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“USE OF SONICATION/ACOUSTIC CAVITATION WITH ADVANCED OXIDANTS TO TREAT PETROLEUM HYDROCARBONS-CONTAMINATED SURFACE WATERS AND GROUNDWATERS”

by

Robert W. Peters, Ph.D., P.E. and
Professor of Environmental Engineering
Department of Civil and Environmental Engineering
University of Alabama at Birmingham
Birmingham, AL  35294-4440
phone: (205)-934-8434
FAX: (205)-934-9855
e-mail: rpeters@eng.uab.edu

Joseph J. Gauthier, Ph.D.
Associate Professor of Biology
Department of Biology
University of Alabama/Birmingham
Birmingham, AL  35294
phone: (205)-934-5659
FAX: (205)-975-6097
e-mail: gauthier@uab.edu

Jan Mohammad
Graduate Student
Department of Civil and Environmental Engineering
University of Alabama at Birmingham
1075 13th Street South
Birmingham, AL  35294-4440
Phone: (205)-934-8430
FAX: (205)-934-9855

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Abstract

Groundwater is one of our most valuable natural resource. More than 50% of the U.S. population depends on groundwater for domestic use and more than 95% of the rural population is dependent on groundwater. A major portion of industries and agriculture use groundwater. These numbers suggest that the personal and economic health of the nation is dependent on groundwater. Contamination of groundwater is a major cause of concern because of its negative implications in terms of public health and economics. The largest source of groundwater contamination involves underground storage tanks (U.S.T). As of September 30, 2006, EPA reported more than 460,000 [U.S. EPA, 2006] confirmed releases from underground storage tanks. The majority of underground storage tanks contain gasoline, diesel, and other petroleum products, which are the most frequently found contaminants in groundwater. One of the most dangerous chemicals found in petroleum products are a group of chemicals known as BTEX. The BTEX group consists of benzene, toluene, ethylbenzene, and xylene. Benzene, a member of the BTEX group found in groundwater contaminated with petroleum products, is a known carcinogen. Toluene, ethylbenzene, and xylenes as well as methyl-tert-butyl ether (MTBE) are toxic chemicals, and their presence in drinking water represents a grave danger to public health. This concern has resulted in considerable research into development of technologies to remove hazardous contaminants such as petroleum hydrocarbons from groundwater. Many advanced water purification techniques including vapor stripping/carbon adsorption, biological treatment, and advanced oxidation processes, have been applied to remove these contaminants from groundwater. All these technologies have their advantages and disadvantages in terms of their practical applications, costs, and process efficiencies.

An innovative technology (sonication as an advanced oxidation process) was tested to remove volatile organic compounds, such as petroleum hydrocarbons, from solution. Sonication is an application of ultrasound processes. Ultrasound has been used for a variety of different applications including plastic welding, emulsification, medical imaging, and atomization of particles. Sonication as a new advanced treatment process promotes the ultrasonic destruction of organic compounds. Most previous attempts in this field rely on the chemical consequences of ultrasound for water and groundwater treatment. Different than previous studies, this study investigated the effect of ultrasound for destruction of BTEX compounds.

This research project investigated the removal of petroleum hydrocarbons from groundwater using air sparging in combination with sonication. Experiments were performed to optimize the air flow rate for efficient and economical air sparging. Groundwater contaminated with petroleum hydrocarbons was subjected to air sparging treatment alone, sonication treatment alone, and air sparging combined with sonication treatment. Results are presented from the operation of the three systems (sonication alone, air sparging alone, and combined sonication + air sparging). Analysis of the results shows air sparging (vapor stripping) combined with sonication system performed best among the three systems tested. Air sparging combined with sonication removed in excess of 90% of the benzene, toluene, ethyl benzene, and o-xylene (BTEX) contaminants from groundwater. It is expected that bioremediation after the combination of air sparging and sonication treatment will further improve the system performance.

The research described in this final report addresses the technological and economic complexities associated with groundwater remediation. Using sonication-based technology, groundwater treatment is expected to be considerably cheaper, quicker, and a more efficient process. The following describe some benefits of the integrated air sparging/sonication technology.

- Treatment is performed in-situ thus avoiding having to deal with technical, economical, and legal problems associated with handling or disposal of contaminated water and sludge;
- The treatment systems complement each other by operating in a synergistic manner – combining them has the potential to greatly improve the treatment efficiency and reduce the treatment time;
- The integrated system can be aided by other *in-situ* treatment technologies such as other advanced oxidants (e.g., O₃ and H₂O₂);
- The system has the ability to destroy hard-to-degrade contaminants or convert them into more easily degradable compounds;
- The system has potential for future improvements in performance with advancements in sonication and air sparging technologies such as development of high power, high frequency sonication equipment;
- The system is cost-effective and has ease of installation and operation;
- Minimal degradation intermediates are formed; and
- The technology minimizes human exposure to hazardous chemicals.
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# Table of Contents

Abstract ............................................................................................................................................ i  
Acknowledgments .......................................................................................................................... iii 
List of Tables ................................................................................................................................. vi  
List of Figures ............................................................................................................................... vii  
1 Introduction ................................................................................................................................. 1  
2 Nature, Scope and Objective ........................................................................................................ 2  
3 Background ................................................................................................................................... 2  
3.1 Brief Discussion of Technology ............................................................................................... 3  
3.2 Previous Research Studies Involving Treatment of Waters Contaminated with Petroleum  
Hydrocarbons using Advanced Oxidation Techniques ............................................................... 4  
4 Methodology .................................................................................................................................. 8  
4.1 Task 1. Conduct batch sonication experiments to determine preliminary optimal  
conditions for subsequent continuous-flow experiments .............................................................. 8  
4.2 Task 2. Perform batch experiments to determine the effects of oxidants (O3, H2O2, etc.) on  
SVOC degradation and the volatility and biodegradability of the resultant product ......................... 9  
4.3 Task 3. Perform preliminary systems analysis and economic analysis for system scale-up  
for a field demonstration .............................................................................................................. 11  
4.4 Procedure for the Different Tasks ........................................................................................... 11  
4.4.1 Task 1. Conduct batch sonication experiments to determine preliminary optimal  
conditions for subsequent continuous flow experiments .............................................................. 11  
4.4.2 Task 2. Perform batch or continuous-flow experiments to determine the effects of  
oxidants (O3, H2O2, etc.) on SVOC degradation and the volatility and biodegradability of the resultant product ...................................................................................................................... 12  
4.4.3 Task 3. Perform preliminary systems analysis for system scale-up for a field  
demonstration ............................................................................................................................... 15  
5 Results and Discussion ............................................................................................................... 16  
5.1 Results for Task 1 – Conduct batch sonication experiments to determine preliminary  
onimal conditions for subsequent experiments ........................................................................... 16  
5.1.1 Air sparging experimental results ......................................................................................... 16  
5.1.2 Sonication experimental results ........................................................................................... 19  
5.2 Results for Task 3 – Perform batch or continuous-flow experiments to determine the  
effects of oxidants (O3, H2O2, etc.) on SVOC degradation and the volatility and  
biodegradability of the resultant product ..................................................................................... 20  
5.2.1 Combinations of experimental systems ............................................................................ 20  
5.2.2 Effect of initial contaminant concentration ......................................................................... 23  
5.2.3 Effect of co-contaminants .................................................................................................. 24  
5.2.4 Effect on process performance from addition of hydrogen peroxide .................................. 27  
5.2.5 Effect on process performance from UV light .................................................................... 27  
5.2.6 Comparison of treatment processes on removal of benzene, toluene, ethylbenzene,  
and o-xylene from solution ....................................................................................................... 29  
5.2.7 Effect of hydroxyl radical scavengers on system performance ......................................... 31
5.3 Results for Task 3 – Perform preliminary systems analysis for system scale-up for a field demonstration ....................................................................................................................32
6 Summary and Conclusions ..........................................................................................34
7 Synopsis ..................................................................................................................38
8 Publications .............................................................................................................40
9 References Cited ......................................................................................................43
List of Tables

Table 4-1. Physical properties of the petroleum hydrocarbons of interest for this study ........10
Table 5-1. Comparison of the rate constants for removal of BTEX compounds from solution using air sparging operations. ..............................................................17
Table 5-2. 1st-order rate constants for removal of benzene from solution employing sonication + air sparging for various initial benzene concentrations .........................................................24
Table 5-3. 1st-order rate constants of the target contaminant (benzene or ethylbenzene) with and without a co-contaminant present). ........................................................................................................25
Table 5-4. Comparison of the 1st-order rate constants for various treatment processes in removing benzene from solution ........................................................................................................32
Table 5-5. Summary of 1st-order rate constants using various treatment processes for removal of benzene, toluene, ethylbenzene, and o-xylene from solution .................................................................34
List of Figures

Page

Figure 4-1. Experimental set up for the sonication-alone system................................................. 12
Figure 4-2. Experimental set up for the air-sparging system........................................................ 13
Figure 4-3. Experimental set up for the combined sonication + air-sparging system.............. 13
Figure 4-4. UV irradiation system. ............................................................................................... 14
Figure 4-5. UV photoreactor stand for insertion into the UV irradiation system....................... 15
Figure 4-6. Experimental set up for the combined sonication, air-sparging, and UV irradiation system .......................................................................................................................... 16
Figure 5-1. Comparison of removal efficiency of benzene using air sparging employing different air flow rates ......................................................................................................................... 17
Figure 5-2. Comparison of removal efficiency of toluene using air sparging employing different air flow rates......................................................................................................................... 18
Figure 5-3. Comparison of removal efficiency of ethylbenzene using air sparging employing different air flow rates......................................................................................................................... 18
Figure 5-4. Comparison of removal efficiency of o-xylene using air sparging employing different air flow rates ......................................................................................................................... 19
Figure 5-5. Comparison of fractional residual BTEX compounds remaining from sonication alone treatment (20 kHz, ~38 W/cm²). ......................................................................................................................... 20
Figure 5-6. Comparison of residual benzene remaining in solution using different treatment systems................................................................................................................................. 21
Figure 5-7. Comparison of residual toluene remaining in solution using different treatment systems................................................................................................................................. 21
Figure 5-8. Comparison of residual ethylbenzene remaining in solution using different treatment systems................................................................................................................................. 22
Figure 5-9. Comparison of residual o-xylene remaining in solution using different treatment systems ................................................................................................................................. 22
Figure 5-10. Comparison of treatment systems (sonication, air sparging, and combined sonication + air sparging) for removal of BTEX compounds from solution............................................. 23
Figure 5-11. Effect of initial benzene concentration for combined sonication + air sparging treatment ........................................................................................................................................... 24
Figure 5-12. Effect of co-contaminants on treatment performance using sonication + air sparging .................................................................................................................................................. 25
Figure 5-13. Effect of co-contaminants (MTBE and phenol) on treatment performance using sonication + air sparging for removal of benzene from solution.................................................. 26
Figure 5-14. Effects of adding hydrogen peroxide on removal of benzene from solution using sonication + air sparging treatment .................................................................................................. 27
Figure 5-15. Effect of adding UV light on removal of benzene from solution using sonication + air sparging treatment .................................................................................................................. 28
Figure 5-16. Effect of adding UV light on removal of toluene from solution using sonication + air sparging treatment .................................................................................................................. 28
Figure 5-17. Treatment system performance comparison for various treatment techniques for removing benzene from solution ................................................................. 29
Figure 5-18. Treatment system performance comparison for various treatment techniques for removing toluene from solution ................................................................. 30
Figure 5-19. Treatment system performance comparison for various treatment techniques for removing ethylbenzene from solution ............................................................... 30
Figure 5-20. Treatment system performance comparison for various treatment techniques for removing o-xylene from solution ................................................................. 31
Figure 5-21. Effect of •OH radical scavengers (sodium carbonate/sodium bicarbonate) on removal of benzene from solution using sonication + air sparging ........................................ 32
Figure 5-22. Synergistic effects of combining advanced oxidation processes for removal of benzene from solution .................................................................................. 33
1 Introduction

This project addressed the major water resources problems for the State of Alabama pertaining to Ground Water (1.A) for the quantity and quality of ground water, particularly for development of improved methods of groundwater remediation; and to Surface Water (2.A) for water quality concerns for surface water supplies related to both point-source and non-point source contamination, and developing models for predicting contaminant fate and transport.

An underground storage tank (UST) is a tank (or combination of tanks) and connected piping having at least 10% of their combined volume underground [U.S. EPA, 2001a]. The tank system includes the tank, underground connected piping, and any containment system. Underground storage tanks have been used to store petroleum hydrocarbons. Gasoline, leaking from service stations, is one of the most common sources of groundwater pollution [U.S. EPA, 2001a]. Because approximately one-half of the U.S. population relies on groundwater as their source of drinking water, groundwater pollution is a serious problem. Many municipal and private wells have had to be shut down as a result of releases from UST systems. Over time, storage tanks corrode and leak, resulting in petroleum hydrocarbons percolating through the subsurface soil and potentially contaminating ground water and surface water supplies. Leaking underground storage tanks (LUSTs) are a significant source of environmental contamination and can pose the following threats to health and safety: fire and explosion; inhalation of dangerous vapors; contamination of soil and groundwater; contamination of drinking water; and contamination of streams, rivers, and lakes [Illinois EPA, 2001b]. Environmental laws and regulations governing LUSTs are found in the Environmental Protection Act, Title XVI, Petroleum Underground Storage Tanks; in Title 35, Illinois Administrative Code (IAC), Subtitle G, Part 731, Underground Storage Tanks; and Part 732, Petroleum Underground Storage Tanks [Illinois EPA, 2001a]. The U.S. EPA [2001a] reports that “as of March 31, 2001, more than 417,000 releases have been reported from UST systems”, about 375,000 cleanups have been initiated, and nearly 259,000 cleanups have been completed [U.S. EPA, 2001c]. Nearly 1.5 million substandard USTs have been closed and (when closed properly) no longer pose a threat to the environment. There are about 716,000 USTs that are currently active, located at about 269,000 sites nationwide [U.S. EPA, 2001d].

