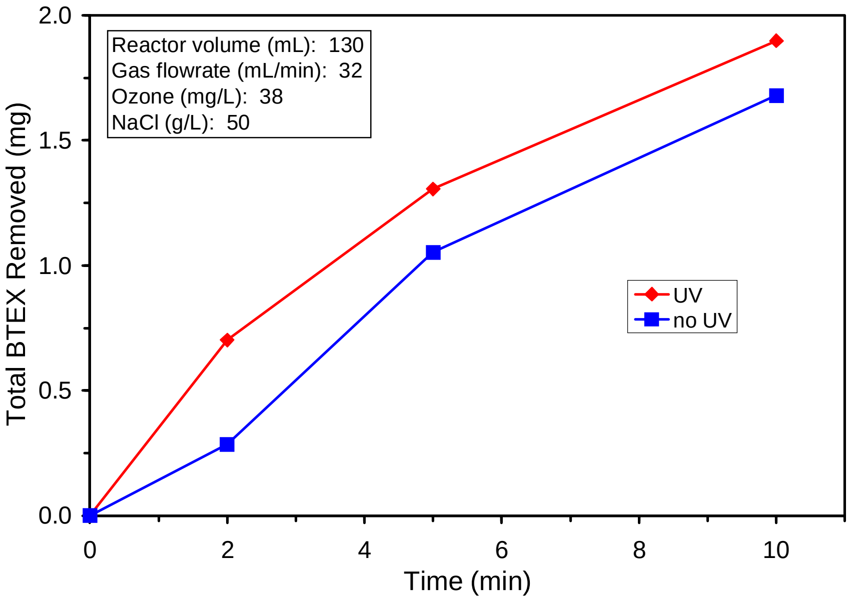


Fig. 10. Effect of UV irradiation on destruction of BTEX by ozonation.

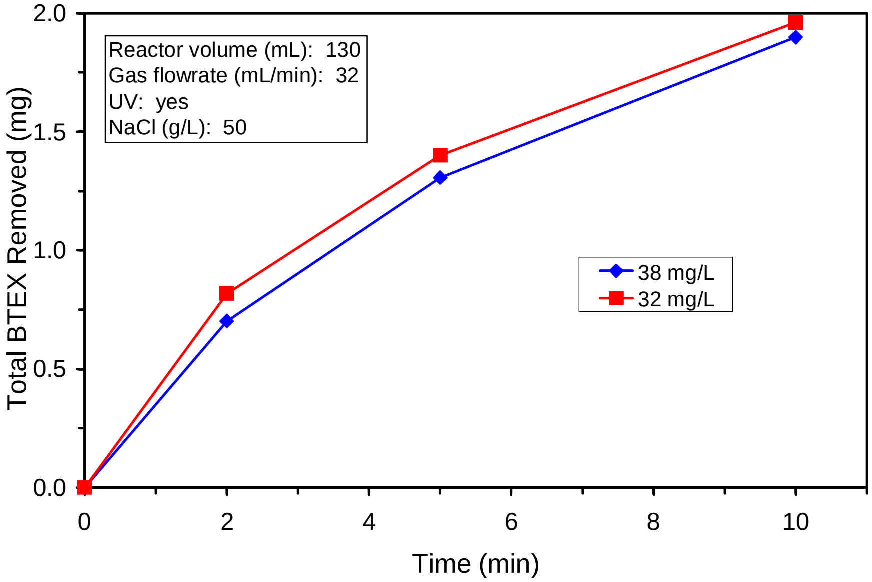


Fig. 11. Effect of ozone concentration on destruction of BTEX by ozonation.

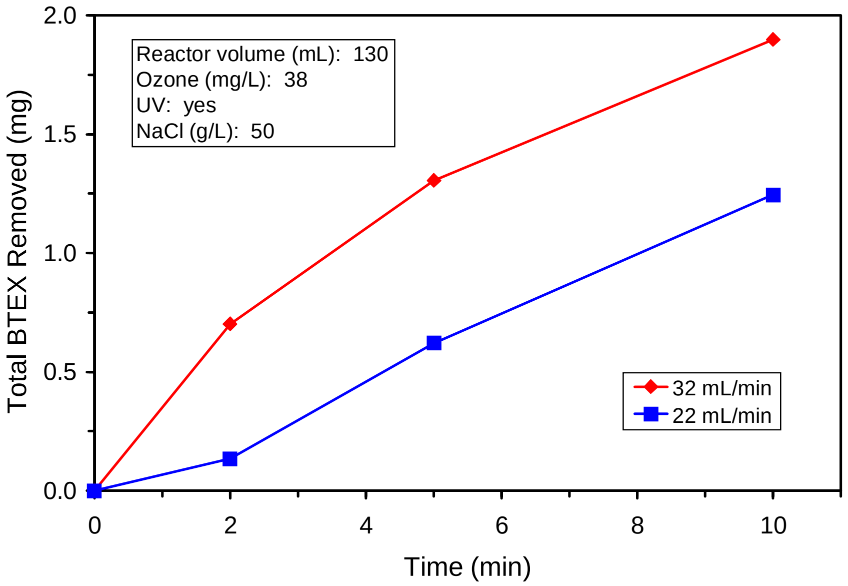


Fig. 12. Effect of gas flow rate on destruction of BTEX by ozonation.

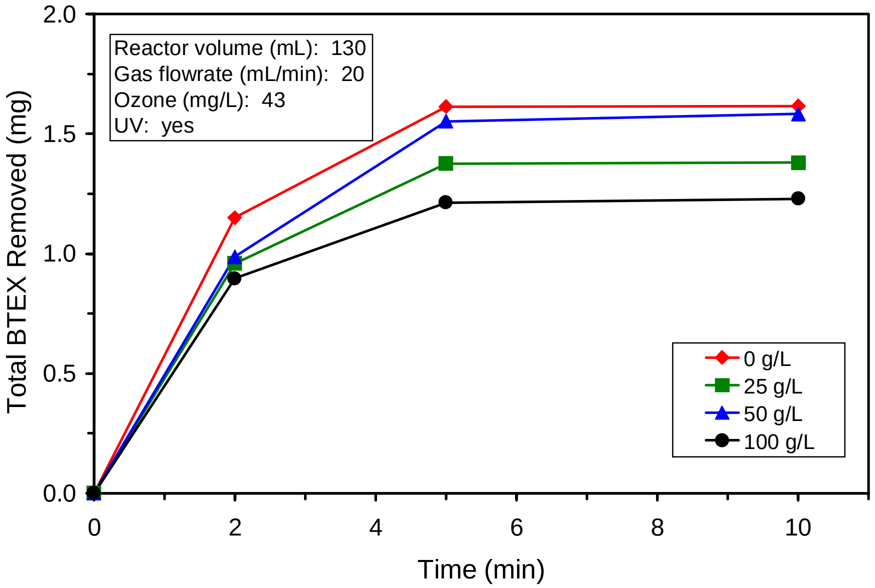


Fig. 13. Effect of salt concentration on destruction of BTEX by ozonation.

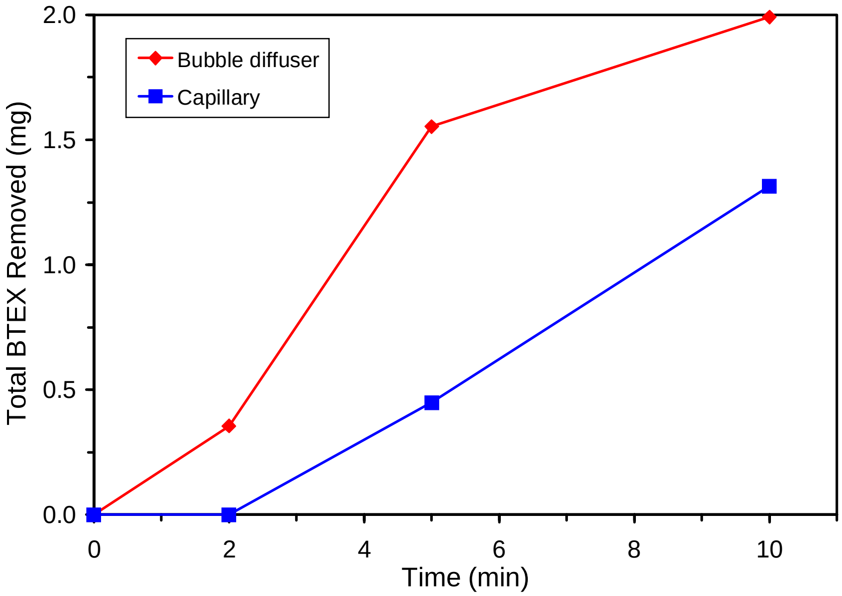


Fig. 14. Effect of bubble size on destruction of BTEX by ozonation.

The effect of pH and hydrogen peroxide (H_2O_2) on the oxidation of organics to CO_2 was studied in a slightly more complex solution with model organics. In these experiments 10 mg/L benzene, 10 mg/L toluene, 500 mg/L acetic acid, 250 mg/L formic acid, 50 mg/L propionic acid, 25 mg/L butanoic acid, 10 mg/L benzoic acid, and 5 mg/L *ortho*-methylphenol in 100 g/L NaCl were added to sparged bottle reactors and shaken for 3 days after which the liquid was acidified and the gas phase was analyzed for CO_2. The results showed that neither pH nor hydrogen peroxide addition improved the oxidation (Fig. 15).

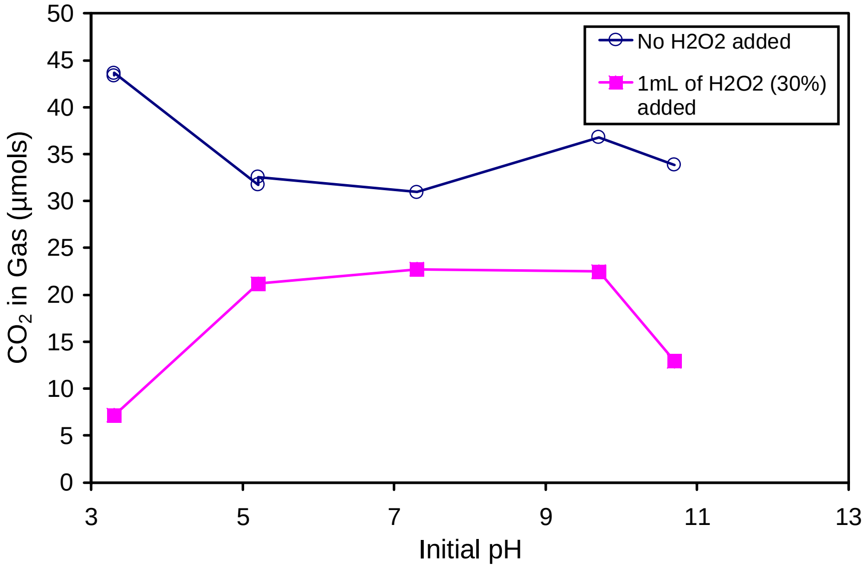


Fig. 15. Effect of pH and H_2O_2 on the oxidation of model organics to CO_2.

4.4 OZONATION OF HEXANOIC ACID

Several experiments were conducted to determine the ability for destruction of higher molecular-weight organic acids, using hexanoic acid as the model compound. The experimental setup was essentially identical to that used with the BTEX and the UV-ozonation reactor except that the solution volume was reduced to 120 mL of solution due to "foaming" in the reactor. Experimental conditions were held at those that resulted in high destruction of BTEX. The significant result of these experiments is that the data indicate that the destruction of hexanoic acid increased as initial pH of the solution treated increases (Fig. 16). Ozonation at a higher pH is better for organic acids; however, this means that many of the low molecular-weight organic acids will scavenge much of the ozone, preventing effective oxidation of extractable water solubles.

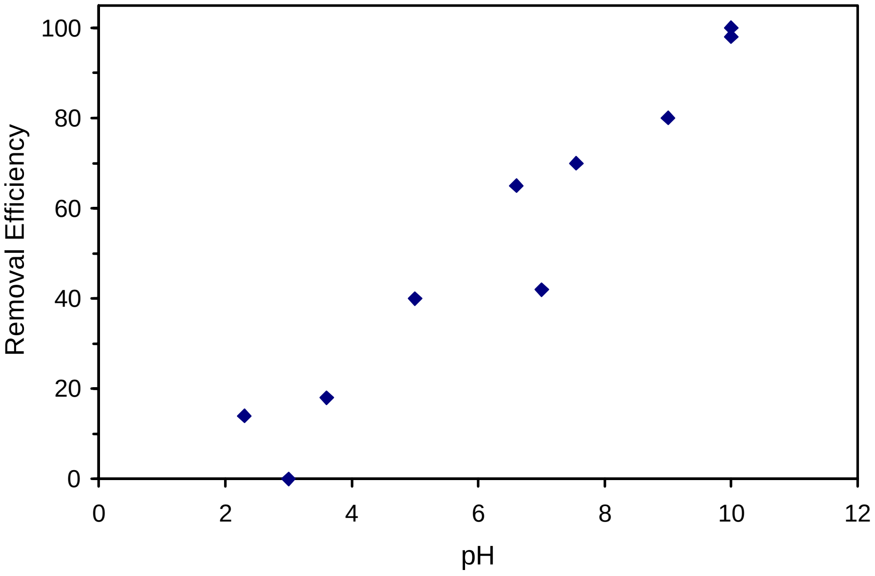


Fig. 16. Effect of pH on hexanoic acid removal. Conditions: 185 mg/L initial hexanoic acid concentration in 50 g/L NaCl; gas flow rate – 10 mL/min; ozone concentration – 38 mg/L; no UV applied.

4.5 OZONATION OF SYNTHETIC PRODUCED WATER FROM OIL-WATER SEPARATOR EXPERIMENTS

The destruction of organics in synthetic produced water was tested in several types of reactors (described on pages 7–10). Small-scale (160 mL) batch experiments were conducted under very controlled conditions. The effect of ozone requirements was tested by adding different amounts of produced water to the same amount of ozone. The results of these experiments are shown in Fig. 17 and 18. Carbon dioxide is a product from complete oxidation (mineralization) of organics. The presence of CO_2 in the gas phase in sealed bottles does not necessarily prove oxidation because some of this CO_2 is present in the contaminated water as carbonate, which generates CO_2 when the samples are acidified. Carbon dioxide may also be produced as fractions of large carbon chains are completely oxidized. Fig. 17 shows the presence of CO_2 in ozonated and oxygenated samples. The results show that the amount of CO_2 present in the gas phase as a result of carbonate levels in the water is proportional to the amount of produced water added to the bottle. Higher levels of CO_2 are observed in bottles with ozone indicating full carbon oxidation of some of the organics (or chain fractions). The destruction of organics (as PEM) is shown for this experiment in Fig. 18. The destruction efficiency was essentially the same in each of the experiments. However, only an incremental amount of CO_2 was generated (Fig. 17) when more water (and thus more mass of organics) was treated. This additional amount of CO_2 found in the gas phase is attributed to carbonates. Thus, we must conclude that the amount of ozone present in these experiments was sufficient enough to cause conversion of extractable organics to non-extractable species, but that the conversion was not a complete oxidation (mineralization).

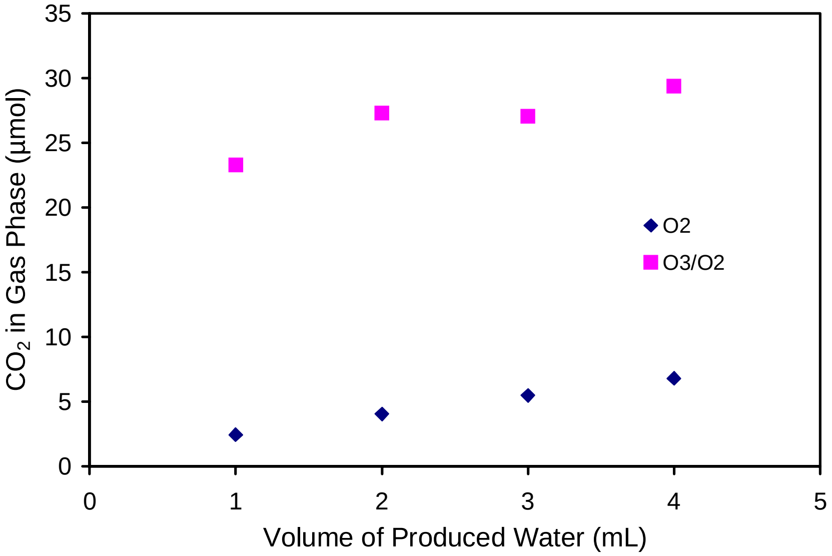


Fig. 17. Presence of CO_2 in the gas phases in ozonated and oxygenated samples synthetic produced water. Approximately 5 mg ozone was added to bottles for ozonation. The contact time was 3 days.

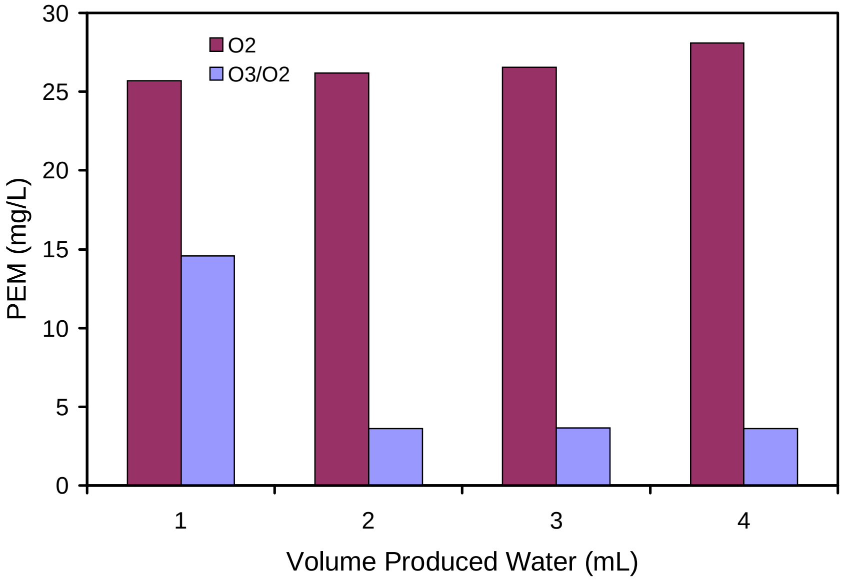


Fig. 18. PEM concentration in ozonated and oxygenated samples from synthetic produced water. The contact time was 3 days and the initial concentration of PEM was 28 mg/L.

Experiments were conducted with synthetic produced water in a column (120 mL) test with a bubble diffuser with continuous ozone addition and with or without UV irradiation. The collected water samples were acidified and extracted with hexane. The hexane fraction was analyzed using the TD-700 fluorometer. As shown in Fig. 19, positive results were obtained. Greater than 90% removal was achieved in 5 minutes of treatment. In addition, it was found that UV irradiation was not necessary to achieve nearly complete removal; in fact, removal was slightly lower for the test with UV but it is within experimental error.

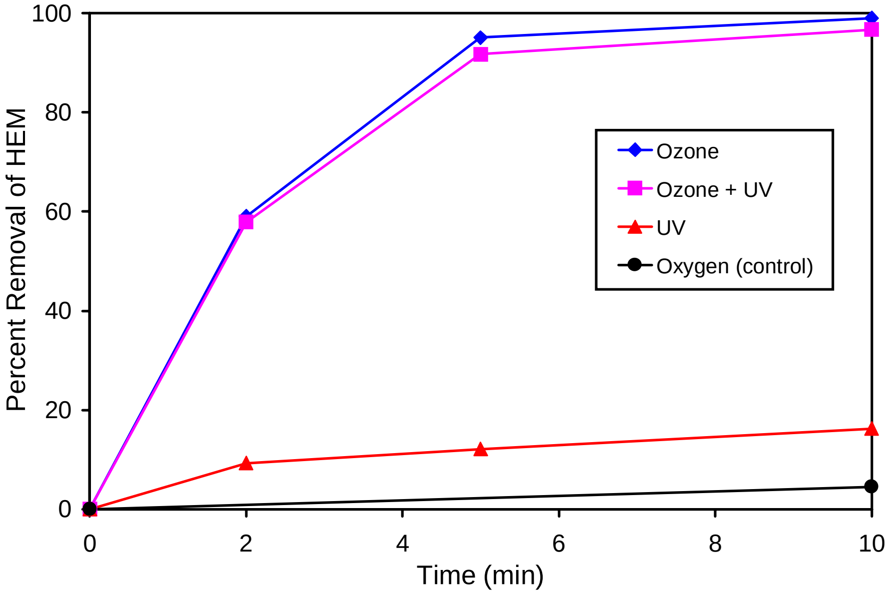


Fig. 19. Ozonation of hexane-extractable materials (via fluorometry) from synthetic produced water. Conditions: gas rate – 10 mL/min; ozone concentration – 38 mg/L.

