OZONE TREATMENT OF SOLUBLE ORGANICS IN PRODUCED WATER (FEAC307)

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Milestone Report:
Letter Report with the Summarized Results from Continuous-flow Testing

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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%. By 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. GOM 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 is an extension of previous research to improve the applicability of ozonation and will help address the petroleum industry-wide problem of treating water containing soluble organics. The goal of this project is to maximize oxidation of water-soluble organics during a single-pass operation. The project investigates: (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. Industrial collaborators include Chevron, Shell, Phillips, BP Amoco, Statoil, and Marathon Oil through a joint project with the Petroleum Environmental Research Forum (PERF).

The research and demonstration program consists of three phases:

1. Laboratory testing in batch reactors to compare effectiveness of organics destruction using corona discharge ozone generation methods with hydrogen peroxide 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. Field testing of a prototype system in close collaboration with an industrial partner to generate performance data suitable for scale-up and economic evaluation.

INTRODUCTION

Ozone is an extremely powerful oxidant that can attack organic materials and convert them to nonhazardous products. Ozone is sparingly soluble in water. It has been determined that the main limitation in ozonation systems comes from the low mass transfer rate of ozone from the gas phase to the liquid phase (Gurol and Singer, 1983; Gurol, 1985; Gurol and Vatistas, 1987; Yurteri and Gurol, 1987; Zhu et al., 1989; Xu and Liu, 1990). 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 (Gurol and Singer, 1983; Xu and Liu, 1990; Zhou et al., 1994). 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 (Ahmad and Farooq, 1983; Sharma, 1993). 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.

During the first year of study, laboratory testing in batch reactors was conducted to compare effectiveness of organics destruction using hydrogen peroxide generated sonochemically and ozone generated via corona discharge. In the batch experiments, three water matrix types were used: (1) benzene, toluene, ethylbenzenes, xylenes, and hexanoic acid (BTEXH) in deionized water, (2) BTEXH in salt water (100 g/L), and (3) salt water as described in ASTM D1141-90 (less trace metals) mixed with light crude from the Gulf of Mexico. The results of that testing are summarized as follows:

- Sonochemical oxidation destroyed some compounds such as BTEX; however, no destruction of hexanoic acid was measured. Because of the relatively slow destruction of BTEX at significant power levels ($k \approx 0.07$ min^{-1} at 0.5 W/L), and no destruction of hexanoic acid, further testing of the sonochemical technique was not pursued.
- Effective destruction of hexane-extractable materials was achieved by ozonation in a reasonable time period (less than 5 minutes). Improved ozonation rates were achieved by enhancing mass transfer through microbubble injection (see Figure 1).
- An effective means to employ electrostatic spraying for production of microbubbles in high-ionic-strength solutions such as produced water was not found. However, small bubble sizes were achieved in such solutions using bubble diffusers.

- UV irradiation contributed significantly to destruction of BTEX by ozonation; however, UV irradiation was not found to significantly improve ozonation of simulated produced water.
- The ozonation of hexanoic acid was highly pH dependent, which may have significant processing implications.



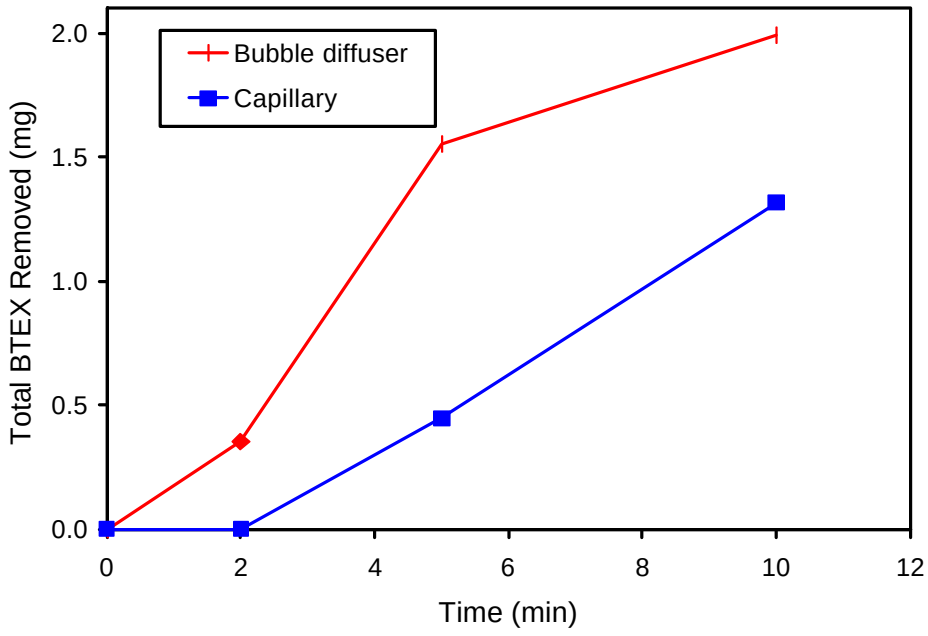


Figure 1. Illustration of the effect of bubble size on organics destruction by ozonation. Top images compare bubbles produced by a sparger (left), and a fine bubble diffuser (right) at the same gas flow rate; graph below shows representative ozonation results.