These leaking underground storage tanks (LUSTs) can result in serious environmental contamination; to compound the problem, the cleanup of these LUST releases are expensive. Costs of remediating sites with soil contamination generally vary between $10,000 and $125,000 [U.S. EPA, 1994, 1995]. Depending on the extent of contamination, costs for remediating sites with groundwater contamination can range from $100,000 to over $1,000,000 [U.S. EPA, 1994, 1995]. One of the main factors in the high cleanup costs is the use of ineffective cleanup methods. Pump-and-treat is the most commonly used method for remediating contaminated groundwater; this often results in unsuccessful cleanups. Even when properly operated, U.S. EPA [1994, 1995] notes that pump-and-treat systems have inherent limitations: they don’t work well in complex geologic settings or heterogeneous aquifers; they often stop reducing contamination long before reaching intended cleanup levels; and they often make sites more difficult to remediate by smearing contamination across the subsurface. EPA encourages the use of alternative technologies that have the ability to perform cleanups faster, more effectively, and less costly than traditional treatment options such as pump-and-treat or excavation and disposal in a landfill [U.S. EPA, 1994, 1995]. It is the goal of the proposed research to investigate the use of downhole (in-situ) sonication/ acoustic cavitation coupled with vapor stripping (air sparging) as a means to effectively destroy petroleum hydrocarbons in a cost-effective manner.
2 Nature, Scope and Objective

This project investigated treatment of petroleum-hydrocarbon contaminated groundwater using a combination of sonication, air sparging, and advanced oxidants as a means to cleanup the groundwater.

During the study year, three separate tasks were performed. Batch and continuous flow experiments were performed using sonication alone, vapor stripping (air sparging) alone, and combined sonication/vapor stripping. These experiments were performed both in the absence and presence of advanced oxidants such as ozone (O\textsubscript{3}) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). The project determined the removal of the parent petroleum hydrocarbon contaminant and identified and quantified any degradation products formed during the advanced oxidation treatment. As a part of the research activities, a preliminary process performance assessment was performed.

The objectives of the proposed research are to investigate the in-situ degradation of petroleum hydrocarbon contaminants present as semi-volatile organic compounds (SVOCs) and to:

- Determine the system performance of the combined in-well sonication, air sparging, and biodegradation to destroy volatile organic compounds (VOCs) and transform SVOCs into VOCs;
- Determine how the combined in-well sonication/air sparging remedial system functions together at the laboratory-scale to remove SVOCs and VOCs;
- Quantify the degradation products formed from sonication/air sparging treatment of petroleum hydrocarbon-contaminated groundwater; and their biodegradability; and
- After water is treated in the well with sonication and VOCs are partially removed through in-well air sparging, determine the role of volatilization and microbial activity on water containing VOCs that is forced to infiltrate through the unsaturated zone.

The three tasks performed during this research study are described briefly below.

1. Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent continuous-flow experiments;
2. Perform batch experiments to determine the effects of oxidants (O\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, etc.) on SVOC degradation and the volatility and biodegradability of the resultant product; and
3. Perform preliminary systems analysis and economic analysis for system scale-up for a field demonstration.

3 Background

Gasoline, leaking from underground storage tanks, is one of the most common sources of groundwater pollution [U.S. EPA, 2001a]. Because approximately one-half of the U.S. population relies on groundwater as their source of drinking water, groundwater pollution is a serious problem. EPA has an expressed interest in exploring the use of alternative technologies for their use in remediating contaminated groundwaters. U.S. EPA [1994, 1995] has identified a number of alternative cleanup technologies that could be used in cleaning up underground storage tank sites, including the use of soil vapor extraction, bioventing, biopiles, landfarming, low-temperature thermal desorption, air sparging, biosparging, natural attenuation, in-situ bioremediation, and dual-phase extraction. Past research performed by the PI has shown that sonication coupled with vapor stripping (air sparging) effectively
destroys chlorinated solvents present as contaminants in groundwater [Ayyildiz et al., 1998; Kuo et al., 1997; Peters et al., 2001; 2000a,b; 1999a,b,c; 1998a,b; 1997; Peters, 2000; Wilkey et al., 1999]. This project extended that work to treat petroleum-hydrocarbon contaminated groundwater, and is consistent with EPA goals of using alternative technologies in groundwater cleanups, by enhancing the performance of air sparging.

3.1 Brief Discussion of Technology

Acoustic cavitation (commonly termed sonication) involves the application of sound waves being transmitted through a liquid as a wave of alternating cavitation cycles. Compression cycles exert a positive pressure on the liquid, pushing molecules together, while expansion cycles exert a negative pressure, pulling molecules away from each other. The chemical effects of sonication are a result of acoustic cavitation. During rarefaction, molecules are torn apart forming tiny microbubbles that grow to a critical size during the alternating cavitation cycles, and then implode releasing a large amount of energy. Temperatures on the order of 5,000°K and pressures up to 500 to 1,000 atmospheres have been observed in microbubble implosions, while the bulk solution stays near ambient. The collapsing bubble interface results in the formation of hydroxyl and hydrogen radicals. These radicals destroy chlorinated organic and petroleum hydrocarbon compounds very effectively. Acoustic cavitation will be employed in-well serving as the first stage of treatment (i.e., pretreatment) in the integrated treatment system, in order to enhance the performance of the in-well vapor stripping (air sparging) and in-situ biodegradation steps (all of which are performed below grade). Further discussion of the sonication and vapor stripping technologies is provided in Appendix I.

The performance can be further enhanced through the addition of advanced oxidants (e.g., ozone (O₃), hydrogen peroxide (H₂O₂), etc.), and incorporation of recent advancements in the acoustic cavitation field. The destruction of organic pollutants can occur via several mechanisms. The organic pollutant inside the cavity and in the interfacial region can undergo pyrolysis reactions (or combustion reactions if oxygen is present) during the implosion. Free radicals (e.g., •OH, •H) formed due to thermolysis of water molecules may react with the organic in the interfacial region or in the solution near the interface. Three primary pathways have been identified for compound degradation, including: (1) hydroxyl radical oxidation, (2) direct pyrolytic degradation, and (3) supercritical water reactions. In aqueous solution, water vapor present in the microbubble is homolytically split during bubble collapse to yield •H and •OH radicals, while chemical substrates present either within or near the gas-liquid interface of the collapsing microbubble are subject to direct attack by •OH. Volatile compounds such as benzene, toluene, ethylbenzene, xylene, and MTBE readily partition into the vapor of the growing cavitation microbubbles and then undergo direct pyrolysis during transient collapse.

Vapor stripping (air sparging) operations have as their goal to transfer the volatile contaminants from the liquid phase (i.e., groundwater) to the vapor phase (i.e., air). The combination of sonication and aeration/ozonation/hydrogen peroxide results in enhanced organic destruction and better liquid/vapor
contact (i.e., better mixing) to facilitate the transfer of the degraded or partially degraded products into the gas phase. The addition of ozone (made through electric discharge of oxygen) into the liquid phase coupled with application of sonication considerably enhances the formation of hydroxyl radicals resulting in enhanced destruction of chlorinated organic compounds in solution. Hydroxyl radicals (•OH) are highly reactive non-specific reactants capable of oxidizing a wide variety of contaminants to carbon dioxide, hydrochloric acid (if chlorinated organics are present), and water. After mass transfer from the liquid phase into the gas phase, the water is pumped to a packer in the dual extraction well, resulting in the water (stripped of the volatile organic compounds (VOCs)) being returned into the subsurface, while the VOC-enriched vapor phase is passed through the second well and is sent to an above-ground vapor treatment system (that could involve capture on activated carbon/regeneration using ultrasonics, or thermal oxidation).

3.2 Previous Research Studies Involving Treatment of Waters Contaminated with Petroleum Hydrocarbons using Advanced Oxidation Techniques

Von Sonntag [1996] noted that most aromatic compounds are only slowly degraded by ozone, but the •OH radical generated through the interaction of ozone with other advanced oxidation processes) reacts very rapidly with these compounds, giving rise to hydroxycyclohexadienyl-type radicals. They react reversibly with oxygen. Thoma et al. [1998] studied the destruction of benzene and toluene in water using ultrasonic irradiation in a parallel plate Near Field Acoustic (NAP) processor; the system was capable of degrading both benzene and toluene in a continuous stirred tank reactor configuration. The reaction kinetics were first-order for the disappearance of the parent compound; the 1st-order rate constants ranged from $2.7 \times 10^{-3}$ to $3.7 \times 10^{-2}$ min$^{-1}$ over an applied power density range of 0.6 to 3.6 watts/mL and target concentrations of 25 to 900 μmoles/L. The rate constant was inversely proportional to the target compound concentration, which indicated higher order reaction kinetics. Wu et al. [2004] investigated aquasonicysis rates and products of selected cyclic C₆Hₓ hydrocarbons (benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexane, cyclohexene, and methylcyclopentane). The sonolysis of these compounds in aqueous solution followed 1st-order kinetics, and the aquasonicysis rate correlated well with the water solubility. Of the compounds studied, the degradation rate of benzene was the smallest (k~0.025 min$^{-1}$). The degradation rate decreased with an increase of the initial hydrocarbon concentration. The effect of initial concentration on the degradation of cyclohexene was more significant than that of benzene. The transfer process of organic solutes between cavitation bubbles and the bulk liquid affected the rates and products resulting from aquasonicysis treatment.

Okuno et al. [2000] studied the sonolysis of benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, biphenyl, polychlorinated biphenyls such as 2- and 4-chlorobiphenyl, and 2,2′-dichlorobiphenyl in aqueous solution. Using 200 kHz ultrasound with an intensity of 6 W/cm² under an argon atmosphere. Approximately 80-90% of the initial amount of these compounds were degraded within 30 to 60 minutes of sonication for initial concentrations in the range of 10 to 100 μmole/L. The degradation rate of these compounds increased with an increase in their vapor pressures. In all cases of sonolysis of the chlorinated organic compounds, an appreciable amount of liberated chloride ion was observed (indicating complete mineralization). de Visscher et al. [1996] studied the breakdown of benzene, ethylbenzene styrene, and o-chlorotoluene in aqueous solution using 520 kHz ultrasonic waves for various initial contaminant concentrations in the millimolar range. First-order reaction rates were obtained; these rates were dependent on the initial concentration and sonication time. The data was modeled as a first-order pyrolysis in which the cavitations yield both reactive volatile and inert/nonvolatile products, along with lowering of the maximum cavitation temperature due to the presence of the organic compounds in the bubble phase.
Gul et al. [1999] studied the change in chemical oxygen demand (COD) of various substituted aromatic compounds (including benzoic acid, p-aminobenzoic acid, p-toluenesulfonic acid, sulfanilic acid, nitrobenzene, resorcinol, p-cresol, o-cresol, o-toluidine, aniline, and 8-hydroxyquinoline) using ozone doses of 5, 10, 15, and 20 mg O₃/min. High ozone doses were needed to obtain better elimination of the initial compounds and to further improve degradability of the ozonation products. C.H. Kuo et al. [1997] performed a comparative study of the benzene/ozone reaction in gaseous-phase and aqueous-phase reactors at atmospheric pressure and 25°C. In distilled water with pH in the range of 5.2 to 5.4, the reaction rate was half-order with respect to both concentrations of dissolved benzene and ozone. The overall rate constants were 0.0011 and 2.67 sec⁻¹, respectively, in the vapor and liquid phase reactors.