These promising results above could not be repeated when similar experiments were conducted in a stirred reactor (no ozone sparging, just stirring) and PEM was used as measurement of extractable organics. The PEM/IR technique is based on C–H bond in the extractables, while the HEM/Fluorometer technique only detects C=C bonds in aromatics. It is very likely that the compounds with double bonds are more reactive than those without this configuration, which is supported by literature data.[13] This demonstrates the importance of selecting analytical methodologies.

The concentration profiles for key components for the stirred reactor experiment are shown in Fig. 20 and 21. In Fig. 20, we are demonstrating the difference in apparent and actual concentration of CO_2 in the gas phase of the reactor. The apparent CO_2 concentration is the result of analysis via gas chromatography; however, we have shown that ozone reacts with the GC column coating producing CO_2, thus the detected CO_2 is artificially high.[14] The data for the actual concentration presented in Fig. 20 are the results of adjusting this apparent concentration by incorporating ozone measurements. In Fig. 21 we have summarized the results.

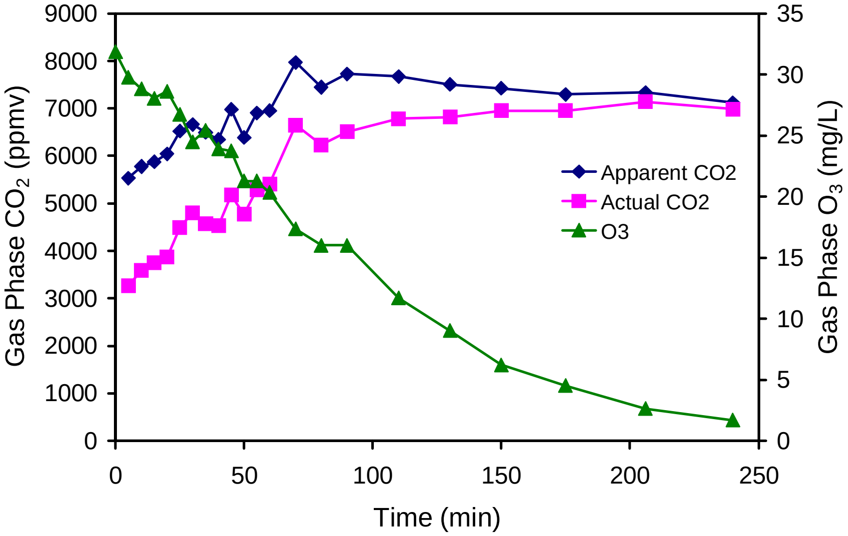


Fig. 20. Measurements of gas phase concentration of ozone and CO_2 in large-scale batch experiments with synthetic produced water at 80°C and pH 2.

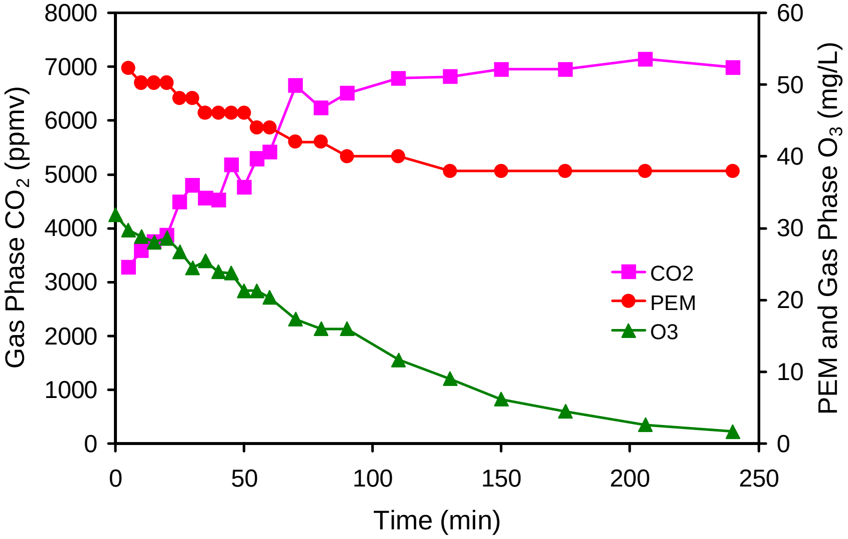


Fig. 21. Summary data from large-scale batch experiments with synthetic produced water at 80°C and pH 2.

4.6 BATCH EXPERIMENTS WITH PRODUCED WATER FROM INDUSTRIAL PARTNERS

Several experiments have been conducted using samples of actual produced water collected by our industrial partners (Company A and Company B). The original produced water from these companies came in 1-L bottles and was refrigerated when not used. Visual inspection showed that at the top of each bottle there was a layer of organic and inorganic particles (Fig. 22). Three stock solutions were made from the solution of each source. The first sample was labeled "clear" and was taken from the bottom of the bottles. Care was taken to avoid particles in the water. The second sample was termed "cloudy". It was taken approximately 2 cm underneath the top layer of the bottle and included particles. The third sample was also taken from the cloudy area but was then filtered through a 0.2-µm-pore filter and was thus called the "filtered" sample.

Fig. 22. Samples of produced water from Company A (left) and Company B. Samples from Company A contained a thick layer of oil on top of the water. Both samples contained particulates that could easily be resuspended.

Batch experiments were conducted using 160-mL bottles without adjusting the pH of the produced water. Results showed that the concentration of PEM in untreated samples was 62.9 ppm for the clear, 317.1 ppm for the cloudy samples, and 26.2 ppm for the filtered samples from Company A. These concentrations, however, were different for a different set of similar stock solutions prepared at a different time. For example, a second set of stock solutions that was prepared had PEM corresponding to 40.5±5 ppm for the clear samples, 118.8±5 ppm for the cloudy samples, and 16.7±5 ppm for the filtered samples. Clearly, there is a great deal of variation in the produced water. This fact caused a difference in results and was sometimes difficult to compare results between experiments.

Although there was a significant difference among the initial concentration of PEM for the three types of solutions, the PEM were converted by ozonation to non-extractable compounds. A comparison of concentrations before and after ozonation is shown in Fig. 23 for cloudy, clear, and filtered samples of Company A and Company B produced water, respectively.

The effect of hydrogen peroxide on the complete destruction of organics to carbon dioxide was measured for various ozone-to-produced water ratios. It can be seen in Fig. 24 that even at high concentration of hydrogen peroxide, minimal additional carbon dioxide was produced. Thus, it appears that there is little incentive to use hydrogen peroxide in combination with ozone.

Carbon dioxide is the product from complete oxidation (mineralization) of organics. The presence of CO_2 in the gas phase in experiments does not necessarily prove complete oxidation because some of this CO_2 is present in the contaminated water as carbonate, which generates CO_2 when the samples are acidified. Fig. 25 shows the presence of CO_2 in ozonated and oxygenated samples from Company A in sealed-bottle experiment. The result shows that the amount of CO_2 present in the gas phase as a result of carbonate levels in the water is proportional to the amount of produced water added to the bottle. In bottle reactors with ozone, higher levels of CO_2 are observed indicating full carbon oxidation of some of the organic fractions. The conversion of organics (measured as PEM) are shown for this experiment in Fig. 26. The destruction efficiency was essentially the same in each of the experiments, but there was not considerably more CO_2 generated when more water (and thus more mass of organics) was treated. Thus, we must conclude that the amount of ozone present in these experiments was sufficient enough to cause conversion of extractable organics to non-extractable species, but that the conversion was not a complete oxidation. Results for corresponding experiments with produced water from Company B are shown in Fig. 27 and Fig. 28. The production of CO_2 in these experiments followed the same type of pattern as in the experiments with Company A's produced water. The same amount of CO_2 was produced via oxidation regardless of the amount of produced water present. The conversion of PEM can be seen in Fig. 28. Here we note that the amount of PEM after ozonation increased with time. Thus, we must conclude that there was not enough ozone to convert the organics to non-extractable species.

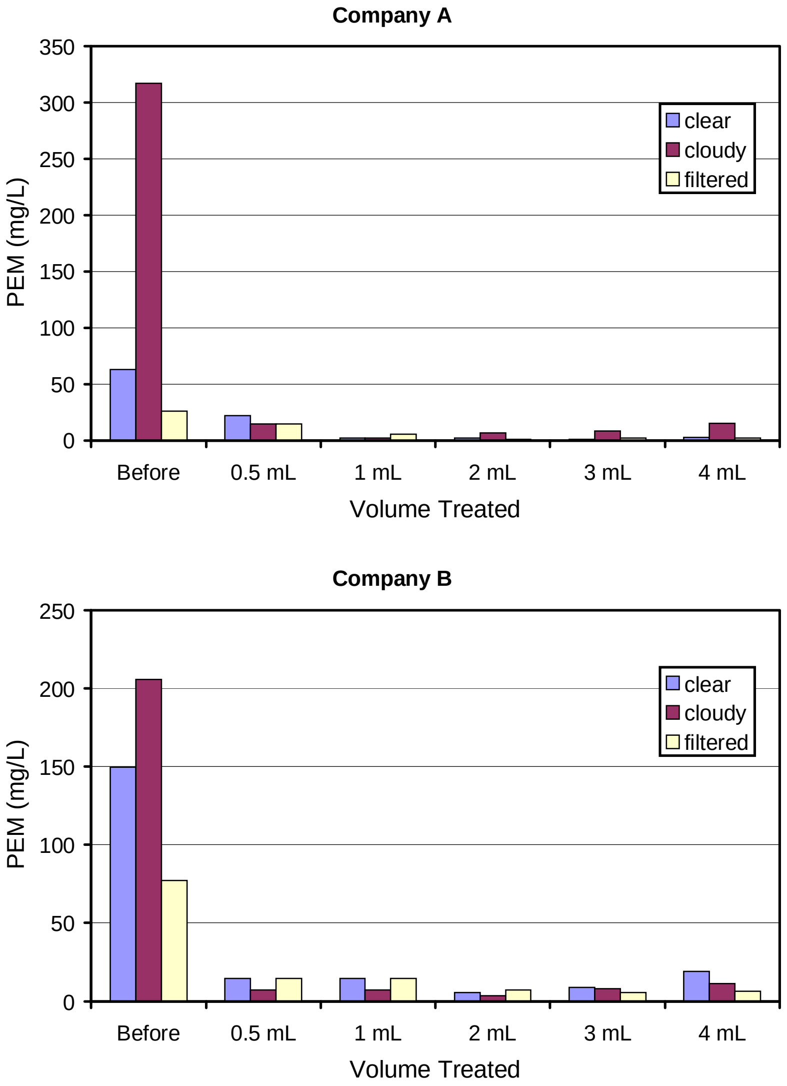


Fig. 23. Concentration of extractable organics in different fractions of produced water samples. The results show concentrations before and after treatment of the produced water. All sample volumes were treated with 6.4 mg O_3. The contact time was 3 days.

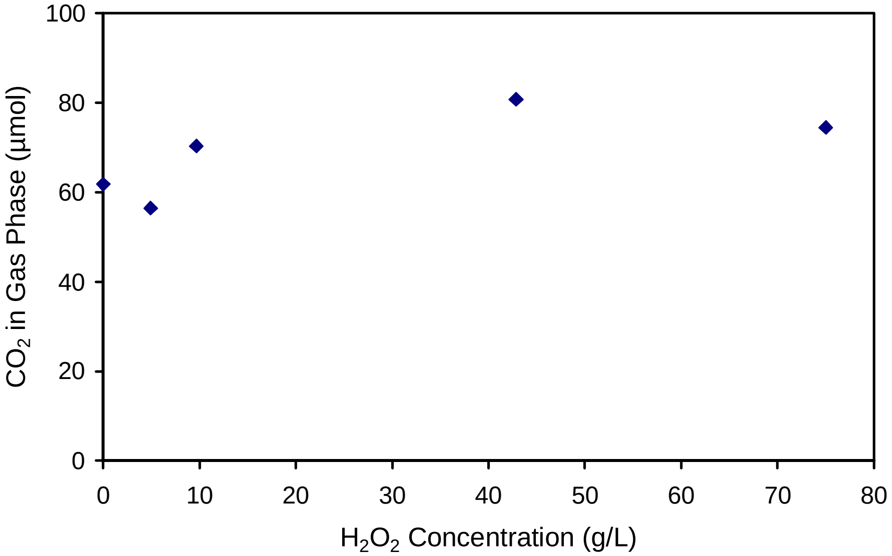


Fig. 24. Effect of hydrogen peroxide on CO_2 production in ozonation of produced water samples from Company A. The contact time was 3 days and the initial ozone concentration was 40 mg/L.

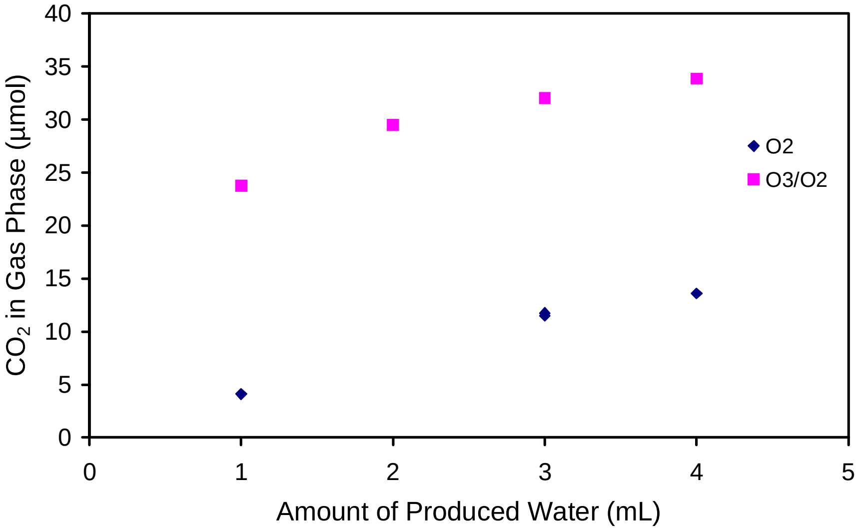


Fig. 25. Presence of CO_2 in the gas phase in ozonated and oxygenated filtered produced water samples from Company A. Approximately 5 mg ozone was added to bottles for ozonation. The contact time was 3 days.

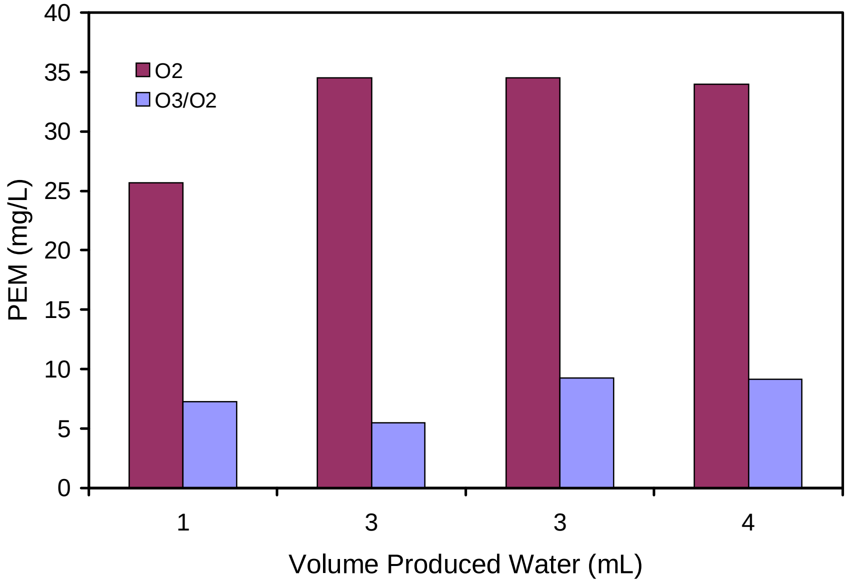


Fig. 26. Extractable organics (as PEM) in ozonated and oxygenated filtered samples from Company A. The contact time was 3 days and the initial concentration of PEM was 44 mg/L.

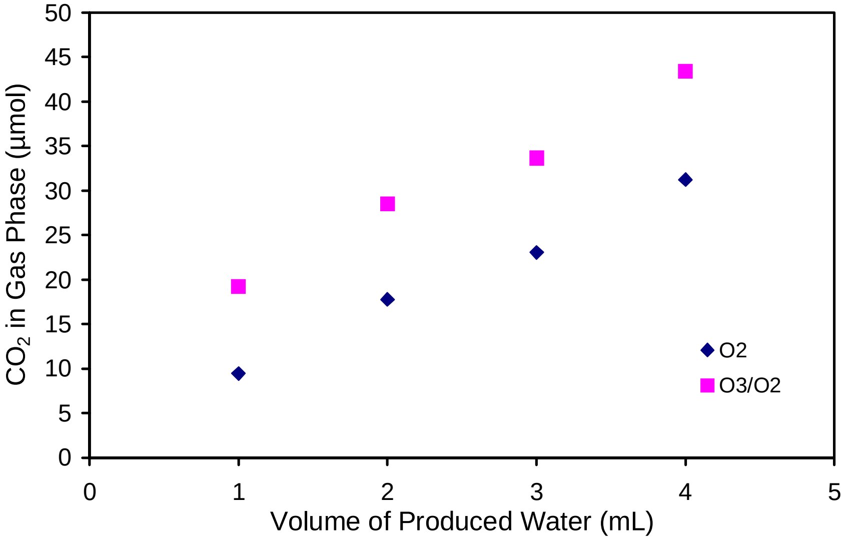


Fig. 27. Presence of CO_2 in the gas phases in ozonated and oxygenated filtered produced water samples from Company B. Approximately 5 mg ozone was added to bottles for ozonation. The contact time was 3 days.

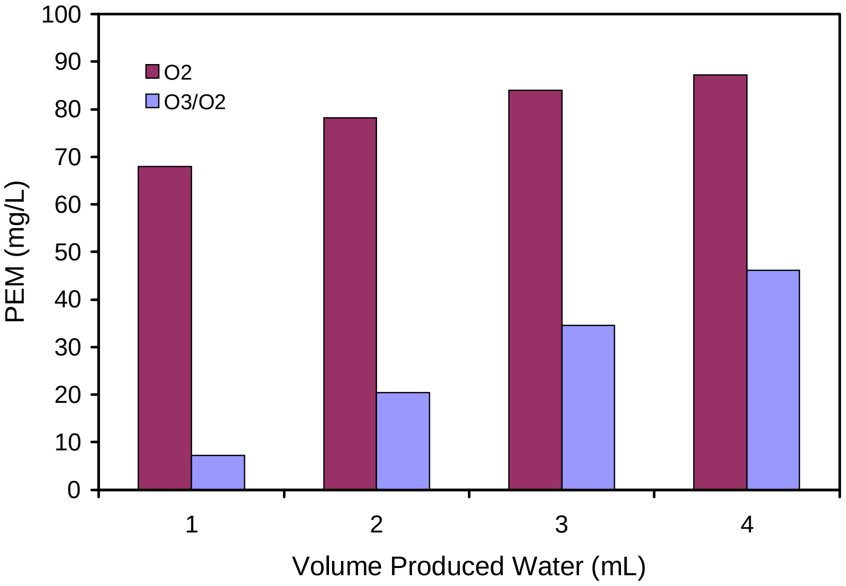


Fig. 28. Extractable organics (as PEM) in ozonated and oxygenated filtered samples from Company B. The contact time was 3 days and the initial concentration of PEM was 104 mg/L.

4.7 LARGE-SCALE BATCH EXPERIMENTS

Several large-scale experiments were conducted to monitor the oxidation of PEM as a function of time. Data such as this may be used to estimate kinetics of the destruction. In Fig. 29 and 30, we have summarized the data collected from experiments using produced water from Company A and Company B.

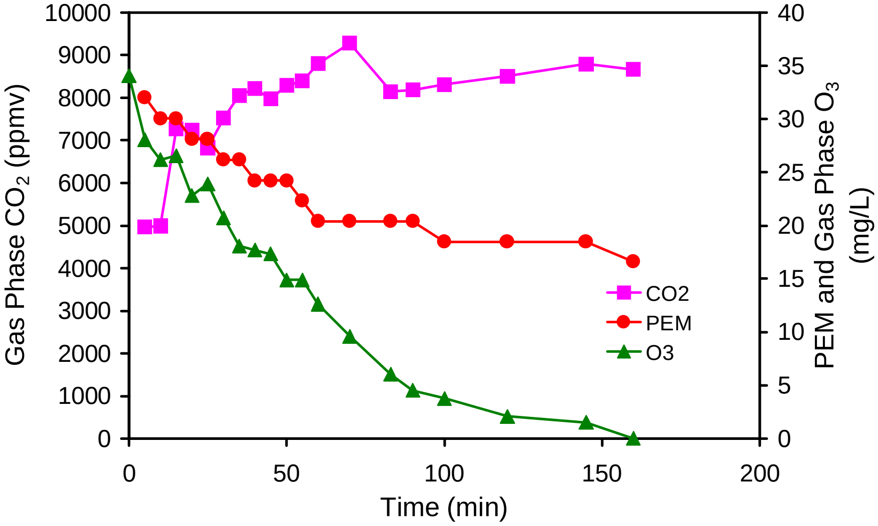


Fig. 29. Summary results from large-scale batch experiments conducted at 80°C and pH 2 with Company A's filtered produced water.