DISCUSSION OF CURRENT ACTIVITIES

An initial set of continuous-flow testing was performed using BTEXH and simulated produced water feed. The tests involved countercurrent gas-liquid in 350-mL reactors, with ozonated gas injection using porous injectors (diffusers) for microbubble formation. The results (see Figure 2) indicated that good removal efficiency, as measured by the reduction of hexane-extractable materials quantified by fluorometry, is possible at reasonable residence times and ozone loading.

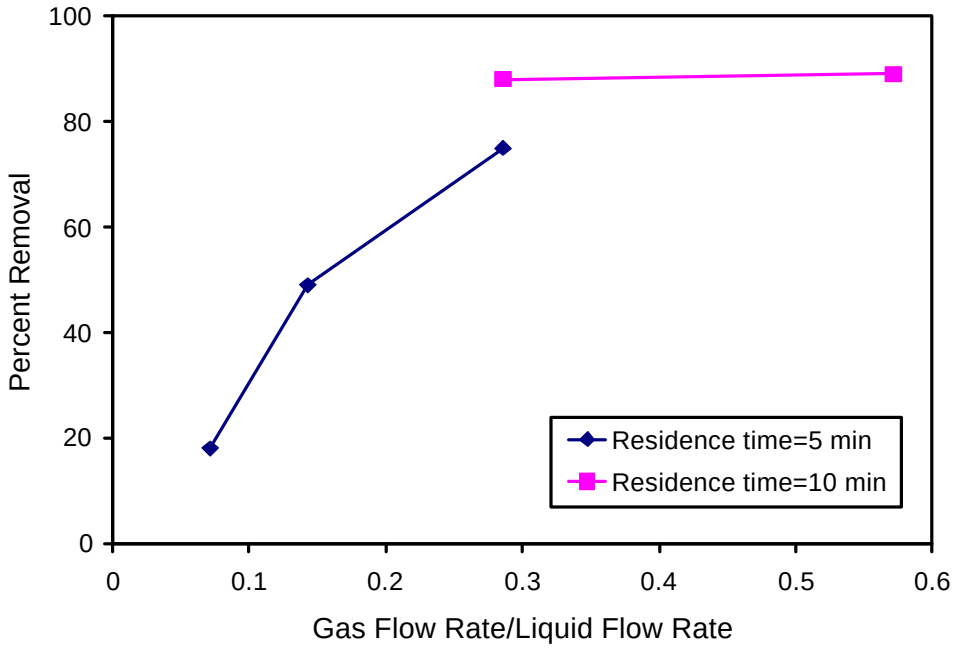


Figure 2. Example results from continuous-flow tests. Experimental conditions: Feed – simulated produced water (25 ppm hexane-extractable); 350-mL reactor, ozone concentration – 40 mg/L ozone; no UV.

On October 7–8, 1999, the Petroleum Environmental Research Forum (PERF) steering committee reviewed the results obtained in this project. They recommended that additional bench-scale research be conducted prior to scale-up and demonstration to answer several technical questions that remained regarding the feasibility of field application of ozonation. The scope of the continuous-flow study task was adjusted to meet those needs and the research activities shifted to two types of testing: (1) microbubble formation and (2) oxidation performance.

Several experiments have been conducted using simulated produced water and samples of actual produced water collected by our industrial partners (Company A and Company B). Microbubble formation tests involved long-term experiments to determine the impact of, and means for avoiding, possible fouling during ozonation by ferric oxide, calcium carbonate, and evaporative salt deposits. Oxidation tests were continued using laboratory-scale continuous-flow column reactors and small batch systems. The work involved multiple experiments with improved synthetic solutions to determine the effect of major process variables including gas flow rate, use of air or oxygen as the feed gas, presence of immiscible oil droplets in the water, and solution pH. No continuous experiments could be completed with actual produced water samples as the sample quantities obtained from the industrial collaborators were insufficient for continuous studies. Instead, we focused the work with actual produced water samples on batch experiments, collecting necessary data for preliminary scale-up information and cost estimation.

EXPERIMENTAL SYSTEMS

Several experimental systems were employed to address the effect of different variables. These systems are displayed in Table 1 and Figure 3–5.

RESULTS

Batch Experiments

Stock solutions of samples were made from produced water 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 during storage. Visual inspection showed that at the top of each bottle there was a layer of organic and inorganic particles (see Figure 6). 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.

Table 1. Experimental Systems Used in Current Studies.

System	Description	Variables Studied or Type of Experiments
Batch	Sealed glass bottles (60 and 160 mL) with Teflon-lined caps (see Figure 3)	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 gas chromatograph (GC) for analysis of 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
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. Simulated produced water was fed from the top of the column (see Figure 5). 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: Fouling Removal via flotation O_3/O_2 versus O_3/air mixtures for oxidation Gas-liquid flow ratio pH
Large Columns	Two continuous gas-flow column with 105- and 150-mm internal diameter. Air was supplied from the bottom through bubble diffusers. Equipped with automatic cleaning mechanism for the gas diffusers to correct fauling problems. (see Figure 4). Typical working volumes were 4.2 and 15 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



Figure 3. Photo of the type of reactor used in small batch experiments(160 mL).

