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**MTBE REMEDIATION USING
HOLLOW FIBER MEMBRANE AND
SPRAY AERATION VACUUM EXTRACTION
TECHNOLOGIES**

by

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1.0 EXECUTIVE SUMMARY

This report summarizes the results of a demonstration of selected technologies used to treat groundwater contaminated with dissolved Methyl Tertiary Butyl Ether (MTBE) and other Volatile Organic Compounds (VOCs). The specific technologies include Spray Aeration Vacuum Extraction (SAVE), developed by Remediation Service International (RSI), and Hollow Fiber Membrane (HFM) degasification, developed by the University of California at Santa Barbara. The test was conducted at the Department of Defense Hydrocarbon National Test Site located at the Naval Construction Battalion Center at Port Hueneme, California, between June 21 and June 25, 1999.

The SAVE system is a mobile unit designed for *ex-situ* remediation of dissolved hydrocarbons. The partitioning principles of the SAVE system include promotion of a large air-water interface in combination with high operating temperatures and vacuum pressures to facilitate volatile organic constituents (VOC) transfer from water to vapor phases. This can lead to more efficient removal of highly soluble volatile compounds like MTBE. The structure of the HFM provides for a large contact area between vapor and water phases, allowing efficient mass transfer to occur with relatively smaller volumes of air than is typically required of air strippers. In addition, there is no further contact between the VOC and water, minimizing partitioning of VOC back into the liquid phase. Therefore, the removal efficiency is much higher than in conventional air-stripping. Due to its small size, it becomes practical to combine the HFM module with other treatment processes, such as the SAVE system, to achieve desired remediation goals.

The project scope consisted of the demonstration of the combined SAVE and HFM systems at the field scale for treating groundwater contaminated with MTBE and other gasoline components. The main objectives are listed below.

1. Meet a target remediation goal of 5 µg/L for MTBE (the secondary drinking water standard for California water supplies);
2. Quantitatively define the component-by-component performance in terms of removal efficiency and mass transfer coefficient for each technology;
3. Evaluate these treatment technologies from a cost-and-performance perspective; and
4. Develop a set of recommendations for routine application of this combination of remediation technologies.

The actual field set up, from the beginning to the end of the treatment process, was composed of water softener units, water filters, a SAVE system with an internal combustion engine (ICE) (for off-gas treatment and supplemental power), one HFM unit and two Granular Activated Carbon (GAC) units. The system was configured specifically for remediation of dissolved MTBE and volatile petroleum hydrocarbon constituents extracted from a monitoring well. The removal efficiencies were evaluated for several system components at water flow rates between 3.8 and 40 liter per minute (1 and 10 gallons per minute (gpm)). The water temperature in the system was maintained at temperatures lower than 54°C (130°F). The first 2 field days were dedicated to evaluating the HFM system. The combined SAVE/HFM system was evaluated the following three days.

In general, the SAVE and HFM removal efficiencies were better at lower water flowrates and higher temperatures. For MTBE, the HFM (without the SAVE treatment system) achieved a

removal efficiency 49% to greater than 76% at water flowrates below 11 liter per minute (3 gpm) in the temperature range of 41 to 56°C (105 to 132°F). At a water flow rate of 19 liters per minute (5 gpm), the HFM MTBE removal efficiency ranged from 46% to 77% in the temperature range of 38 to 56°C (100 to 133°F). The HFM removal efficiency was below 30% at water flow rates higher than 27 liters per minute (7 gpm) for the temperature range of 32 to 40°C (90 to 104°F).

The SAVE system (without the HFM component) achieved MTBE removal efficiencies ranging from 91% to greater than 99% at water flow rates below 11 liters per minute (3 gpm) in the temperature range of 40 to 43°C (105 to 109°F). At a water flow rate of 19 liters per minute (5 gpm), the MTBE removal efficiency of the SAVE system ranged from 65% to greater than 99% for the temperature range of 35 to 50°C (95 to 122°F). The SAVE MTBE removal efficiency ranged from 74% to 88% at water flow rates higher than 27 liters per minute (7gpm) for temperatures ranging from 33 to 36°C (92 to 97°F).

For the combined SAVE-HFM system, the MTBE removal efficiency ranged from 81% for the highest flow rates (30 liters per minute, or 8gpm) to greater than 99% for the lowest flow rates (3.8 liters per minute, or 1gpm) for the temperatures ranging from 40 to 43°C (105 - 110°F). The combined SAVE-HFM system removal efficiency for Benzene was difficult to quantify due to the low influent concentrations, since the effluent basically did not have detectable Benzene concentrations.

The complete system configuration used during the demonstration (including SAVE, HFM, water softeners and GAC units) consistently achieved removal efficiencies of MTBE, benzene and toluene greater than 99.9% for flow rates between 1 to 9 gpm and temperatures ranging from 32 to 56°C (89 to 133°F). No breakthrough of MTBE, benzene, or toluene occurred in either of the GAC units. During the 5-day demonstration effort, approximately 34,200 L (9,000 gallons) of contaminated groundwater was treated while continuously meeting the project's MTBE clean up goal of 5 µg/L.

2.0 INTRODUCTION AND BACKGROUND

This report presents the results of a demonstration of a treatment system for groundwater contaminated with dissolved Methyl Tertiary Butyl Ether (MTBE) and other Volatile Organic Compounds (VOCs) which treats three phases at once: groundwater, soil and air-stripping vapors, and contaminated soil. For this demonstration, only groundwater was treated. The specific technologies include Spray Aeration Vacuum Extraction (SAVE), developed by Remediation Service International (RSI), and Hollow Fiber Membrane (HFM) degassification, developed by the University of California at Santa Barbara. The test was conducted at the Department of Defense Hydrocarbon National Test Site (HNTS) located at the Naval Construction Battalion Center at Port Hueneme, California, between June 21 and June 25, 1999. The HNTS provides sites for demonstrating remediation technologies for the treatment of petroleum-based contamination.

MTBE has been used as a gasoline additive to increase octane and reduce air pollution in the U.S. since 1979. It was originally added to gasoline to replace lead compounds. MTBE is currently the most common gasoline additive used in North America and elsewhere. Although relatively volatile, MTBE is water soluble, and therefore has a low Henry's constant. Since it does not tend to sorb to sediment particles or naturally occurring organic material, there is virtually no retardation, so it can move at the same rate as ground water. MTBE undergoes biodegradation slowly under aerobic and anaerobic conditions (Fujiwara et. al., 1984; Jensen and Arvin, 1990; Yeh and Novak, 1994). MTBE may cause ecological damage and human health effects (CAL-EPA, 1998). According to the National Water Quality Assessment program of the United States Geological Society (USGS), MTBE is found at thousands of Underground Storage Tank (UST) sites. There are many cases where the MTBE concentration is higher than regulatory action levels (Keller et. al., 1998).

There are currently a number of available technologies to treat VOCs in contaminated groundwater. The most commonly used methods include soil vapor extraction, air stripping and granular activated carbon (GAC). In addition, several innovative treatment technologies, such as SAVE and advanced oxidation processes (AOP) using ozone/hydrogen peroxide are currently under development (Keller et al., 1999).

Soil vapor extraction (SVE) is commonly used for removing volatile constituents from ground water, and for delivering nutrients to zones which may favorably respond by stimulating microbes capable of degrading organic materials. Inefficiencies due to preferential pathways and scaling can inhibit SVE removal efficiencies. In addition, since MTBE is very soluble, removing it from groundwater in-situ simply by extracting the vapors above the contaminated groundwater may be inefficient and costly. Groundwater plume containment and treatment is necessary to achieve significant reductions in MTBE concentrations.

Air stripping is a reliable and flexible technology for removing dissolved organic materials from an aqueous stream. However, the treatment cost can increase substantially if air treatment is required.

The SAVE system can combine positive attributes associated with SVE and air stripping by either directly treating vapors from the subsurface or by treating extracted ground water. To date, the SAVE system has been used successfully at many VOC sites. However, experience related to MTBE extraction and treatment is limited.

Several investigators have tried to use GAC for MTBE removal because it is a simple, reliable, and proven technology. Although GAC is efficient for removal of most organic materials, it is not very effective for removal of MTBE, especially at high concentrations. This is due to the fact that MTBE has a low affinity for organic carbon. The disposal and regeneration costs for spent GAC is also a concern.

AOP has no need for air treatment or disposal of hazardous waste. However, this method can be expensive at low flow rates. In addition, MTBE removal can be inhibited by the presence of other organic compounds. There is also a concern that AOP intermediate products (e.g., bromate, tert-butyl alcohol) and other oxidized compounds can pose a significant health risk, greater than MTBE itself.

The hollow fiber membrane (HFM) technology is a relatively new method for removing dissolved organic materials from an aqueous stream. One distinct advantage is that HFM has a very small footprint when compared to other available technologies. However only a small number of field tests have been performed. The scaling on the fiber surface and subsequent plugging of fiber pores may reduce the removal efficiency. In addition, the useful membrane life range has yet to be determined at the field scale.

Keller et. al. (1999) compared the cost and performance of various treatment technologies for MTBE contaminated water at various flow rates and concentrations. When air treatment is not required, they found that air stripping is the lowest cost technology for high flow rate (100 to 1000 gpm), while HFM is the lowest cost technology for low flow rate (10 to 100 gpm).

This effort will serve to evaluate the performance and identify several logistical concerns regarding the use of HFM techniques and HFM techniques combined with additional VOC removal methods, namely the SAVE system, on a field scale.

2.1 TEST OBJECTIVES

The demonstration objectives are listed below.

1. Meet a target remediation goal of 5 µg/L for MTBE (the secondary drinking water standard for California water supplies).
2. Quantitatively define the component-by-component performance in terms of removal efficiency and mass transfer coefficient for each technology.
3. Evaluate these treatment technologies from a cost-and-performance perspective.
4. Develop a set of recommendations for routine application of these remediation technologies.