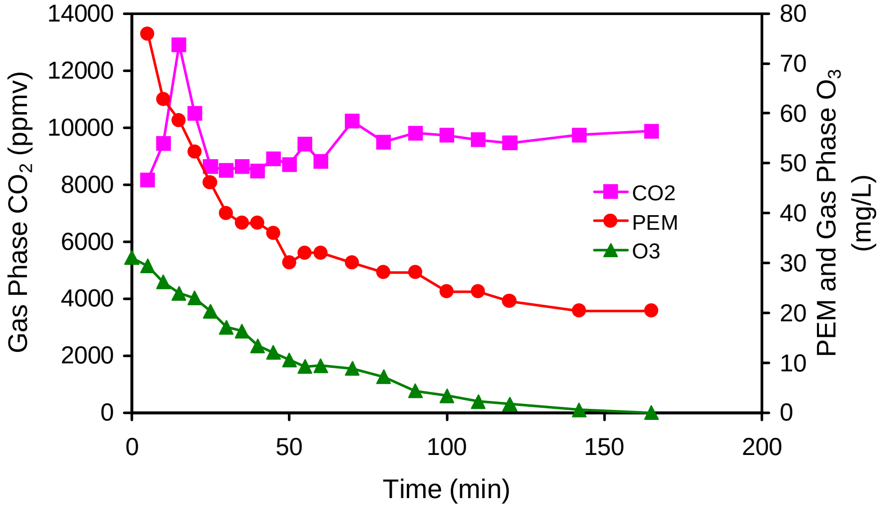


Fig. 30. Summary results from large-scale batch experiments conducted at 80°C and pH 2 with Company B's filtered produced water.

The results presented in Fig. 21 and Fig. 29 indicate that CO_2 was a product of oxidation when the synthetic produced water and the Company A-supplied produced water were treated with ozone. This was not the case with the Company B-supplied produced water. (Fig. 30) It should also be noted that in all cases, there is an initial amount of CO_2 present in the gas phase due to the liberation of dissolved CO_2 present in all the produced water samples. It is also clear that the PEM decreased during the experiments and that the decrease stopped when the ozone was depleted from the gas phase.

During the large-scale batch experiments, selected water samples were analyzed for organic acids. It is clear from the results presented in Fig. 31 and Fig. 32 that the low-molecular-weight acids present in the actual produced water samples were not affected by the ozonation. There was no net accumulation of new acids, nor was there any net destruction of these acids. Produced water from Company A and B contained approximately 1250 and 85 mg/L of organic acids, respectively.

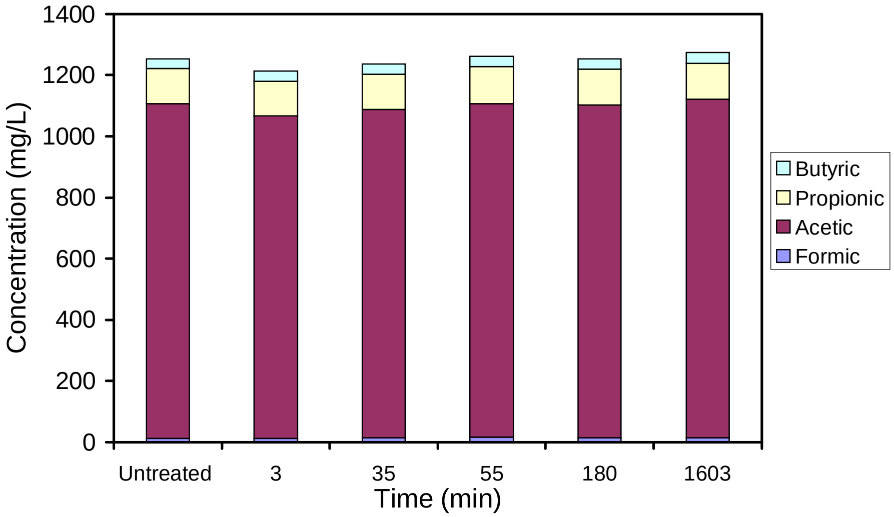


Fig. 31. Acids analyses results from large-scale batch experiments conducted with Company A-supplied filtered produced water at 22°C.

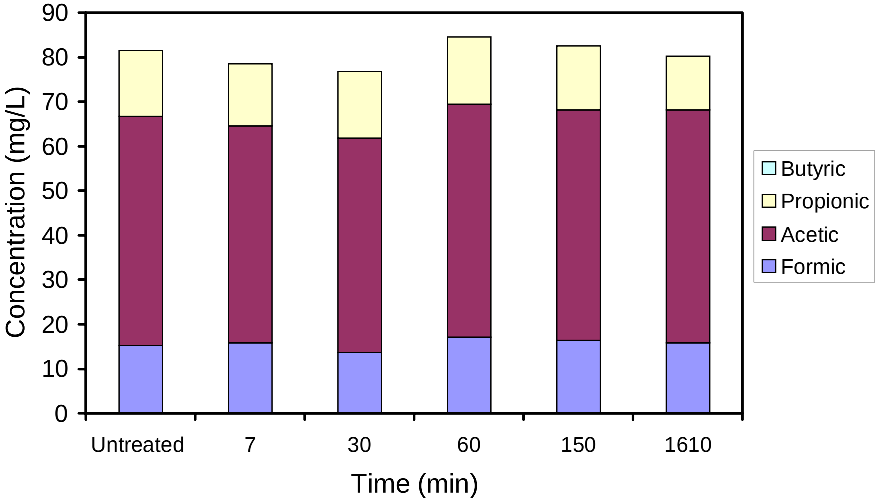


Fig. 32. Acids analyses results from large-scale batch experiments conducted with Company B-supplied filtered produced water at 22°C.

4.8 BATCH DATA KINETICS OF PCE EXTRACTABLE ORGANICS BY OZONE

To estimate the rate of reaction for the destruction of PEM, the following simplified direct reaction scheme was used:[4]

$$\text{PEM} + n\text{O}_3 \rightarrow \text{products} \qquad (3)$$

Assuming the rate of reaction is dependent on the concentration of PEM and O_3, we can write the following rate expression:

$$-\mathrm{d}[PEM]/\mathrm{d}t = k\,[PEM]\,[O_3]^n \qquad (4)$$

where d*[PEM]*/d*t* is the rate of PEM disappearance and *k* is the reaction rate constant. The expression may be rearranged to

$$-\mathrm{d}[PEM]/\mathrm{d}t/[PEM] = k\,[O_3]^n, \qquad (5)$$

suggesting that a plot of $-\mathrm{d}[PEM]/\mathrm{d}t/[PEM]$ as a function of $[O_3]$ should lead to some insight about the values of *k* and *n*. The above mathematical expressions are based on the assumptions that mass transfer of ozone to the organics is not limiting and that the change in reactor water volume is not substantial. To estimate the rate of disappearance, a cubic spline subroutine was used to smooth the data and obtain derivatives at each sampling point.[15] These derivatives were then divided by the concentration of PEM and plotted as a function of ozone concentration, $[O_3]$. The result is shown graphically in Fig. 33.

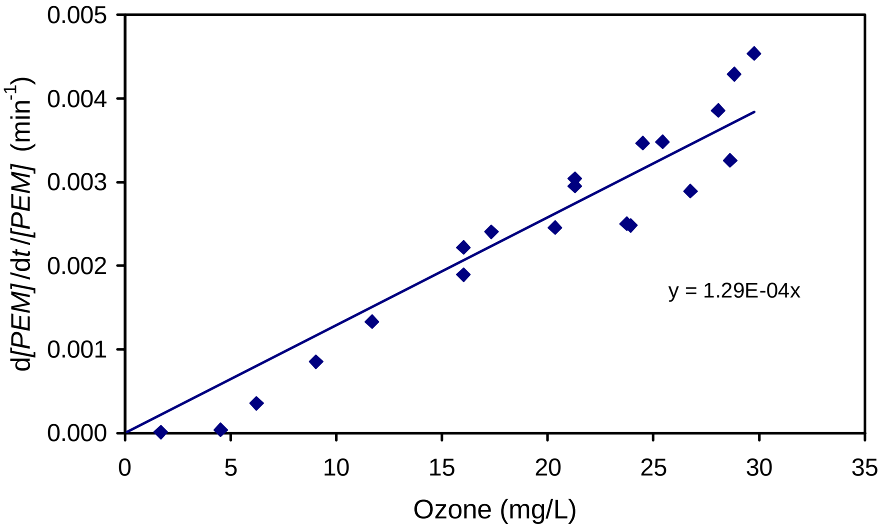


Fig. 33. Graphical determination of rate constant for reaction of filtered synthetic produced water organics with ozone.

The data appeared to fall on a straight line, indicating that *n* in Eqs. 3–5 has a value close to 1.0 and that *k* was approximately $1.3\cdot10^{-4}$ L/mg·min. The same kind of mathematical treatment was performed with data from experiments with filtered produced water from the Company A and Company B. In both cases, *n* was determined to be close to 1 and the values for *k* were $3.5\cdot10^{-4}$ and $9.5\cdot10^{-4}$ (L/mg·min), respectively. There is a significant amount of scatter in data of this type, thus the values for *k* are only approximate values. Using standard statistical methods (Student t), the values of *k* with 95% confidence interval are shown in Table 5 with data from experiments conducted at room temperature (21–23°C) and at 80°C. As is noted the *k*-value is higher at the higher temperature. It can also be seen that the organics in the Company B produced water sample reacted approximately twice as fast as the organics in the Company A produced water sample.

Table 5. Rate constants determined for the different produced water types.

	***k*-Value with 95% confidence [L/(mg·min)]**	
Source of produced water	**22°C**	**80°C**
Synthetic		0.000120–0.000138
Company A	0.0000505–0.0000880	0.000297–0.000396
(duplicate experiment)	0.0000506–0.000115	
Company B	0.000231–0.000400	0.000867–0.00104

In another experiment, ozone-containing oxygen was continuously flushed through the large-scale batch reactor and the concentration of PEM was monitored as a function of time. The result of this experiment is shown in Fig. 34. The smooth curve shows the concentration of ozone in the liquid. It is interesting to note that there was an initial increase, followed by a plateau, and then a slow decrease in concentration. One possible explanation is that there are different types of reactions contributing to the breakdown of the PEM or the partially oxidized products. The results from the experiments also show that there were not severe mass transfer limitations, as the concentration of ozone in the liquid was well above zero. The data presented in Fig. 34 was used to determine the kinetics for degradation by calculating the value of the left-hand side of Eq. 3 (specific rate) for each of the sample events. The average specific rate (d*[PEM]*/dt/*[PEM]*) was 0.00557–0.00825 (95% confidence interval), and the average gas phase ozone concentration during the experiment was 52.0–57.2 mg/L. This would mean that the *k* value was 0.000097–0.000159 L/(mg·min), which is about half of the value obtained using data from experiments where the ozone concentration decreased with time (Table 5 for 22°C, Company B). It is not clear why there was a difference.

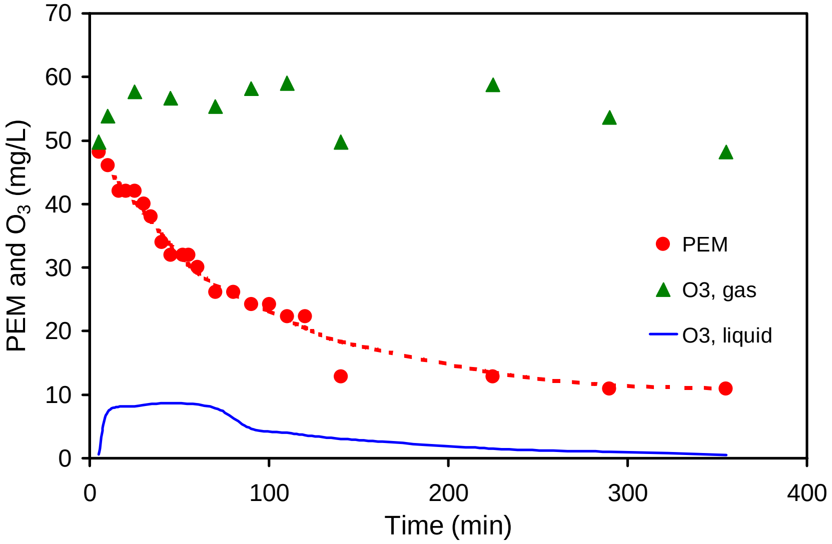


Fig. 34. Degradation of PEM in a batch reactor at 22°C using filtered produced water from Company B. Ozone was continuously purged in the gas phase.

This kinetic data can be used to correlate removal efficiency to contact time. This correlation is shown in Fig. 35 for an ozone concentration of 40 mg/L. As is noted, the data show that long contact times between ozone and produced water would be needed to obtain high removal efficiency.

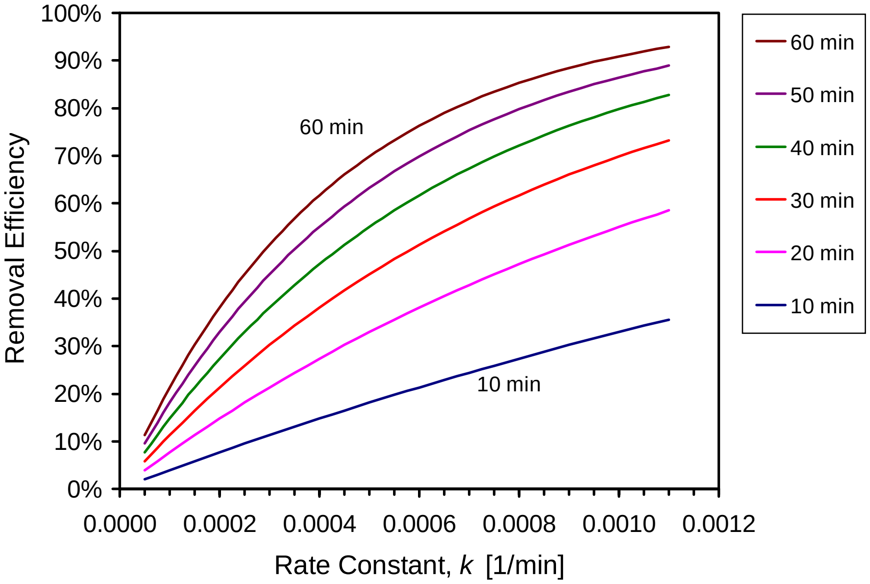


Fig. 35. Prediction of PEM removal efficiency as a function of reaction rate constant for various contact times. The data applies to an ozone concentration of 40 mg/L in air.

4.9 MASS BALANCE AND OZONE REQUIREMENTS

The ozone demand is an important parameter to consider when a full technology assessment is required. The data collected in the large-scale batch reactors were reviewed and plotted in a manner that would determine the ozone demand. The results are shown in Fig. 36 and 37, where the concentration of PEM has been plotted as a function of the ozone concentration. For the experiments conducted at room temperature, the slope of a line through the data was 0.4 for experiments conducted with Company A and synthetic produced water. The slope was 1.1 in the experiment with Company B's water. In the experiments conducted at 80°C, the slope was 0.7 for Company A and synthetic produced water and 2.1 for Company B's water. Considering that the gas volume and liquid volume in these reactors were on average 4.3 and 0.18 L. The ozone demand can be calculated to be 11–80 mg O_3/mg PEM, depending on the operating conditions (Table 6).

The amount of carbon converted from its oxidation state in PEM to carbon dioxide is seen in Fig. 38. Here, the molar amount of carbon in carbon dioxide has been plotted as a function of the estimated molar amount of carbon in reacted PEM (assuming that PEM is 86% (w/w) carbon). These results indicate (from the slopes of the trend lines) that only 6 to 25% of the carbon in the PEM removed is completely oxidized to carbon dioxide. To summarize, the decrease in PEM is clear but CO_2 accounts for less than 25% of the potential products.

Carbon dioxide was a detectable product of the ozonation; however, the majority of the CO_2 did not come from complete conversion of PEM. The majority of the CO_2 detected in the batch experiments (after correction for carbonates) could not be contributed to a decrease in PEM. Based on the trends displayed in Fig. 38, approximately 20.7 µmol CO_2 was generated in small-scale batch experiments for Company B and synthetic produced water without a decrease in PEM. With water from Company A, 8.6 µmol CO_2 was generated without a decrease in PEM. There are several possible explanations:

1. Portions of the carbon structure could be converted into CO_2, while still remain a PEM. This cannot be true as the amount of CO_2 generated in some experiments exceeds the amount of carbon contained in the PEM.
2. Ozone is oxidizing some organics that cannot be classified as PEM. Acids analyses on samples do not indicate that there is a decrease in the organic acids concentration. The accuracy of the organic acids measurement is appropriate to observe a decrease in the acids if all the CO_2 generated originated from acids degradation.
3. The most likely explanation is that the source of carbon dioxide is that organics, not extractable with PCE under acidic conditions, are responsible for the majority of CO_2 production.

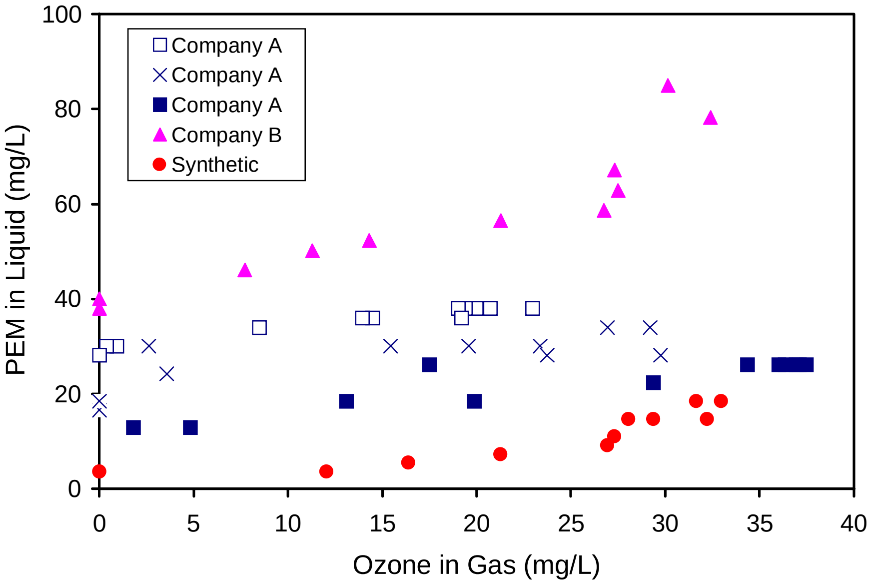


Fig. 36. PEM remaining in the liquid as a function of ozone remaining in the gas phase in experiments conducted at room temperature (22°C). Data for several duplicate experiments have been included for Company A.

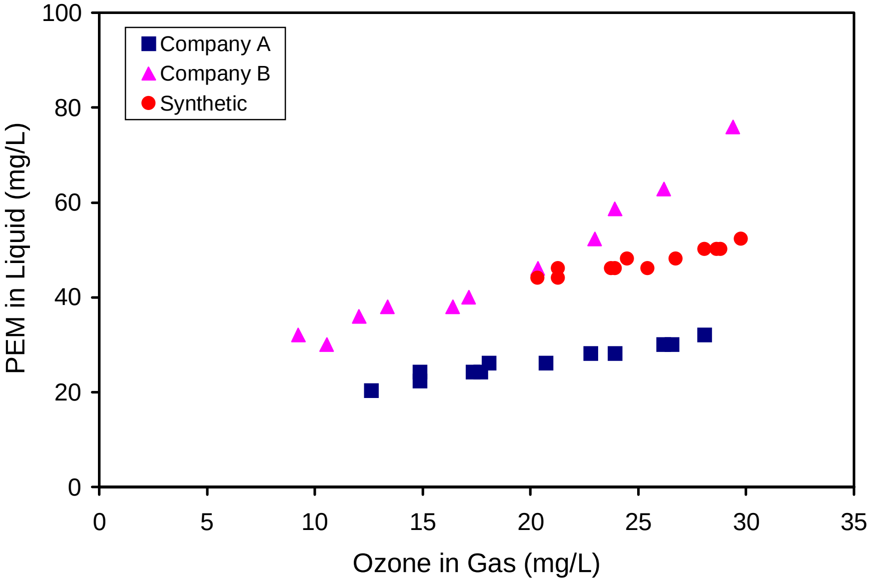


Fig. 37. PEM remaining in the liquid as a function of ozone remaining in the gas phase in experiments conducted at 80°C.