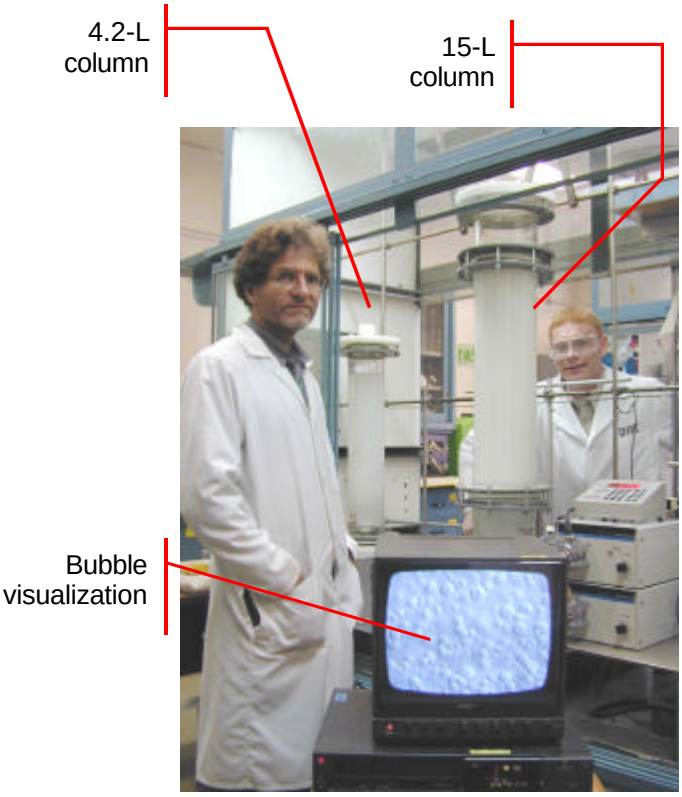


Figure 4. Photo of the type of reactors used in large-scale column experiments.



Figure 5. Photo of the type of reactor used in small column, continuous-flow experiments (350 mL).



Figure 6. Samples of produced water from Company A (right) and Company B (left). Samples from Company A contained a thick layer of oil on top of the water. Both samples contained particulates that could easily be resuspended.

One set of experiments included twelve different conditions by varying produced-water (Company A) volume and concentration of hydrogen peroxide. The initial ozone concentration in the bottles, before the addition of produced water, was 40.8 mg/L in the gas phase. Results from experiments showing complete oxidation of produced water organics are shown in Figure 7, where the CO_2 in the gas after the completion of the experiment is plotted versus the liquid volume treated. Experiments conducted without H_2O_2 added show that the CO_2 concentration reached a limiting value when more than 2 mL of produced water was treated. The results suggest that the volume of ozone containing gas at concentration 40.8 mg/L needed to oxidize produced water from Company A was more than 160 mL per 2 mL of produced water. The second curve of Figure 7 corresponds to results from experiments where hydrogen peroxide (0.1 mL) was added. It was found that, for treatment of small volumes of produced water, the CO_2 produced in the absence of H_2O_2 was slightly higher than when H_2O_2 was used. When treating more than 2 mL of produced water (at which volumes the ozone in the gas phase was not enough to complete the ozonation reactions) addition of H_2O_2 led to higher production of CO_2. Comparison of results from the experiments with and without H_2O_2 suggests that H_2O_2 does not have a synergistic effect with ozone in oxidizing organic compounds that are not oxidized by ozone alone.

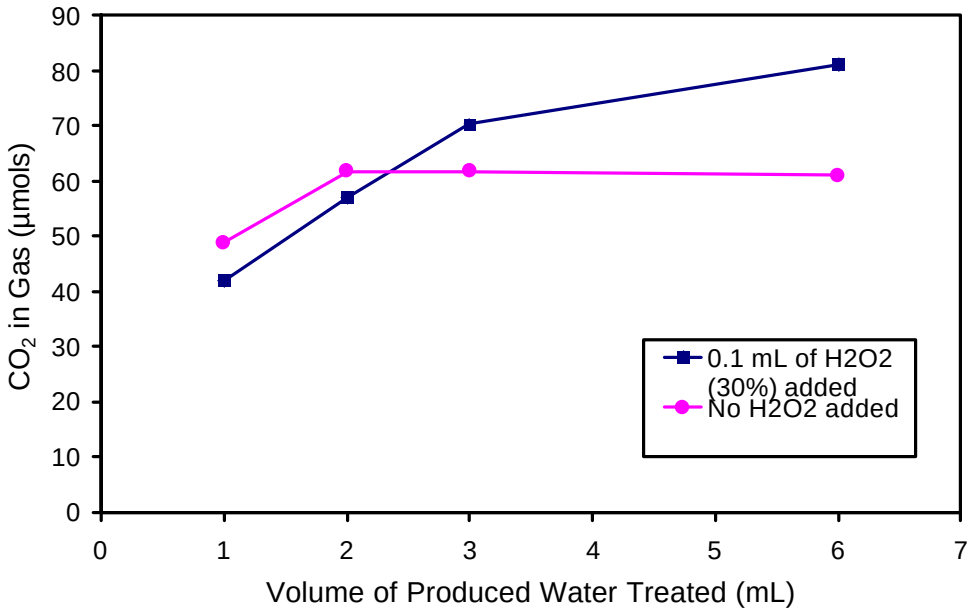


Figure 7. Effect of hydrogen peroxide on batch ozonation of produced water (Company A).