2.2 TECHNOLOGICAL OVERVIEW

The SAVE system is a mobile unit for *ex-situ* remediation. The remediation mechanisms of the system involve air stripping at high operating temperatures and vacuum pressures. Higher temperature and vacuum conditions enhance the stripping

process by increasing the transfer of VOCs from water to gas phases. These allow for more efficient removal of less volatile and more soluble organic compounds like MTBE. Similar concepts apply to the removal of VOCs by HFM. The HFM structural components provide for a large contact area between gas and water phases, allowing for mass transfer to occur with relatively small air volumes. The system effectively behaves like a small, highly efficient, air-stripping unit. Due to the small modular size, it is easy to combine HFM with other treatment processes, especially the SAVE system, to achieve desired remediation goals. In addition, the membrane does not allow VOCs in the gas phase to contact the water phase again, significantly increasing the removal efficiency.

2.3 DEMONSTRATION SCOPE

The scope of this effort was to conduct a field scale cleanup of the MTBE and gasoline contaminated groundwater using HFM and SAVE remediation technologies. The test was designed to evaluate the MTBE and gasoline removal efficiencies for each system component at varying operational conditions (i.e., water flow rates and temperature).

3.0 SITE DESCRIPTION

The test was conducted at the Department of Defense Hydrocarbon National Test Site (HNTS) located at the Naval Construction Battalion Center at Port Hueneme, California. The HNTS was established for the demonstration of innovative technologies related to the remediation of soils and groundwater contaminated with fuel hydrocarbon. Government officials report that leaded and unleaded fuels leaked from underground storage tanks (USTs) from September 1984 to March 1985 (Kram and Lory, 1998). According to records maintained by the Naval Exchange, approximately 42 cubic meters (11,000 gallons) of regular unleaded gasoline were released during that period. In their study, Kram and Lory (1998) report that a resulting dissolved benzene plume extended to approximately 330-m (1,080-ft) downgradient of the source. In addition, MTBE concentrations as high as 16,000 ppb were measured approximately 457m (1,500 ft) from the source.

The region is a semi-perched aquifer zone consisting of fluvial-deltaic sediments approximately 7.6 m (25 feet) thick. The uppermost silty sands grade into sand and silty sand at depths ranging from 2.3 to 7.6 m (7.5 to 25 ft) below ground surface (BGS). The unconfined water table ranges from 2.6 to 3.7 m (8.5 to 12 ft) BGS. Therefore, the thickness of saturated aquifer is approximately 4.6 m (15 ft), depending on the location within the plume. The hydraulic conductivity ranges from 0.2×10^{-3} to 1.4×10^{-3} meters per second. The average linear velocity in the unconfined aquifer ranges from approximately 70 to 440 m (230 to 1450 ft) per year, assuming a porosity of 0.3.

In this demonstration, groundwater was pumped from Well CBC-10 and Well CBC-19, both located approximately 10 m (33 ft) downgradient of the source, approximately 7 m (20 ft) apart from each other (Figure 3-1).

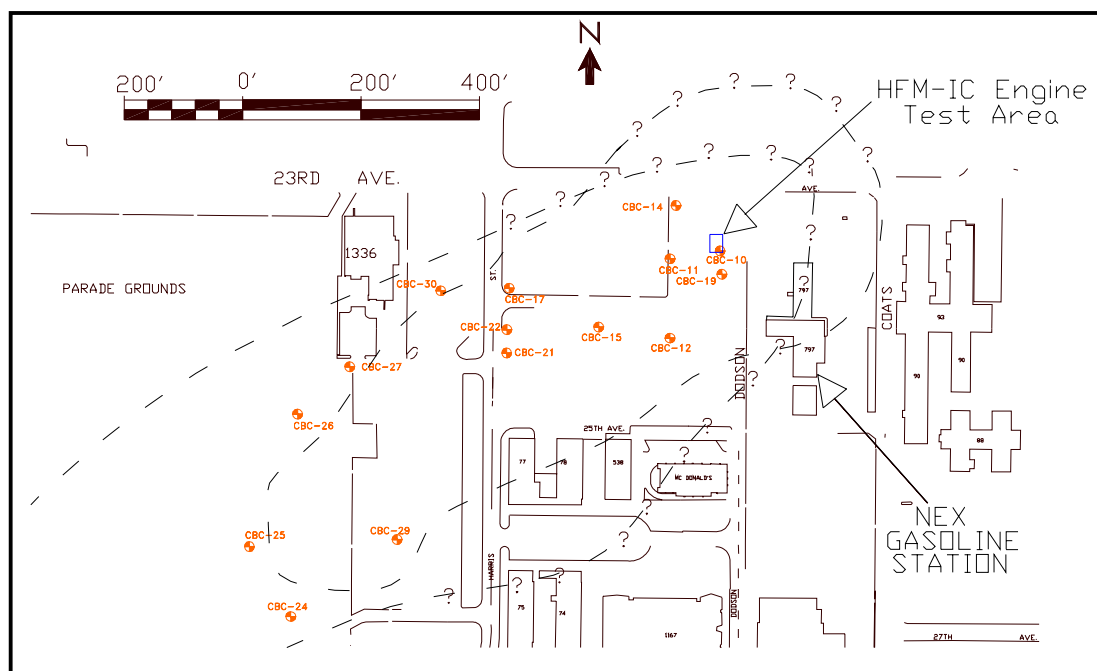


Figure 3-1. Test site.

4.0 DEMONSTRATION DESCRIPTION

In this demonstration, the contaminated groundwater was treated by the Spray Aeration Vacuum Extraction system and a Hollow Fiber Membrane unit using several configurations in a field-scale application. This section describes the principles and configurations of the treatment systems, as well as test plans and sampling program used during the demonstration.

4.1 TECHNOLOGY PRINCIPLES

Spray Aeration Vacuum Extraction (SAVE) System: The SAVE system is a mobile remediation system designed for removal and treatment of hydrocarbon contaminants in groundwater through the principles of air stripping and combustion (Figure 4-1). The stripping process of the SAVE system is enhanced by maximizing the surface area between water and air using a spray nozzle to produce a fine water vapor. The movement of contaminants from water to air is optimized by applying vacuum pressure and increasing the operating temperature using waste heat generated by the Internal Combustion Engine (ICE) as well as electrical resistances powered by the ICE's generator. Therefore, the vapor pressure of the contaminants increases, leading to partitioning of volatile contaminants into the air phase. The ICE also supplies the vacuum that is used to remove vapor phase constituents and reduce required volatilization temperatures. In the case of petroleum hydrocarbons and MTBE, the extracted contaminants are also used as fuel for the ICE, supplemented with propane as needed. The detailed specifications and operating conditions for the SAVE system are provided in Appendix C.

Hollow Fiber Membrane (HFM) Unit: The HFM unit is a compact degasification module designed for separation of volatile gases from water by using a bundle of hydrophobic hollow fiber membranes as a contacting device (Figure 4-2). Schematic drawings of the HFM are shown in Figures 4-3 and 4-4. The configuration of the fiber bundle is designed to maximize the contact interface between water and gas phases. The contaminated water is passed through the inner part of the membrane and a counter current air flow is pulled by vacuum applied to the outer part of the membrane. The dissolved contaminants are transferred to the gas phase, induced by a concentration gradient and a vacuum. A concentration gradient is established between the contaminants in the ground water and clean air, leading to transfer of the volatile constituents through the membrane. The selective physicochemical properties of the membrane allow only the organic compounds to transfer across the membrane to the air phase. The HFM unit used during this demonstration was a porous hydrophobic fiber with an inner diameter of 50 – 100 μm , an outer diameter of 0.15 m, and a length of 0.5 m.



Figure 4-1. SAVE system.

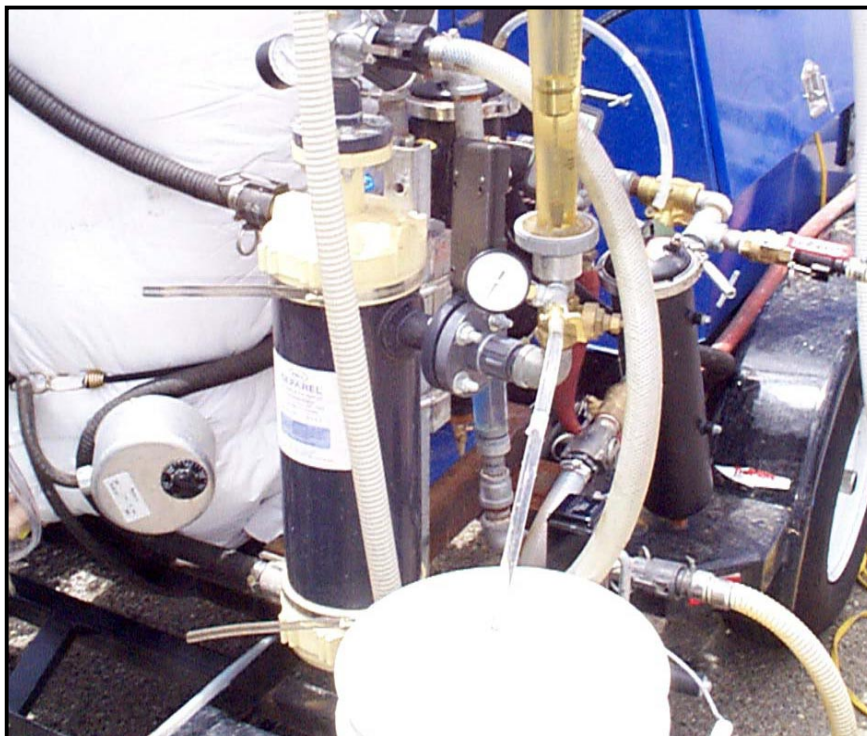


Figure 4-2. HFM unit in the field.