Table 6. Calculated ozone demand in large-scale batch experiments.

Temperature	Produced water source	Ozone demand
22°C	Company A & Synthetic	80 mg O_3/mg PEM
	Company B	22 mg O_3/mg PEM
80°C	Company A & Synthetic	34 mg O_3/mg PEM
	Company B	11 mg O_3/mg PEM

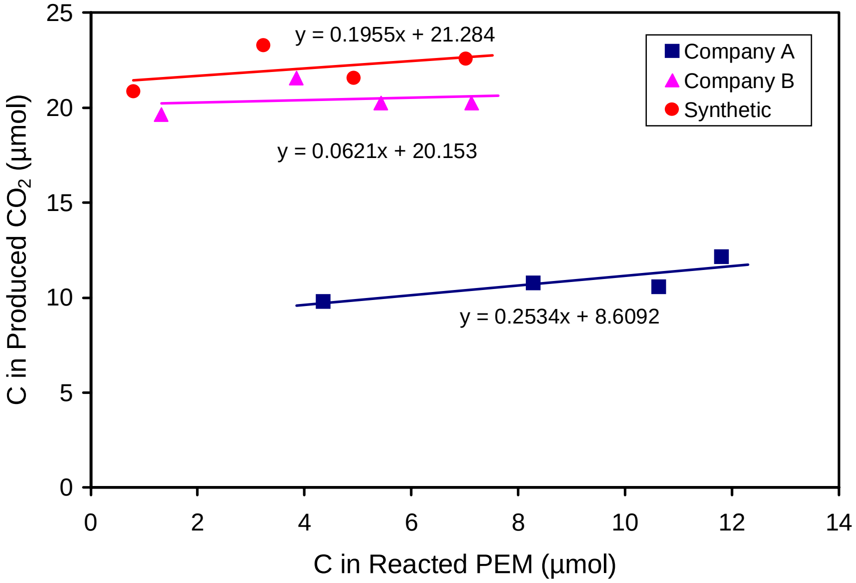


Fig. 38. Mass balance for carbon data taken from small-scale batch experiments at 22°C. Both the CO_2 and PEM levels were corrected with control experiment conducted with pure oxygen. Different amounts of produced water (1–4 mL) were contacted with either O_2 or 5.4 mg O_3 in O_2 for 3 days.

4.10 IDENTIFICATION OF OZONATION PRODUCTS OF PRODUCED WATER BY GC-MS

A preliminary GC-MS analysis of PEM in produced water from Company A, before and after ozonation, was performed (Fig. 39). The peaks represent carbon compounds present in the samples, which unfortunately could not be recognized by the mass-spectroscopy library used in this work. (Subsequent samples were sent to Georgia Institute of Technology for GC-MS analysis). The top graph in Fig. 39 (before ozonation) contains more peaks than the bottom graph (after ozonation), indicating that several compounds have been destroyed by ozone.

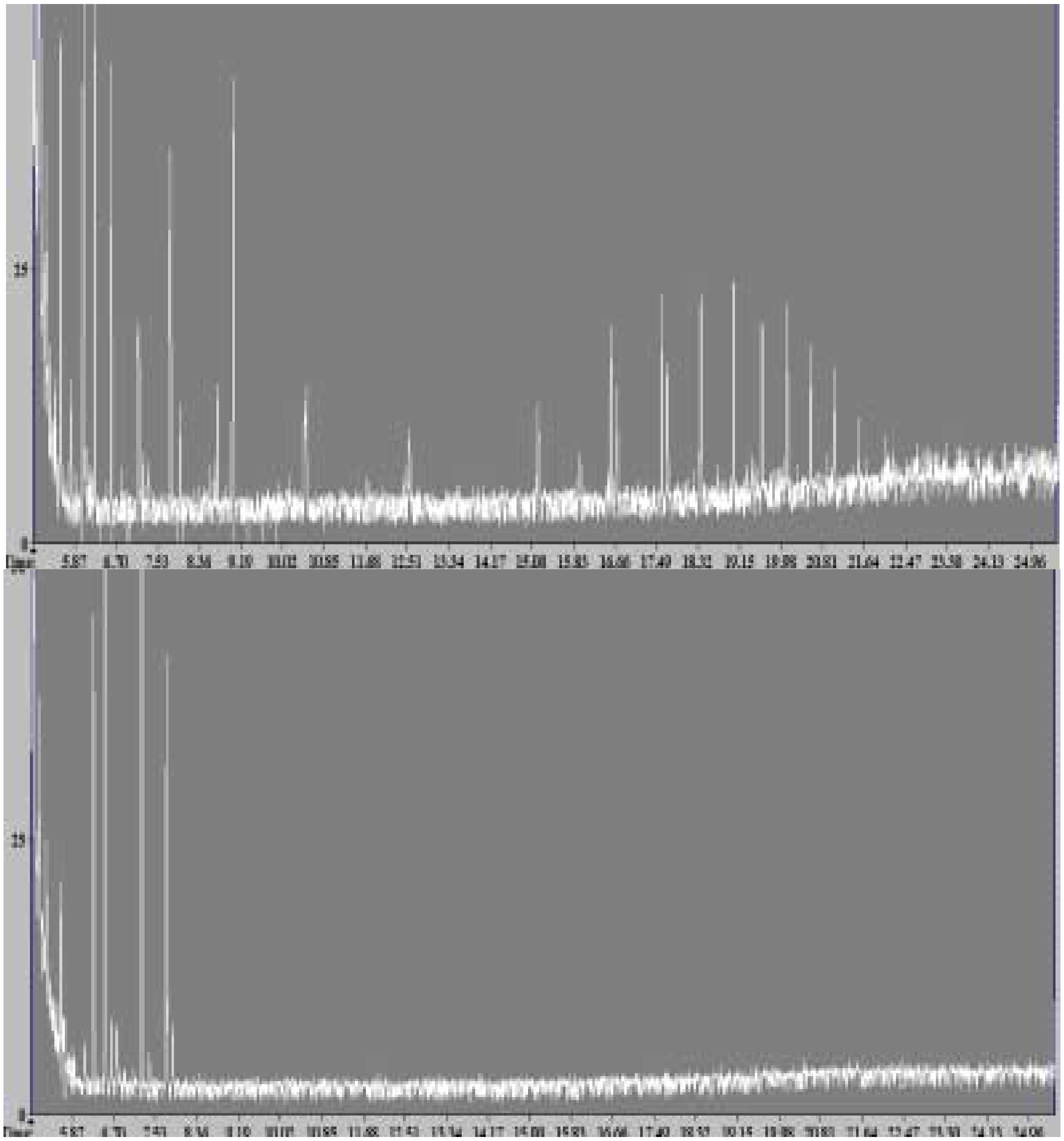


Fig. 39. GC-MS analysis of produced water from Company A before (top) and after (bottom) ozonation.

To attempt to identify the organic compounds in produced water before, during, and after prolonged ozonation, the Georgia Institute of Technology performed GC-MS analysis. Their complete report, including tables with identified compounds, is attached as Appendix A. The HPLC grade dichloromethane (99%, Aldrich Chemical Co., Mich., USA) was used as a solvent and samples of (a) non-ozonated solutions, (b) partially ozonated solutions, and (c) prolonged ozonated solutions were used for analysis.

The intermediates and by-products of the ozone oxidation process were expected to include oxygen atoms. We found that most of the intermediates and by-products of both partially and prolonged oxidation were acids, while others did not contain oxygen atoms. This phenomenon may be due to reactions between the compounds in the samples and radical species formed by ozone reactions with water or organic compounds.

Most of the peaks in the chromatogram of the Company B sample, in Fig. 40(a), fall in the range of 110°C to 165°C on the GC temperature ramp. The unstable baseline may be a result of contamination of the column or impurities in the sample. The results confirmed the presence of cyclopentanecarboxylic acid, cyclopentaneacetic acid, and cyclohexanecarboxylic acid in the sample.

The results of partial oxidation of produced water from Company B [Fig. 40(b)] showed that new compounds were created during the ozonation process while some of the original compounds were still present. Results of prolonged oxidation of produced water from Company B [Fig. 40(c)] show that some compounds, previously created in the partially oxidizing step, disappeared but others remained. For prolonged oxidation, some new products were formed. The intermediates during ozonation of Company B samples were 2-ethyl-4-methyl-1,3-dioxolane, 1,3-dibromo-3-methylbutane, and 4-nitrophenyl-ester-2-butenoic acid, and the products of prolonged oxidation were 1-bromo-3-methyl-2-butene, dibromochloromethane, 2,3-dichloro-2-methylbutane, butanamide, tribromomethane, and 2,2-dichloropentane. Among the oxidation by-products only butanamide contains oxygen atom, while the others contain halogen atoms.

For Company A (Fig. 41), the components in the non-ozonated produced water were different from those of Company B (Fig. 40). The non-ozonated produced water from Company A contained propanoic, butanoic, and pentanoic acids, which were not found in the Company B sample. Some peaks in this chromatogram appear to contain the silicon atom, which may come from the column itself. These peaks were also found in some of the other samples but at very low concentrations.

The only compound, which was found in both non-ozonated and partially oxidized produced water from Company A, was butanoic acid while others disappeared. The intermediate compounds resulting from ozonation of produced water from Company A were 1,4-dibromopentane, 1,3-dibromo-3-methylbutane, hexanoic acid, heptanoic acid, and octanoic acid. The products of prolonged oxidation were 1-bromo-3-methyl-2-butene, dibromochloromethane, butanamide, tribromomethane, 2,2-dichloropentane, 2-piperidinone, and 3-hexene-2-one.

Substances that contained the silicon atom were found in the non-ozonated synthetic produced water (Type 4) [Fig. 42(a)]. All of these substances were also found in the non-ozonated produced water from Company A [see Fig. 41(a)]. Prolonged oxidation of the synthetic produced water [Fig. 42(b)] produced almost every compound that were found in Company A prolonged oxidized sample [Fig. 41(c)]. The ozonation by-products for synthetic produced water were 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane.

GC-MS results demonstrated that ozonation destroyed some organic compounds creating some unique products. Some of the products of ozonation with Company A, Company B, and synthetic produced water samples were the same. Common ozonation by-products were 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane. There were some intermediates formed during the ozonation process. Each intermediate and product was formed at different ozonation periods. An interesting finding was the formation of compounds that contain halogen atoms rather than oxygen atom. This result is presumed to be due to reactions of organic compounds with radicals formed by ozone reactions with water and organics. In addition, some of the compounds formed during ozonation may substitute oxygen with halogens from solvent molecules, e.g., NaCl.

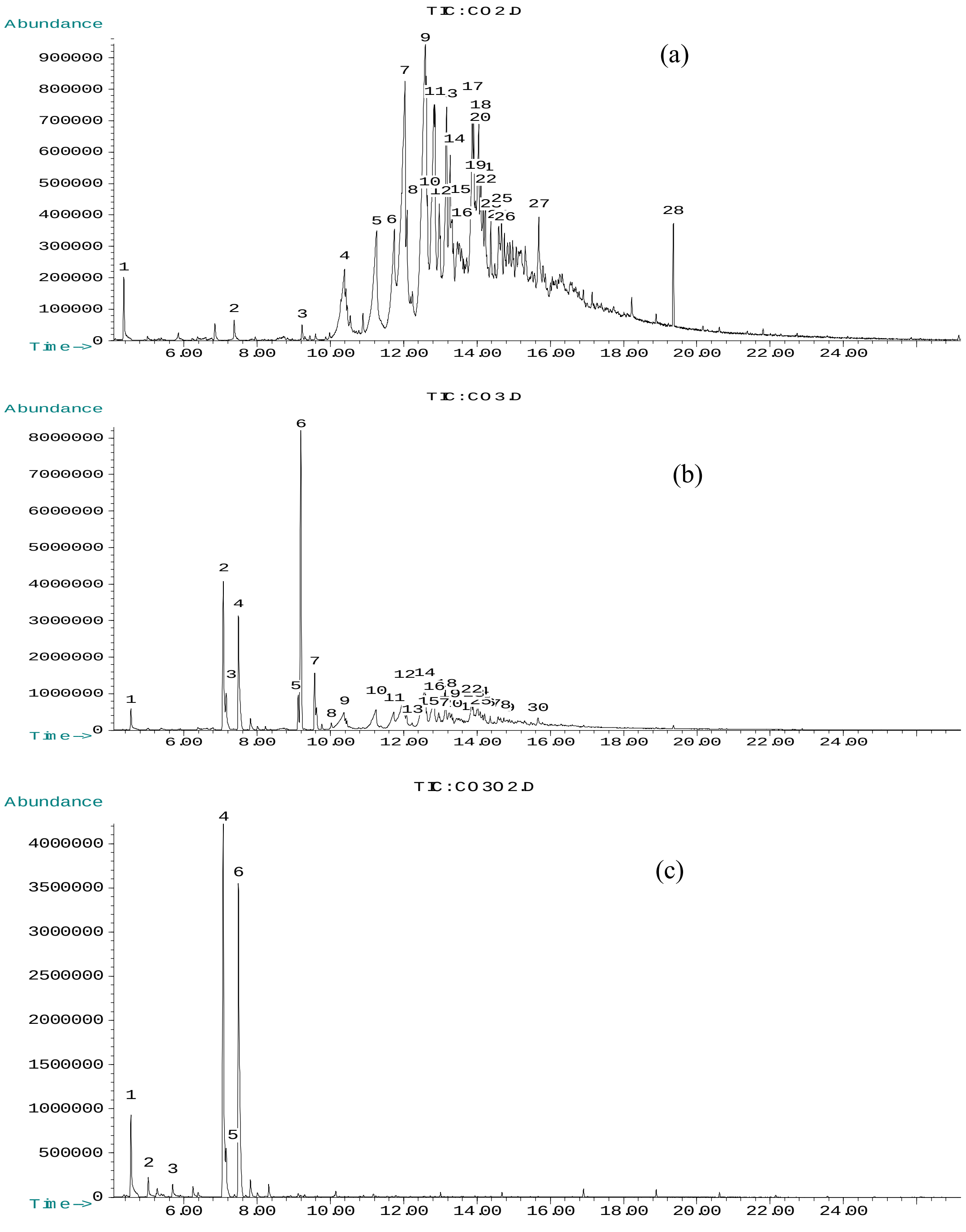


Fig. 40. Chromatograms of samples from (a) non-ozonated, (b) partially ozonated, and (c) prolonged ozonated produced water from Company B.

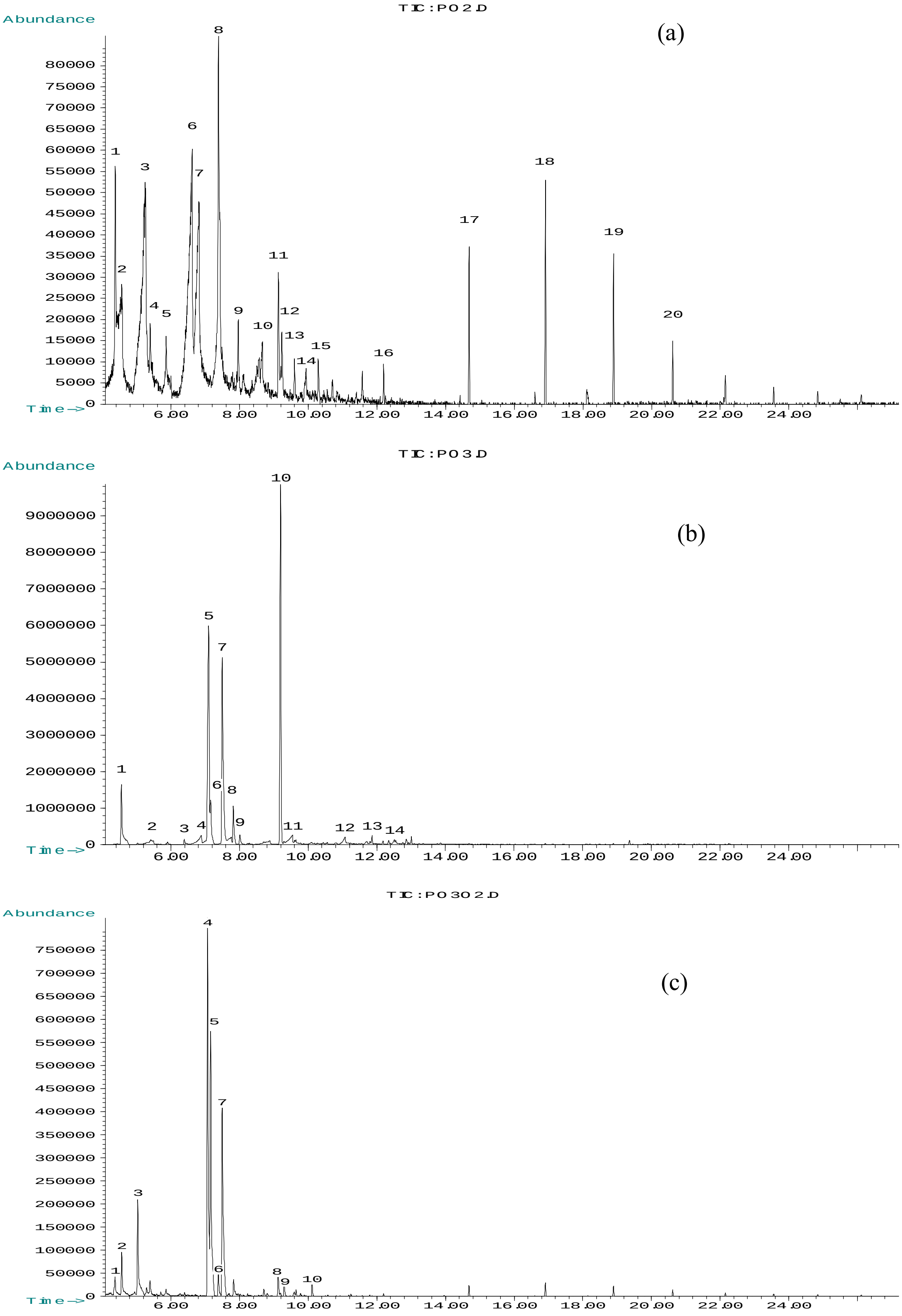


Fig. 41. Chromatograms of samples from (a) non-ozonated, (b) partially ozonated, and (c) prolonged ozonated produced water from Company A.

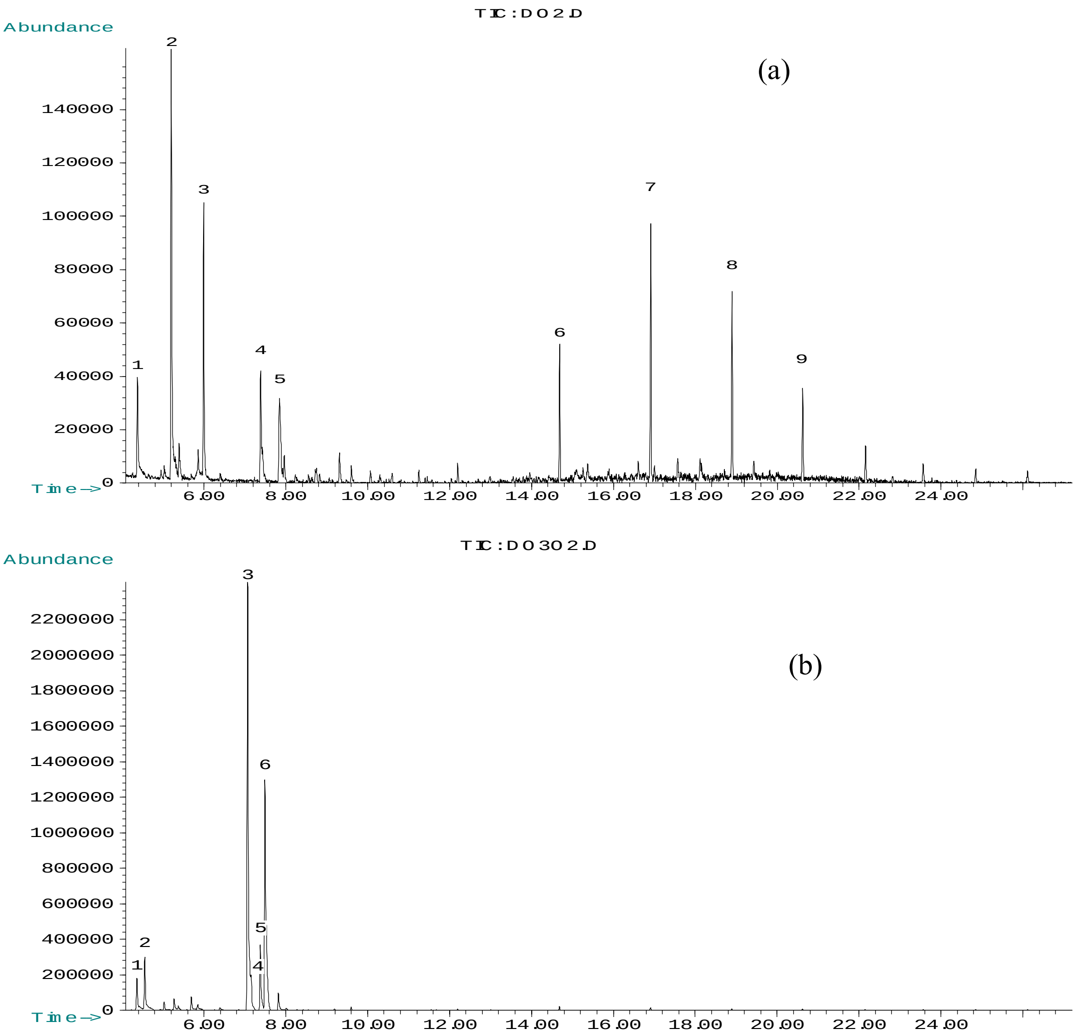


Fig. 42. Chromatograms of samples from (a) non-ozonated, and (b) prolonged ozonated synthetic produced water.