The effect on CO_2 production by the amount of H_2O_2 added is shown in Figure 8. In these experiments, 3 mL of produced water from Company A was treated which, according to the results in Figure 7, cannot be completely oxidized by 160-mL volume of O_3/O_2 mixture. Figure 8 shows that the CO_2 concentration in the gas did not increase significantly with addition of H_2O_2. This is another indication that H_2O_2, when used with ozone, does not enhance oxidation of organics.

Another set of batch experiments used produced water from two sources: Company A and Company B. All experiments were conducted using 160-mL bottles without adjusting the pH of the produced water. As previously described, we distinguish between three types of water samples: clear, taken from the bottom of the source container; cloudy, taken from the top of the container underneath the organic layer; and filtered, that is a cloudy sample passed through a 0.2-µm-pore-size filter. Results showed that the concentration of PCE extractables was 62.9 ppm for the clear, 317.1 ppm for the cloudy samples, and 26.2 ppm for the filtered 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 PCE extractables corresponding to 40.5±5 ppm for the clear, 118.8±5 ppm for the cloudy samples, and 16.7±5 ppm for the filtered. Clearly, there is a great deal of variation in the produced water.

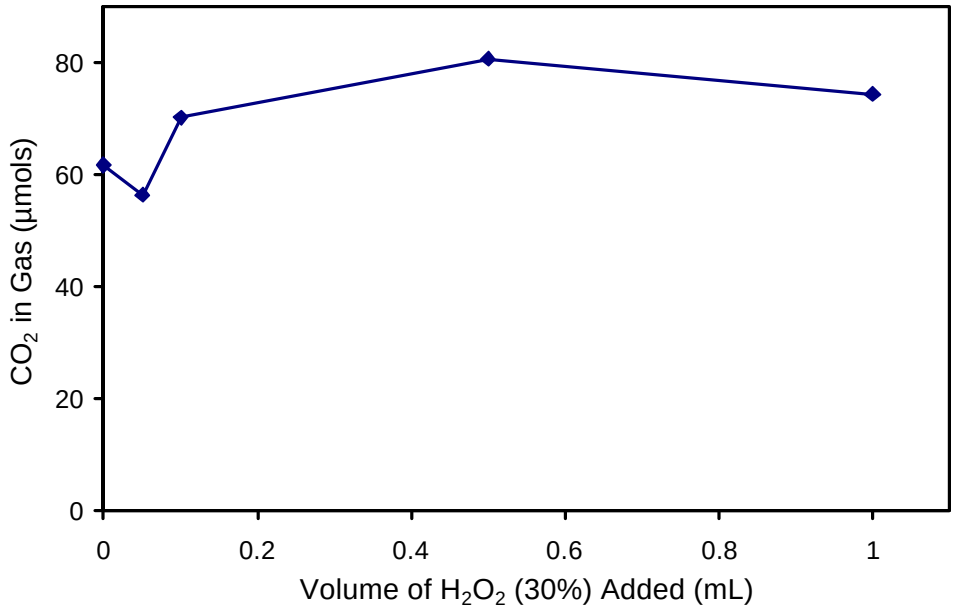


Figure 8. Effect of hydrogen peroxide on batch ozonation of 3 mL of produced water (Company A).

Although there was a significant difference among the concentration of PCE extractables for the three types of solutions, the PCE extractables were destroyed by ozonation. A comparison of concentrations before and after ozonation is shown in Figure 9 for cloudy, clear, and filtered samples of Company A and Company B produced water, respectively.

The quantity of carbon dioxide formed by ozonation of produced water from both companies is plotted in Figure 10 for clear, cloudy, and filtered samples. Two notable observations from Figure 10 are:

1. there is no clear distinction among the different types of samples (i.e., clear, cloudy, and filtered) from each company, and
2. produced water from Company A consistently yielded higher amounts of carbon dioxide.

The implication of the first observation is that complete oxidation of all PCE extractables was not achieved.