Suri et al. [1993] investigated the use of several catalysts that were obtained commercially and/or prepared in the laboratory. These catalysts were examined for their photoactivity. The catalysts studied included: TiO₂, Pt-TiO₂ with platinum loading ranging from 0.5 to 100% by weight, SrTiO₃, and 1.5% NiO-SrTiO₃. The following organic contaminants were tested: trichloroethylene (TCE), toluene, methyl ethyl ketone (MEK), salicylic acid, and 2,4-dinitrophenol, with initial concentrations ranging from 0.1 to 10.0 mg/L. The activity of the photocatalysts can be improved by 2-4 times over commercially available catalysts. Groundwater contaminated by BTEX compounds was treated using advanced oxidation processes (AOPs) such as TiO₂ photocatalysis and iron (Fe²⁺)/H₂O₂ exposed to solar light with an average intensity of 1.7 mW/H₂O₂ exposed to solar light with an average intensity of 1.7 mW/cm² at 365 nm [Cho et al., 2006b]. Near complete degradation of BTEX and total petroleum hydrocarbons (TPH) was observed within 2 and 4 hours, respectively. The AOP processes involving Fe²⁺/H₂O₂/solar light and TiO₂/H₂O₂/solar light were effective ex situ techniques for remediating groundwater contaminated with petroleum hydrocarbons. The photooxidation of p-xylene and o-nitrotoluene were studied by Ghaly [2005] in a closed bench-scale unit using hydrogen peroxide or hydrogen peroxide/Fe²⁺ as a photocatalyst. Results of the photo-Fenton process (UV/H₂O₂/Fe²⁺) were compared with the UV/H₂O₂ process; the results indicated that the photo-Fenton process resulted in a higher efficiency degradation of the selected compounds and reduced energy consumption. The degradation reactions were 1st-order; the value of the reaction rate constant k was ~5x higher for the photo-Fenton process than that in the case of the UV/H₂O₂ system. The quantity of both H₂O₂ and Fe²⁺ must be properly selected the pH properly adjusted to optimize the process. For their particular system studied, the optimum reaction conditions were: 0.03 mole H₂O₂/L using the UV/H₂O₂ system and 0.01 mole H₂O₂/L, 1.0 mmole Fe²⁺/L at pH ~3 for the photo-Fenton process. Schreier and Pucik [2002] investigated the treatment of groundwater containing methyl tert-butyl ether (MTBE) and other petroleum hydrocarbons in water employing Fenton’s reagent. Treatment of groundwater with 1% H₂O₂ and 5 mmole/L Fe²⁺ at pH 3 destroyed greater than 99.8% MTBE, >93.2% total petroleum hydrocarbons (TPH), and >98.5% BTEX compounds within 24 hours. Less than 0.01% of the MTBE, 5.1% of the TPH, and <0.7% of the BTEX compounds were volatilized. The rates and amounts of O₂ and heat generated depended on the amounts of H₂O₂ and Fe²⁺ used. Using UV irradiation combined with H₂O₂ treatment, Cater et al. [2000] investigated treatment of MTBE using this advanced oxidation process. The degradation of MTBE followed pseudo-first-order kinetics. The researchers showed that MTBE can be easily and effectively treated with the UV/H₂O₂ process. Augusti et al. [1998] studied the destruction of benzene and other benzene derivatives using Fenton’s reagent (Fe²⁺/H₂O₂) in water; membrane introduction mass spectrometry (MIMS) was used to investigate the kinetic behavior. Their data analysis suggested that cleavage of the benzene C-H bond occurs as the reaction rate controlling step. Fenton’s reagent has also been used to treat gasoline contaminated soils [Watts et al., 2000]. They studied the effects of H₂O₂ concentration, iron catalyst concentration, and pH on the degree of treatment for soils contaminated with BTEX compounds, along with nonane, decane, and dodecane. Oxidation of the aromatic compounds required less iron and less H₂O₂ than did oxidation of the aliphatic compounds, while proceeding more effectively at near-neutral pH. Greater than 95% of the BTEX compounds were destroyed at near neutral pH using 2.5% H₂O₂ and 12.5 mmole/L, while only 37% nonane, 7% decane, and 1% dodecane were achieved under the same conditions.
Lou and Lee [1995] studied treatment of benzene, toluene, and xylene (BTX) using Fenton’s reagent under batch conditions. BTX can be effectively oxidized in aqueous solutions with Fenton’s reagent. At a $\text{H}_2\text{O}_2$:BTX:Fe$^{2+}$ ratio of 12:1:60 (mg/L), the dissolved BTX can be completely removed for treatment times of less than 10 minutes. Tiburtius et al. [2005a,b] observed that BTEX could be effectively oxidized using a near UV-assisted photo-Fenton process. The treatment permits nearly total degradation of BTEX compounds and removal exceeding 80% of the phenolic intermediates for reactions times of ~30 minutes. Heterogeneous photocatalysts and $\text{H}_2\text{O}_2$/UV systems show slower degradation efficiency, which they attributed to the heterogeneous character of the TiO$_2$-mediated system and loss of photonic efficiency of the $\text{H}_2\text{O}_2$/UV system in the presence of highly colored intermediates. Using high energy electron beam irradiation, Cooper et al. [1992] investigated the removal and destruction of halogenated ethenes, benzene, and substituted benzenes contained in waters of different quality, including potable water, and raw and secondary wastewaters. Removal efficiencies ranged from 85 to >95% and varied with water quality, solute concentration, dose and contaminant compound.

The ozonation and peroxone oxidation of toluene in aqueous solutions was studied by Kuo and Chen [1996]. They investigated the kinetics of the aqueous-phase oxidation or toluene by ozone and ozone-hydrogen peroxide mixtures at 25°C. The oxidation kinetics were 1st-order with respect to ozone concentration; the reaction order in toluene varied with pH and the presence or absence of H$_2$O$_2$. The peroxone oxidation was half-order with respect to H$_2$O$_2$ in distilled water (initial pH of 5.4) and other solutions of higher pH. In acidic solutions with an initial pH ≤ 3, the overall kinetics was 2nd-order; the direct oxidation of toluene by ozone molecules was predominant in determining the slow rate of reaction. The reaction became very fast and enhanced with the addition of H$_2$O$_2$, if present, in alkaline solutions with an initial pH of 10 or higher. Under those conditions, the reaction was controlled by hydroxyl radical reactions and was independent of the toluene concentration.

Walker et al. [2001] investigated use of ozonation of aqueous solutions containing benzene, toluene, ethylbenzene, and xylenes. Salt solutions ranging from 0 to 2.0 moles/L were used in the study. Microbubbles were formed either by an electrostatic spraying method or by a small-pore bubble diffuser. Although electrostatic spraying is an effective technique for BTEX removal in low-conductivity solutions, it is not suitable for microbubble formation in high ionic solutions. Bench-scale studies were conducted to assess the efficiency of ozonation (O$_3$) and advanced oxidation processes such as O$_3$/UV, O$_3$/H$_2$O$_2$, UV/H$_2$O$_2$, and O$_3$/UV/H$_2$O$_2$ for treatment of o-nitrotoluene as a benzene derivative, by Ghaly et al. [2001]. The direct reaction between o-nitrotoluene and O$_3$ resulted in a slow oxidation rate of o-nitrotoluene and was pseudo 1st-order. At higher pH or by the combination of O$_3$ with UV or H$_2$O$_2$, Ozonation results in more efficient and faster oxidation rates of o-nitrotoluene due to hydroxyl radicals (•OH) in the oxidation of o-nitrotoluene. Kuo and Soong [1984] studied the oxidation of benzene using ozone in aqueous solutions for temperatures ranging from 5 to 35°C. The solution pH ranged from 3 to 7. The O$_3$ reaction was half-order with respect to both O$_3$ and benzene concentration in acidic solutions. In neutral solution, the reaction was 1st-order in O$_3$ concentration and nearly independent of benzene concentration. At 25°C, the half-life of the reaction decreased from 20 to less than 0.2 sec, and the 1st-order rate constant increased from 0.012 to 12 sec$^{-1}$ as the solution pH increased from 3 to 7. Both benzoquinone and hydroquinone (1,4-dihydroxybenzene) were formed in the neutral solutions as detected by gas chromatography techniques.

Bian et al. [2001] studied the sonochemical degradation of toluene in an airproof aqueous solution. The sonication time had a great effect on the removal rate of toluene; the degradation followed pseudo-first-order kinetics. After irradiation for 40 minutes, 90-95% of the toluene was removed. The types of dissolved gas and pH also had some effect on the system performance. Results confirmed that radical-oxidation controlled the sonochemical oxidation of toluene. The primary middle products included benzaldehyde, bibenzyl, and dibutyl phthalate. The final products were carbon dioxide and water.
Gunukula and Tittlebaum [2001] investigated the use of an advanced oxidation process (TiO$_2$ combined with ozone) to treat oil and grease, total petroleum hydrocarbons, chemical oxygen demand, benzene, toluene, ethylbenzene, and xylene generated during barge cleaning operations. Significant reductions on oil and grease, and TPH were observed. Oxygen alone indicated a 50% removal efficiency for oil and grease and TPH. Ozone exhibited a treatment efficiency of 86% for oil and grease and TPH at a dosage rate of 12 standard cubic feet per minute (SCFM) and 82% for a dosage of 6 SCFM. Using solar light combined with titanium dioxide (TiO$_2$) photocatalysts, greater than 70% degradation of BTEX and total petroleum hydrocarbons (TPH) was achieved within 4 hours treatment time [Cho, et al., 2006a]. Solar light used alone or solar light combined with hydrogen peroxide (H$_2$O$_2$) did not show any significant removal within the same treatment period. Both TiO$_2$ immobilized systems were able to reduce BTEX and TPH levels effectively, provided 10 mM H$_2$O$_2$ was added. The removal efficiency of BTEX and TPH increased with larger solar collector area of the reactor. Lichtin et al. [1992] studied the TiO$_2$-catalyzed oxidative decomposition of 16 organic pollutants in water, including: Arochlor 1254, Aroclor 1260, benzene, chlorobenzene, chloroform, 2-chlorophenol, N,N-dimethylformamide (DMF), EDTA, ethylene glycol monomethyl ether, Freon 113 (C$_2$Cl$_3$F$_3$), glycerol, methanol, 2-nitrotoluene, phenol, toluene, and trichloroethylene (TCE). The destructions were promoted by photocatalytic oxidation using H$_2$O$_2$. All components of a mixture of six pollutants underwent oxidation decomposition, but relative rates in the mixture were not the same as for the separately, reacted components.

The effectiveness of the H$_2$O$_2$/UV process for treating aqueous solutions containing trichloroethylene (TCE), tetrachloroethylene (PCE) benzene, and toluene, was investigated by Kang and Le [1997]. Low pressure mercury lamps of wavelength 254 nm served as the UV source. For irradiation of aromatic compounds such as benzene and toluene at high concentrations, by-products formed were found to reduce the oxidation rate; the by-products acted as UV absorbers in competition with the parent compounds. Addition of peroxy enhanced the oxidation rate. The overall rate of the H$_2$O$_2$/UV system was dependent on the relative importance of the •OH radical pathway, the direct photolysis reaction rates, and the absorptivity of by-products at 254 nm. Kuo et al. [2000] studied the oxidation of toluene and 2,4,6-trinitrotoluene (TNT) by ozone and hydrogen peroxide mixtures (known as perozone oxidation) in solution at 25°C. The overall reaction in alkaline solution was 1st-order with respect to the concentration of dissolved ozone and was nearly independent of the pollutant concentrations. The oxidation of toluene was half-order in hydrogen peroxyde concentration; the rate constant changed in proportion to the hydroxyl ion concentration with an exponent of 0.67. Lawson and Adams [1999] studied treatment employing ozone and hydrogen peroxyde (H$_2$O$_2$) to treat toluene, benzene, xylene, tetrachloroethylene (PCE), trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA). Ozone, H$_2$O$_2$, and scavenger concentrations, and solution pH, all had a significant effect on the advanced oxidative scrubber system. Zeff and Barich [1992] reported that halogenated contaminants such as trichloroethylene, perchloroethylene, and other halogenated compounds have been successfully treated using UV/ozone or UV/hydrogen peroxyde UV with ozone and peroxyde. Contaminants such as benzene, toluene, xylene, hydrazines, phenols, chlorophenols, dioxanes, PCBs, and pesticides in wastewaters and groundwaters have also been reduced to acceptable discharge standards.

In a mechanistic study, Destaillats et al. [2000] studied the treatment of aqueous azo dye solutions. The degree of mineralization employing 500-kHz sonication of azobenzene or methyl orange solution increased from ~20% to more than 80% in the presence of ozone (O$_3$). The authors speculated that the synergism of combining sonication with ozone involved the fast oxidation by ozone of free radical or unsaturated species generated by •OH radical attack on otherwise refractory products. The products probably included saturated mono- and dicarboxylic acids, known to be resistant to O$_3$ oxidation. The increased high reactivity was attributed to HO$_2$• and O$_2$• radicals.
Manolache et al. [2004] studied the treatment of artificially contaminated water containing aromatic compounds (benzene, ethylbenzene, and xylenes) treated with dense medium plasma (DMP) environments in the presence of oxygen. Prior to optimization of the DMP technology, contamination levels decreased from 600 to 1,000 ppm to ppb levels for treatment times as low as 1 minute.

4 Methodology

The four tasks performed during this study are described briefly below.

4.1 Task 1. Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent continuous-flow experiments

Batch laboratory experiments were conducted to identify key process parameters such as solution pH values, steady-stated operating temperature, ultrasonic power intensities, initial petroleum hydrocarbon concentration, and oxidant concentrations. Petroleum hydrocarbons targeted for the study included: benzene, toluene, ethylbenzene, and o-xylene. Physical properties of these compounds are listed in Table 4-1. Additionally, several experiments were performed with multiple petroleum hydrocarbon contaminants present to investigate the effect of co-contaminants being present. Replicate experiments and chemical analyses were performed as part of the quality assurance/quality control.