4.11 CONTINUOUS-COLUMN EXPERIMENTS

A few continuous-flow experiments were conducted with synthetic and actual produced water in the system depicted in Fig. 6. Initial experiments with synthetic produced water (100 g/L salt; 1 g/L light crude GOM oil) were designed to find suitable operating conditions for the actual produced water studies. These results are shown in Fig. 43. All the studies were conducted in a 200-mL column with a liquid residence time of 10 min. Based on this data, it must be concluded that the majority of PEM removed was removed via floatation and that little was removed via ozonation.

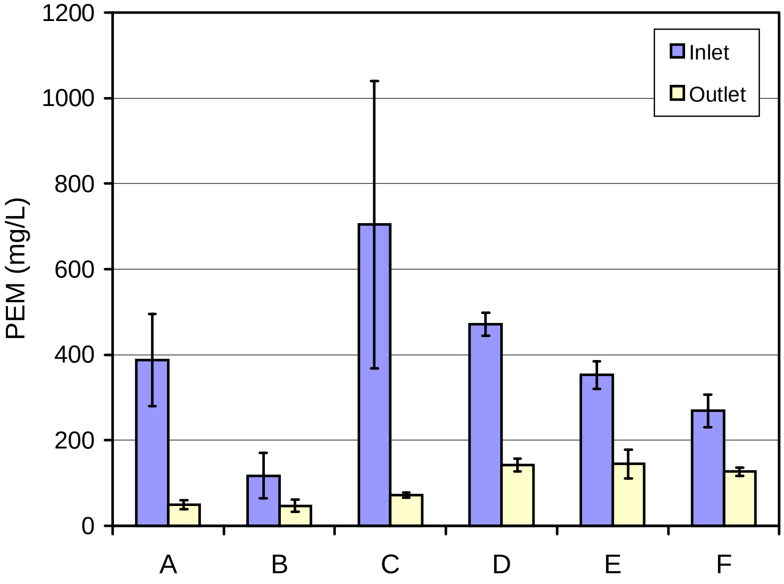


Fig. 43. Continuous-flow experiments with synthetic water. The operating conditions were: A–pH 8, 53 mg O_3/L in O_2 at 1000 mL/min; B–pH 8, 53 mg O_3/L in O_2 at 90 mL/min; C–pH 8, 500 mL O_2/min; D–pH 8, 100 mL O_2/min; E–pH 8, 33 mg O_3/L in air at 100 mL/min; F–pH 5, 33 mg O_3/L in air at 100 mL/min.

The results from experiments with synthetic produced water were confirmed when a study with produced water from Company A was conducted in the same column. The operation conditions were similar with a reactor volume of 210 mL and a liquid residence time of 10 min. The ozone concentration was 47 mg/L and the flow rate was 400 mL/min O_3 in O_2. The inlet PEM concentration was 114 mg/L and the effluent concentration was 104 mg/L. Thus, it was concluded that the majority of the PEM in Company A's produced water consisted of water-soluble species that would not be removed via floatation or via ozonation for these short retention times.

Long-term experiments of microbubble formation were conducted using synthetic saltwater containing 35 g/L sea salt, 65 g/L sodium chloride and a concentration of 30 ppm ferrous chloride that was oxidized, forming a precipitate phase. The experiments indicated that after sufficient time, depending on the gas flow rate, gas diffuser area, and solution concentration, pore fouling occurs, leading to decreased gas flow rate at constant pressure or increased gas pressure required for a given flow rate. Fouling was encountered only as a result of evaporative salt deposition rather than ferric oxide or calcium carbonate formation. This problem was effectively overcome by periodically flowing a small amount of water through the injectors to dissolve the salt deposits in the pores (Fig. 44).

We tested two larger-size columns and continuous cleaning of bubble diffusers with the objective to develop a robust approach for continuous, long-term formation of large contact area for ozone transfer from bubbles to the solution. These columns were 105 and 150 mm in diameter and 500 and 990 mm in length, respectively. The pore size of the diffusers was 10–16 µm. The gas flow rates ranged between 4.5 and 21 L/min. The effect of the gas flow rate and salt concentration on bubble size is illustrated in Fig. 45. As is noted, the bubble-size in salt water is approximately 10 times smaller than it is in fresh water.

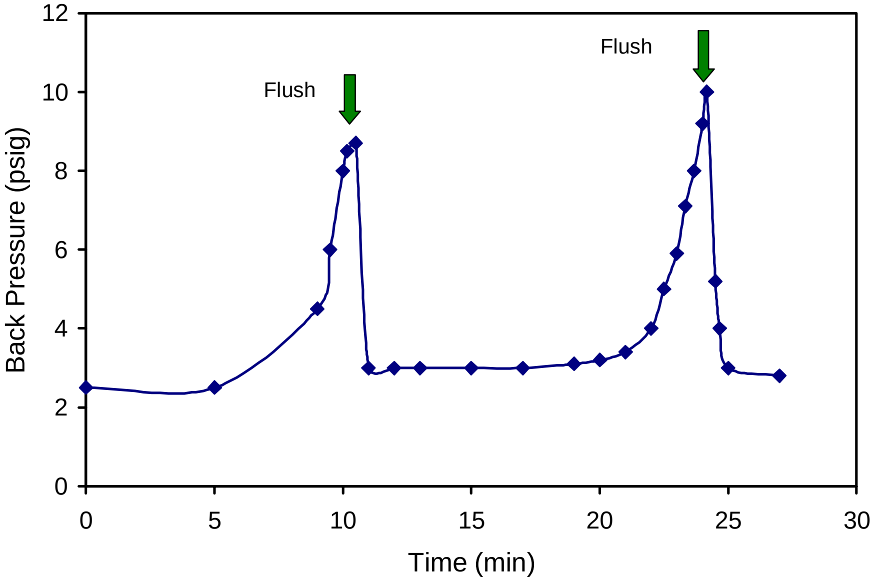


Fig. 44. Example results of salt deposition and water flush for gas flow through a porous injector. Conditions: liquid flow – 10 mL/min salt water; gas flow – 300 mL/min oxygen containing ozone, distilled water flush – 0.3 mL/min.

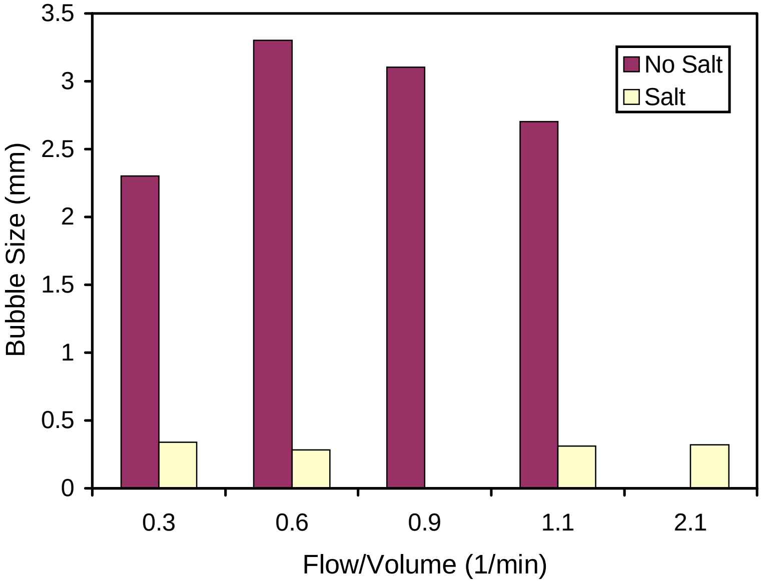


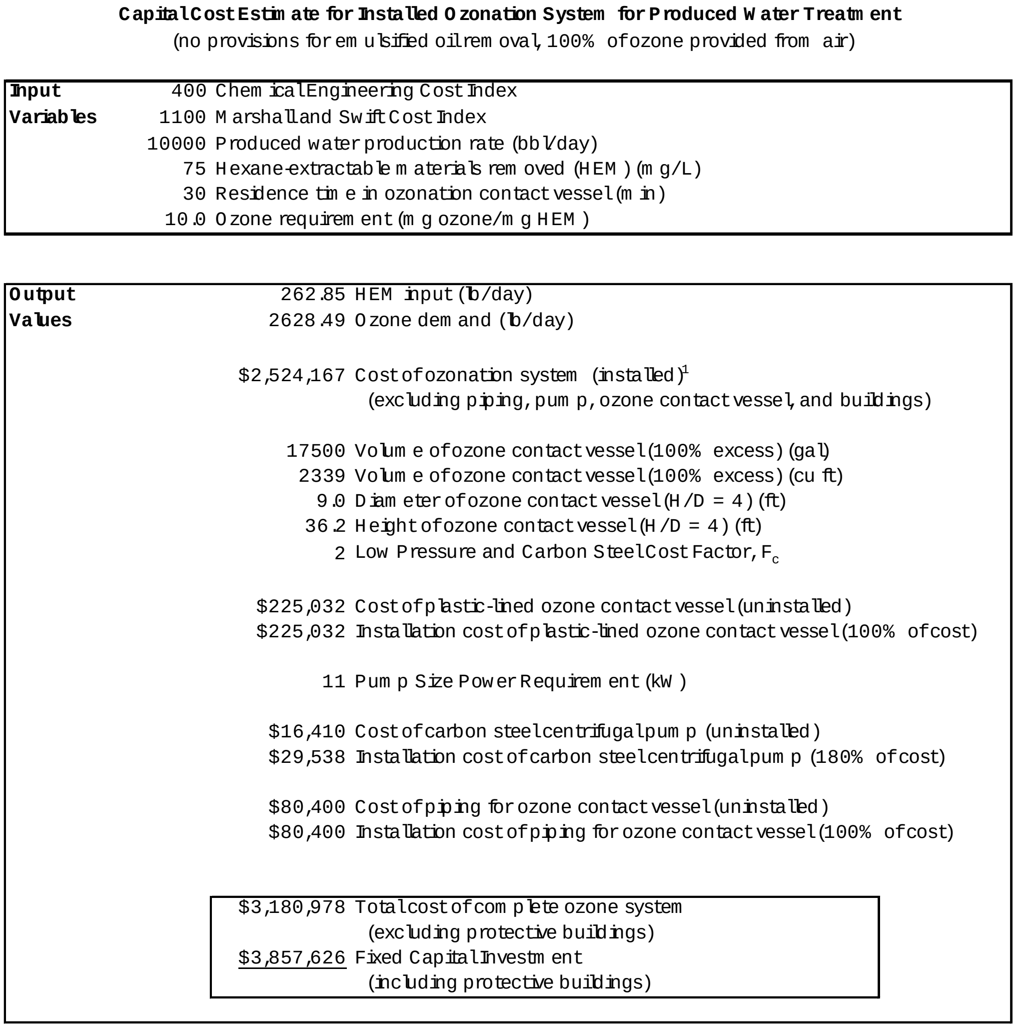
Fig. 45. Bubble size in large columns for different gas flow to contactor volume ratio.

During the extended testing in the large columns, the highest flow rate was used, and every 15 min, fresh water was pumped into the gas line before the diffuser at a rate of 500 mL/min for 20 sec. After a few weeks of operation in this mode, salt water from the column was used in place of the fresh water for flushing. This method of flushing worked just as well. The system operated for several months without problems, other than replacement of metal parts with glass parts when the flushing stream was altered to salt water.

A third larger column, 230 mm in diameter and 760 mm in length with an industrial type of bubble diffuser, was also tested. Small bubbles were formed for several weeks of continuous operation, demonstrating that the cleaning approach for the pores worked well.

4.12 ECONOMIC EVALUATION OF OZONATION FOR PRODUCED WATER TREATMENT

The estimated economic calculations were based on the extrapolation of experimental results. The rate of produced water was 10,000 bbl/day (17,500 gal/hr) with an initial content of 100 ppm of extractable organics. A liquid residence time of 30 minutes and 75% destruction of extractable organics was assumed with an ozone consumption of 10 g ozone/g PEM. The calculations were performed in a Microsoft Excel spreadsheet that allowed for change in parameters. The fixed capital cost and annual operating cost spreadsheets are shown in Fig. 46 and 47. The estimations are in US dollars and updated to approximately mid-2001;[16] the Chemical Engineering Cost Index and Marshal & Swift Index used in the calculations are 400 and 1100, respectively. The fixed capitol investment for the ozonation treatment facility (without buildings) is estimated to cost of \$3.2 million. It should be noted that treating this volume of produced water would require a very large contact vessel (36 feet tall). The economic evaluation is based on information from Katz.[17] Again using information from Katz, the operating cost for this facility on a basis of 1000 gallons treated is \$7.31. The operating cost includes depreciation estimated as 10% of the fixed capital investment; the major operating expenses are operating labor at 26%, electricity at 4%, maintenance and operating supplies at 10%, and depreciation at 42%.[18–20]



Capital Cost Estimate for Installed Ozonation System for Produced Water Treatment

(no provisions for emulsified oil removal, 100% of ozone provided from air)

Input Variables	400	Chemical Engineering Cost Index
	1100	Marshall and Swift Cost Index
	10000	Produced water production rate (bbl/day)
	75	Hexane-extractable materials removed (HEM) (mg/L)
	30	Residence time in ozonation contact vessel (min)
	10.0	Ozone requirement (mg ozone/mg HEM)

Output Values	262.85	HEM input (lb/day)
	2628.49	Ozone demand (lb/day)
	$2,524,167	Cost of ozonation system (installed)[1] (excluding piping, pump, ozone contact vessel, and buildings)
	17500	Volume of ozone contact vessel (100% excess) (gal)
	2339	Volume of ozone contact vessel (100% excess) (cu ft)
	9.0	Diameter of ozone contact vessel (H/D = 4) (ft)
	36.2	Height of ozone contact vessel (H/D = 4) (ft)
	2	Low Pressure and Carbon Steel Cost Factor, F_c
	$225,032	Cost of plastic-lined ozone contact vessel (uninstalled)
	$225,032	Installation cost of plastic-lined ozone contact vessel (100% of cost)
	11	Pump Size Power Requirement (kW)
	$16,410	Cost of carbon steel centrifugal pump (uninstalled)
	$29,538	Installation cost of carbon steel centrifugal pump (180% of cost)
	$80,400	Cost of piping for ozone contact vessel (uninstalled)
	$80,400	Installation cost of piping for ozone contact vessel (100% of cost)
	$3,180,978	Total cost of complete ozone system (excluding protective buildings)
	$3,857,626	Fixed Capital Investment (including protective buildings)

Fig. 46. Capital cost estimation spreadsheet.

Annual Operating Cost Estimate for Installed Ozonation System for Produced Water Treatment

(24 hr/day, 365 days/year operation)

Input Variables	$3,857,626	Fixed Capital Investment
	$0.05	Cost of electricity ($/kWh)
	$0.03	Cost of cooling water ($/gal)
	4	Required labor (# of 12-hr shift positions)

			Quantity	$/Quantity	
Output Values	Direct Costs				
	Operating labor		2	$31,746	$63,492
	Supervisory & clerical labor (15% of operating labor)				$9,524
	Utilities	Electricity (kWh)	9582474	$0.05	$479,124
		Cooling water (gal)	27661031	$0.03	$830
	Maintenance (2% of fixed capital investment)				$77,153
	Operating supplies (20% of maintenance)				$15,431
	Laboratory charges (20% of operating labor)				$12,698
	Indirect costs				
	Depreciation (10% of fixed capital investment)				$385,763
	Taxes and insurance (2% of fixed capital investment)				$77,153
	TOTAL ANNUAL OPERATING COST				$1,121,166
	Operating cost per 1000 gal treated				$7.31
	Investment per 1000 bbl per day				$385,763

Fig. 47. Annual operating cost of ozonation of produced water.

The sensitivity of costs to contact time and ozone demand is shown in Fig. 48 and 49. If a reduction of the contact time from 30 min to 10 min could be achieved, the capital costs would be reduced by approximately 10%, but the size of the vessel would be reduced by 67%.

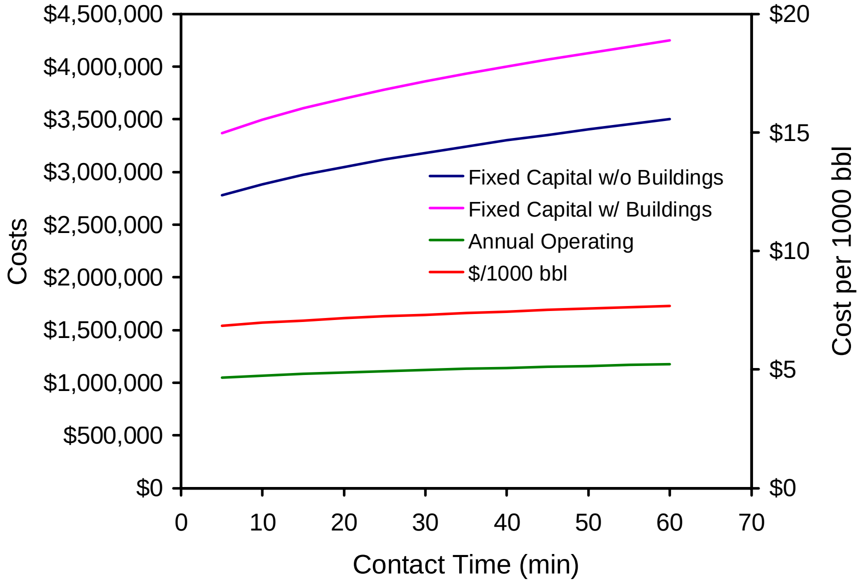


Fig. 48. Sensitivity to the cost associated with ozonation of produced water. Baseline was a 30-min contact time and an ozone demand of 10 g/g.

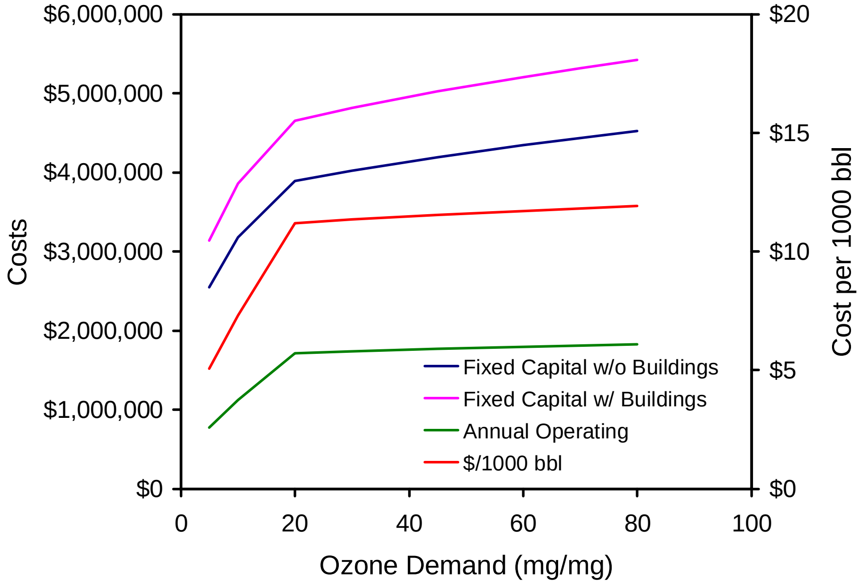


Fig. 49. Sensitivity to the cost associated with ozonation of produced water. Baseline was a 30-min contact time and an ozone demand of 10 g/g.