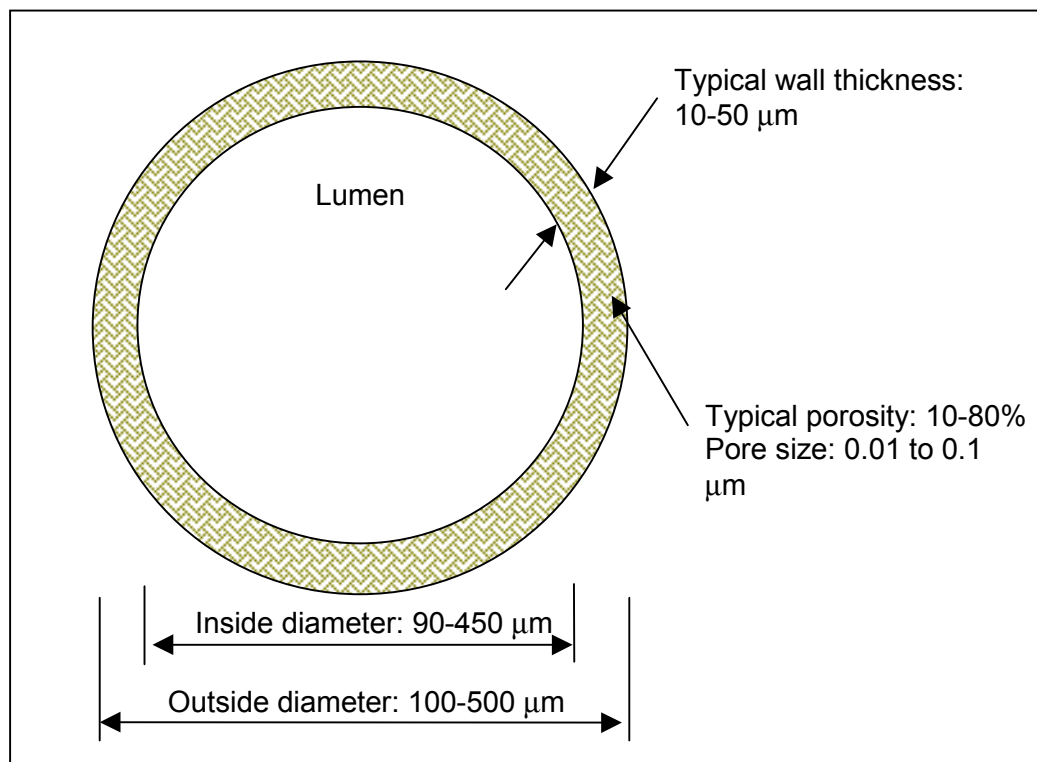


Figure 4-3. HFM cross-section.

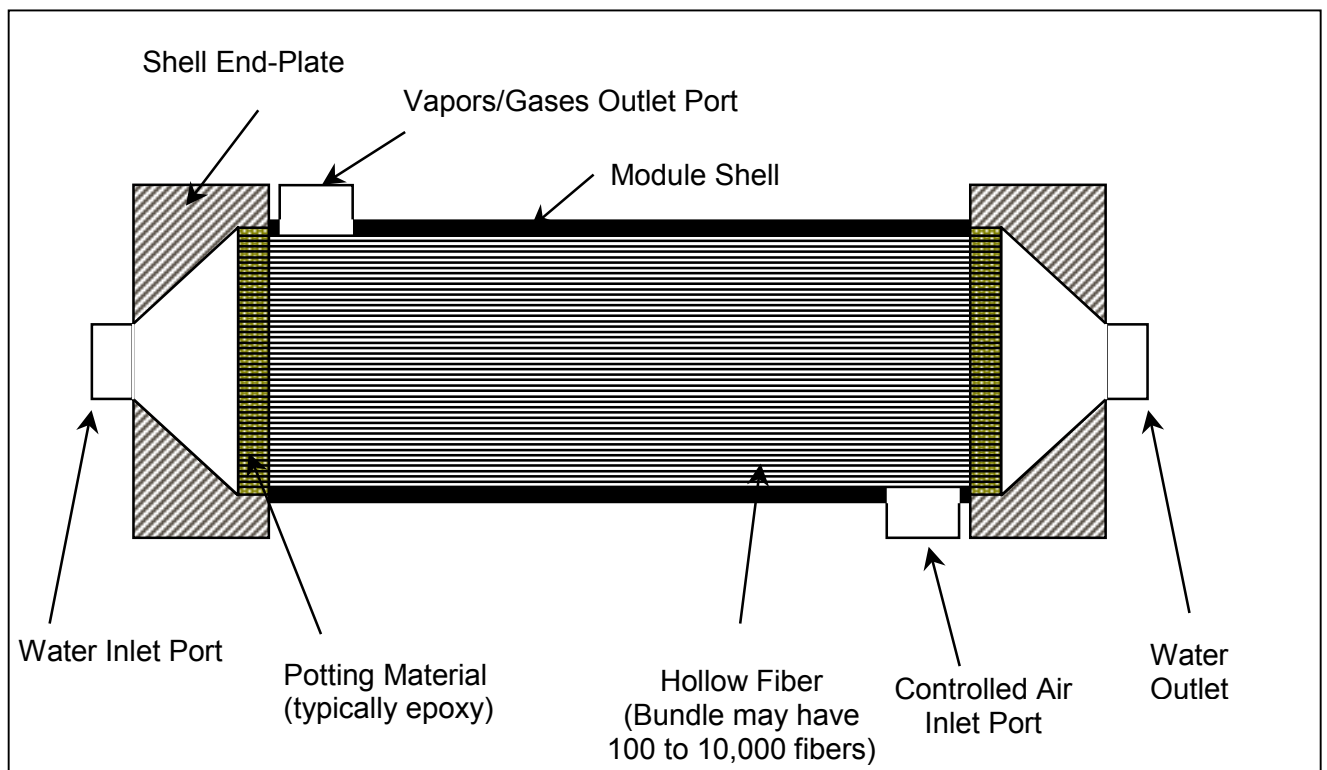


Figure 4-4. HFM flow schematic.

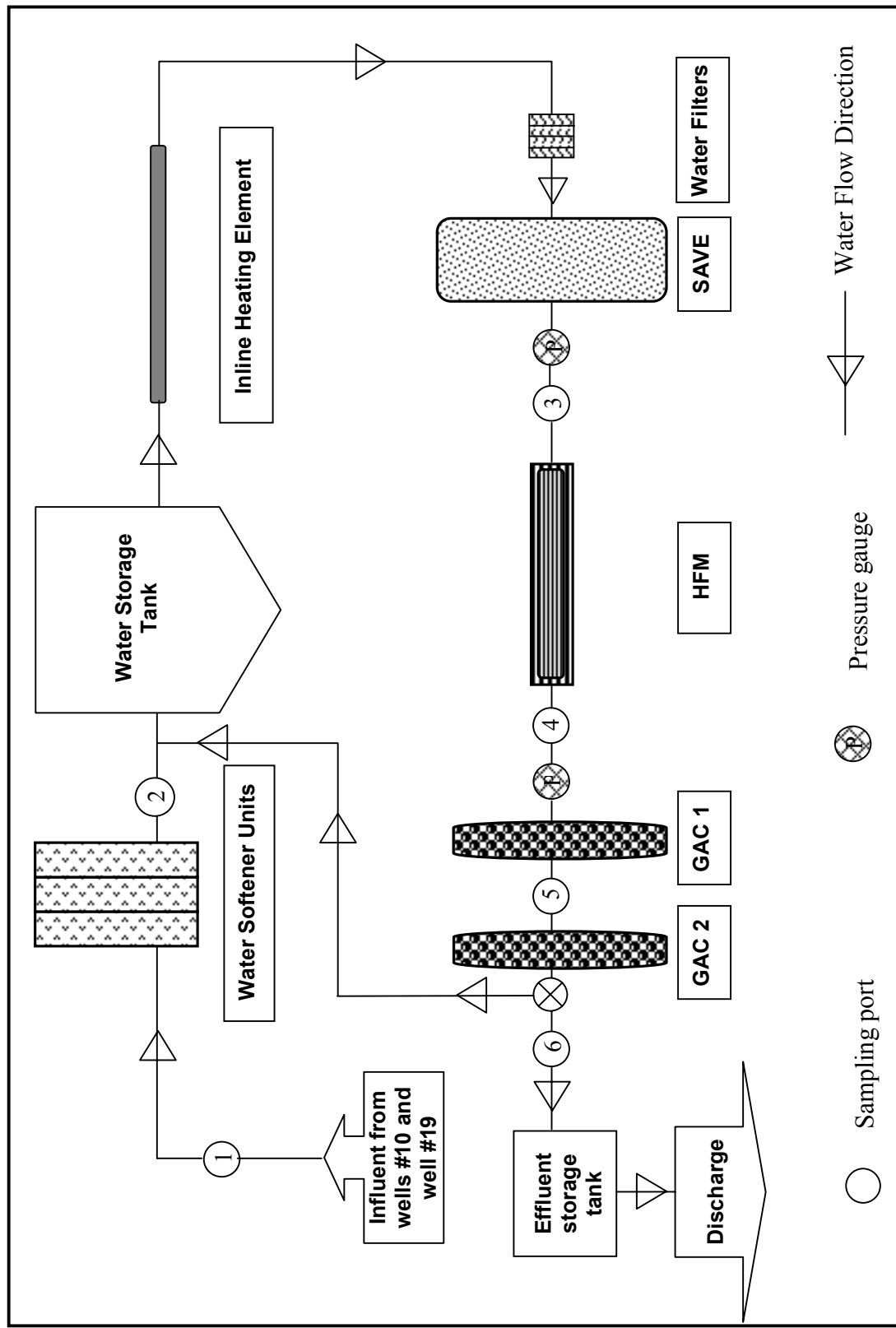


Figure 4-5. Water flow diagram.

4.2 FIELD TEST CONFIGURATION

The field-scale system was composed of water softener units, water filters, one SAVE system with ICE, one HFM unit and two Granular Activated Carbon (GAC) units. The system was setup for on-site remediation of dissolved MTBE and petroleum hydrocarbons.