Petroleum hydrocarbons will be spiked into artificial groundwater solutions, to closely simulate conditions that may be experienced in the field. The recipe for the artificial groundwater is listed below:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration to Prepare Artificial Groundwater</th>
<th>Quantity of Chemical Required to Prepare 20-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium sulfate [MgSO₄ • 7 H₂O]</td>
<td>60 mg/L</td>
<td>1.20-g</td>
</tr>
<tr>
<td>Potassium nitrate [KNO₃]</td>
<td>20 mg/L</td>
<td>0.40-g</td>
</tr>
<tr>
<td>Sodium bicarbonate [NaHCO₃]</td>
<td>36 mg/L</td>
<td>0.72-g</td>
</tr>
<tr>
<td>Calcium chloride [CaCl₂]</td>
<td>35 mg/L</td>
<td>0.70-g</td>
</tr>
<tr>
<td>Calcium nitrate [Ca(NO₃)₂]</td>
<td>35 mg/L</td>
<td>0.70-g</td>
</tr>
<tr>
<td>Calcium sulfate [CaSO₄ • 2H₂O]</td>
<td>25 mg/L</td>
<td>0.50-g</td>
</tr>
<tr>
<td>Hydrochloric acid [HCl]</td>
<td>0.35 mL</td>
<td>7.0-mL</td>
</tr>
<tr>
<td>Monobasic sodium phosphate dihydrate [NaH₂PO₄]</td>
<td>0.2 μM (~0.0312 mg/L)</td>
<td>0.624-g</td>
</tr>
</tbody>
</table>

Sonication/air sparging experiments were performed in a reactor used to treat the petroleum hydrocarbon contaminants in groundwater employing sonication alone, air sparging alone, or combined sonication/air sparging. The reactor was a glass vessel with an ultimate capacity of 1.0-L; normally the
reactor was operated using a sample volume of \( \sim 500\)-mL. Batch experiments were performed separately on each of the petroleum hydrocarbon contaminants (benzene, toluene, ethylbenzene, and xylene). The initial contaminant concentrations ranged anywhere from \( \sim 1\) to \( \sim 100\) mg/L. The sonicator has an ultrasonic frequency of 20 kHz; the applied power intensity was nominally 12.3-, 25.3-, and 35.8 W/cm\(^2\). The batch reactions were operated normally for up to 10 minutes treatment time, with samples withdrawn for GC analysis every 2 minutes. The batch experiments were operated using either sonication alone, air sparging alone, or using the combined sonication/air sparging technique. Air injection rates used in these experiments were nominally 0- (sonication alone), 250-, 500-, 750-, and 1000-mL/min.

Several batches of “simulated” groundwater containing both the contaminant-of-concern (COC) and any other significant competing contaminants were prepared. In this project, significant contaminants-of-concern included volatile organics such as benzene, toluene, ethylene benzene, and \( o\)-xylene. In the PI’s previous acoustic cavitation studies on chlorinated solvents conducted at Argonne National Laboratory, the following degradation products were identified for various chlorinated compounds:

<table>
<thead>
<tr>
<th>Sample</th>
<th>CCl(_4)</th>
<th>CHCl(_3)</th>
<th>CH(_2)Cl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediates</td>
<td>C(_2)Cl(_4), C(_2)Cl(_6)</td>
<td>CCl(_4), C(_2)Cl(_4), C(_2)Cl(_6)</td>
<td>CH(_2)Cl(_3)</td>
</tr>
<tr>
<td>Final Products</td>
<td>Cl(^-)</td>
<td>Cl(^-)</td>
<td>Cl(^-)</td>
</tr>
</tbody>
</table>

Similar studies were performed involving petroleum hydrocarbons. These batches of simulated groundwater mimicked the actual groundwater found at the selected LUST sites. Several test runs were conducted using the experimental treatment system. Concentrations of the COC as well as other significant contaminants were measured before and after passing through the experimental treatment system.

Task 3. Perform batch experiments to determine the effects of oxidants (O\(_3\), H\(_2\)O\(_2\), etc.) on SVOC degradation and the volatility and biodegradability of the resultant product.

Potential enhancements of the destruction of the parent SVOCs and VOCs by addition of oxidants (such as O\(_3\), H\(_2\)O\(_2\), etc.) were investigated in batch and/or continuous flow sonication experiments. The influence of these oxidants were addressed in terms of the organic degradation products.
Table 4-1. Physical properties of the petroleum hydrocarbons of interest for this study.

<table>
<thead>
<tr>
<th>Parent Compound or Degradation Product</th>
<th>Molecular Formula</th>
<th>Molecular Weight, (g/mole)</th>
<th>Boiling Point, (°C)</th>
<th>Freezing Point, (°C)</th>
<th>Flash Point, (°C)</th>
<th>Melting Point, (°C)</th>
<th>Density, (g/mL)</th>
<th>Vapor Pressure</th>
<th>Vapor Density</th>
<th>Lower Explosive Limit (LEL), (%)</th>
<th>Upper Explosive Limit (UEL), (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent Compounds:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>78.12</td>
<td>80.09</td>
<td>---</td>
<td>12 (cc)</td>
<td>5.51</td>
<td>0.8794@ 20°/4°C</td>
<td>100 mm@26.1°C</td>
<td>2.77</td>
<td>1.4</td>
<td>8.0</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C₆H₁₀</td>
<td>106.18</td>
<td>136.2</td>
<td>-94.9</td>
<td>59°F</td>
<td>-94.9</td>
<td>0.8669@ 20°/4°C</td>
<td>10 mm@25.9°C</td>
<td>3.66</td>
<td>1.2</td>
<td>6.8</td>
</tr>
<tr>
<td>Methyl tert-Butyl Ether (MTBE)</td>
<td>CH₃OC₄H₉</td>
<td>88.15</td>
<td>55.0</td>
<td>---</td>
<td>-10.0</td>
<td>-109</td>
<td>0.7405</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>128.18</td>
<td>217.9</td>
<td>---</td>
<td>174°F (oc)</td>
<td>80.1</td>
<td>1.162; 1.145@ 20°/4°C</td>
<td>1 mm@52.6°C</td>
<td>4.42</td>
<td>0.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>92.15</td>
<td>110.4-110.7</td>
<td>-94.5</td>
<td>40°F (cc)</td>
<td>-95.0 to -94.5</td>
<td>0.866@ 20°/4°C</td>
<td>36.7 mm@30°C</td>
<td>3.14</td>
<td>1.27</td>
<td>7.0</td>
</tr>
<tr>
<td>Xylene:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>C₈H₁₀</td>
<td>106.18</td>
<td>144.4</td>
<td>---</td>
<td>115°F (cc)</td>
<td>-25.2</td>
<td>0.880@ 20°/4°C</td>
<td>---</td>
<td>---</td>
<td>1.0</td>
<td>6.0</td>
</tr>
<tr>
<td>p-Xylene</td>
<td></td>
<td></td>
<td>138.3</td>
<td>---</td>
<td>77-81°F (cc)</td>
<td>13-14</td>
<td>0.8611@ 20°/4°C</td>
<td>10 mm@27.3°C</td>
<td>3.66</td>
<td>1.1</td>
<td>7.0</td>
</tr>
</tbody>
</table>
The untreated water and the sonicated-treated water (containing degradation products, identified in Task 2) were compared in terms of the degradation products. The volatility and biodegradability of the resultant organic compounds will be determined. The volatility of the target organic contaminants can be determined by measuring the residual contaminant concentrations using a laboratory-scale air sparging unit.

For the biodegradability of the resultant organic compounds, triplicate samples of untreated water and sonicated treated material will be subjected to shake flask biodegradation studies. Initially, soil inoculum from sites contaminated with the parent compound(s) were needed to determine the biodegradability of the untreated and treated material. Comparisons were made using GC/MS and HPLC of material before and after biotreatment. It is possible that an acclimation period may be required to provide for sufficient degradation to occur. These studies were conducted under aerobic and anaerobic conditions.

4.3 Task 3. Perform preliminary systems analysis and economic analysis for system scale-up for a field demonstration.

A preliminary systems analysis was performed on this integrated in-well sonication system, based upon the data collected in the above tasks. A comparison was made between this in-well sonication process and conventional pump-and-treat techniques, addressing wattage input and economics. The systems analysis approach was used to identify any major operational problems that require attention, potential intermediate degradation/emission products formed during the process, effect of co-contaminants (such as other organic contaminants, hardness (calcium and magnesium salts), etc.). This information can be used for design of pilot-scale equipment.

4.4 Procedure for the Different Tasks

4.4.1 Task 1. Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent continuous-flow experiments.

Figure 4-1 shows the experimental set up of the sonication system used to treat the various BTEX compounds.

The nominal experimental conditions employed are listed below:

- Bulk solution temperature was room temperature (~26°C);
- pH was near neutral (pH ~ 6-7);
- Bulk pressure: 1.0 atmospheres;
- Initial BTEX concentration: 100 mg/L
- Sonication frequency: 20 kHz
- Sonication power: 12, 24, and 36 W/cm²;

The reactor is 1.0-L in capacity; typically, the reactor was operated to hold 500-mL of liquid contents. The reactor has a series of injection/production ports to enable liquids to be delivered to and from the reactor, as well as provide means to add the advanced oxidants (hydrogen peroxide and ozone) to the reactor, plus provide means to obtain liquid samples for gas chromatography analysis, along with providing a means for the air space above the reactor to be sent through an activated carbon column for analysis with purge-and-trap techniques of the contaminants retained on the activated carbon column.
Task 2. Perform batch or continuous-flow experiments to determine the effects of oxidants (O₃, H₂O₂, etc.) on SVOC degradation and the volatility and biodegradability of the resultant product.

Figures 4-2 through 4-3 show the experimental system for acoustic treatment of BTEX-contaminated solutions using air sparging (volatilization) alone and sonication combined with air sparging, respectively. The air sparging system employed a diffused gas sparger to distribute the air in the form of gas bubbles throughout the reactor liquid contents. Note in Figure 4-2 the lack of the sonication equipment, while the system shown in Figure 4-3 allowed operation of the combined sonication and air sparging systems simultaneously. In addition to the nominal experimental conditions outlined for the sonication system, the following additional nominal operating conditions were employed for the combined sonication + advanced oxidants systems:

- Air flow rate: 0-, 250-, 500-, 750- and 1,000-mL/min
- Hydrogen peroxide (H₂O₂) dose: 100 ppm
- Sodium carbonate and sodium bicarbonate dose: 50 mg/L (to consume hydroxyl radicals)
- Ultraviolet light (mercury lamps): 16 lamps operating at 8 watts each

The hydrogen peroxide was added as a nominal 3% solution so that upon delivery to the reactor (after dilution) the hydrogen peroxide has a nominal concentration of 100 mg/L. The ultraviolet light equipment is shown in Figure 4-4. A UV-photoreactor stand was constructed to allow combined treatments involving sonication, air sparging, and UV irradiation to be operated in combination. The photo-reactor stand is shown in Figure 4-5. Figure 4-6 shows the experimental set up for the combined system employing sonication, air sparging, and UV irradiation.
Figure 4-2. Experimental set up for the air-sparging system.

Figure 4-3. Experimental set up for the combined sonication + air-sparging system.
Figure 4-4. UV irradiation system.
Figure 4-5. UV photoreactor stand for insertion into the UV irradiation system.

Task 3. Perform preliminary systems analysis for system scale-up for a field demonstration.

This task involves analysis of the data collected in Tasks 1 and 2 with a focus on the systems analysis.
5 Results and Discussion

5.1 Results for Task 1 – Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent experiments

5.1.1 Air sparging experimental results

Initial experiments involved performing air sparging on solutions containing 100 mg/L of benzene, toluene, ethylbenzene, and o-xylene using different air injection rates (250-, 500-, 750-, and 1,000-
Results from those experiments are shown in Figures 5-1, 5-2, 5-3, and 5-4 for benzene, toluene, ethylbenzene, and \( \alpha \)-xylene, respectively. These figures show that an air flow rate of 250-mL/min was insufficient for adequate removal of the BTEX compounds. However, the results for the other flow rates (500-, 750-, and 1,000-mL/min) resulted in nearly the same removal for any particular compound, with only marginal improvement for the flow rates of 750- and 1,000-mL/min compared to 500-mL/min; as a result, an air flow rate of 500-mL/min was used in the other experiments in which sonication was combined with air sparging operations.

The ease of removal of these BTEX compounds is shown by looking at the 1st-order rate constant \( k \) (which is the numerical value of the exponent in the base e term). The results are summarized in the table below. Comparison of the rate constants indicates that there is only marginal improvement in the removal of the BTEX compounds for air flow rates of 500-mL/min or greater. The removal of benzene, toluene, and ethyl benzene are comparable; removal of \( \alpha \)-xylene is the most difficult, as evidenced by it having the lowest 1st-order rate constants.

Table 5-1. Comparison of the rate constants for removal of BTEX compounds from solution using air sparging operations.

<table>
<thead>
<tr>
<th>Petroleum Hydrocarbon Compound</th>
<th>Air Flow Rate, (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0523</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0481</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.0857</td>
</tr>
<tr>
<td>( \alpha )-Xylene</td>
<td>0.0368</td>
</tr>
</tbody>
</table>

Figure 5-1. Comparison of removal efficiency of benzene using air sparging employing different air flow rates.
Figure 5-2. Comparison of removal efficiency of toluene using air sparging employing different air flow rates.

Figure 5-3. Comparison of removal efficiency of ethylbenzene using air sparging employing different air flow rates.
Figure 5-4. Comparison of removal efficiency of o-xylene using air sparging employing different air flow rates.

An observation was made during the experiments that Henry’s law constant effects a contaminant removal from water by air sparging. The results show ethylbenzene which has the highest Henry’s law constant has the highest removal efficiency. The highest removal rate for ethylbenzene compared to the other BTEX compounds is due to its higher Henry’s law constant.