4.13 COMPARISONS WITH PREVIOUS OZONATION STUDIES

The PERF Project 93-23 (Removal of Soluble Oil from Produced Water: Technology Evaluation) investigated the removal of water-soluble oil from produced water in the early 1990s.[21] In these studies, ozone (16.7 mg/L) in air was introduced at a gas flow rate of 175 L/min to a reactor containing 102 L water at 35°C. The water flow rate to the reactor was set to 2.23, 5.03, 11.0, and 20.1 L/min, corresponding to a liquid residence time of 46, 20, 9, and 5 min, respectively. This operation resulted in an overall (as measured by IR) removal rate of 39.3, 33.0, 21.0 and 22.5 %, respectively. This data can be used to suggest an overall rate constant in these experiments from the predictions presented in Fig. 35. Such an approach suggests that the rate constant was in the range of 0.00065–0.0014 min^{-1}, when adjusted for the lower ozone concentration. This rate constant value is of the same order of magnitude as those found in our experiments (see Table 5). The ozone dosing-rate was 79 mg O_3/mg extractables removed in the earlier PERF study. They noted better performance (measured as overall removal efficiency) when UV light was applied. The two best conditions, resulting in the highest removal efficiencies, corresponds to an over rate constant of 0.0011 (at 51% removal efficiency and 46 min residence time) and 0.0012 min^{-1} (at 61% removal efficiency and 56 min residence time). In a batch type operation, they recirculated 757 L of water through the reactor at 39 L/min and supplied ozone at approximately 36 mg/L, 21% removal was observed in 120 min and 48% removal was observed in 360 min. This corresponds to an overall removal rate constant of 0.0004 min^{-1}.

5. CONCLUSIONS

A large number of experiments, to determine the feasibility of ozone as an oxidation agent, were performed on a variety of synthetic and actual produced water in this project. The limited supply of actual produced water made it impossible to conduct continuous flow experiments for extended period of times. Synthetic water could be produced in large amounts but is possibly not very representative of produced water as it pertains to the water-soluble organics. In the synthetic produced water, the majority of “extractables” consisted of oil droplets, which in some of the continuous studies were removed via floatation. In other experiments, these particulates contributed to a great variability in the untreated water samples. The removal of extractable organics via ozonation proved to be a slow process with reaction rates similar to those found in previous pilot-scale studies conducted by PERF. This agreement in results suggests that destruction of soluble organics may require large contact vessels for sufficient contact times. The large equipment results in higher capital cost and annual operating expenses. If the majority of the extractable organics are small droplets, our data indicate that floatation may be an effective means by which these could be removed.

6. REFERENCES

1. A. N. Sachanen, *The Chemical Constituents of Petroleum*, Rinehold Publishing Corp., New York, 1945.
2. D. T. Bostick et al., *Characterization of Soluble Organics in Produced Water*, Department of Energy Petroleum Energy Research Forum Project 98-04, to be published at Oak Ridge National Laboratory, Oak Ridge, Tenn..
3. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., vol. 17, ed. J. I. Kroschwilz, John Wiley & Sons, New York, 1991, p. 960.
4. J. Hoigne and H. Bader, “Rate Constant of Reactions of Ozone with Organic and Inorganic Compounds in Water-I Dissociating Organic Compounds,” *Water Res.* **17**, 185 (1983).
5. *Water Quality and Treatment*, 4th ed., ed. F, W. Pontius, American Water Works Association, McGraw-Hill, New York, 1990.
6. B. P. Tissot and D. H. Welte, *Petroleum Formation and Occurrence*, Springer-Verlag, New York, 1984.
7. C. Yurteri and M. D. Gurol, “Removal of Dissolved Organic Contaminants by Ozonation,” *Environ. Prog.* **6**, 240 (1987).
8. S. J. Masten and S. H. R. Davies, “Use of Ozonation to Degrade Organic Contaminants in Wastewaters,” *Environ. Sci. Technol.* **28**, 180A (1994).
9. J. F. Walker, Jr. and R.L. Cummins, *Development of a Centrifugal Downhole Separator*,” Proceedings of the 1999 Offshore Technology Conference, Houston, Texas, May 1999.
10. *Standard Methods for the Examination of Water and Wastewater*, 17th ed., eds. L. S. Cleceri, A. E. Greenberg, and R.R. Trussell, American Public Health Organization, Washington, D.C., 1989, p 4.162.
11. W.-T. Shin, S. Yiacoumi, and C. Tsouris, “Experiments on Electrostatic Dispersion of Air in Water,” *Ind. Eng. Chem. Res.* **9**, 3647 (1997).
12. U. Hofmeier, V. V.Yaminsky, and H. K. Christenson, “Observations of Solute Effects on Bubble Formation,” *J. Colloid. Interf. Sci.* **174**(1), 199 (1995).
13. J. Hoigne and H. Bader, “Rate Constant of Reactions of Ozone with Organic and Inorganic Compounds in Water-I Non-Dissociating Organic Compounds,” *Water Res.* **17**, 173 (1983).
14. K. T. Klasson, S. A. Jones, and A. B. Walker, “Measurement of Ozone via an Indirect Gas Chromatography Method,” *Ozone Sci. Eng.*, submitted for publication (2001).

15. K. T. Klasson, “Experimental Data Analysis: An Algorithm for Smoothing of Data and Determining Enzyme and Microbial Kinetic Rates,” *Appl. Biochem. Biotechnol.* **63/65**, 339 (1997).

16. *Chemical Engineering Magazine*, (March 2001), p. 138.

17. J. Katz, *Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water*, Noyes Data Corp., Park Ridge, N. J., 1980.

18. A. Chauvel et al., *Manual of Economic Analysis of Chemical Processes*, McGraw Hill, New York, 1981.

19. J. M. Douglas, *Conceptual Design of Chemical Processes*, McGraw Hill, New York, 1988.

20. G. D. Ulrich, *A Guide to Chemical Engineering Process Design and Economics*, John Wiley, New York, 1984.

21. Z. I. Khatib, *Removal of Soluble Oil from Produced Water: Technology Evaluation*, Technical Progress Report WTC xxx-97, Joint Industry Project PERF 93-23, Shell Development Company, Houston, Texas, May 1997.

APPENDIX A

IDENTIFICATION OF OZONATION PRODUCTS OF PRODUCED WATER BY GC-MS

Prepared by:

Sotira Yiacoumi and Viriya Vithayaveroj

School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, Georgia GA 30332-0512

for

Oak Ridge National Laboratory

(May 2001)

APPENDIX A: IDENTIFICATION OF OZONATION PRODUCTS OF PRODUCED WATER BY GC-MS

1. OBJECTIVE

The objective of this study is to identify the organic compounds in produced water before, during, and after ozonation, by using GC-MS.

2. INTRODUCTION

2.1 Ozonation

Ozone is an unstable reactive gas and has widely been used as an oxidant in water/wastewater treatment processes. It reacts with organic substances in two different mechanisms: direct reaction with ozone and indirect reaction with free hydroxyl radicals that are produced by ozone decomposition. The direct reactions with ozone can be classified into two ways: an electrophilic addition and a cyclo-addition. The electrophilic addition occurs at the electron rich parts of organic molecules like carbon-carbon double bonds at neutral to acidic conditions. The cyclo-reaction is selective to unsaturated carbon-carbon double bonds and forms carbonyl compounds (aldehydes or ketones). The reactivity of ozone depends on the electron density at the reaction sites. At alkaline conditions ozone decays mostly to hydroxyl radicals and by chain reactions to other radicals, which effect an unspecific radical reaction with organic substances.

2.2 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography (GC) is a common analytical technique for separating volatile compounds and can provide a representative spectral output. The advantages of GC are speed of analysis, resolution, ease of operation, excellent quantitative results, and moderate costs. GC however, is unable to verify the identity or structure of any peaks, and therefore GC data alone cannot be used to identify compounds (McNair and Miller, 1998). Mass spectrometry (MS) on the contrary provides quantitative data as well as qualitative identification of unknown compounds. Furthermore, MS is easily coupled to a GC system.

When a sample is injected into a GC system, it will be vaporized. The different chemical and physical characteristics of molecules determine how each substance in the sample interacts with the GC column surface. The column allows the various substances to partition themselves. After the compounds emerge from the column, they enter the ionization chamber. A 70-eV electron beam draws out electrons from a tungsten filament. These high-energy electrons strike the neutral analyte molecules, causing ionization and fragmentation. Each fragment is charged and travels to the accelerator as an individual particle. In a quadrupole mass analyzer, the ions are separated according to their mass-to-charge (*m/z*) ratio by electric field. Depending on the produced electric field, only ions of a particular *m/z* will be focused on the detector.

GC-MS has been employed in several investigations. Feigel and Holmes used GC-MS to analyze waste and wastewater for low-level contaminants such as polyaromatic hydrocarbons (PAH). Glover and Bullin (1989) examined seven unweathered heavy residual oils by using both GC and GC-MS and compared the results to source samples for identification purposes. The long-side-chain alkylaromatics in crude oil were also investigated using GC-MS by Dutta and Harayama (2000). Maldonado et al. (1999) studied the presence of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. Zeng et al. (2000) focused on an integrated treatment of benzo[*a*]pyrene involving sequential chemical oxidation and biological degradation. The qualitative and quantitative determinations of benzo[*a*]pyrene, intermediates, and reaction products were carried out by GC and GC-MS.

Since the produced water is generated in the oil production, it is expected to contain hydrocarbon compounds. Toluene and xylenes are common compounds found in any crude oil and oil products. The present study used toluene, xylenes, and combinations of both as standard solutions for reference. The temperature program was obtained by considering the separation of standard solutions and compounds in the samples, as well as by examining temperature programs found in the literature. The optimal temperature program chosen was the one that gave the best results.

3. EXPERIMENTAL INSTRUMENTS AND PROCEDURE

3.1 Test Apparatus and Instruments

The specifications of the major apparatus and instruments used in this study are listed below:

- An HP 6890 series gas chromatograph (Hewlett Packard Co., CA, USA).
- An HP 5973 mass selective detector (MSD) (Hewlett Packard Co., CA, USA).
- An HP 6890 series injector and autosampler (Hewlett Packard Co., CA, USA).
- An HP-5MS 5% Phenyl Methyl Siloxane capillary column (30 m × 0.25 mm I.D. × 0.25 μm film thickness, Hewlett Packard Co., CA, USA). The column length of 30 m provides a good compromise between resolution and speed of analysis. The column diameter of 250 μm represents the best concession between resolution, speed, sample capacity, and ease of operation. A standard film thickness of 0.25 μm represents a compromise between the high resolution attainable with thin films and the high capacity available with thick films.
- An HP Chemstation software (Hewlett Packard Co., CA, USA).
- A 10 μL autosampler syringe.
- 2 mL vials.
- 4 mL wash vials.

3.2 Chemicals and Samples

- Helium gas was employed as a carrier gas.
- The HPLC grade dichloromethane (Aldrich Chemical Co., MI, USA) was used as a solvent.
- As toluene and xylenes were expected to be present in the samples, they were used to prepare standard solutions.
- Eight samples of produced water were categorized into three groups: non-ozonated samples indicated with *NO*, partially ozonated (ozonated for 5 minutes) samples indicated with *O5*, and prolonged ozonation (50 min) samples indicated with *O50* These samples came from Company A, Company B, and a synthetic produced water (SPW). The samples from Company A and Company B included all three groups,

while those from SPW included only non-ozonated and prolonged ozonated samples. Later, four Company A samples ozonated for different time periods were provided to study the effect of ozonation time on the chemical composition in the sample.

3.3 Experimental Procedure

This study consisted of two phases:

I. Identifying the parent compounds, intermediates, and oxidation by-products in the non-ozonated samples, partially ozonated samples, and samples ozonated for 50 minutes.
II. Comparing the compounds in the samples that underwent oxidation by ozone for different time periods.

The principal procedures included the following steps:

1. Preparing 1000 ppm stock standard solutions by spiking chemicals into 10 mL of dichloromethane. Diluting the solutions with dichloromethane to 20 ppm and filling them in 2 mL vials. These solutions were used as reference.
2. Varying the temperature program, pressure, and helium gas flow rate by considering temperature programs from the literature. The goal was to achieve the optimal program that gives the best results.
3. Employing the autosampler to inject 1 μL of solution into the GC-MS system.
4. Identifying organic compounds in the sample by using the NBS75K library.

The performance of the GC-MS system was verified with the experimental configuration and conditions summarized in Table A-1. The quadrupole mass selective detector was operated under the scan mode to obtain spectral data for identifying the compounds.

Table A-1: Instrument Conditions

Gas Chromatograph	
Oven Program:	38°C, 4 min; 10°C/min to 250°C and hold for 2 min.
Carrier Gas:	Helium, 1.2 mL/min
Injector Temperature:	250°C
Mass Spectrometer	
Ion Source Temperature:	230°C
Quadrupole Temperature:	160°C
Solvent Delay:	4 min
Electron Energy:	70 eV
Mass Range:	50-550 a.m.u.
Scans/sec:	1.5

The experimental results were obtained by using the ChemStation integrator and the default integration events, shown in Table A-2.

Table A-2: Integration Events

Initial Area Reject:	1
Initial Peak Width:	0.02
Shoulder Detection:	OFF
Initial Threshold:	18

4. EXPERIMENTAL RESULTS

The experimental results were given in terms of the highest match quality. Some statistics, such as percent impurity, confidence factor, contamination factors can also be obtained by using the ChemStation software. Since these values followed the same trend as the match quality, only the highest match quality is shown in the results.

4.1 Standard Solutions

As toluene and xylenes are expected to be present in the samples, they were used to make standard solutions. Three solutions - (1) toluene solution, (2) xylenes solution, and (3) toluene-xylenes mixture - were prepared. Figure A-1 shows the chromatogram of toluene separation. One significant peak was found at retention time (RT) about 4.35 min. This peak was identified as toluene with 94% match quality. In addition, there are 6 very small peaks at 18.90, 20.62, 22, 23, 24, and 26 min. A similar chromatogram was obtained in the separation of xylenes solution as shown in Figure A-2. The peak appeared at 7.37 min and the library recognized it as *p*-xylene with 97% match quality. Six small peaks were also observed but at a lower value of abundance as compared to those in toluene solution. Two high peaks are shown in Figure A-3, which presents the chromatogram of toluene-xylenes mixture. The first one appeared at 4.36 min, which is toluene, while the second one appeared at 7.37 min, which is *p*-xylene. The separation of this mixture gave the same percent match quality as in the separation of the single compound solutions. Those six small peaks observed in the separation of toluene and xylenes solutions are still present in this chromatogram.

4.2 Sample Solutions (Phase I)

4.2.1 Sample Solutions of Company B

Company B *NO* sample represents non-ozonated produced water. Several peaks were observed in the chromatogram, as shown in Figure A-4. Most of them fall in the range of 10.39 to 19.36 min RT. As expected, toluene and *p*-xylene were found to be present in this sample. The baseline is unstable; it increased its slope at 10 min, decreased after 12.59 min, and then reached a stable state around 26 min. The percent match quality values are not as good as those obtained in the separation of standard solutions but they represent the best results of all the experimental runs for this sample. The results confirmed the presence of cyclopentanecarboxylic acid, cyclopentaneacetic acid, and cyclohexanecarboxylic acid in the sample.

Company B *O5* sample represents produced water that was oxidized by ozone for 5 min. Figure A-5 shows that the peaks observed in the *NO* are still present in the *O5* sample and about 10 new peaks appeared. These new compounds have relative high abundance as compared to the compounds found in the *NO* sample. The highest peak was identified as 2,4-dibromopentane. Toluene and xylenes were not detected in this chromatogram. The baseline has the same trend as in the *NO* sample.

Company B *O50* sample represents produced water after prolonged (50 min.) ozonation. Figure A-6 illustrates that some compounds that were formed under partial oxidation still appear in this chromatogram, while some are gone especially the highest peak, 2,4-dibromopentane. The compounds found in the *NO* sample also disappeared. The small peaks, which were found in the toluene and xylenes solutions but not in Company B *NO* and *O50* samples, appear in this case. The baseline of this chromatogram is stable.

4.2.2 Sample Solutions of Company A

The chromatogram of Company A *NO* sample has an unstable baseline in the first 12 min and then reaches a stable state, as shown in Figure A-7. Most of the peaks were also displayed in the first 12 min. Small peaks in the range of 18 to 26 min were also found, and some of them showed relatively high abundance. The results illustrate that the sample contains toluene and *p*-xylene. The compounds found in this sample are quite different from those found in the Company B *NO* sample. The library identified that this sample contains propanoic, butanoic, and pentanoic acids (in some cases methyl-substituted).

Figure A-8 demonstrates that new compounds were created in the Company A *O5* sample. Most of them are similar to those created in the Company B *O5* sample. Most of the peaks found in Company A *NO* sample disappeared. Acids such as hexanoic acid, heptanoic acid, and octanoic acid were discovered while propanoic acid disappeared. However, butanoic acid and pentanoic acid were still present in the sample.

Figure A-9, the chromatogram of the Company A *O50* sample, is similar to Figure A-6. The difference is the level of abundance. Moreover, the Company A *O50* sample seems to show more peaks than the Company B *O50* sample.

4.2.3 Sample Solutions of SPW

SPW *NO* sample displayed fewer peaks than the other *NO* samples, as shown in Figure A-10. Toluene and *p*-xylene were found in this case. The highest peak was identified as 3-methyl-2-buten-1-ol. The peaks at RT of 14.69, 16.91, 18.90, and 20.62 min, which were also identified in the Company A *NO* sample, were found in relatively high abundance.

SPW *O50* sample has a similar chromatogram (Figure A-11) as those of Company A *O50* and Company B *O50* samples, but with a smaller number of peaks than the Company A *O50* sample.

4.3 Sample Solutions (Phase II)

These samples came from experiment with filtered Company A produced water. They went through the ozone oxidation process for different time periods. Figure A-12 displays the chromatogram of sample *A18-2* that was ozonated for 3 minutes. Two peaks were discovered at 9.11 and 9.56 min RT and were identified as 2-ethyl-4-methyl-1,3-dioxolane and 1-bromo-3-methyl-2-butene, respectively.

The chromatograms of samples *A18-6* (35-min ozonation) and *A18-10* (180-min ozonation) (Figure A-13 and A-14) exhibited similar results but different from those of sample *A18-2*. There were three peaks at RT of 7.04, 7.47, and 9.20 min and were recognized as butanamide, 2,2-dichloropentane, and 1,3-dibromo-3-methylbutane, respectively. The chromatogram of sample *A18-11* (24-hr ozonation) shown in Figure A-15 presents almost the same results as those of samples *A18-6* and *A18-10* but has one peak less. The compounds found in this sample are butanamide and 2,2-dichloropentane. One can notice that these chromatograms have much fewer peaks than those of partially and completely ozonated samples.

5. DISCUSSION

Varying the temperature program, pressure, and flow rate has effect on the separation of compounds. The retention time and percent match quality depend on the conditions used. However, the shapes of all chromatograms for each sample are the same irrespectively of the conditions employed. The results presented in this report are the best results obtained based on the percent match quality.

5.1 Standard Solutions

The HP-5MS column exhibited a good capability to separate toluene and xylenes. Toluene was separated at temperature around 38.6°C while *p*-xylene was separated at 68.8°C. The small peaks observed in all chromatograms of standard solutions may come from the solvent itself or some contaminants in the column.

5.2 Sample Solutions (Phase I)

The intermediates and by-products of the ozone oxidation process were expected to include oxygen atom. One can see, however, that some of the intermediates and by-products of both partially and completely ozonated samples do not contain any oxygen atom. This phenomenon may be due to reactions between the compounds in the samples and radicals formed by ozone destruction.

5.2.1 Sample Solutions of Company B

Most of the peaks in the chromatogram of the Company B *NO* sample are able to separate in the range of temperature of 110°C to 165°C. The unstable baseline may be a result of contamination of the column or impurities in the sample. The small peaks could not be identified because their abundances are low as compared to other compounds in the sample. The obtained match quality showed that this column is unable to separate very well the unknown compounds in the sample.

The results of the Company B *O5* sample showed that new compounds are created during the ozonation process while the compounds found in the Company B *NO* sample are still present in the sample. Comparing these results to the results obtained in the separation of 50-min. ozonated Company B sample (Figure A-6), one can see that some compounds that are created in the partially oxidizing step disappear but others are still present in the sample. This observation indicates that the compounds that have disappeared in the 50-min. ozonated sample are intermediates. On the other hand, the compounds that are still present in the 50-min. ozonated sample are considered as ozonation by-products.