In this demonstration, contaminated water was pumped from Well CBC-10 and Well CBC-19 (Figure 3-1) using a set of peristaltic pumps operating from 3 to 8 gpm. The groundwater was treated in the water softener units first to prevent scaling in the SAVE and HFM, and then pumped to a storage tank before further treatment. Waste heat emitted by the ICE was used to assist with water preheating. In addition, an in-line heating element (8 kW) was installed to maintain high water temperatures for the influent.

The water softeners consisted mainly of cation resins manufactured by Puretec®. The resins were small polymeric orange beads with a diameter of about 1 mm. The hardness was removed by the exchange of multivalent cation (i.e. Ca^{2+} , Fe^{2+} , Mg^{2+}) with Na^+ . Each water softener unit was filled with 37 cubic feet of resin beads and was setup to handle water flow up to 150 gpm. In practice, it is not necessary to oversize the water softeners.

The water was pumped from the storage tank through 50 μm water filters to remove suspended particles before entering the SAVE system. The SAVE system components used in this demonstration included a spray aeration tank, a propane driven ICE, and a system controller with display panels from which several system parameters were monitored and adjusted. The filtered water entered the spray aeration tank, was heated, and sprayed in the aeration tank. During this test, if the water flow rate was higher than 3 gpm, the extra heating element was used to preheat the water before entering the SAVE system. The effluent from the SAVE system was then pumped through the HFM. The spray aeration tank was not used to treat the water for all diagnostic runs. Specifically, the first two days were dedicated to evaluation of the HFM, so the tank was only used for heating purposes, not for stripping.

The air current for both SAVE and HFM was created by vacuum generated by the ICE. The air stream consisting of stripped volatile organic compounds (VOCs) was fed back to the ICE to be incinerated. Finally, the effluent from HFM was passed through two GAC units and stored in a water tanker prior to discharge. The GAC units used were manufactured by Pure Effect Incorporated. Each unit was rated at 10 gpm capacity and contained 4 cubic feet of GAC materials.

4.3 TEST PLAN

The test was scheduled for 5 consecutive days. The removal efficiencies of MTBE and petroleum hydrocarbons were evaluated for several system components at various water flow rates and temperatures. The maximum water temperature in the system was maintained at temperatures below 54°C (130°F) to avoid damage to the HFM.

Water samples were collected from the following locations in the aqueous flow stream (Figure 4-5). Water temperature, airflow rate, water flow rate, vacuum pressure

and ambient temperature were recorded every half an hour and during each sampling event. The sampling ports are designated as follows:

Location 1	Between the ground water wells and the water softener;
Location 2	Between the water softener and the SAVE system (SAVE influent);
Location 3	Between the SAVE system and the HFM system (HFM influent);
Location 4	Between the HFM unit and the first GAC unit (HFM effluent);
Location 5	Between the two GAC units; and
Location 6	Between the final GAC unit and the water storage truck (discharge).

The sampling plan was designed to evaluate the efficiency of HFM (only using the SAVE for energy and heat requirements) during the first two days, and to evaluate the whole system (HFM and SAVE treatment in series) during the last three days. Table 4-1 presents the sample frequency, flow rates, sample port location for each round, analytes, and daily objectives. Water samples from both Well CBC10 and Well CBC19 (Location 1) were collected at the beginning and the end of each day. In addition to MTBE and BTEX analysis, general mineral analysis was performed for water samples collected from Locations 1 and 2 at the beginning and the end of each day to determine water softener efficiencies.

Water samples from Location 5 had been sent to a certified laboratory to ensure that the concentration of MTBE and BTEX was below 5 µg/L before the water was discharged. The plan was to only analyze samples from Location 6 (system effluent following the second GAC unit) if breakthrough occurred in the first GAC unit. If breakthrough occurred in the second GAC, all the stored effluent water for that day's effort would have been run through the entire system again time until all water was clean to levels below 5 µg/L.

Table 4-1. Test Plan

Day	Time After Start (minutes)	Water Flow Rate (gpm)	Sampling Location	Temperature (°F)	Chemical Analyses*	Objective
06-21-99	0	5	1,2,4,5	Not exceed 130	Minerals, MTBE&BTEX	To evaluate the HFM for removal efficiency at 5 gpm. No spray aeration.
	10	5	2,4,5	Not exceed 130	MTBE&B&T	
	40	5	2,4,5,6	Not exceed 130	MTBE&B&T	
	100	5	2,4,5	Not exceed 130	MTBE&B&T	
	160	5	2,4,5	Not exceed 130	MTBE&B&T	
	220	5	2,4,5	Not exceed 130	MTBE&B&T	
	280	5	2,4,5	Not exceed 130	MTBE&B&T	
	340	5	2,4,5,6	Not exceed 130	MTBE&B&T	
	400	5	1,2,4,5,6	Not exceed 130	Minerals, MTBE&BTEX	
06-22-99	0	1	1,2,4,5	Not exceed 130	Minerals, MTBE&BTEX	To evaluate the HFM for removal efficiency at various flow rates. No spray aeration.
	10	1	2,4,5	Not exceed 130	MTBE&B&T	
	40	1	2,4,5	Not exceed 130	MTBE&B&T	
	70	1	2,4,5	Not exceed 130	MTBE&B&T	
	80	3	2,4,5	Not exceed 130	MTBE&B&T	
	110	3	2,4,5,6	Not exceed 130	MTBE&B&T	
	140	3	2,4,5	Not exceed 130	MTBE&B&T	
	170	3	2,4,5	Not exceed 130	MTBE&B&T	
	180	7	2,4,5	Not exceed 130	MTBE&B&T	
	210	7	2,4,5	Not exceed 130	MTBE&B&T	
	240	7	2,4,5	Not exceed 130	MTBE&B&T	
	270	10	2,4,5,6	Not exceed 130	MTBE&B&T	
	300	10	2,4,5,6	Not exceed 130	MTBE&B&T	
	330	10	1,2,4,5,6	Not exceed 130	Minerals, MTBE&BTEX	

Table 4-1. Test Plan (continued)

Day	Time After Start (minutes)	Water Flow Rate (gpm)	Sampling Location	Temperature (°F)	Chemical Analyses*	Objective
06-23-99	0	5	1,2,3,4,5	Not exceed 130	Minerals, MTBE&BTEX	To evaluate the SAVE and HFM for removal efficiency at 5 gpm. SAVE operated throughout the test.
	10	5	2,3,4,5	Not exceed 130	MTBE&B&	
	40	5	2,3,4,5	Not exceed 130	MTBE&B&T	
	100	5	2,3,4,5,6	Not exceed 130	MTBE&B&T	
	160	5	2,3,4,5	Not exceed 130	MTBE&B&T	
	220	5	2,3,4,5	Not exceed 130	MTBE&B&T	
	280	5	2,3,4,5	Not exceed 130	MTBE&B&T	
	340	5	2,3,4,5,6	Not exceed 130	MTBE&B&T	
	400	5	1,2,3,4,5,6	Not exceed 130	Minerals, MTBE&BTEX	
06-24-99	0	1	1,2,3,4,5	Not exceed 130	Minerals, MTBE&BTEX	To evaluate the SAVE and HFM for removal efficiency at various flow rates. SAVE operated throughout the test.
	10	1	2,3,4,5	Not exceed 130	MTBE&B&T	
	40	1	2,3,4,5	Not exceed 130	MTBE&B&T	
	70	1	2,3,4,5	Not exceed 130	MTBE&B&T	
	80	3	2,3,4,5	Not exceed 130	MTBE&B&T	
	110	3	2,3,4,5,6	Not exceed 130	MTBE&B&T	
	140	3	2,3,4,5	Not exceed 130	MTBE&B&T	
	170	3	2,3,4,5	Not exceed 130	MTBE&B&T	
	180	7	2,3,4,5	Not exceed 130	MTBE&B&T	
	210	7	2,3,4,5	Not exceed 130	MTBE&B&T	
	240	7	2,3,4,5,6	Not exceed 130	MTBE&B&T	
	270	10	2,3,4,5	Not exceed 130	MTBE&B&T	
	300	10	2,3,4,5	Not exceed 130	MTBE&B&T	
	330	10	1,2,3,4,5,6	Not exceed 130	Minerals, MTBE&BTEX	

Table 4-1. Test Plan (continued)

Day	Time After Start (minutes)	Water Flow Rate (gpm)	Sampling Location	Temperature (°F)	Chemical Analyses*	Objective
06-25-99	10	5	1,2,3,4,5	110	Minerals, MTBE&BTEX	To evaluate the SAVE and HFM for removal efficiency at 5 gpm and various temperatures.
	70	5	2,3,4,5	110	MTBE&B&T	
	130	5	2,3,4,5	110	MTBE&B&T	
	160	5	2,3,4,5,6	110	MTBE&B&T	
	220	5	2,3,4,5	110	MTBE&B&T	
	230	5	2,3,4,5	110	MTBE&B&T	
	290	5	2,4,5	130	MTBE&B&T	
	320	5	2,4,5,6	130	MTBE&B&T	
	350	5	1,2,3,4,5,6	120	Minerals, MTBE&BTEX	

*Minerals (including: alkalinity, bicarbonate, carbonate, hydroxide, pH, total hardness, chloride, fluoride, nitrate as N, sulfate, conductivity, Total Dissolved Solids, MBAS surfactants, Color, Turbidity, calcium, Copper, Iron, Magnesium, manganese, Potassium, Sodium, Zinc) only run for samples collected from Locations 1 and 2 to evaluate water softener unit.

BTEX = Benzene, Toluene, Ethyl Benzene and Xylene

B&T = Benzene and Toluene

4.4 CHEMICAL ANALYSIS

General Minerals. The water samples were collected in plastic bottles and sent to CAPCO Analytical Services located in Ventura, California. Samples were analyzed using method SW 846 (USEPA, 1993).