5.1.2 Sonication experimental results

Experiments were performed to determine the removal efficiency of BTEX compounds using sonication alone (conducted at 20 kHz, ~38 W/cm²). The results are shown in Figure 5-5 for the four petroleum hydrocarbons studied (benzene, toluene, ethylbenzene, and o-xylene). After 10 minutes treatment time, sonication alone removed 45.8% of benzene, 47.2% of toluene, 50.9% of ethylbenzene, and 40.7% of o-xylene. The 1ère-order rate constants were 0.0608 min⁻¹, 0.0635 min⁻¹, 0.0702 min⁻¹, and 0.0497 min⁻¹, for benzene, toluene, ethylbenzene, and o-xylene, respectively. The value of the 1ère-order rate constant for benzene of 0.0608 min⁻¹ was very close to the 1ère-order rate constant reported by C.H. Kuo et al. [1997] of 0.066 min⁻¹ for benzene. Our results show sonication alone method is most effective in removing ethylbenzene (highest rate constant of 0.0702 min⁻¹) and least effective in removing o-xylene (lowest rate constant of 0.0497 min⁻¹). Removal rates for the different BTEX compounds are in the order ethyl benzene > toluene > benzene > o-xylene. This is in agreement with the order of the Henry’s law constants for the BTEX compounds. Ethylbenzene has the highest Henry’s law constant and hence is easily removed compared to the other BTEX compounds. The results of these experiments indicate that the Henry’s law constant plays an important role in removal of contaminants from water by sonication. The results also indicate sonication alone is not very effective in removing BTEX from water. This low removal rate can be attributed to several factors including degassing effect during sonication, improper frequency, temperature, power intensity, and the extremely volatile nature of BTEX compounds.
Comparison of Removal Rates of BTEX by Sonication Alone

<table>
<thead>
<tr>
<th>Compound</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$y = 0.9654e^{-0.0608x}$</td>
<td>0.9883</td>
</tr>
<tr>
<td>Toluene</td>
<td>$y = 0.9231e^{-0.0635x}$</td>
<td>0.9217</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>$y = 0.9938e^{-0.0702x}$</td>
<td>0.9902</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>$y = 0.9616e^{-0.0497x}$</td>
<td>0.9595</td>
</tr>
</tbody>
</table>

Figure 5-5. Comparison of fractional residual BTEX compounds remaining from sonication alone treatment (20 kHz, ~38 W/cm²).

5.2 Results for Task 2 – Perform batch or continuous-flow experiments to determine the effects of oxidants (O₃, H₂O₂, etc.) on SVOC degradation and the volatility and biodegradability of the resultant product

5.2.1 Combinations of experimental systems

Experiments were conducted in which advanced oxidants were added to solutions. For the benzene system, the following treatment systems were investigated:

- Air sparging alone;
- Sonication alone (at 20 kHz);
- UV alone;
- Sonication + air sparging;
- Sonication + UV;
- Air sparging + UV;
- UV + H₂O₂;
- Sonication + air sparging + H₂O₂;
- Sonication + air sparging + UV; and
- Sonication + air sparging + H₂O₂ + UV.

Results of these various systems (used singly or in combination) are presented in Figure 5-6. Figures 5-7 through 5-9 show the results for the toluene, ethylbenzene, and o-xylene systems, respectively, employing sonication alone (operated at 20 kHz), air sparging alone (employing an air flow rate of 500 mL/min), and the combined sonication + air sparging system.
Performance of Different Systems for Removal of Benzene

- Air sparging alone
  \[ y = 1.0582e^{-0.1347x} \]
  \[ R^2 = 0.9834 \]

- Sonication alone
  \[ y = 0.9654e^{-0.0608x} \]
  \[ R^2 = 0.9883 \]

- UV alone
  \[ y = 0.9951e^{-0.2289x} \]
  \[ R^2 = 0.9955 \]

Comparison of residual benzene remaining in solution using different treatment systems.

Sonication + Air sparging + UV
  \[ y = 1.0943e^{-0.2886x} \]
  \[ R^2 = 0.9955 \]

Sonication + UV
  \[ y = 0.9951e^{-0.2289x} \]
  \[ R^2 = 0.9955 \]

Figure 5-6.

Comparing system performance for toluene removal

- Air sparging alone
  \[ y = 0.984e^{-0.1381x} \]
  \[ R^2 = 0.9867 \]

- Sonication alone
  \[ y = 0.9231e^{-0.0635x} \]
  \[ R^2 = 0.9217 \]

- Sonication + Air sparging
  \[ y = 1.3823e^{-0.2443x} \]
  \[ R^2 = 0.9054 \]

Figure 5-7.
Comparing system performance for Ethylbenzene

Figure 5-8. Comparison of residual ethylbenzene remaining in solution using different treatment systems.

Comparing System Performance for o-xylene

Figure 5-9. Comparison of residual o-xylene remaining in solution using different treatment systems.
Figure 5-10 shows a comparison of the removal of benzene, toluene, ethylbenzene, and \( o \)-xylene, employing sonication alone, air sparging alone, and the combined sonication + air sparging system for a treatment time of 20 minutes. For a treatment time of 10 minutes, removal by sonication alone, air sparging alone, and the combined sonication + air sparging system ranged from 41.0 – 51.0%, 75.0 – 77.0%, and 90.0 – 94.0%, respectively.

![Comparison of Treatment Systems for Removal of BTEX](image)

5.2.2 Effect of initial contaminant concentration

Figure 5-11 shows the results of treating benzene in solution using combined sonication (operated at 20 kHz) + air sparging (using an air injection rate of 500-mL/min), for different initial benzene concentrations. Nominal initial benzene concentrations were 25, 50, 100, and 200 mg/L. The removal curves all exhibit similar behavior. The 1st-order rate constants for these four initial benzene concentrations are summarized below in Table 5-2. The data indicate that nearly identical 1st-order rate constants are obtained for all four initial benzene concentrations (ranging from 25 to 200 mg/L). This indicates that the reaction is 1st-order reaction, independent of the initial concentration.

Contaminants are usually present in water as a mixture of more than one contaminant. In the case of BTEX compounds, most often they are present in water as a mixture of all four BTEX compounds. Other contaminants such as methyl tert-butyl ether (MTBE) may also be present. Presence of more than one contaminant complicates the treatment process and may affect its efficiency to remove the contaminants. Additional experiments were performed to study the effect of co-contaminants on the effectiveness of the integrated sonication + air sparging system. Benzene and ethylbenzene were used as co-contaminants for each other and the effect of one on the removal efficiency of the other was studied. MTBE and phenol...
were also used as co-contaminant for benzene and the effect of their presence on the removal of benzene with the sonication + air sparging system studies. Concentrations used for all contaminants were maintained at 100 mg/L for the sake of uniformity.

5.2.3 Effects of co-contaminants

Figure 5-12 shows the effects of having a co-contaminant present. In this case, experiments using benzene and ethylbenzene were conducted (in the absence and presence of each other). By having the other compound present as a co-contaminant, the removal of the target compound (either benzene or ethylbenzene) was enhanced. Table 5-3 compares the removal of benzene and ethylbenzene in the absence and presence of a co-contaminant).

![Graph showing the effects of having a co-contaminant present](image.png)

**Figure 5-11.** Effect of initial benzene concentration for combined sonication + air sparging treatment.

**Table 5-2.** 1st–order rate constants for removal of benzene from solution employing sonication + air sparging for various initial benzene concentrations.

<table>
<thead>
<tr>
<th>Initial Benzene Concentration, (mg/L)</th>
<th>1st-Order Rate Constant, (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.2325</td>
</tr>
<tr>
<td>50</td>
<td>0.2316</td>
</tr>
<tr>
<td>100</td>
<td>0.2234</td>
</tr>
<tr>
<td>200</td>
<td>0.2276</td>
</tr>
</tbody>
</table>

24
Table 5-3. 1st-order rate constants of the target contaminant (benzene or ethylbenzene) with and without a co-contaminant present.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Co-Contaminant</th>
<th>1st-Order Rate Constant, (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>None</td>
<td>0.2234</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>None</td>
<td>0.2684</td>
</tr>
<tr>
<td>Benzene</td>
<td>Ethylbenzene</td>
<td>0.2795</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Benzene</td>
<td>0.3122</td>
</tr>
</tbody>
</table>

Figure 5-12. Effect of co-contaminants on treatment performance using sonication + air sparging.

Figure 5-13 shows the effect of having co-contaminants (MTBE and phenol) present for removal of benzene from solution using sonication + air sparging. The presence of these co-contaminants hindered the removal of benzene from solution; the 1st-order rate constant decreased from 0.2234 min⁻¹ (in the absence of MTBE and phenol) to 0.2066 min⁻¹, a decrease of 7.5%. The presence of MTBE and phenol as co-contaminants hindered the removal of benzene slightly, but not to a great degree.
The tables and graphs above show co-contaminants did not significantly affect the performance of the sonication + air sparging system. This insensitivity of the process to co-contaminants may be due to the reaction mechanism. The dominant reaction mechanism seems to be pyrolysis. The minor reaction mechanism is oxidation by \( \cdot \)OH radicals. Pyrolysis refers to the incineration or burning of the contaminant due to high temperature during the cavity implosion events. The more contaminants there are; the more of them are incinerated; therefore, the effect of co-contaminants on the pyrolysis is insignificant.

In the first case, benzene and ethylbenzene were used as co-contaminants for one another and the effect of the presence of one was studied on the removal rate of the second contaminant. A concentration of 100 mg/L of both benzene and ethylbenzene were used. An unexpected observation was seen for removal of both benzene and ethylbenzene when treated in the presence of one another. The percentage of benzene and ethylbenzene removed with 10 minutes treatment when treated in presence of one another was greater than the removal when each of them was treated separately. When treated separately, the sonication + air sparging removed 90% benzene and 94% ethylbenzene, while in presence of ethylbenzene, the removal of benzene reached 93% and removal of ethylbenzene increased to 95%. The increase in removals may be due to the two contaminants working as co-solvents for one another.

For the case of MTBE and phenol as co-contaminants, the percent removal was reduced from 90% to 86%. Though the reduction is within the error margin, it is possible the presence of MTBE and phenol affect the \( \cdot \)OH reactions. MTBE and phenol compete with benzene for \( \cdot \)OH radicals, thus slightly inhibiting the degradation of benzene by \( \cdot \)OH radicals. The small reduction in the removal rate of benzene in presence of the co-contaminants also indicates that the dominant reaction mechanism for the system is pyrolysis.
The observed impunity of the system to the inhibitory effects of co-contaminants is a positive factor favoring better system performance in real-life application of the technology. In most cases, the contaminants are present in water as a mixture of more than one contaminant and any system deployed for remediation must deal with co-contaminants which can adversely affect the system performance.

5.2.4 Effect on process performance from addition of hydrogen peroxide

Figure 5-14 shows the effect of adding 100 ppm of hydrogen peroxide (H₂O₂) to sonication combined with air sparging for treatment of benzene. The addition of hydrogen peroxide causes a slight enhancement on the removal of benzene from solution, increasing the 1st-order rate constant from 0.2150 min⁻¹ to 0.2234 min⁻¹. The effect is more pronounced during the early part of treatment (~2 to 6 minutes), whereas the removal is nearly the same with or without H₂O₂ after 8 minutes of treatment time.

5.2.5 Effect on process performance from UV light

Figures 5-15 and 5-16 show the effect of adding ultraviolet (UV) light coupled with the use of sonication and air sparging for removal of benzene and toluene, respectively, from solution. The UV experimental treatment set up was shown in Figure 4-6; 16 UV tubes of 8-watts each were used for the UV treatment. Figures 5-15 and 5-16 show that addition of UV light enhanced the removal of benzene and toluene from solution, increasing the 1st-order rate constant from 0.2166 min⁻¹ to 0.2866 min⁻¹ and from -0.2359 min⁻¹ to 0.3512 min⁻¹ for benzene and toluene, respectively.
Figure 5-15. Effect of adding UV light on removal of benzene from solution using sonication + air sparging treatment.

Figure 5-16. Effect of adding UV light on removal of toluene from solution using sonication + air sparging treatment.
5.2.6 Comparison of treatment processes on removal of benzene, toluene, ethylbenzene, and \textit{o}-xylene from solution

Figure 5-17 shows the system performance for the various treatment systems used for removing benzene from solution; the treatment systems are ranked in terms of their system performance, from lowest treatment efficiency to highest treatment efficiency. The treatment time used in the system was 10 minutes. The lowest treatment efficiency was 26% using UV light alone, whereas the highest efficiency was 95% achieved using sonication + air sparging + UV light and sonication + air sparging + UV + H\textsubscript{2}O\textsubscript{2}. Greater than 90% benzene removal was achieved using the following techniques:

- sonication + air sparging
- sonication + air sparging + H\textsubscript{2}O\textsubscript{2}
- sonication + air sparging + UV light
- sonication + air sparging + UV + H\textsubscript{2}O\textsubscript{2}

Figures 5-18 through 5-20 shows the system performance for the various treatment systems used for removing benzene from solution; the treatment systems are ranked in terms of their system performance, from lowest treatment efficiency to highest treatment efficiency. The treatment systems investigated were: sonication alone (operated at 20 kHz); air sparging alone (using an air injection rate of 500 mL/min); sonication + air sparging; sonication + UV light; and sonication + air sparging + UV light. The lowest removal efficiency was achieved using sonication alone – 47%, 51%, and 41% for toluene, ethylbenzene, and \textit{o}-xylene, respectively. The highest efficiency was achieved using the combined sonication + air sparging + UV light, resulting in removals of 97%, 99%, and 93% for toluene, ethylbenzene, and \textit{o}-xylene, respectively, after 10 minutes treatment time. Approximately 90% or greater removal efficiencies were achieved using sonication + air sparging and sonication + air sparging + UV light.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{system_comparison.png}
\caption{System Comparison for Benzene Removal Efficiency for 10 min Treatment Time}
\end{figure}

Figure 5-17. Treatment system performance comparison for various treatment techniques for removing benzene from solution.
Figure 5-18. Treatment system performance comparison for various treatment techniques for removing toluene from solution.