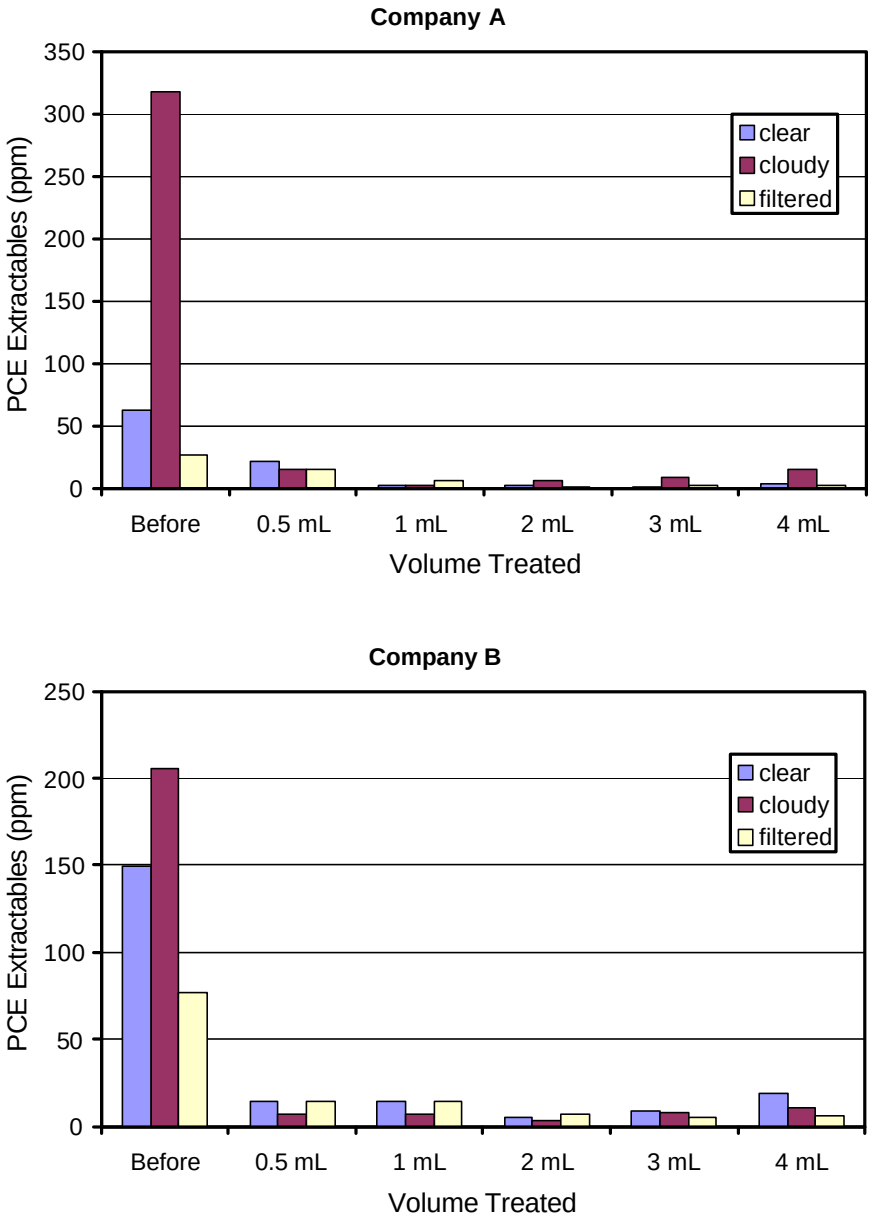


Figure 9. Concentration of extractable organics in different fractions of produced water samples. The results show concentrations before and after treatment of the produced water. All sample volumes were treated with 160 mL O_3/O_2 mixture and O_3 concentration of approximately 40 mg/L.

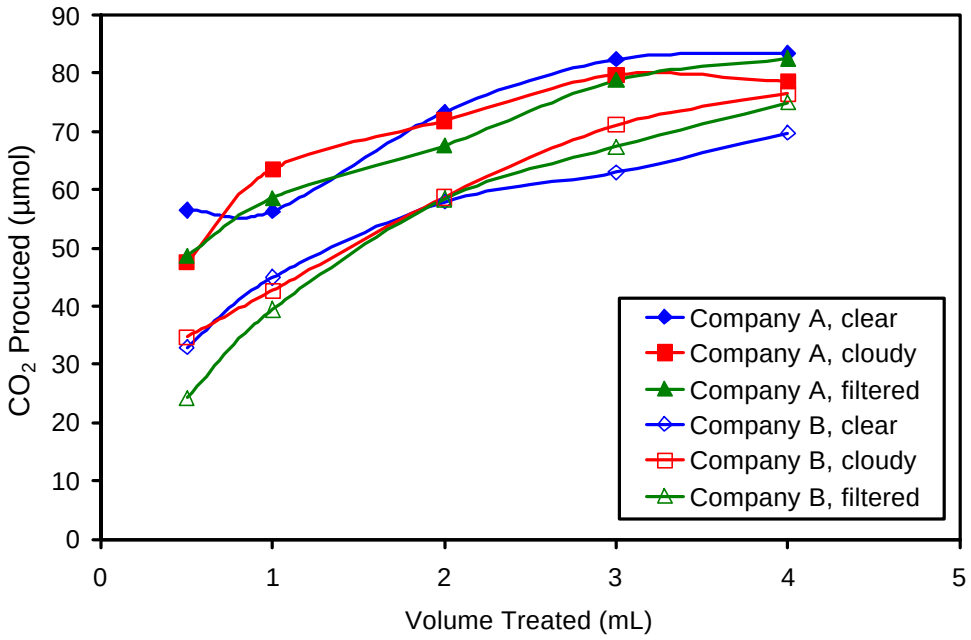


Figure 10. Comparison of the quantity of carbon dioxide formed by ozonation of produced water from Company A and Company B.