MTBE and BTEX. The water samples were collected in 40 ml amber vials and stored at 4°C. In the middle and the end of every test day, samples from Location 5 were sent to CAPCO for rapid turnaround results.

All other samples were extracted using a Solid Phase Micro-Extraction (SPME) technique. In this analysis, Polydimethyl Siloxane Carboxen fiber was used to extract MTBE, Benzene and Toluene from a liquid phase, and the fiber was then placed in the GC injection port at 250°C. The analyses were performed using a Hewlett Packard 5890 Gas Chromatograph equipped with a Flame Ionization Detector (FID). The temperature of the detector was set at 250°C. A VOLCOL (Supelco) capillary column (30 m x 0.25 mm with 0.25 µm film) was used. The column temperature was programmed from 100 to 120°C at an increasing rate of 12.0°C/min. All analyses were run in duplicate with reproducibility of $\pm 10\%$.

Selected samples of the water softener resins used in the field were tested for their sorption ability for MTBE, Benzene and Toluene in the Bren School laboratory at the University of California, Santa Barbara. Four sets of treatments with controls and a set of blanks were prepared in 40-mL amber vials. The blanks were prepared by adding 37 ml

of deionized water to 10 g of the water softener resins. The four treatments were prepared by adding 37 mL of spiked water solution to 10 g of water softener resins. The water solutions consisted of 0.25, 0.5, 1 and 5 part per million (ppm) of MTBE, benzene, and toluene, individually and as mixtures with equal concentrations of each compound. The controls were prepared in the same way as the treatments but with no water softener resins. The mixtures were kept at room temperature and the concentrations of the solutions were measured after 3 and 5 days. The sorption capacity was calculated by considering the change in mass in the aqueous solution as a function of time, which is assumed to transfer mostly to the polymeric resins.

5.0 TECHNOLOGY PERFORMANCE EVALUATION

In this section, the performance for each technology component, as well as overall system performance, is assessed and summarized. The performance data for each component is presented in an order consistent with the system flow stream configuration depicted in Figure 4-5. The performance of the overall process is subsequently evaluated and presented at the end of the section.

5.1 PERFORMANCE OF INDIVIDUAL COMPONENTS

Pretreatment Processes: This section describes the water chemistry measured in each extraction well, and following treatment by the water softener units. The pre- and post-treatment water softener analytical results are summarized in Table 5-1. Appendix D contains a complete list of the analytical results.

For general water chemistry, the results indicate that the ground water has high Total Hardness ranging from 960 to 1060 mg/L. The water softener units reduced the Total Hardness to values ranging from non-detect to 170 mg/L. Although it was originally assumed that the treatment would not affect VOC concentrations, there was considerable removal of MTBE, Benzene and Toluene at this step. Prior to the water softeners, MTBE concentrations ranged from 260 to 8,090 ppb, Benzene concentrations ranged from below 5 to 47,300 ppb, and Toluene concentrations ranged from below 5 to 12,000 ppb. Following the water softeners, MTBE concentrations ranged from below 5 to 700 ppb, Benzene concentrations ranged from below 5 to 64 ppb, and Toluene concentrations were all below 5 ppb.

The resin sorption experimental results (Table 5-2) indicate that among the three species, MTBE has the lowest affinity for the material and Toluene has the highest. At equilibrium with a solution of 5 ppm, MTBE can sorb onto the material up to 7.7 µg/g, Benzene can sorb onto the material up to 9.8 µg/g, and Toluene can sorb onto the material up to 14.9 µg/g. The results also indicate that at these concentrations, sorption is essentially linear with concentration and is below the maximum sorption capacity of the resins (Figure 5-1 to 5-4).

Because the water filters remove particles mainly by mechanical means, the change in dissolved VOC concentrations due to the water filters was not expected. During the demonstration, the filter bags were changed once after the end of the third day (after treated about 19,000 L (5,000 gallons) of water). Photographs of the filter bags were taken to compare the new filters bags with the used ones (Fig 5-5). No significant scaling was found in the filter bags, nor a significant change in pressure drop across the filter. There was a slight coloring due to iron deposits on the bags, but not enough to decrease the filtering capacity. This suggests that the softening system is effectively removing most of the Ca^{2+} and Fe^{2+} present and that little or no scaling should occur in either the SAVE or HFM systems.

Table 5-1. Summary of Inorganic Groundwater Chemistry from Well #CBC-10 and Well #CBC-19 (before the water softener units and after the water softeners)

Compound	Concentration Before Water Softeners	Concentration After Water Softeners	Units
<u>General Minerals</u>			
Alkalinity	450-530	480-540	mg/L
pH	7.3-7.4	7.4-7.8	
Total Hardness	960-1060	N.D. (10)-170	mg/L
Conductivity	1870-11600	2370-11900	uMHOs/cm
TDS.	1730-1860	1760-1840	mg/L
Turbidity	40-58	0.77-8.5	NTUs
Calcium	330-350	N.D. (2)-47	mg/L
Magnesium	80-83	N.D. (1)-11	mg/L
Iron	2.0-5.4	0.08-0.81	mg/L
Sodium	170-210	530-820	mg/L
<u>VOC's</u>			
MTBE	260-8,090	N.D. (5)-700	ppb
Benzene	N.D. (5)-47,300	N.D. (5)-64	ppb
Toluene	N.D. (5)-12,200	N.D. (5)	ppb

TDS: Total Dissolved Solids

ND Not-detected

NTUs: Nephelometric turbidity units

VOC's: Volatile organic compounds

uMHOs/cm: micromhos/cm

Table 5-2. Sorption Capability of the Cation Resins for MTBE, Benzene, Toluene

Contaminants	Concentration (ppm)	Sorption (µg/g)	
		Pure	Mixture of the Three species
MTBE	5	7.7	6.4
	1	1.6	0.8
	0.5	0.3	0.2
	0.25	0.3	0.3
Benzene	5	9.8	11.4
	1	2.4	2.2
	0.5	1.4	0.6
	0.25	0.9	0.5
Toluene	5	14.9	12.0
	1	1.9	2.0
	0.5	1.2	0.9
	0.25	0.9	0.5

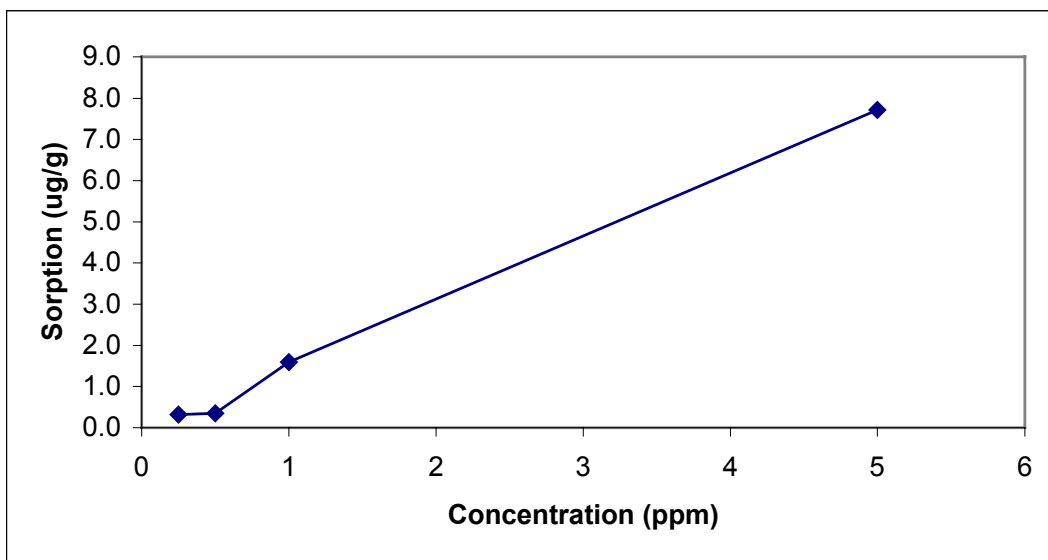


Figure 5-1. Sorption of MTBE onto the water softener materials at different concentrations of MTBE.

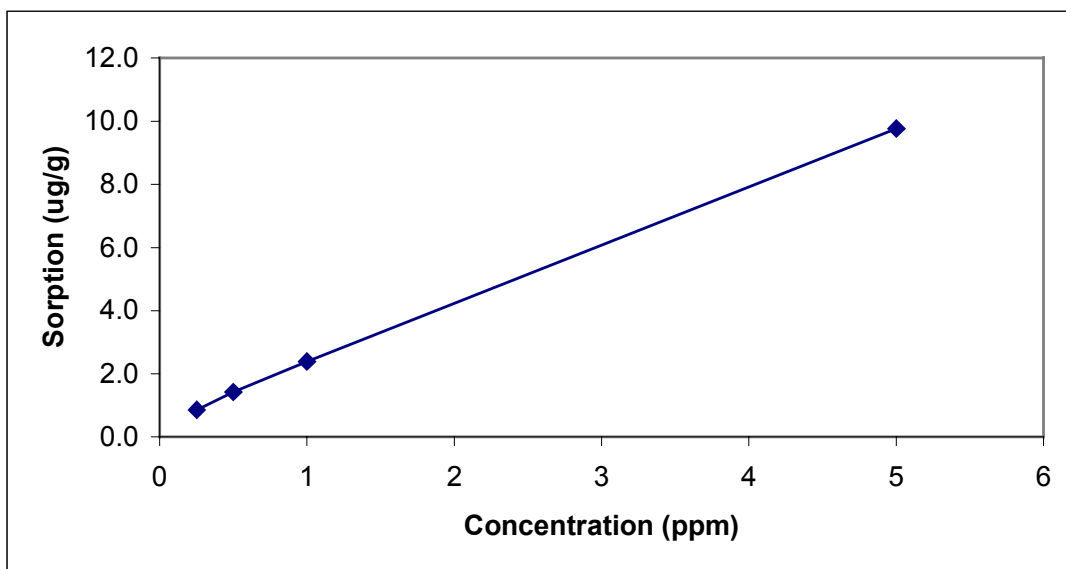


Figure 5-2. Sorption of benzene onto the water softener materials at different concentrations of benzene.