Figure 5-19. Treatment system performance comparison for various treatment techniques for removing ethylbenzene from solution.
Figure 5-20. Treatment system performance comparison for various treatment techniques for removing o-xylene from solution.

5.2.7 Effect of hydroxyl radical scavengers on system performance

Figure 5-21 shows the effect of having hydroxyl radical (•OH) scavengers present (carbonate and bicarbonate ions, present at 100 mg/L as CaCO₃ each, on the removal of benzene from solution. The presence of the •OH radical scavengers does have a small effect on the removal of benzene from solution. The presence of the carbonate and bicarbonate ions caused a reduction in the 1ˢᵗ-order rate constant from 0.2234 min⁻¹ to 0.2017 min⁻¹, a reduction of 9.7%.
Figure 5-21. Effect of OH radical scavengers (sodium carbonate/sodium bicarbonate) on removal of benzene from solution using sonication + air sparging.

5.3 Results for Task 3 – Perform preliminary systems analysis for system scale-up for a field demonstration.

Figure 5-22 presents a comparison of the predicted performance for the combined treatment system (sonication + air sparging + UV light) along with the individual treatment systems (sonication alone, air sparging alone, and UV light alone). The predicted rate constant for the combined treatment process was obtained by adding the respective rate constants for the individual processes (sonication and air sparging). The combination of these treatment systems represents a process synergism, resulting in a 27.6% enhancement over the case of combining the rate constants for the separate systems. The results are summarized in Table 5-4 below.

Table 5-4. Comparison of the 1st-order rate constants for various treatment processes in removing benzene from solution.

<table>
<thead>
<tr>
<th>Treatment Process</th>
<th>1st-Order Rate Constant, (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonication alone</td>
<td>0.0608</td>
</tr>
<tr>
<td>Air sparging alone</td>
<td>0.1347</td>
</tr>
<tr>
<td>UV light alone</td>
<td>0.0307</td>
</tr>
<tr>
<td>Combined (sonication + air sparging + UV light) – predicted</td>
<td>0.2262</td>
</tr>
<tr>
<td>Combined (sonication + air sparging + UV light) – observed</td>
<td>0.2886</td>
</tr>
</tbody>
</table>
Comparison of Observed and Predicted Fractional Residual Benzene Concentrations Using Sonication + Air Sparging + UV Light

Sonication:

\[ y = 0.9654e^{-0.0608x} \]
\[ R^2 = 0.9883 \]

Air Sparging:

\[ y = 1.0582e^{-0.1347x} \]
\[ R^2 = 0.9834 \]

UV Light:

\[ y = 0.9951e^{-0.0307x} \]
\[ R^2 = 0.9905 \]

Sonication+Air Sparging+UV (observed):

\[ y = 1.0943e^{-0.2886x} \]
\[ R^2 = 0.9955 \]

Sonication+Air Sparging+UV (predicted):

\[ y = e^{-0.2262x} \]
\[ R^2 = 1 \]

Figure 5-22. Synergistic effects of combining advanced oxidation processes for removal of benzene from solution.

Using the data presented in this section, the process synergism of combining technologies can be assessed. The technologies considered were sonication alone (operated at 20 kHz), air sparging alone (using an air injection rate of 500-mL/min), and the combination of sonication and air sparging. The process synergism was assessed for benzene, toluene, ethyl benzene, and o-xylene. The data are summarized in Table 5-5 on the following page. The predicted rate constant for the combined treatment process was obtained by adding the respective rate constants for the individual processes (sonication and air sparging). In every case the experimental observed rate constant was higher than the predicted rate constant. The enhancement of combining the processes was approximately 10.8%, 21.2%, 56.3%, and 13.3% for benzene, toluene, ethylbenzene, and o-xylene, respectively. Combining the processes results in process synergism, thereby enhancing the system removal efficiency, and results in a more cost-effective process.
Table 5-5. Summary of 1st-order rate constants using various treatment processes for removal of benzene, toluene, ethylbenzene, and o-xylene from solution.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Treatment Process</th>
<th>1st-Order Rate Constant, (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Sonication alone</td>
<td>0.0608</td>
</tr>
<tr>
<td></td>
<td>Air sparging alone</td>
<td>0.1347</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (predicted)</td>
<td>0.1955</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (observed)</td>
<td>0.2166</td>
</tr>
<tr>
<td>Toluene</td>
<td>Sonication alone</td>
<td>0.0635</td>
</tr>
<tr>
<td></td>
<td>Air sparging alone</td>
<td>0.1381</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (predicted)</td>
<td>0.2016</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (observed)</td>
<td>0.2443</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Sonication alone</td>
<td>0.0702</td>
</tr>
<tr>
<td></td>
<td>Air sparging alone</td>
<td>0.1655</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (predicted)</td>
<td>0.2357</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (observed)</td>
<td>0.3684</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Sonication alone</td>
<td>0.0497</td>
</tr>
<tr>
<td></td>
<td>Air sparging alone</td>
<td>0.1385</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (predicted)</td>
<td>0.1882</td>
</tr>
<tr>
<td></td>
<td>Combined sonication + air sparging (observed)</td>
<td>0.2132</td>
</tr>
</tbody>
</table>

6 Summary and Conclusions

Batch experiments were conducted for removal of benzene, toluene, ethylbenzene, and o-xylene from solution, using sonication, air sparging, and combined sonication and air sparging. The experimental results indicate that increasing the air flow rate enhances mass transfer efficiency, but the enhancement of mass transfer rate with respect to air flow rate is not linear. The experimental data indicated that an air flow rate of 250-mL/min was insufficient for adequate removal of the BTEX compounds, whereas the results for the other flow rates (500-, 750-, and 1,000-mL/min) resulted in nearly the same removal for any particular compound, with only marginal improvement for the flow rates of 750- and 1,000-mL/min compared to 500-mL/min; as a result, an air flow rate of 500-mL/min was used in the other experiments in which sonication was combined with air sparging operations. Bubbles are coalesced as the air flow increases and the coalescence of the bubbles lowers the enhancement of interfacial area [Miller, 1983]. As a consequence, the coalescence of the bubbles limits the mass transfer efficiencies of organic compounds in bubble column reactors.

Sonication alone method is most effective in removing ethylbenzene and least effective in removing o-xylene. Removal rates for the different BTEX compounds are in the order ethyl benzene > toluene > benzene > o-xylene, which is in agreement with the order of the Henry’s law constants for the BTEX compounds. Ethylbenzene has the highest Henry’s law constant and hence is more easily removed compared to the other BTEX compounds. The results of these experiments indicate that the Henry’s law constant plays an important role in removal of contaminants from water by sonication. The results also indicate sonication alone is not very effective in removing BTEX from water.

Experiments were performed to determine the BTEX removal efficiency for sonication combined with air sparging system. The combined sonication + air sparging system removed 90% of benzene compared to 46% by sonication alone and 75% by air sparging alone. The removal of toluene by combined system is 92% compared to 47% by sonication alone and 77% by air sparging alone. The
combined sonication + air sparging system also removed 94% of ethylbenzene compared to 51% by sonication alone and 81% by air sparging alone while the removal of o-xylene by combined sonication + air sparging system is 89% compared to 41% by sonication alone and 75% by air sparging alone. The two systems when combined, act synergistically and improve the removal efficiency of BTEX compounds from solution. This synergism exists due to the fact that dissolved gases play a critical role in determining the efficiency of a sonication system. The presence of dissolved gases dramatically enhances the contaminant removal efficiency of the sonication system. The absence of dissolved gases adversely affects performance of the sonication system. By combining air sparging with the sonication process, the presence of dissolved gases in the solution is enhanced. These dissolved gases provide nucleation sites for the cavitation microbubbles. The presence of dissolved gases lowers the cavitation threshold and results in the generation of higher numbers of microbubbles, which in turn enhances the contaminant removal efficiency of the integrated sonication system.

Contaminant removal efficiency of all the systems (air sparging, sonication, and sonication+air sparging) is affected by the contaminant’s Henry’s law constant. Contaminants with higher Henry’s law constants are more easily removed from water while contaminants with lower Henry’s law constant are harder to remove. This work shows all three treatment systems (air sparging alone, sonication alone, and sonication + air sparging) are more effective in removing ethylbenzene which has the highest Henry’s law constant, but less effective in removing o-xylene which has the lowest Henry’s law constant.

Although air sparging alone removes a high percentage of BTEX compounds from water and the combined sonication + air sparging system enhances the removal by less than 25% over the air sparging alone system, the combined system has several key advantages over the air sparging alone system. Air sparging does not destroy the contaminant; it merely facilitates a phase transfer from the liquid phase into the gaseous phase. The contaminant removed by air sparging still pose a danger to the environment. The contaminants removed by air sparging exist in vapor form above the liquid surface. These contaminant vapors must be captured through soil vapor extraction system (SVE) and must be treated before they are released into the environment. Additional treatment is required to comply with existing legal requirements and to avoid soil and air contamination. Post-treatment techniques generally used along with air sparging include incineration and chemical treatment after vapor extraction from an air sparging site. The combines sonication + air sparging system, on the other hand, destroys the contaminant in-situ. The combined system eliminates the need for post-treatment thus cutting cost of remediation. The combined system also eliminates the need for SVE system for capturing contaminant vapors thus reducing cost, installation time, maintenance cost. Also the contaminated vapors generated collected during air sparging are brought up to the surface for further treatment which triggers compliance with RCRA. Once the contaminant vapors are brought up to the surface, the contaminated vapors, water, the sludge, are removed, and the recovered contaminants must be handled as toxic substances. The combined sonication + air sparging system eliminates the above surface vapor treatment and the technical and legal issues associated with it.

Sonication results in degassing of the liquid; for an efficient sonication process, a dissolved gas supply must be maintained. Combining air sparging with sonication greatly improves the contaminant removal efficiency. Air sparging helps maintain the dissolved gases supply in the liquid, thereby ensuring high removal efficiency of sonication system. The two processes act synergistically and the overall efficiency of a combined system is better than either of the two systems alone. The results from this project show air sparging and sonication works best in combination with each other. The performance of sonication + air sparging far exceeds that of the two separate systems operating separately.

The presence of co-contaminants did not significantly affect the performance of the sonication + air sparging system. This insensitivity of the process to co-contaminant may be due to the reaction
mechanism. The dominant reaction mechanism seems to be pyrolysis, while the minor reaction mechanism is oxidation by \( \bullet \text{OH} \) radicals.

Benzene and ethylbenzene were used as co-contaminants for one another and the effect of the presence of one was studied on the removal rate of the other contaminant. When treated in presence of one another, the percentage of benzene and ethylbenzene when treated in presence of one another was greater than the removal when each of them was treated separately. The increase in removal may possibly be due to the two working as co-solvent for one another.

For the case of MTBE and phenol as co-contaminants, the percent removal of benzene was reduced. It is likely that the presence of MTBE and phenol effect the \( \bullet \text{OH} \) reactions. MTBE and phenol compete with benzene for \( \bullet \text{OH} \) radicals, thereby slowing down the degradation of benzene by \( \bullet \text{OH} \) radicals. The insignificantly small reduction in the removal rate of benzene in presence of co-contaminants, also indicates that the dominant reaction mechanism for the system is pyrolysis.

For initial benzene concentrations of 25-, 50-, 100-, and 200 mg/L, treatment results indicated that the effect of initial concentration on performance of sonication + air sparging to remove benzene was insignificant. This suggests that the dominant reaction mechanism is pyrolysis. The initial concentration greatly influences the rate of contaminant destruction by \( \bullet \text{OH} \) radicals, because with increased initial concentration the number of contaminant molecules overwhelm the \( \bullet \text{OH} \) radicals available to attack the contaminant molecules, thereby decreasing the rate of contaminant destruction. However the process of pyrolysis is minimally affected by the initial concentration. With increased initial concentration, more of the contaminant is destroyed during pyrolysis. The fact that initial concentration does not affect the removal rate by sonication + air sparging indicates the dominant reaction mechanism is pyrolysis.

In order to investigate the reaction mechanism for the integrated sonication + air sparging treatment process and determine which of the two is the dominant mechanism; experiments were performed in presence of \( \bullet \text{OH} \) radical scavengers with the view that the \( \bullet \text{OH} \) radical scavengers negatively affect a system performance where dominant reaction mechanism is by \( \bullet \text{OH} \) radical reactions. The \( \bullet \text{OH} \) radicals did not significantly affect the benzene removal rate. When treated in presence of \( \bullet \text{OH} \) scavengers (such as carbonate and bicarbonate ions), the decrease in the benzene removal rate was insignificant. The \( \bullet \text{OH} \) scavenger’s failure to significantly reduce the efficiency of the sonication + air sparging system performance indicates that the reaction by \( \bullet \text{OH} \) radicals to degrade benzene is not the dominant reaction mechanism; the results indicated the dominant reaction mechanism of the sonication + air sparging system was pyrolysis.