In the prolonged (50 min.) ozonation process, some new products that had not been found in the previous two samples are formed. These are considered as by-products as well. The intermediates of ozonation of Company B samples are 2-ethyl-4-methyl-1,3-dioxolane, 1,3-dibromo-3-methylbutane, and 4-nitrophenyl-ester-2-butenoic acid, and the by-products are 1-bromo-3-methyl-2-butene, dibromochloromethane, 2,3-dichloro-2-methylbutane, butanamide, tribromomethane, and 2,2-dichloropentane. Among the oxidation by-products only butanamide contains oxygen atom, while the others contain halogen atoms.

5.2.2 Sample Solutions of Company A

For Company A, the non-ozonated results are different from those of Company B. Most of the compounds were located in the temperature range of 35°C to 120°C. This sample contains fatty acids, which were not discovered in the Company B sample. Some peaks in this chromatogram consist of silicon atom, which may come from the column itself. These peaks are also found in some of the other samples but at very low abundance. They appear in this chromatogram at very high concentration because the concentration of other compounds in the sample is low compared to the other samples.

The only compound, found in both non-ozonated and 5-min. ozonated samples, is butanoic acid while the others are all gone. This result may be a consequence of the concentrations of compounds in the non-ozonated sample, which are greatly smaller than those in the partially oxidation sample. Some of the new compounds are similar to those found in the Company B *O5* sample.

It is interesting to note that the disappeared substances in the 5-min. ozonated sample are discovered in the 50-min. ozonated sample. This phenomenon may be explained by the concentration effect. The intermediates of ozonation for the Company A samples are 1,4-dibromopentane, 1,3-dibromo-3-methylbutane, hexanoic acid, heptanoic acid, and octanoic acid. The by-products are 1-bromo-3-methyl-2-butene, dibromochloromethane, butanamide, tribromomethane, 2,2-dichloropentane, 2-piperidinone, and 3-hexene-2-one.

5.2.3 Sample Solutions of SPW

Substances that consist of silicon atom are found in the non-ozonated SPW sample. All of them are also found in the non-ozonated Company A sample. The reasons for that were discussed in Section 5.2.2.

Fifty-minute ozonation produces almost every compound as found with the Company A sample. The results confirmed that toluene and *p*-xylene are not destroyed under ozonation. Since there was no 5-min. ozonation sample from SPW, the ozonation intermediates cannot be detected. The ozonation by-products are 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane.

5.3 Sample Solutions (Phase II)

The compounds found in *A18-2* are dissimilar to those in *A18-6*, *A18-10*, and *A18-11*. However, when these compounds were compared to the substances in the 5-min. and 50-min. ozonated Company A samples, it was found that the first compound is an intermediate and the second one is a by-product. This result indicates that after the sample undergoes ozonation for a few minutes, the intermediate, 2-ethyl-4-methyl-1,3-dioxolane, is formed as well as the by-product, 1-bromo-3-methyl-2-butene. By continuing the ozonation for several minutes, those compounds in the first sample disappear, while two products and an intermediate are formed. These products are butanamide and 2,2-dichloropentane. The intermediate is 1,3-dibromo-3-methylbutane. The chromatograms of *A18-6* and *A18-10* are identical. Maintaining the ozonation for a longer time (*A18-11*), the intermediate disappears, while the two by-products are still present in the sample.

6. CONCLUSIONS

A GC-MS instrument accompanied with the HP Chemstation software and using the NBS75K library was employed in this study to identify ozonation products of produced water. The results were obtained by means of match quality. The quality of some identified compounds, however, was not high enough, which indicates that the HP-5MS capillary column is not the best column to separate these compounds and the samples themselves may have some impurities.

All the results demonstrate that ozonation may be used to destroy some organic compounds. On the other hand, ozonation also creates by-products. Some of the ozonation by-products of Company A, Company B, and SPW samples are the same. The common ozonation by-products are 1-bromo-3-methyl-2-butene, butanamide, tribromomethane, and 2,2-dichloropentane. There are some intermediates formed during the ozonation process. Each intermediate or by-product is formed at different ozonation periods.

The non-ozonated Company B sample includes the most compounds as compared to the other samples. The main compounds are cyclopentanecarboxylic acid, cyclopentaneacetic acid, and cyclohexanecarboxylic acid. The compounds of Company A samples are fatty acids such as butanoic acid and pentanoic acid. The results of SPW samples are pretty much the same as those of Company A but with fewer compounds. None of the fatty acids is found in any of the SPW samples.

7. REFERENCES

Dutta, T.K. and Harayama, S., “Analysis of Long-Side-Chain Alkylaromatics in Crude Oil for Evaluation of Their Fate in the Environment,” *Environ. Sci. Technol.*, **35**, 102-107, 2001.

Feigel, C. and Holmes, W., “The Determination of Polyaromatic Hydrocarbons,” *Varian Application Note: Number 10*, www.varian.com.

Glover, C.J. and Bullin, J.A., “Identification of Heavy Residual Oils by GC and GC-MS,” *J. Env. Sci. & Health*, **A24**, 57-75, 1989.

Maldonado, C., Bayona, J.M., and Bodineau, L., “Sources, Distribution, and Water Column Processes of Aliphatic and Polycyclic Aromatic Hydrocarbons in the Northwestern Black Sea Water,” *Environ. Sci. Technol.*, **33**, 2693-2702, 1999.

McNair, H.M. and Miller, J.M., “*Basic Gas Chromatography*,” John Wiley & Sons, Inc., New York, 1998.

Zeng, Y., Hong, P.K.A., and Wavrek, D.A., “Integrated Chemical-Biological Treatment of Benzo[*a*]pyrene,” *Environ. Sci. Technol.*, **34**, 854-862, 2000.

CHROMATOGRAMS OF ALL SAMPLES

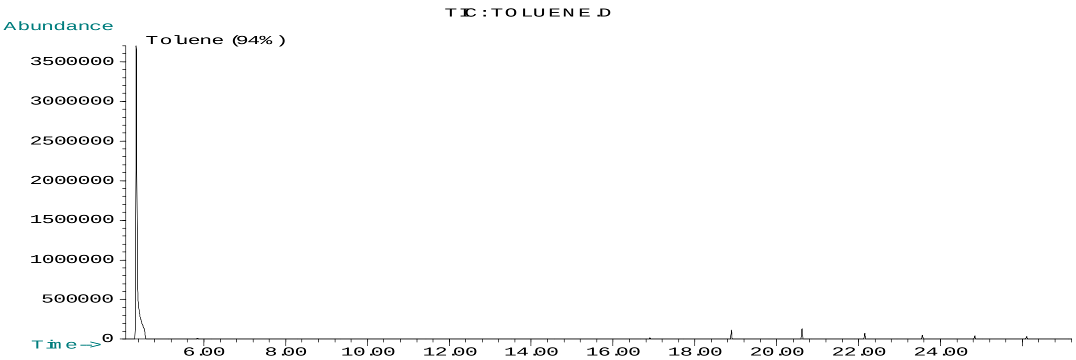


Figure A-1. Chromatogram of toluene solution.

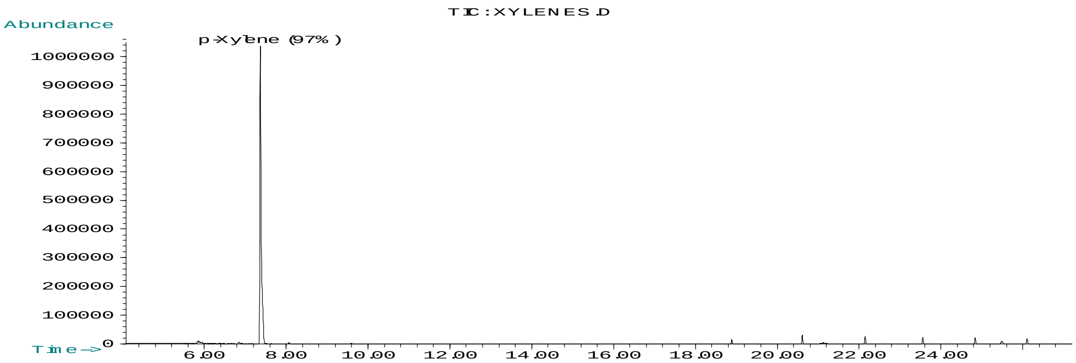


Figure A-2. Chromatogram of xylenes solution.

Figure A-3. Chromatogram of toluene-xylenes mixture.

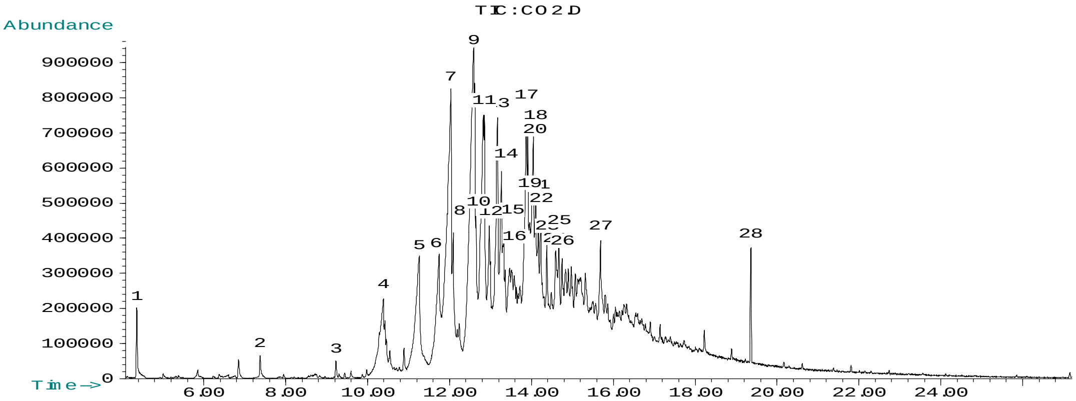


Figure A-4. Chromatogram of non-ozonated Company B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	90
2	7.38	*p*-Xylene	C_8H_{10}	95
3	9.23	Phenol	C_6H_6O	97
4	10.39	Cyclopentanecarboxylic acid	$C_6H_{10}O_2$	74
5	11.26	Cyclobutanecarboxylic acid, 2,2-dimethyl	$C_7H_{12}O_2$	17
6	11.75	Cyclopentaneacetic acid	$C_7H_{12}O_2$	53
7	12.04	Cyclohexanecarboxylic acid	$C_7H_{12}O_2$	76
8	12.09	2(3H)-Furanone, dihydro-4,5-dimethyl	$C_6H_{10}O_2$	38
9	12.59	Cyclohexanemethanol	$C_7H_{14}O$	43
10	12.65	Cyclopentane, 1-methyl-3-(1-methylethyl)	C_9H_{18}	49
11	12.85	2-Octenal, (E)-	$C_8H_{14}O$	46
12	12.97	Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-	C_9H_{16}	43
13	13.17	1,10-Dicyanodecane	$C_{12}H_{20}N_2$	35
14	13.27	Cyclohexane, 1-pentyl-	$C_{11}H_{20}$	35
15	13.33	1,4-Hexadiene, 2-methyl-	C_7H_{12}	38
16	13.47	Undecylenic acid	$C_{11}H_{20}O_2$	52
17	13.87	Cyclopentaneundecanoic acid	$C_{16}H_{30}O_2$	38
18	13.92	Cyclohexanemethanol, 4-methyl-,trans-	$C_8H_{16}O$	38
19	13.96	Cyclohexane, 1-ethyl-4-methyl-,cis-	C_9H_{18}	35
20	14.05	Cyclohexanemethanol, 2-methyl-	$C_8H_{16}O$	47
21	14.11	Cyclopropanemethanol,2,2,3,3-tetramethyl-	$C_8H_{16}O$	38
22	14.23	Cyclohexane, methylene	C_7H_{12}	30
23	14.38	Cyclohexane, ethylidene-	C_8H_{14}	50
24	14.60	1-Methyl-2-methylenecyclohexane	C_8H_{14}	45
25	14.67	Cyclohexanemethanol, 4-methyl-,cis	$C_8H_{16}O$	47
26	14.75	1-Hexadecyne	$C_{16}H_{30}$	53
27	15.69	1-Methyl-3-(1'methylcyclopropyl)cyclopentene	$C_{10}H_{16}$	38
28	19.36	Cyclopentane, 1,1'-ethylidenebis	$C_{12}H_{22}$	50

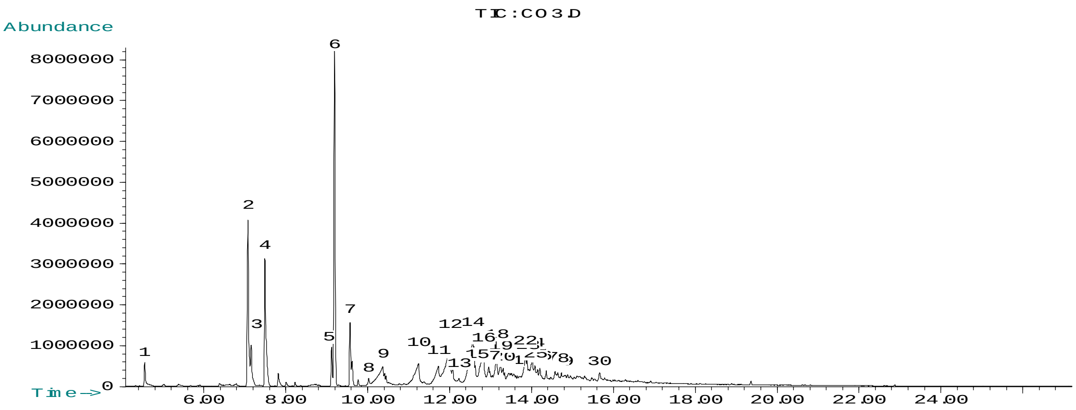


Figure A-5. Chromatogram of partially oxidized (5-min ozonation) Company B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	7.08	Butanamide	C_4H_9NO	45
3	7.16	Methane, Tribromo-	$CHBr_3$	97
4	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25
5	9.12	1,3-Dioxolane, 2-ethyl-4-methyl-	$C_6H_{12}O_2$	59
6	9.19	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	43
7	9.57	2-Butene,1-bromo-3-methyl	C_5H_9Br	32
8	10.02	2-Butenoic acid, 4-nitrophenyl ester	$C_{10}H_9NO_4$	37
9	10.38	Cyclopentanecarboxylic acid	$C_6H_{10}O_2$	83
10	11.24	Cyclobutanecarboxylic acid, 2,2-dimethyl	$C_7H_{12}O_2$	35
11	11.73	Cyclopentaneacetic acid	$C_7H_{12}O_2$	59
12	12.02	Cyclohexanecarboxylic acid	$C_7H_{12}O_2$	93
13	12.08	Pentanal, 3-(hydroxymethyl)-4,4-dimethyl	$C_8H_{16}O_2$	32
14	12.57	Cyclohexanemethanol	$C_7H_{14}O$	47
15	12.63	Cyclopentane, 1-methyl-3-(1-methylethyl)	C_9H_{18}	46
16	12.84	3-Octyne, 2-methyl-	C_9H_{16}	30
17	12.96	Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-	C_9H_{16}	43
18	13.16	1,10-Dicyanodecane	$C_{12}H_{20}N_2$	35
19	13.25	Cyclohexene, 1-pentyl-	$C_{11}H_{20}$	43
20	13.31	Benzocyclodecene, tetradecahydro-	$C_{14}H_{26}$	43
21	13.45	1-Heptadecyne	C_7H_{32}	43
22	13.49	5-Eicosyne	$C_{20}H_{32}$	38
23	13.86	Cyclopentane, 1,1'-ethylidenebis	$C_{12}H_{22}$	43
24	13.89	Cyclohexane, 1-(cyclohexylmethyl)	$C_{13}H_{24}$	50
25	14.03	m-Menthane, (1S,3R) - (+) -	$C_{10}H_{20}$	43
26	14.09	Cyclohexane, 1-ethyl-4-methyl-,cis-	C_9H_{18}	43
27	14.21	Cyclohexane, methylene	C_7H_{12}	43
28	14.37	Cyclohexane, ethylidene-	C_8H_{14}	46
29	14.58	Methylenecyclooctane	C_9H_{16}	55
30	14.73	Cyclohexanol, 5-methyl-2-(1-methylethenyl)-	$C_{10}H_{18}O$	78
31	15.66	1-Methyl-3-(1'methylcyclopropyl)cyclopentene	$C_{10}H_{16}$	38

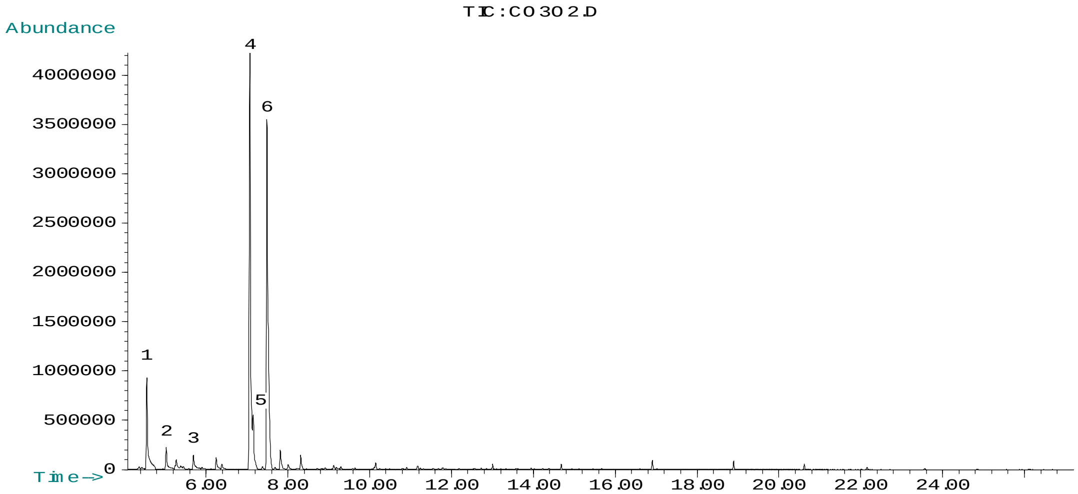


Figure A-6. Chromatogram of prolonged (50 min.) ozonated Company B sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	5.03	Methane, dibromochloro	$CHBr_2Cl$	97
3	5.70	Butane, 2,3-dichloro-2-methyl-	$C_5H_{10}Cl_2$	90
4	7.08	Butanamide	C_4H_9NO	45
5	7.16	Methane, Tribromo-	$CHBr_3$	95
6	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25

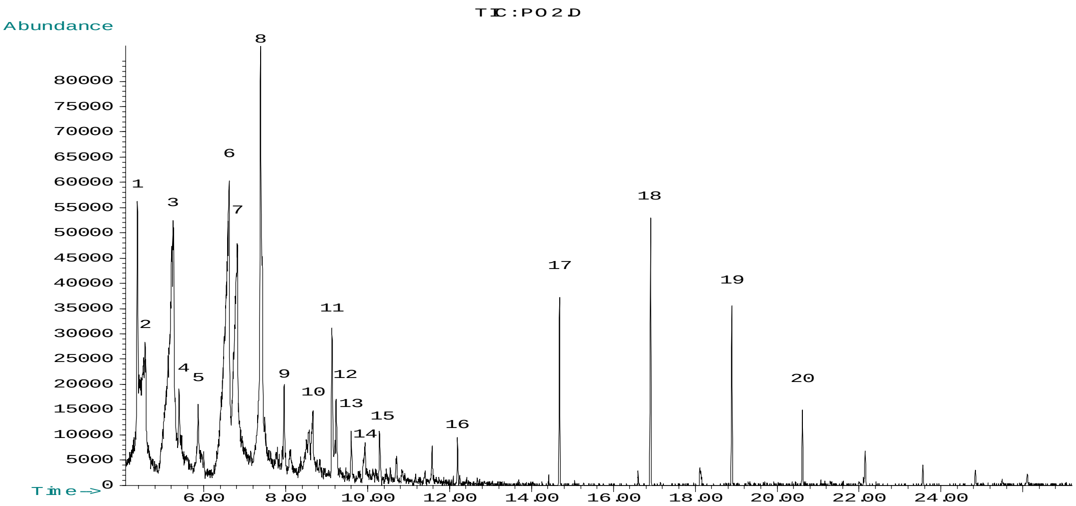


Figure A-7. Chromatogram of non-ozonated Company A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.38	Toluene	C_7H_8	58
2	4.56	Propanoic acid, 2-methyl-	$C_4H_8O_2$	53
3	5.25	Butanoic acid	$C_4H_8O_2$	86
4	5.39	Ethanol, 2-[(2-ethylhexyl)oxy]-	$C_{10}H_{22}O_2$	40
5	5.86	Cyclotrisiloxane, hexamethyl	$C_6H_{18}O_3Si_3$	78
6	6.62	Butanoic acid, 3-methyl-	$C_5H_{10}O_2$	39
7	6.82	Pentanoic acid, methyl ester	$C_6H_{12}O_2$	25
8	7.38	*p*-Xylene	C_8H_{10}	91
9	7.96	Bicyclo[2.2.2]octane, 1-bromo-4-methyl	$C_9H_{15}Br$	38
10	8.66	Pentanoic acid, 4-methyl-	$C_6H_{12}O_2$	9
11	9.13	1,4-Dioxane, dimethyl	$C_6H_{12}O_2$	59
12	9.23	Phenol	C_6H_6O	80
13	9.60	Cyclotetrasiloxane, octamethyl	$C_8H_{24}O_4Si_4$	56
14	9.94	Azetidine, 1-nitroso-	$C_3H_6N_2O$	7
15	10.29	Cycloheptene, methyl	C_8H_{14}	40
16	12.20	Cyclopentasiloxane, decamethyl-	$C_{12}H_{36}O_4Si_5$	56
17	14.68	Cyclohexansiloxane, dodecamethyl-	$C_{12}H_{32}O_6Si_6$	78
18	16.91	1,1,1,3,5,7,9,9,9-Nonamethylpentasiloxane	$C_9H_{30}O_4Si_5$	38
19	18.90	Silane, [[4-[1,2-bis[(trimethylsilyl)oxy]ethyl]-1,2-phenylene]bis(oxy)]bis[trimethyl-	$C_{20}H_{42}O_4Si_4$	37
20	20.62	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	$C_{13}H_{40}O_5Si_6$	59