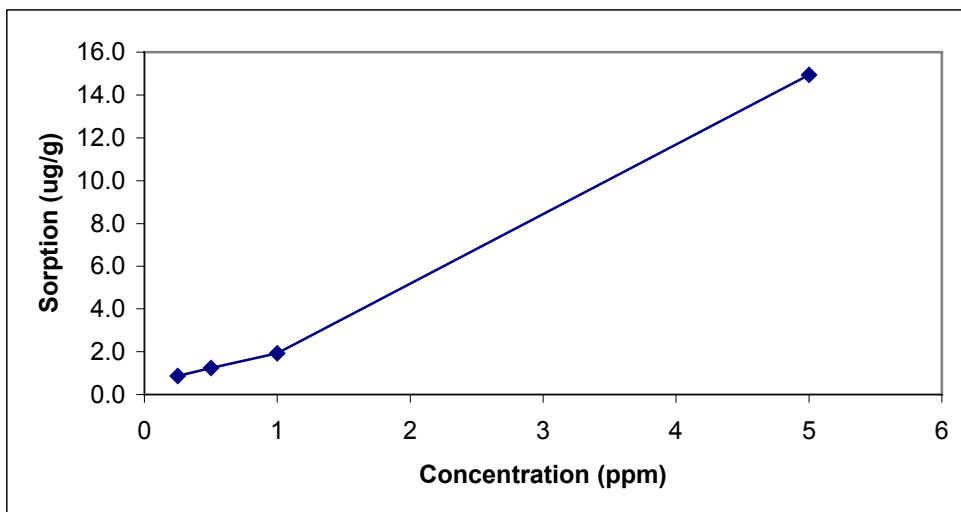


Figure 5-3. Sorption of toluene onto the water softener materials at different concentrations of toluene.

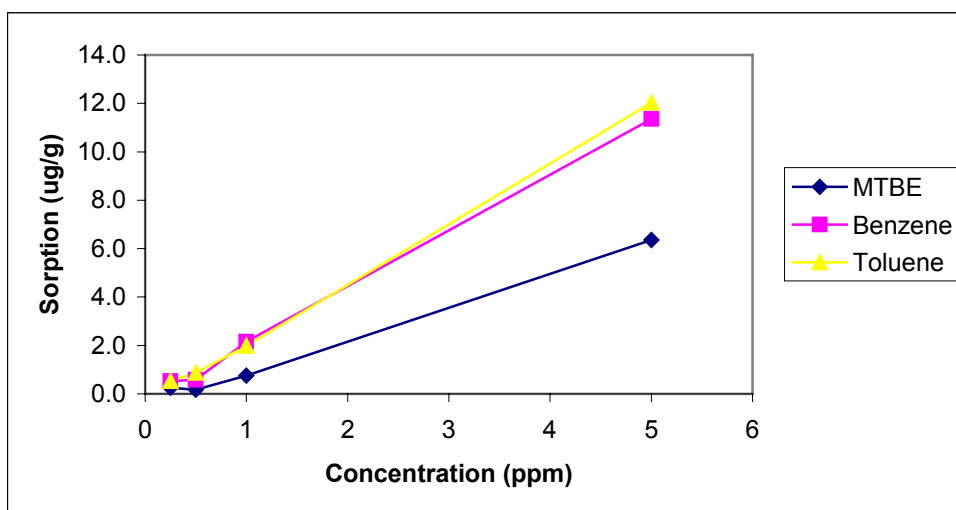


Figure 5-4. Sorption of MTBE, benzene, and toluene onto the water softener materials at different concentrations of mixture of the three species.



Figure 5-5. Water filters (new filters are on the right).

HFM Removal of MTBE, Benzene, and Toluene: This section describes the removal of MTBE, Benzene and Toluene by measuring concentrations at Locations 3 and 4 (Figure 4-5). The pre- and post-HFM treatment analytical results are summarized in Tables 5-3 and 5-4.

At a water flow rate (Q_w) below 11 liter per minute (L/min) (3 gpm), the MTBE removal efficiency is in the range of 49% to greater than 76% in the temperature range of 44 to 56°C (105 to 132°F). At Q_w of 19 L/min (5 gpm), the MTBE removal efficiency ranged from 46% to 77% in the temperature range of 38 to 56°C (100 to 133°F). The MTBE removal efficiency was below 30% at Q_w higher than 27 L/min (7 gpm) for temperature range of 32 to 40°C (90 to 104°F).

The removal efficiency of Benzene was greater than 80% at Q_w below 19 L/min (5 gpm) in the temperature range of 38 to 56°C (101 to 132°F). However, since the initial concentration of Benzene was rather low, it is quite possible that the HFM can achieve removal efficiencies well above 80%, as shown in laboratory experiments.

A comparison of the experimental vs. theoretical removal efficiency of MTBE by HFM is depicted in Figure 5-6. According to this study, the experimental removal efficiency slightly exceeds the theoretical removal efficiency. However, the relationship is very close to 1:1. A detailed derivation of the theoretical removal efficiency is presented in Appendix A.

The removal efficiency data from this study was used to determine the overall gas-liquid mass transfer coefficient across the HFM (K_{La}). The mass transfer coefficient

for MTBE was calculated using methods described in Keller et al., (1998). The relationship between K_{La} and temperature is presented in Figure 5-7. This relationship can be used to predict the removal efficiency for HFM for a given fiber length. The design equations required to calculate K_{La} and the corresponding theoretical removal efficiencies are presented in Appendix A.

Table 5-3. Summary of MTBE Removal Efficiency by HFM

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)	% Removal by HFM
3.8	1	43/110	32 / 10	68
3.8	1	50/122	284 / 86	70
3.8	1	52/125	374 / 89	76
3.8	1	56/132	238 / 63	74
11	3	41/105	257 / 132	49
11	3	43/109	296 / 147	50
11	3	44/112	294 / 123	58
11	3	52/125	21 / <5	> 76
11	3	56/133	22 / 8	65
19	5	32/89	538 / 281	48
19	5	32/90	443 / 239	46
19	5	35/95	187 / 99	47
19	5	37/99	150 / 79	47
19	5	38/100	469 / 218	54
19	5	38/101	493 / 209	58
19	5	38/101	567 / 210	58
19	5	38/101	496 / 255	49
19	5	38/101	451 / 216	52
19	5	38/101	144 / 62	57
19	5	38/101	154 / 60	61
19	5	38/101	165 / 62	52
19	5	41/105	19 / <5	> 74
19	5	42/108	289 / 149	48
19	5	42/109	53 / 20	62
19	5	50/122	59 / 11	81
19	5	54/129	134 / 30	77
19	5	56/133	82 / 19	77
27	7	34/94	36 / 28	21
27	7	35/95	35 / 28	21
27	7	36/97	216 / 177	18
27	7	36/97	245 / 201	18
27	7	36/97	379 / 233	38
27	7	41/104	400 / 253	37
30	8	33/92	61 / 44	27
30	8	34/94	324 / 292	10
30	8	34/94	58 / 43	25
30	8	36/96	50 / 39	22
34	9	33/92	334 / 302	10
34	9	33/92	377 / 341	9

Table 5-4. Benzene Removal Efficiency by HFM

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)	% Removal by HFM
3.8	1	56/132	25 / <5	> 80
11	3	56/133	26 / <5	> 80
19	5	38/101	25 / <5	> 80
19	5	38/101	27 / <5	> 81
19	5	42/109	24 / <5	> 80

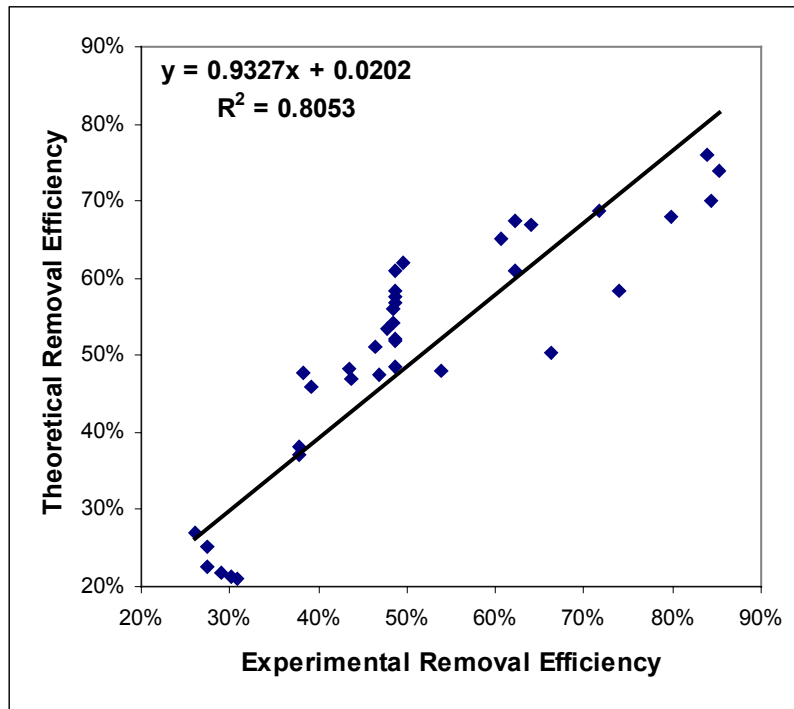


Figure 5-6. Theoretical versus experimental removal efficiency of MTBE by HFM.