The effect of two advanced oxidants, hydrogen peroxide \( (\text{H}_2\text{O}_2) \) and ultraviolet light \( (\text{UV}) \), was studied on the overall performance of the combined sonication + air sparging system to remove benzene. The results showed that both \( \text{H}_2\text{O}_2 \) and UV light enhanced the performance of the sonication + air sparging system. However, the enhancement resulting from addition of UV light was much larger compared to the enhancement by \( \text{H}_2\text{O}_2 \). Since the enhancement of system performance for removal of benzene by addition \( \text{H}_2\text{O}_2 \) was insignificant compared to the enhancement resulting from addition of UV, \( \text{H}_2\text{O}_2 \) was not tried for the rest of the contaminants. Only sonication + air sparging + UV light system was tested for the remaining three contaminants.

\( \text{H}_2\text{O}_2 \) breaks under sonication releasing \( \bullet \text{OH} \) radicals thus enhancing removal of benzene by \( \bullet \text{OH} \) radical reaction. Removal of benzene by \( \bullet \text{OH} \) radical reaction is only a very small portion of the overall reaction; the dominant process is the removal of benzene by pyrolysis. The fact that UV light has a much more positive effect on the system performance compared to \( \text{H}_2\text{O}_2 \) is likely due to the fact that \( \text{H}_2\text{O}_2 \) only affects the minor process of removal of benzene by \( \bullet \text{OH} \) radicals, but has little, if any, effect on the
dominant reaction mechanism of pyrolysis, which is responsible for removal of the bulk of the benzene from water. UV light, on the other hand, can affect both types of reaction mechanisms. UV light causes water to dissociate, generating •OH radicals, thus enhancing the removal of benzene by •OH radical reaction mechanism. Light is a form of energy and addition of UV light means addition of more energy to the system. The added energy due to addition of UV light results in a lower cavitation threshold and more intense temperature. Both these factors enhance pyrolysis, thus increasing the over efficiency of the system.

The lowest treatment efficiency for removal of benzene was using UV light alone, whereas the highest efficiency was achieved using sonication + air sparging + UV light and sonication + air sparging + UV + H₂O₂. Greater than 90% benzene removal was achieved using the following techniques:

- sonication + air sparging
- sonication + air sparging + H₂O₂
- sonication + air sparging + UV light
- sonication + air sparging + UV + H₂O₂

The lowest removal efficiency for removal of toluene, ethylbenzene, and o-xylene, was achieved using sonication alone. The highest efficiency was achieved using the combined sonication + air sparging + UV light. Approximately 90% or greater removal efficiencies were achieved using sonication + air sparging and sonication + air sparging + UV light.

The results of this research project are summarized as below:
1. An optimum air flow rate exists for the air sparging system.
2. The Henry’s law constant plays an important role in determining system efficiency.
3. Stand alone sonication system is not a very efficient or cost-effective remediation technique.
4. Combining sonication with air sparging synergistically enhances the system performance.
5. Initial concentration does not significantly affect the system performance.
6. The presence of a co-contaminant may slightly enhance or slightly depress contaminant removal rate depending on the type and nature of the co-contaminant.
7. The dominant reaction mechanism is pyrolysis.
8. Adding hydrogen per oxide (H₂O₂) does not significantly affect the contaminant removal rate.
9. Sonication combined with UV light can be developed into an efficient remediation system.
10. Advanced oxidants such as UV light can dramatically enhance the sonication + air sparging system performance.
7 Synopsis

Below is the Synopsis that was submitted to the Alabama Water Resources Research Institute.

“USE OF SONICATION/ACOUSTIC CAVITATION WITH ADVANCED OXIDANTS TO TREAT PETROLEUM HYDROCARBONS-CONTAMINATED SURFACE WATERS AND GROUNDWATERS”

Project Synopsis  You should provide a synopsis of your research project, single-spaced, one inch margins on all sides, and not to exceed three (3) pages, which incorporates:

a. A statement of the problem and research objectives:

This project seeks to treat petroleum-hydrocarbon contaminated groundwater using a combination of sonication, vapor stripping, and advanced oxidants as a means to cleanup the groundwater.

b. A brief explanation of methodology:

Four separate tasks are to be performed in this study. Batch and continuous flow experiments will be performed using sonication alone, vapor stripping alone, and combined sonication/vapor stripping. The study focused on treatment of benzene, toluene, ethylbenzene, and o-xylene (BTEX). Initial contaminant concentrations were generally held constant at 100 mg/L. The sonicator had an ultrasonic frequency of 20 kHz, and the power intensity was ~38 W/cm². For those experiments involving air stripping, the air injection rate was normally held constant at 500 mL/min. Additional experiments were conducted for removal of benzene, toluene, ethylbenzene, and o-xylene, using different air flow rates, of 250, 500, 750, and 1,000 mL/min. Batch reactions were operated for up to 10 minutes treatment time, with samples drawn for gas chromatography analysis every 2 minutes. Experiments were performed both in the absence and presence of advanced oxidants such as ozone (O₃) and hydrogen peroxide (H₂O₂). The project determined the removal of the parent petroleum hydrocarbon contaminant and identify and quantified any degradation products formed during the advanced oxidation treatment. As a part of the project, a preliminary economic and process performance assessment were performed.

c. Principal findings and significance;

Results from air stripping treatment for 10 minutes are summarized below in Table 1. The results indicate that little improvement in terms of contaminant removal is achieved for air flow rates exceeding 500 mL/min. This flow rate was deemed to be the optimum air flow rate for the other experiments performed in conjunction with sonication.
Table 1. Summary of Results from Air Sparging Experiments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Removal Efficiency, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air Flow Rate, (mL/min)</td>
</tr>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Benzene</td>
<td>37.46</td>
</tr>
<tr>
<td>Toluene</td>
<td>39.98</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>53.00</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>55.37</td>
</tr>
</tbody>
</table>

Figure 1 summarizes the removal efficiency of benzene, toluene, ethylbenzene, and o-xylene obtained after 10 minutes treatment using various treatment technologies (sonication alone, air sparging alone, sonication+air sparging, sonication+UV light, and sonication+air sparging+UV light).

Figure 1. Comparison of Removal Efficiencies of BTEX Compounds Using Different Treatment Processes.

d. A list of all publications/presentations and manuscripts produced:

A list of all publications/presentations and manuscripts produced during the conduct of this project (when the project synopsis was submitted), a total of six technical/scientific presentations and one conference proceedings were produced. These publications/presentations are listed below.
Conference Proceedings:


Conference Presentations:


Poster Papers Presented at Regional Conferences:


e. A list of all students (and their educational level) supported on the project:

- Mr. Jan Mohammad – seeking M.S. degree in environmental engineering
  Department of Civil and Environmental Engineering
  University of Alabama at Birmingham
  Birmingham, AL 35294-4440
8 Publications

Publications and conference presentations resulting from this project are listed below.

Publications:


Presentations at National/Regional Conferences:


Poster Papers Presented at Regional Conferences:


Copies of these papers and presentations are available upon request.
9 References Cited


43


International Conf. on Advanced Oxidation Technologies for Water and Air Remediation, p.33 (abstract), Orlando, FL, (September 23-26).


APPENDIX I. BRIEF DESCRIPTION OF SONICATION/ACOUSTIC CAVITATION AND VAPOR STRIPPING TECHNOLOGIES

INTRODUCTION

Following the declassification of sonication technology and materials by the military, considerable scientific and innovative advances have been made within the last few years in the field of acoustic cavitation (sonication). Sonication can no longer be thought of simply as a "jewelry cleaner" technique, but incorporates significant advances in the areas of much higher power/densities, multiple frequency devices, miniaturization of acoustic cavitation equipment, improved focusing and directionalizing of acoustic waves, etc., have enabled significant advances to today’s second generation sonication equipment. Applications have been developed for using the technology in the metals, agricultural, energy and environmental sectors. This project outlines an approach for resolving an extremely vexing environmental issue, i.e., organics in groundwater.

The introduction of high power ultrasound (i.e., sound energy with frequencies in the range of 15 kHz to ~1MHz) into liquid reaction mixtures is known to cause a variety of chemical transformations. In recent years, due to the growing need to eliminate undesirable chemical compounds, the utilization of high energy ultrasound for hazardous waste treatment has been explored with great interest [Hua and Hoffmann, 1996; Hua et al., 1995a,b; Hoffmann et al., 1996; Kotronarou et al., 1991, 1992a,b; Kotronarou and Hoffmann, 1995].

Sonication of liquid media results in the formation of microbubbles that grow to a critical size and then implode. Temperatures at the collapsing bubble interface are about 5,000°K and pressures are near 500 atmospheres, but the bulk solution remains near ambient conditions. In these highly reactive conditions, hydroxyl radicals (•OH) and hydrogen ions (H•) are generated; they are very effective at degrading organic compounds. If organic compounds are present in the water, they are rapidly destroyed, either directly or by reacting with the free radicals. The intensity of cavity implosion, and hence the nature of the reactions involved, can be controlled by process parameters such as the ultrasonic frequency, ultrasonic intensity per unit volume of liquid medium, static pressure, choice of ambient gas, and addition of oxidants (e.g., H2O2, O3).

The discussion that follows addresses primarily sonication/acoustic cavitation treatment of chlorinated organics. However, a similar discussion will be applicable for treatment of petroleum hydrocarbons.

The application of ultrasonic irradiation for treatment of hazardous chlorinated organic wastes started in the early 1980s. Argonne National Laboratory has been at the forefront of this research. To demonstrate the feasibility of the ultrasonic detoxification process and to obtain kinetic information about the process, two bench-scale batch-processing units, one pilot-scale batch/continuous-processing unit, and one continuous-flow unit were set up at Argonne. Research activities at Argonne have concentrated on the ultrasonic decomposition of hazardous organic compounds present in aqueous samples (including laboratory-prepared, laboratory-simulated, and real samples received from the field) from industrial waste streams and groundwaters. Results from these experiments indicated that ultrasonics or ultrasonics-enhanced advanced oxidation processes can convert the hazardous organic contaminants to non-toxic or less toxic, simpler organic compounds. For some simpler but toxic organic compounds (such as carbon tetrachloride, trichloroethylene, etc.), the introduced ultrasonic energy completely converts the compounds into non-hazardous compounds such as water, carbon dioxide, and hydrochloric acid. Of the process parameters investigated to date, the intensity of the ultrasonic-wave energy was found to have the largest effect on the destruction rate of the contaminant (which increases with the intensity). The results
verified that the irradiation time required for a given degree of destruction can be further reduced by the addition of a small amount of chemical oxidant such as hydrogen peroxide. Some of these results have been published in the technical journals and conference proceedings.

Ultrasonic irradiation can easily be integrated with existing, conventional treatment systems, making it possible to simultaneously treat hazardous and non-hazardous waste streams. Successful development and deployment of this technology could completely change the remediation of groundwaters contaminated from leaking underground storage tanks.

Physical and Chemical Principles -- Ultrasound

Ultrasonic irradiation of liquid reaction mixtures induces electrohydraulic cavitation, which is a process during which the radii of preexisting gas cavities in the liquid oscillate in a periodically changing pressure field created by the ultrasonic waves. These oscillations eventually become unstable, forcing the violent implosion of the gas bubbles. The rapid implosion of a gaseous cavity is accompanied by adiabatic heating of the vapor phase of the bubble, yielding localized and transient high temperatures and pressures (while the bulk solution remains near ambient conditions). Temperatures on the order of 4,200°K and pressures of 975 bar have been estimated [Mason and Lorimer, 1988]. Experimental values of P = 313 atmospheres and T = 3,360°K have been reported [Sehgal et al., 1977] for aqueous systems, while temperatures in excess of 5,000°K have been reported [Flint and Suslick, 1989, 1991; Suslick et al., 1986] for cavitation of organic and polymeric liquids. Recent experimental results on the phenomenon of sonoluminescence [Crum and Roy, 1994; Crum, 1994] suggest that even more extreme temperatures and pressures are obtained during cavitation bubble collapse [Putterman, 1995]. Thus, the apparent chemical effects in liquid reaction media are either direct or indirect consequences of these extreme conditions.

Even though the basic physical and chemical consequences of cavitation are fairly-well understood, many fundamental questions about the cavitation site in aqueous solution remain unanswered. In particular, the dynamic temperature and pressure changes at the bubble interface and their effects on chemical reactions need further exploration. Since this region is likely to have transient temperatures and pressures in excess of 647°K and 221 bar for periods of microseconds to milliseconds, supercritical water (SCW) has been proposed that provides an additional phase for chemical reactions during ultrasonic irradiation in water [Hua et al., 1995b]. Supercritical water exists above the critical temperature, T_c, of 647°K and the critical pressure, P_c, of 221 bar and has physical characteristics intermediate between those of a gas and a liquid. The physicochemical properties of water such as viscosity, ion-activity product, density, and heat capacity change dramatically in the supercritical region. These changes favor substantial increases for rates of most chemical reactions.

Two distinct sites for chemical reactions exist during a single cavitation event [Hua et al., 1995b; Kotronarou et al., 1991]. They are the gas-phase in the center of a collapsing cavitation bubble and a thin shell of superheated liquid surrounding the vapor phase. The volume of the gaseous region is estimated to be larger than that of the thin liquid shell by a factor of ~2x10^4.

During cavitation/bubble collapse, which occurs within 100 ns, water undergoes thermal dissociation within the vapor phase to give hydroxyl radical and hydrogen atoms as follows:

\[
\text{H}_2\text{O} \rightarrow \text{H}^\bullet + \cdot\text{OH}
\]

[The \text{H}^\bullet in the above reaction equation denotes sonolytic-type treatment].
The concentration of \( \bullet \text{OH} \) at a bubble interface in water has been estimated to be \( 4 \times 10^{-3} \text{ M} \) [Gutiérrez et al., 1991]. Many of the chemical effects of ultrasonically induced cavitation have been attributed to the secondary effects of \( \bullet \text{OH} \) and \( \text{H} \bullet \) production.