A GC/MS analysis of PCE extractables in produced water from Company A, before and after ozonation, was performed (Figure 11). The peaks represent carbon compounds present in the samples, which unfortunately could not be recognized by the mass-spectroscopy library used in this work. The top graph (before ozonation) contains more peaks than the bottom graph (after ozonation), indicating that several compounds have been destroyed by ozone. Although it is demonstrated in Figure 11 that ozonation was effective in removing organic compounds from produced water, further studies are still needed to identify both reactants and products of ozonation. Such studies are the subject of future work.

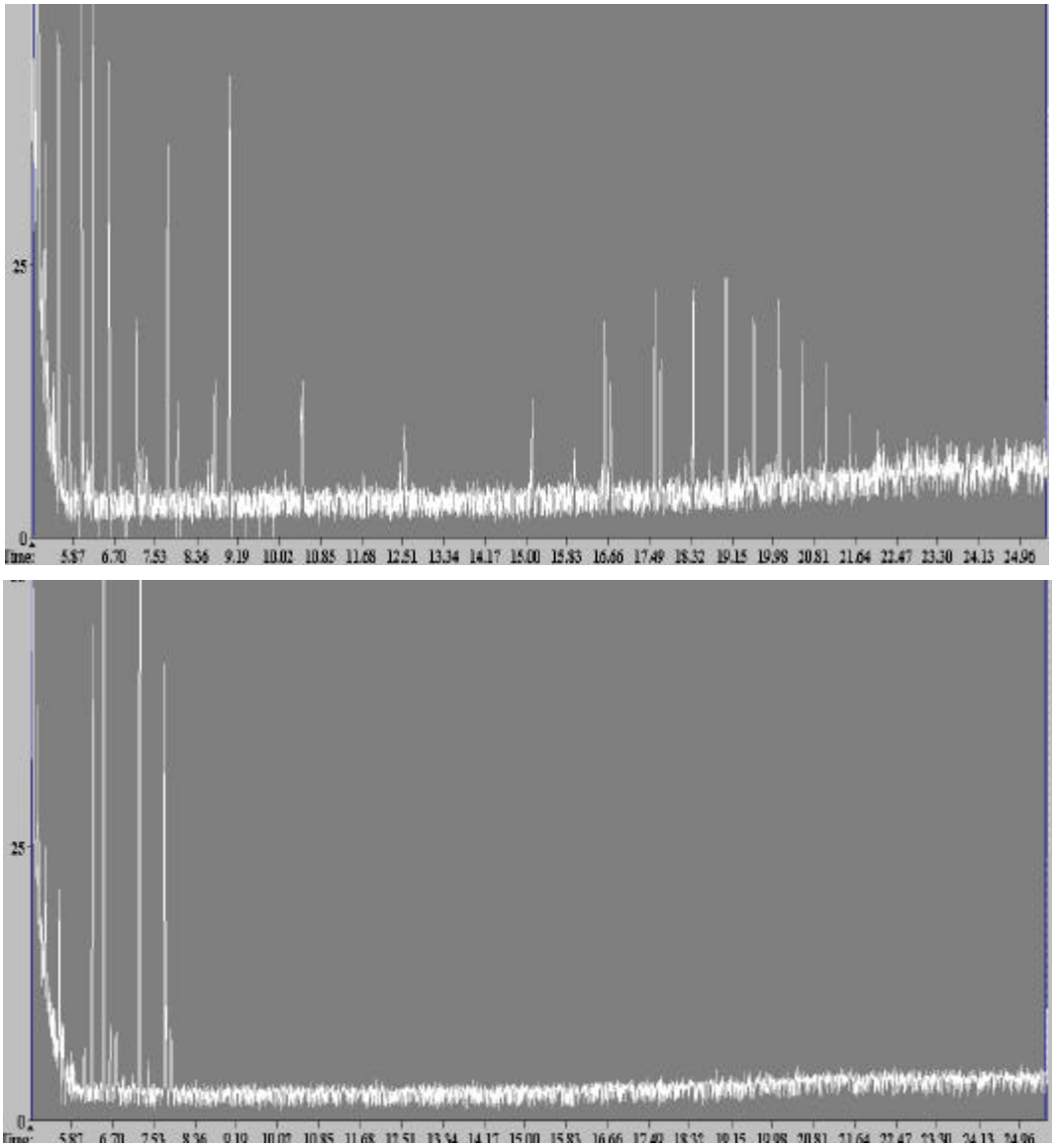


Figure 11. GC/MS analysis of produced water from Company A before (top) and after (bottom) ozonation.

Continuous-Flow Small Column Experiments

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. To date, fouling has been 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.