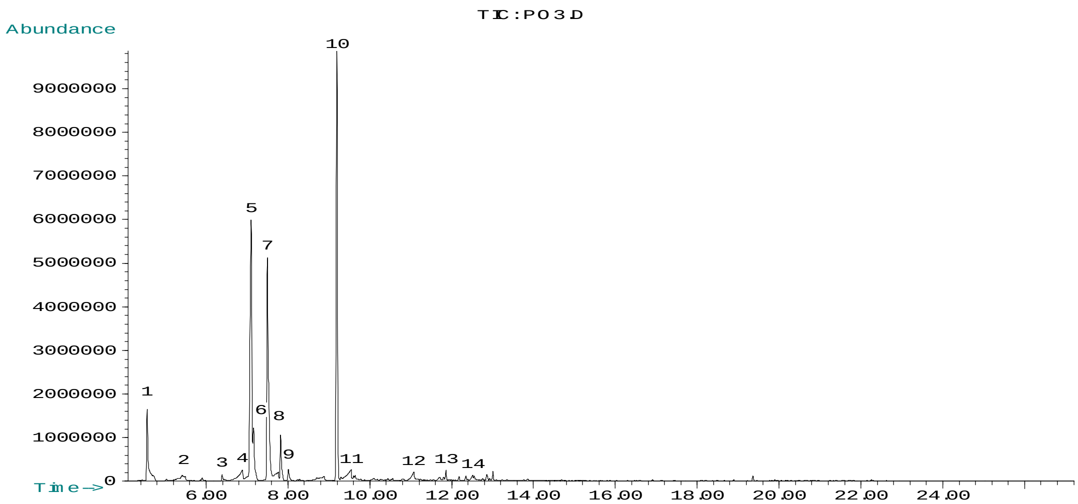


Figure A-8. Chromatogram of partially oxidized (5-min ozonation) Company A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	86
2	5.42	Butanoic acid	$C_4H_8O_2$	58
3	6.39	2-Butene,1-bromo-3-methyl	C_5H_9Br	80
4	6.89	Butanoic acid, 3-methyl-	$C_5H_{10}O_2$	64
5	7.10	Butanamide	C_4H_9NO	45
6	7.16	Methane, Tribromo-	$CHBr_3$	96
7	7.50	Pentane,2,2-dichloro	$C_5H_{10}CI_2$	25
8	7.76	Pentanoic acid	$C_5H_{10}O_2$	78
9	8.01	Pentane,1,4-dibromo	$C_5H_{10}Br_2$	53
10	9.20	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	43
11	9.54	Hexanoic acid	$C_6H_{12}O_2$	83
12	11.08	Heptanoic acid	$C_7H_{14}O_2$	87
13	11.86	Bromisovalum	$C_9H_{18}O_3Br$	38
14	12.51	Octanoic acid	$C_8H_{16}O_2$	72

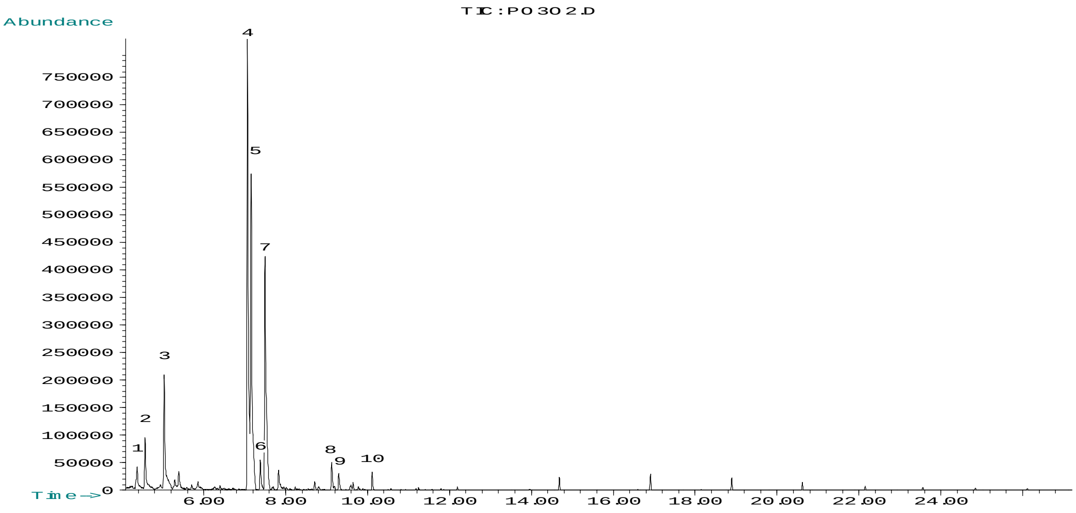


Figure A-9. Chromatogram of prolonged (50 min.) ozonated Company A sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	70
2	4.57	2-Butene,1-bromo-3-methyl	C_5H_9Br	72
3	5.03	Methane, dibromochloro	$CHBr_2Cl$	97
4	7.06	Butanamide	C_4H_9NO	59
5	7.15	Methane, Tribromo-	$CHBr_3$	94
6	7.38	*p*-Xylene	C_8H_{10}	95
7	7.49	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	33
8	9.13	1,4-Dioxane, dimethyl	$C_6H_{12}O_2$	53
9	9.29	2-Piperidinone	C_5H_9NO	89
10	10.11	3-Hexen-2-one	$C_6H_{10}O$	50

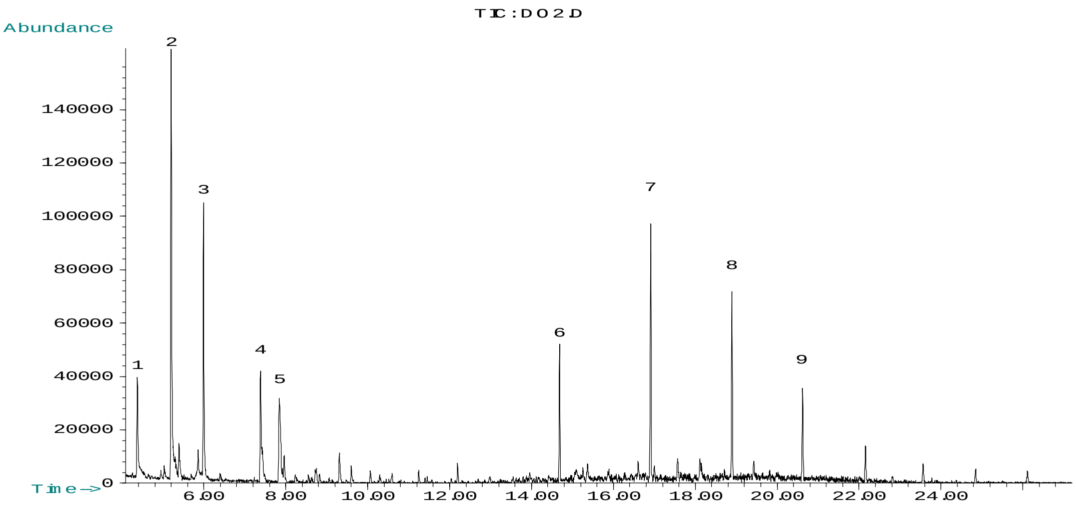


Figure A-10. Chromatogram of non-ozonated SPW sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.38	Toluene	C_7H_8	83
2	5.20	3-Buten-2-ol,2-methyl	C_5H_8O	43
3	5.99	3-Penten-2-ol	$C_5H_{10}O$	43
4	7.38	*p*-Xylene	C_8H_{10}	95
5	7.85	Ethane, 1,1,2,2-tetrachloro-	$C_2H_2Cl_4$	90
6	14.69	Cyclohexasiloxane, dodecamethyl-	$C_{12}H_{32}O_6Si_6$	83
7	16.91	1-(3-Hydroxy-4-methylphenyl)-1,3,3,6-tetramethylindan-5-ol	$C_{20}H_{24}O_2$	27
8	18.90	Silane, [[4-[1,2-bis[(trimethylsilyl)oxy]ethyl]-1,2-phenylene]bis(oxy)]bis[trimethyl-	$C_{20}H_{42}O_4Si_4$	47
9	20.62	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	$C_{13}H_{40}O_5Si_6$	25

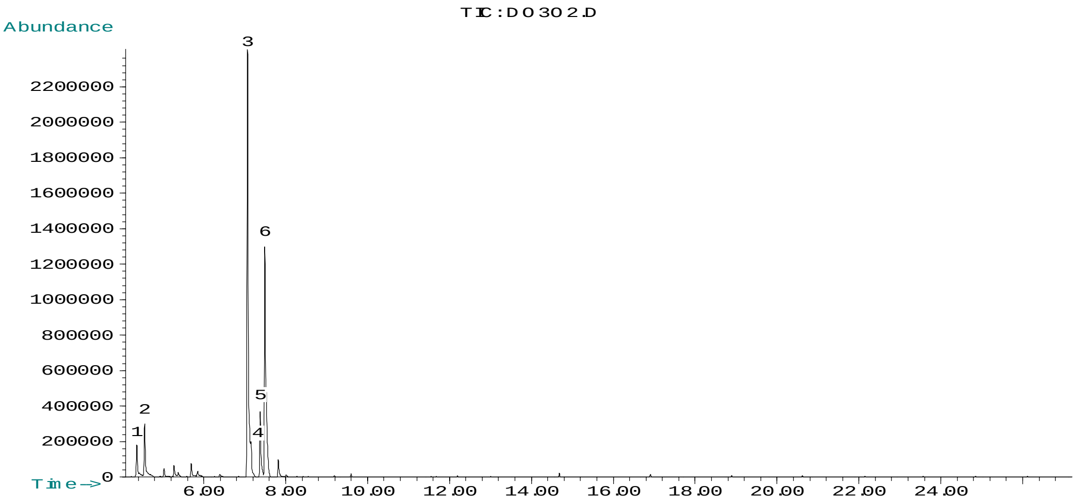


Figure A-11. Chromatogram of prolonged (50 min.) ozonated SPW sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	4.37	Toluene	C_7H_8	91
2	4.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	72
3	7.07	Butanamide	$C_5H_{10}Cl_2$	45
4	7.15	Methane, Tribromo-	$CHBr_3$	95
5	7.38	*p*-Xylene	C_8H_{10}	97
6	7.49	Pentane, 2,2-dichloro	$C_5H_{10}Cl_2$	25

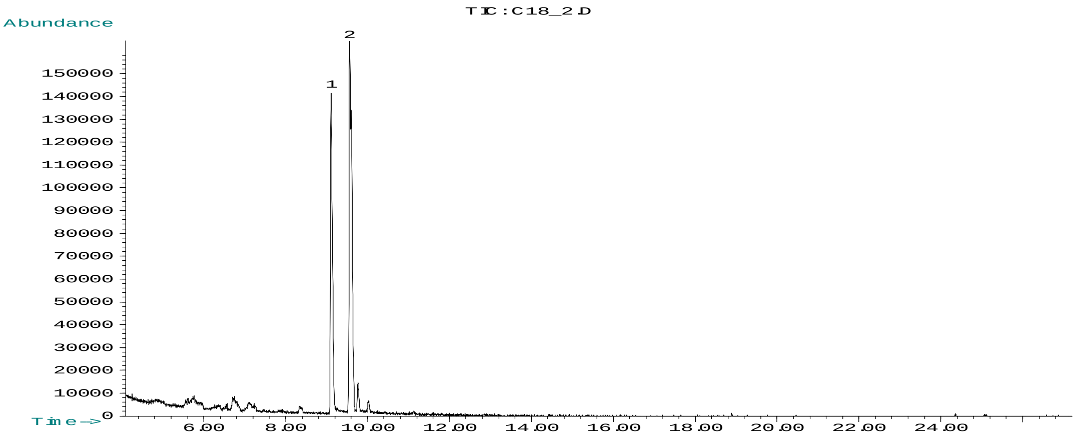


Figure A-12. Chromatogram of Company A (*A18-2*) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	9.11	1,3-Dioxolane, 2-ethyl-4-methyl-	$C_6H_{12}O_2$	50
2	9.56	2-Butene,1-bromo-3-methyl	C_5H_9Br	38

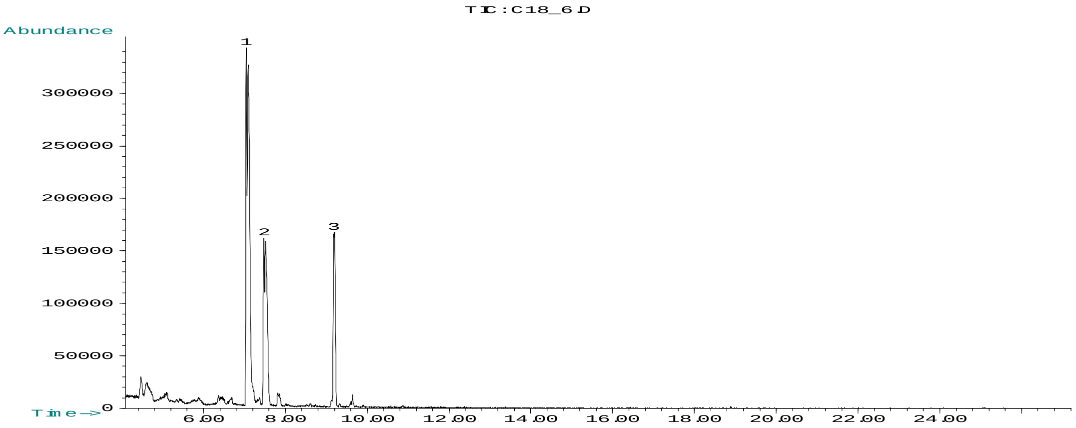


Figure A-13. Chromatogram of Company A (*A18-6*) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	7.04	Butanamide	C_4H_9NO	45
2	7.47	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	25
3	9.20	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	64

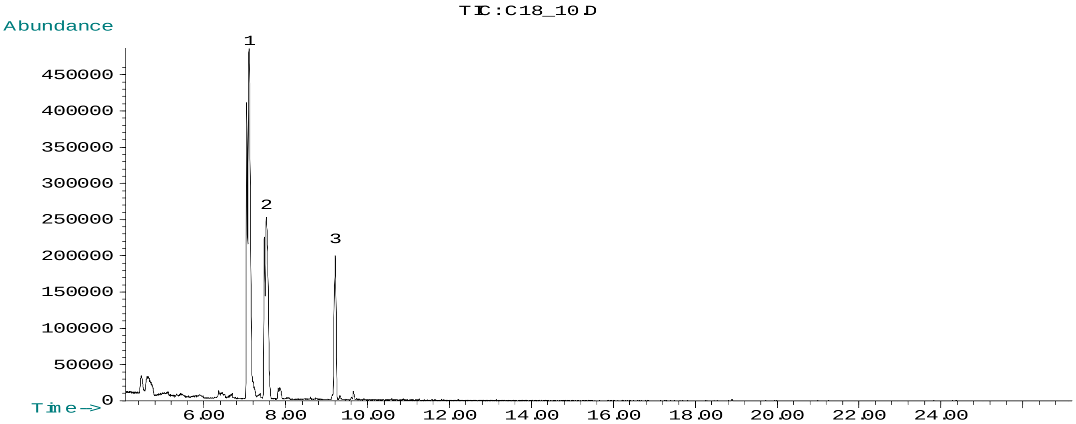


Figure A-14. Chromatogram of Company A (*A18-10*) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	7.05	Butanamide	C_4H_9NO	42
2	7.48	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	36
3	9.21	Butane, 1,3-dibromo-3-methyl	$C_5H_{10}Br_2$	40

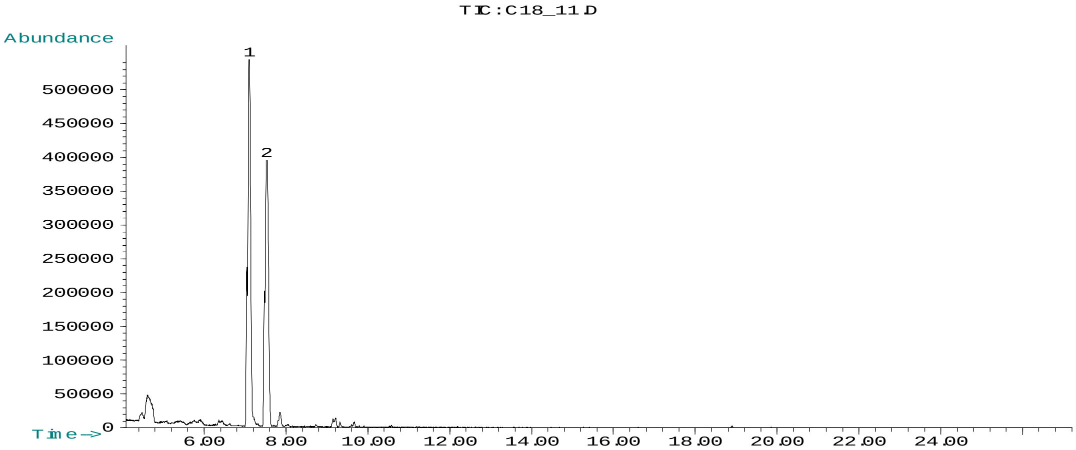


Figure A-15. Chromatogram of Company A (*A18-11*) sample.

Peak	RT	COMPOUND	FORMULA	QUAL
1	7.04	Butanamide	C_4H_9NO	53
2	7.47	Pentane,2,2-dichloro	$C_5H_{10}Cl_2$	17

INTERNAL DISTRIBUTION

1. R. M. Counce
2. B. H. Davison
3. D. W. DePaoli
4. M. D. Dinsmore
5. S. A. Jones
6. R. R. Judkins
7. K. T. Klasson
8. S. M. Robinson
9. T. W. Schmidt
10. C. Tsouris
11. A. B. Walker
12. Central Research Library
13. ORNL Laboratory Records, RC

14–15. ORNL Laboratory Records, OSTI

EXTERNAL DISTRIBUTION

16. V. R. Blackwell, Chevron Texaco ERTC, 100 Chevron Way, P.O. Box 1627, Richmond, CA 94802
17. D. Bourg, Phillips Petroleum Company, 6330 West Loop South, Bellaire, TX 77401
18. N. C. Comstock, DOE National Petroleum Technology Office, P.O. Box 3628, Tulsa, OK 74101
19. M. Dubrovsky, Chevron Texaco ERTC, 100 Chevron Way, P.O. Box 1627, Richmond, CA 94802
20. Mona Hjelsvold, Statoil R&D Centre, Postuttak, Trondheim, Norway N-7005
21. S.-I. Johnson, Technology Resources, T&PD, 241 CPL, Phillips Research Center, Bartlesville, OK 74004
22. Z. I. Khatib, SIEP, SEPTAR-AWW, Volmerlaan 8, 2288 GD, Rijswijk, Netherlands
23. N. J. Spiridakis, Chevron Texaco ERTC, 100 Chevron Way, P.O. Box 1627, Richmond, CA 94802
24. D. Sutterfield, DOE National Petroleum Technology Office, P.O. Box 3628, Tulsa, OK 74101
25. V. Vithayaveroj, School of Civil and Environmental Engineering, Georgia Institute of Technology, 200 Bobby Dodd Way, Atlanta, GA 30332-0512.
26. S. Z. Yiacoumi, School of Civil and Environmental Engineering, Georgia Institute of Technology, 200 Bobby Dodd Way, Atlanta, GA 30332-0512.