For treatment of carbon tetrachloride (CCl\(_4\))-contaminated waters, Wu et al. [1992a,b] speculated that the major reactions involved were bond-cleavage of water and of CCl\(_4\) in the cavitation hole. Destructions greater than 99% were achieved. First-order kinetics were observed within the experimental concentration ranges studied (up to 130 mg/L of CCl\(_4\)). The residual CCl\(_4\) concentration decreased for increasing pH in the range of 3 to 9 (for the same applied sonication period). Better sonication efficiency was observed at higher initial pH values; however, this improvement diminished for pH > 6. In the experimental conditions employed in their study, the researchers concluded that temperature and pH had little effect on the CCl\(_4\) destruction rate; however, the destruction rate was significantly affected by the intensity of the ultrasonic energy. The destruction rate exhibited a linear relationship with the applied power intensity. Adding hydrogen peroxide as an oxidant had a negligible effect on the destruction rate (with or without ultrasonic irradiation), suggesting that the destruction of CCl\(_4\) in water under ultrasonic irradiation was dominated by the high temperature dissociation reactions within the collapsing cavities [Wu et al., 1992b]. Additional data and technology description are discussed by Wu and Peters [1995].

 Destruction of pesticides such as atrazine was shown to be effective using a Fenton's oxidation system, and was enhanced by the application of sonication [Peters and Wu, 1996]. Removal efficiencies of atrazine exceeded 90%, even for treatment times as low as 5 minutes. Sonication improved the removal of atrazine by at least 10% for treatment times of 10 minutes or less. Higher dosages of Fe\(^{2+}\) and H\(_2\)O\(_2\) resulted in higher removals of atrazine from solution. They investigated four separate systems for their ability to remove atrazine from solution: (1) Fenton's oxidation conducted without application of UV light; (2) Fenton's oxidation conducted in the presence of UV light; (3) Fenton's oxidation conducted using sonication in the absence of UV light; and (4) Fenton's oxidation conducted using sonication in the presence of UV light. Of these four systems, the sonication-enhanced Fenton's oxidation resulted in the best treatment of the Fenton's oxidation systems studied. That system promoted the formation of hydroxyl radicals (\( \bullet \text{OH} \)) to more effectively destroy the organic contaminants (e.g., atrazine). Their work showed that addition of oxidants such as H\(_2\)O\(_2\) or Fenton's Reagent could enhance organic destruction using sonication.

 Sonochemical reactions in water are characterized by the simultaneous occurrence of supercritical water reactions, direct pyrolysis, and radical reactions especially at high solute concentrations. Volatile solutes such as carbon tetrachloride [Hua and Hoffmann, 1996] and hydrogen sulfide [Kotronarou et al., 1992b] undergo direct pyrolysis reactions within the gas phase on the collapsing bubbles or within the hot interfacial region as shown below:

\[
\begin{align*}
\text{CCl}_4 & \rightarrow \text{CCl}_3\bullet + \text{Cl}\bullet \\
\text{CCl}_3\bullet & \rightarrow \cdot\text{CCl}_2 + \text{Cl}\bullet \\
\text{H}_2\text{S} & \rightarrow \text{HS}\bullet + \text{H}\bullet
\end{align*}
\]

while low-volatility solutes such as thiophosphoric acid esters [Kotronarou et al., 1992a] and phenylate esters [Hua et al., 1995b; Kotronarou et al., 1992a] can react in transient supercritical phases generated within a collapsing bubble. In the case of ester hydrolysis, reaction rates are accelerated 10\(^2\) to 10\(^4\) times the corresponding rates under controlled kinetic conditions (i.e., same pH, ionic strength, and controlled overall temperature). This effect can best be illustrated by the catalytic effect of ultrasonic irradiation on the rate of hydrolysis of parathion in water at pH 7. The half-life for parathion hydrolysis at pH 7.4, in the
absence of ultrasound at 25°C is 108 days. However, in the presence of ultrasound, the half-life is reduced to 20 minutes [Kotronarou et al., 1992a].

Pyrolysis (i.e., combustion) and supercritical water reactions in the interfacial region are predominant at high solute concentrations, while at low solute concentrations, free radicals are likely to predominate. Depending on its physical properties, a molecule can simultaneously or sequentially react in both the gas and interfacial liquid regions.

In the specific case of hydrogen sulfide gas dissolved in water, both pyrolysis in the vapor phase of the collapsing bubbles and hydroxyl radical attack in the quasi liquid interfacial region occur simultaneously as follows:

\[
\begin{align*}
\text{H}_2\text{S} & \rightarrow \text{HS}^\bullet + \text{H}^\bullet \\
\text{H}_2\text{S} + \cdot\text{OH} & \rightarrow \text{HS}^\bullet + \text{H}_2\text{O}
\end{align*}
\]

Hua and Hoffmann [1996] investigated the rapid sonolytic degradation of aqueous carbon tetrachloride (CCl₄) at an ultrasonic frequency of 20 kHz and at an applied power of 130 W (0.108 W/cm²). The rate of disappearance of CCl₄ was found to be first-order over a broad range of conditions, consistent with the results of Wu et al. [1992a,b]. The observed first-order degradation rate constant was \(3.3 \times 10^{-3} \text{ s}^{-1}\) when \([\text{CCl}_4] = 195 \text{ mM}\); \(k_{\text{obs}}\) was observed to increase slightly to \(3.9 \times 10^{-3} \text{ s}^{-1}\) when \([\text{CCl}_4]\) was decreased by a factor of ten (i.e., \([\text{CCl}_4]\) = 19.5 mM) [Hua and Hoffmann, 1996]. Low concentrations of hexachloroethane, tetrachloroethylene, and hypochlorous acid (HOCl) in the range of 0.01 to 0.1 mM, were detected as transient intermediates, while chloride ion and CO₂ were found to be stable products.

The highly reactive intermediate, dichlorocarbene, was identified and quantified by means of trapping with 2,3-dimethylbutene. Evidence for involvement of the trichloromethyl radical was also obtained and was indirectly implied by the formation of hexachloroethane. The presence of ozone during sonolysis of CCl₄ did not affect the degradation of carbon tetrachloride but was shown to inhibit the accumulation of hexachloroethane and tetrachloroethylene.

The following mechanism was proposed to account for the observed kinetics, reaction intermediates, and final products:

\[
\begin{align*}
\text{CCl}_4 & \rightarrow \cdot\text{CCl}_3 + \text{Cl}^\bullet \\
\text{CCl}_3 & \rightarrow \cdot\text{CCl}_2 + \text{Cl}^\bullet
\end{align*}
\]

Formation of dichlorocarbene, \(\cdot\text{CCl}_2\) is also thought to occur by the simultaneous elimination of two chlorine atoms:

\[
\text{CCl}_4 \rightarrow \cdot\text{CCl}_2 + \text{Cl}_2^\bullet
\]

A third mechanism for dichlorocarbene formation is disproportionation of the trichloromethyl radical that can be inferred from an analogous reaction between the trifluoromethyl radical and the hydrodifluoromethyl radical:

\[
\cdot\text{CCl}_3 + \cdot\text{CCl}_3 \rightarrow \text{CCl}_4 + \cdot\text{CCl}_2
\]

All three pathways are possible at the hot center of the imploding microbubble. The trichloromethyl radical can also couple to form hexachloroethane:
\[ \cdot \text{CCl}_3 + \cdot \text{OH} \rightarrow \text{HOCCl}_3 \]

In the presence of oxidizing species, the trichloromethyl radical can act as a scavenger of hydroxyl radicals:

\[ \cdot \text{CCl}_3 + \cdot \text{OH} \rightarrow \text{HOCCl}_3 \]

or molecular oxygen:

\[ \cdot \text{CCl}_3 + \cdot \text{O-O} \cdot \rightarrow \text{O-OCCl}_3 \]

Based on analogous gas-phase mechanisms, the reactive intermediate \( \text{HOCCl}_3 \) appears to rapidly react to yield phosgene and other products as follows:

\[ \text{HOCCl}_3 \rightarrow \text{HCl} + \text{COCl}_2 \]
\[ \text{COCl}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{HCl} \]
\[ \cdot \text{O-OCCl}_3 + \text{H}_2\text{O} \rightarrow \text{HOCCl}_3 + \text{HO}_2 \]

Phosgene hydrolysis in water is rapid [Manogue and Pigford, 1960] under ambient conditions; and the rate constant is positively correlated with increasing temperature. Thus, the hydrolysis of this intermediate can be enhanced by the occurrence of supercritical water during cavitationsal microbubble collapse:

\[ \text{COCl}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCl} + \text{CO}_2 \]

The dichlorocarbene can be coupled for form tetrachloroethylene:

\[ 2 \cdot \text{CCl}_2 \rightarrow \text{C}_2\text{Cl}_4 \]

or hydrolyze to carbon monoxide and hydrochloric acid:

\[ \cdot \text{CCl}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + 2 \text{HCl} \]

Chlorine atoms can combine to form molecular chlorine, which hydrolyses to hypochlorous acid and chloride ion:

\[ \text{H}_2\text{O} \]
\[ 2 \cdot \text{Cl} \rightarrow \text{Cl}_2 \rightarrow \text{HOCl} + \text{HCl} \]

The formation of the reactive intermediate, dichlorocarbene, is confirmed by the selective trapping of the carbene with 2,3-dimethyl-2-butene to form 1,1-dichloro-2,2,3,3-tetramethylene cyclopropane. In a similar fashion, the trichloromethyl radical is trapped by 2,3-dimethyl-2-butene to yield 2-methyl-2-trichloromethyl-1-butene. These trapped intermediates can be identified and quantified by gas chromatography/mass spectroscopy (GC/MS) techniques.

**In-Well Vapor Stripping**

In-well vapor stripping has been demonstrated at Edwards Air Force Base (AFB) for the removal of dissolved TCE from groundwater. The in-well vapor stripping component of this combined sonication and stripping remedial technology is based on a special well. The well itself is screened at two horizontal
intervals [Gvirtzman and Gorelick, 1992, 1993; Gorelick and Gvirtzman, 1993, 1995]. A lower screened interval is located at depth below the water table and allows groundwater contaminated with VOCs to enter the well. An upper screened interval is located above the water table and allows water depleted in VOCs to enter the well. An eductor pipe is installed inside the well casing creating a well-within-a-well. Inside the inner well, an air line is introduced into which air is injected. The air is released beneath the water table, creating bubbles that rise. A simple separator plate (or well packer) is located within the inner well at an elevation above the water table. As the water/bubble mixture hits this separator plate, the water is forced laterally into the outer well and exits into the vadose zone through the upper screened interval. From there, the water freely infiltrates back to the water table. The air bubbles, enriched in VOCs, are released into the outer well and are extracted to the ground surface under a vacuum.

As discussed previously, in-well vapor stripping operates on two basic principles. The first is that of groundwater recirculation and is accomplished using a dual-screened recirculation well. Air-lift pumping occurs when air is injected into the well. Due to the density difference between the water outside the well and the water/bubble mixture within the inner well, a lift is created [François et al., 1996]. Water and air rise within the inner well, forcing additional water to flow from the aquifer into the well through the lower screened interval. The water and bubble mixture flows upward in the annular space around the air line. Because the water enters the well as the lower screened interval and returned to the water table, a groundwater circulation cell is developed in the vicinity of the well. The second operating principle is that of volatilization [Gvirtzman and Gorelick, 1992]. When contaminated water enters the well at the lower screened interval, it encounters the injected air which has formed bubbles. The VOCs will volatilize and mass is transferred from the water to the gas phase. Given approximately 20 feet of contact distance between the contaminated water and the air bubbles, equilibrium partitioning occurs. The air within the well strips out the VOCs. During the Edwards AFB demonstration, approximately 90% of the TCE was stripped from the water with each pass through the well. This air is separated from water using the separator plate located above the upper screened interval and the VOC-enriched vapor is vacuumed off and treated by sorption onto granular activated carbon. The water exiting the well at the upper screened interval has then been depleted of VOCs and is returned to the aquifer where microbial degradation can occur, depending upon the type of compound, and during sequential passes through the treatment well, additional VOCs are stripped and removed. In-well vapor stripping has efficacy at any level of contaminant concentration and can be particularly effective when VOC concentrations are high.

The combined remedial system will take contaminated water and remove a significant portion of the SVOCs and VOCs in the well (the treatment well). The system operates by employing groundwater recirculation as described previously. Contaminated water enters the well and with each pass through the well contaminants are removed by both sonication and volatilization. A radial clean-up zone is created around the well. Previous work on recirculation wells [Philip and Walter, 1992; Kabala, 1993; Herrling et al., 1991; Gvirtzman and Gorelick, 1992] has shown that a single well can achieve a zone of cleanup that extends radially 2 to 3 times the aquifer thickness. Groundwater entering this zone under regional flow conditions will be recycled and cleaned. It is expected that with each pass through the well, in-well vapor stripping will remove approximately 90 to 99% of the VOCs, and sonication will remove 90+%. Any residual VOCs may be biodegraded as the water enters the unsaturated zone. In addition, the VOC vapors that are produced by the in-well vapor stripping system may be treated at the ground surface or may be degraded in-situ in the unsaturated zone through microbial activity.