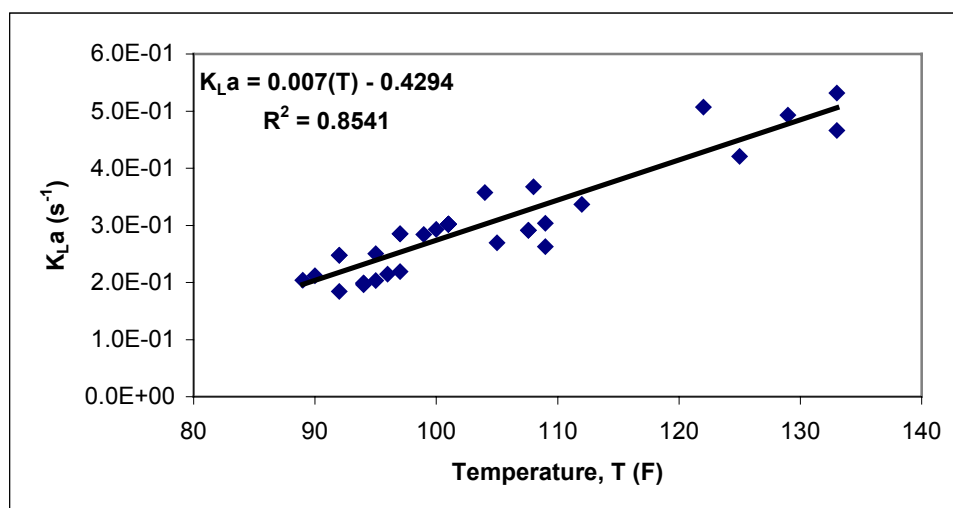


Figure 5-7. Mass transfer coefficient for MTBE using the HFM.

SAVE Removal of MTBE, Benzene, and Toluene: This section describes the removal of MTBE, Benzene and Toluene by measuring concentrations at Locations 2 and 3 (Figure 4-5). The pre- and post-SAVE treatment analytical results are summarized in Tables 5-5 and 5-6.

At a water flow rate (Q_w) below 11 liter per minute L/min (3 gpm), the MTBE removal efficiency ranged from 91% to greater than 99% for the temperature range of 40 to 43°C (105 - 109°F). At Q_w of 19 L/min (5 gpm), the MTBE removal efficiency ranged from 65% to greater than 99% for the temperature range from 35 to 50°C (95 to 122°F). The MTBE removal efficiency ranged from 74% to 88% at water flow rates higher than of 27 liters per minute (7gpm) for temperatures ranging from 33 to 36°C (92 to 97°F).

The removal efficiency of Benzene ranged from 65% at Q_w of 30 L/min (8 gpm) to greater than 86% for Q_w ranging from 3.8 L/min (1 gpm) to 27 L/min (7gpm) in the temperature range from 33 to 36°C (92 to 110°F). The removal efficiency of Toluene was higher than 54% at Q_w of 30 L/min (8 gpm) in the temperature range of 33 to 36°C (92 to 96°F). Again, the low influent concentrations don't provide an accurate assessment of the potential removal efficiency of Benzene and Toluene, since the final concentration is below the detection capability of our analytical instruments. Other field tests by RSI indicate greater than 99% removal efficiency of BTEX under most conditions.

A comparison of the experimental vs. theoretical removal efficiency of MTBE by the SAVE system is depicted in Figure 5-8. The theoretical removal efficiency calculations were based on equations typically used for air stripping towers. The equations for theoretical removal efficiency and for design requirements are presented in Appendix B.

Table 5-5. MTBE Removal Efficiency by SAVE

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)	% Removal by SAVE
3.8	1	43/110	382 / <5	> 99
3.8	1	43/110	344 / 32	91
3.8	1	43/110	254 / <5	> 98
11	3	41/105	260 / 21	92
11	3	42/108	277 / <5	> 98
11	3	43/109	365 / 22	94
19	5	35/95	559 / 187	67
19	5	37/99	531 / 150	72
19	5	38/101	537 / 144	73
19	5	38/101	437 / 154	65
19	5	38/101	550 / 105	81
19	5	41/105	342 / 45	88
19	5	41/105	363 / 19	95
19	5	43/109	435 / 17	96
19	5	43/109	361 / 53	85
19	5	43/110	299 / 34	89
19	5	44/111	420 / <5	> 99
19	5	50/122	351 / 59	83
27	7	34/94	241 / 36	85
27	7	35/95	247 / 35	86
27	7	36/97	243 / 49	80
30	8	33/92	231 / 61	74
30	8	34/94	466 / 58	88
30	8	36/96	268 / 50	81

Table 5-6. Benzene and Toluene Removal Efficiency by SAVE

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)	% Removal by Save
<u>Benzene</u>				
3.8	1	43/110	24 / <5	> 79
3.8	1	43/110	23 / <5	> 78
3.8	1	43/110	22 / <5	> 78
11	3	41/105	24 / <5	> 80
11	3	42/108	25 / <5	> 80
11	3	42/109	25 / <5	> 80
27	7	34/94	27 / <5	> 82
27	7	35/95	32 / <5	> 84
27	7	36/97	37 / <5	> 86
30	8	33/92	31 / <5	> 84
30	8	34/94	64 / 22	65
30	8	36/96	32 / <5	> 84
<u>Toluene</u>				
30	8	33/92	11 / <5	> 54
30	8	36/96	12 / <5	> 55

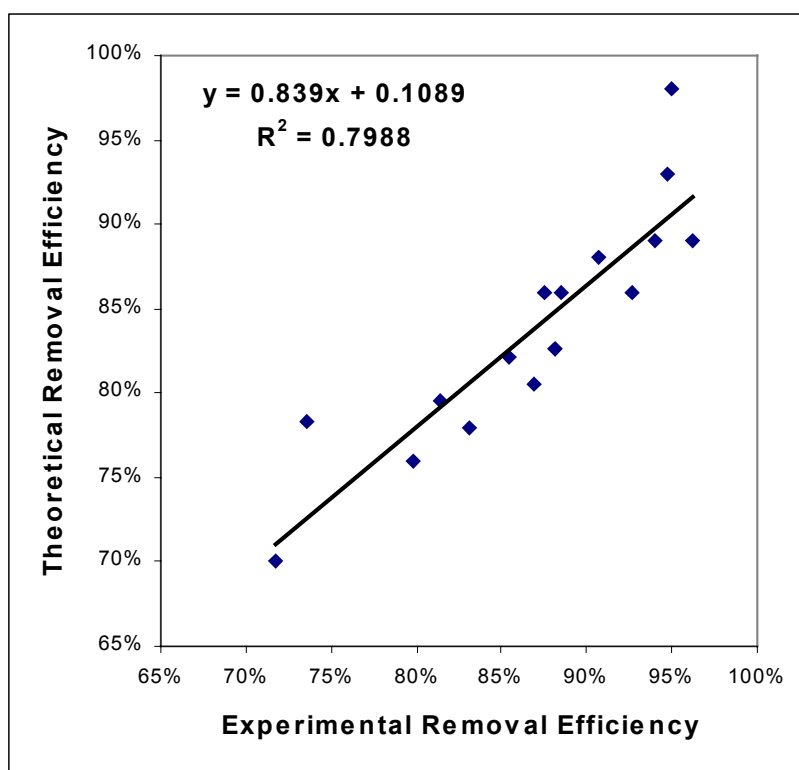


Figure 5-8. Theoretical versus experimental removal efficiency of MTBE by SAVE.

5.2 OVERALL SYSTEM PERFORMANCE

SAVE – HFM Removal of MTBE: This section describes the removal of MTBE, Benzene and Toluene by measuring concentrations at Locations 2 through 4 (Figure 4-5). The pre- and post-SAVE-HFM treatment analytical results are summarized in Tables 5-7 and 5-8.

At Q_w of 3.8 liter per minute (L/min) (1 gpm), the MTBE removal efficiency ranged from 97% to greater than 99% at 43°C (110°F). At Q_w of 11 L/min (3 gpm), the MTBE removal efficiency ranged from 98% to greater than 98% in the temperature range of 41 to 43°C (105 to 109°F). At Q_w of 19 L/min (5 gpm), the MTBE removal efficiency ranged from 82% to greater than 99% in the temperature range of 35 to 43°C (95 to 109°F). As shown in Figure 5-9, the combined removal efficiency at 19 L/min (5 gpm) increases rapidly with temperature until around 40°C (104°F), and then becomes asymptotic once it reaches around 98% removal. At Q_w of 27 L/min (7 gpm), the MTBE removal efficiency ranged from 88% to 89% for temperature ranged of 34 to 36°C (94 to 97°F). At Q_w of 30 L/min (8 gpm), the MTBE removal efficiency ranged from 81% to 91% for temperature range of 33 to 36°C (92 to 96°F).

The combined SAVE-HFM system removal efficiency for Benzene was difficult to quantify due to the low influent concentrations. In all cases, Benzene after the SAVE-HFM treatment was below practical quantification limit.

Complete Process Removal of MTBE, Benzene, and Toluene: The complete system configuration used during the demonstration (including SAVE, HFM, water softeners and GAC units) consistently achieved MTBE, Benzene and Toluene removal efficiencies greater than 99.9% for flow rates between 1 to 9 gpm and temperatures ranging from 32 to 56°C (89 to 133°F). No breakthrough of MTBE, benzene, or toluene occurred in either of the GAC units. During the 5-day demonstration effort, approximately 34,200 L (9,000 gallons) of contaminated groundwater was treated while continuously meeting the project's MTBE clean up goal of 5 µg/L.