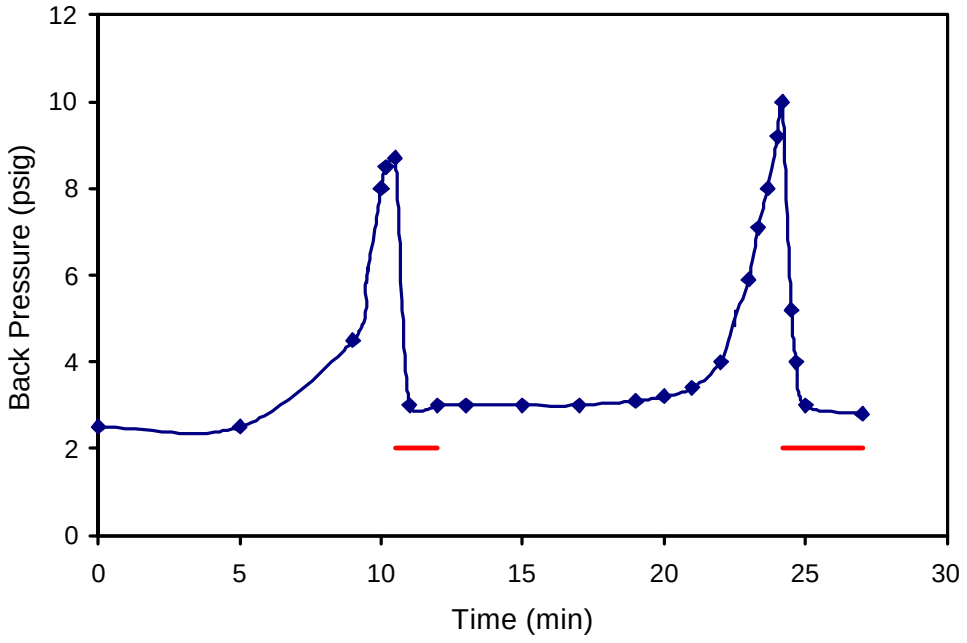


Figure 12. Example results of salt deposition and water flush for gas flow through a porous injector. Conditions: liquid flow – 10 mL/min salt water; gas flow - 300 mL/min oxygen containing ozone, distilled water flush – 0.3 mL/min. Horizontal bars indicate time period for water flush.

Representative results obtained in the continuous-flow ozonation experiments using oil dispersed in simulated seawater at 1-g/L are shown in Figure 13. This figure presents the fate of the carbon that was introduced into the reactor in the liquid feed stream. The results from each experiment is represented by a bar with three segments labeled "residual," "CO_2," and "flotation." "Residual" is the PCE-extractable fraction of the carbon that remained in the water after treatment, "CO_2" is the fraction that was fully converted to carbon dioxide, and "flotation" is the fraction of carbon that was removed by physical flotation of the oil droplets by the gas bubbles. Results from Experiments A and B indicate that, with ozone injection, a significant amount of the total carbon present in the feed solution was transformed into carbon dioxide. A greater gas flow rate in Experiment A than in Experiment B resulted in a more complete oxidation to CO_2. Results from Experiments C and D indicate that negligible oxidation to CO_2 was caused by oxygen alone and that higher gas flow removed more oil via flotation. Results from Experiment E and F show that a small, but measurable, conversion to CO_2 occurred with injection of ozone at lower concentrations (encountered with air feed to the ozone generator). In all cases, flotation was shown to be a major mechanism for dispersed oil removal.

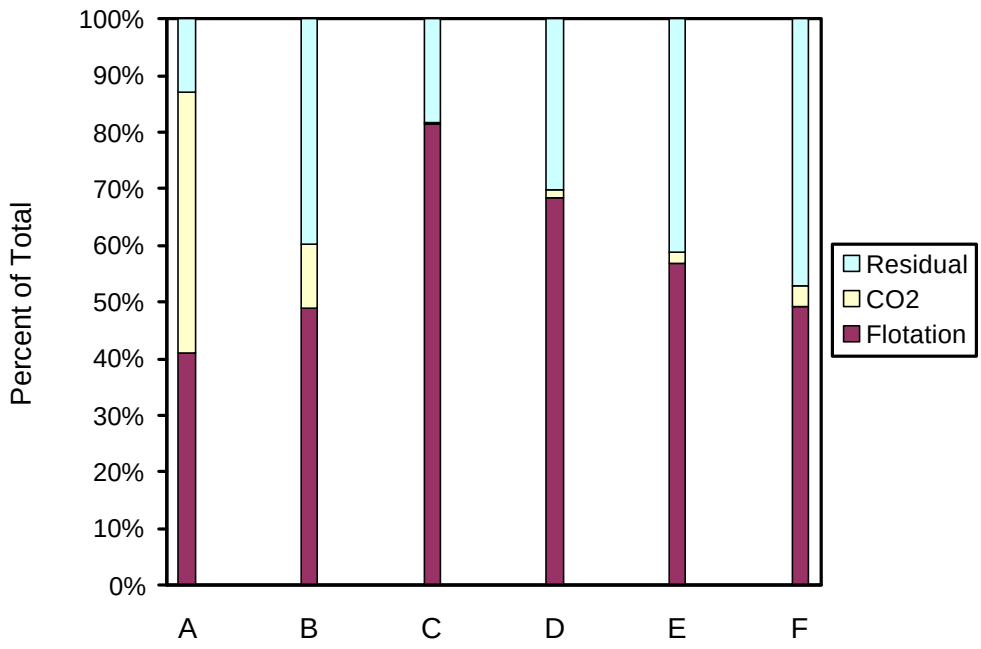


Figure 13. Representative results of continuous-flow ozonation tests with simulated produced water. All experiments run at 20 mL/min liquid flow rate and 10 min liquid residence time. Test conditions:

A: 1000 mL/min gas flow (oxygen/ozone), pH 8
B: 90 mL/min gas flow (oxygen/ozone), pH 8
C: 500 mL/min gas flow (oxygen), pH 8
D: 100 mL/min gas flow (oxygen), pH 8
E: 100 mL/min gas flow (air/ozone), pH 8
F: 100 mL/min gas flow (air/ozone), pH 4.9

The surface potential of oil drops was measured at various pH values to investigate the removal of oil droplets by flotation. It was found that the isoelectric point (zero surface potential) was at pH 4.8, while between pH 2.8 and 10.7 the potential ranged from +60 mV to –125 mV (data not shown). Despite the wide range of surface charge on the oil droplets, the oil removal obtained by flotation alone (using a low flow, 100 mL/min, of air as the feed gas) was not greatly affected by a shift from pH 8 (60% removal) closer to the isoelectric point at pH 4.9 (53% removal). The fact that removal by flotation was not higher at the isoelectric point indicates that the ionic strength was sufficiently high to reduce the role of electrostatic forces.

Continuous Large-Scale Experiments

The objective of this work was to investigate long-term use of larger-size equipment and continuous cleaning of bubble diffusers. The diffusers' pore size was 10–16 μm. The effect of gas flow rate and salt concentration on bubble size may be seen in Figure 14. As is noted, the bubble-size in salt water is approximately 10 times smaller than it is in fresh water.

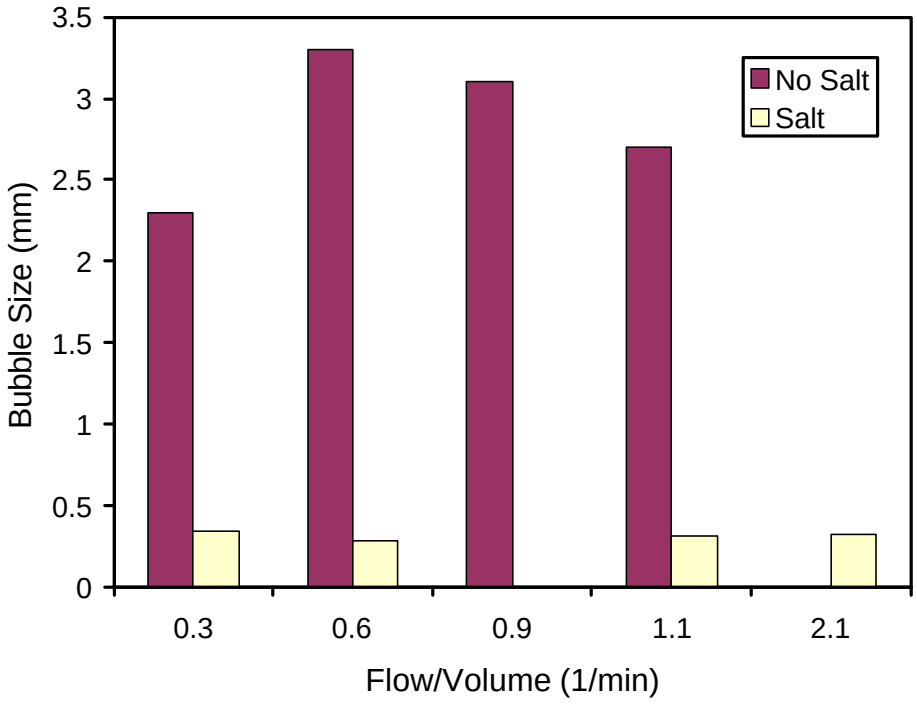


Figure 14. Bubble size in large columns for different gas flow to contactor volume ratio.

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 has operated for several months without problems, other than replacement of metal parts with glass parts when the flushing stream was altered to salt water.

PUBLICATION

A.B. WALKER; C. TSOURIS; D.W. DePAOLI; K.T. KLASSON, "Ozonation of Soluble Organics in Aqueous Solutions Using Microbubbles," accepted for publication in *Ozone Science and Engineering*, February 2001.

PRESENTATION

A.B. WALKER; C. TSOURIS; D.W. DePAOLI; K.T. KLASSON, "Removal of Organics from High-Ionic-Strength Aqueous Solutions," presented at Eleventh Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 17-20, 1999.

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