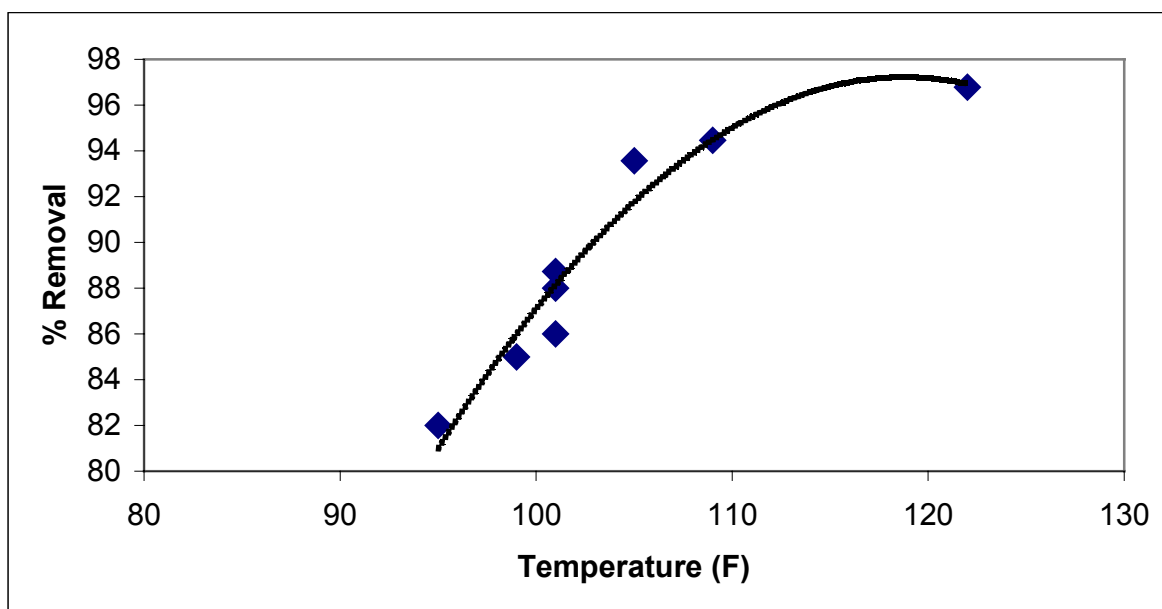


Figure 5-9. MTBE removal by SAVE-HFM at 5 gpm.

Table 5-7. MTBE Removal Efficiency by SAVE-HFM

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)	% Removal by SAVE HFM
3.8	1	43/110	382 / <5	> 99
3.8	1	43/110	344 / 10	97
3.8	1	43/110	254 / <5	> 98
11	3	41/105	260 / <5	> 98
11	3	42/108	277 / <5	> 98
11	3	43/109	365 / 8	98
19	5	35/95	559 / 99	82
19	5	37/99	531 / 79	85
19	5	38/101	537 / 62	88
19	5	38/101	437 / 60	86
19	5	38/101	550 / 62	89
19	5	41/105	342 / 22	94
19	5	41/105	299 / <5	> 98
19	5	43/109	435 / <5	> 99
19	5	43/109	361 / 20	94
19	5	43/110	299 / <5	> 98
19	5	44/111	490 / <5	> 99
19	5	50/122	351 / 11	97
27	7	34/94	243 / 30	88
27	7	35/95	247 / 28	89
27	7	36/97	241 / 28	88
30	8	33/92	231 / 44	81
30	8	34/94	466 / 43	91
30	8	36/96	268 / 39	85

Table 5-8. Benzene Removal Efficiency by SAVE-HFM

Water Flow Rate (L/min)	Water Flow Rate (gpm)	Temperature °C/°F	Concentration Influent/Effluent (ppb)
3.8	1	43/110	24 / <5
3.8	1	43/110	23 / <5
3.8	1	43/110	22 / <5
11	3	41/105	24 / <5
11	3	42/108	25 / <5
11	3	42/109	25 / <5
19	5	41/105	39 / <5
19	5	41/105	41 / <5
19	5	42/109	41 / <5
19	5	50/122	34 / <5
27	7	34/94	27 / <5
27	7	35/95	32 / <5
27	7	36/97	37 / <5
30	8	33/92	31 / <5
30	8	34/94	64 / <5
30	8	36/96	32 / <5

5.3 COSTS

The costs (excluding taxes or labor) for the treatment components used in this study are summarized in Table 5-9. Total monthly costs for the unit operation components listed (one water softener unit, water filter, one SAVE-HFM, and two GACs) are approximately \$6,303. If the concentration of the contaminants is high enough to provide fuel for the SAVE system, this cost can be reduced. Additional costs for each ion exchange replacement are approximately \$250, and \$1,450 for each GAC replacement. Expected lifespans for the water softener resins and GAC activated materials are 2-3 months and 6 months, respectively, depending on the water quality of both influent and effluent.

Table 5-9. Estimated Costs for Each Unit Operation

Equipment	Cost (Dollars)	Unit	Remarks
Water softener unit	143	Rental/month	Replacement of the ion exchange not included
Save-HFM	5,500	Rental/month	Contaminants are not used as fuel for ICE
Water filters	16	Per bag	10 bags/month (replace every 3 day)
GAC unit	250	Rental/month	Two units; Replacement of GAC not included

We assumed that the water would be pumped at rates of 5 gpm and 8 gpm, for 12 and 24 hours per day for 30 days (to derive monthly costs). Results from these four scenarios are presented in Table 5-10. When operating with longer daily durations, it can be useful to use alarm and remote monitoring systems as provided by the SAVE system. With increased throughput through the system, the cost per gallon decreases significantly, since the fixed costs are important.

Table 5-10. Estimated Cost Per Scenario

Process Rate (gpm)	Duration (hr/day)	Throughput (gal/mo.)	Costs/Gallon (\$)
5	12	108,000	0.06
5	24	216,000	0.03
8	12	172,800	0.04
8	24	345,600	0.02

5.4 DISCUSSION

The HFM component of the system was effective at removing MTBE and Benzene (up to 76% and over 80%, respectively). In general, the unit was most effective at lower flow rates and higher temperatures. This was to be expected, since longer residence times and higher temperatures are conducive to VOC partitioning from aqueous phase to vapor phase. Although the relationship may not be valid over the entire range of anticipated field conditions for every site, the relationship between theoretical and experimental removal efficiencies is very close to 1:1 for the conditions encountered during this investigation. The information gathered in this field test and through previous laboratory experiments can be used to design a longer HFM unit capable of removing more than 99% of the MTBE and VOCs present.

The SAVE component of the system was effective at removing MTBE and Benzene (greater than 99% and over 86%, respectively). As with the HFM component, the SAVE unit was most effective at lower flow rates and higher temperatures. This again was to be expected, since longer residence times and higher temperatures are conducive to VOC partitioning from aqueous phase to vapor phase and this might affect the performance of the aeration nozzle spray.

The combined SAVE/HFM system was highly effective at removing MTBE (ranging from 81% to greater than 99%). The combined SAVE-HFM system removal efficiency for Benzene was difficult to quantify due to the low influent concentrations and effluent concentrations below practical quantitation limits. Again, at low flow rates and high temperatures, removal was most effective.

The complete system (including SAVE, HFM, water softeners and GAC units) consistently achieved MTBE, Benzene and Toluene removal efficiencies greater than 99.9% for flow rates between 1 to 9 gpm and temperatures ranging from 32 to 56°C (89 to 133°F). In addition, no breakthrough occurred at either GAC unit. A total of approximately 34,200 L (9,000 gallons) of contaminated groundwater were treated while continuously meeting the MTBE clean-up goal of 5 µg/L. Therefore, this setup will work for the range of concentrations encountered at the site.

Although loss of VOCs due to the water softener units was not anticipated, there was a considerable amount of MTBE, Benzene and Toluene removed during this process. This reduction may be due to the large amount of water softener resins in each water softener unit (37 cubic feet) and the relatively low concentrations of the contaminants in the groundwater. The concentrations of MTBE, Benzene and Toluene entering the SAVE/HFM system were decreased to levels below 1 ppm by the water softener columns. Therefore, the SAVE/HFM removal efficiencies for MTBE and Benzene at higher concentration ranges (higher than one ppm) could not be determined.

Ideas for Improvement. During this investigation, only one HFM unit was used. Due to the small size, it is possible to use a set of HFM components in series or in parallel. However, when doing so, it is necessary to be aware of the potential for reduced air and water flow rates due to resistance in the fibers. Another option would be to re-size the unit to allow for greater flow and potentially greater removal efficiency for the range of flow rates investigated. The data gathered in this field test can be used to design a longer HFM module, using the mass transfer coefficient information.

At this point, the life of the HFM unit under field conditions has not been tested. Since the system is not a filter, regeneration is not necessary. However, depending upon the influent characteristics, scaling can lead to plugging. Therefore, a routine maintenance, which includes reverse flow of soft water and slightly acid solutions, will increase the life span of the unit.

Removal efficiencies can be improved by controlling temperatures at higher flow rates. For the current configuration, a reduction in temperature due to a decrease in residence time adjacent to the heating element was observed. Therefore, for the higher flow rates, removal efficiencies were only evaluated for lower temperature ranges. Insulation, and shorter delivery tube length can help reduce the amount of heat loss prior to the HFM component.

In order to reduce the potential for scaling, a water softener is required for the influent. When testing site water, it is also important to look for constituents, which may not initially seem relevant. A general minerals analysis is recommended before making the final design decisions for a field system.

Future Work. Although the system worked very well for the given site conditions, for sites with higher concentration, it may be necessary to cycle the effluent more than once through the HFM-SAVE system. This is particularly true for areas that require higher flow for hydraulic control of the contaminant plumes. It would be useful to test the same setup under conditions where groundwater concentrations of MTBE are significantly higher. In addition, a heating system, which can maintain temperatures ranging from 110°F to 120°F under water flow conditions ranging from 5 to 15 gpm, is recommended. For sites requiring higher groundwater extraction rates, several systems can be placed in strategic locations. In addition, a longer HFM unit can be constructed to treat contaminants at groundwater flow rates higher than 20 gpm, or alternatively achieve higher contaminant removal.

Methods for Improving Costs. During this investigation, effluent was directed to a temporary water holding truck. After learning of the successful VOC removal results, the treated water was then discharged. To avoid costs, it would be useful to establish an agreement with the regulatory agencies to more effectively handle treated effluent. Once a pilot test of a full-scale system has successfully demonstrated removal efficiencies which meet or exceed regulatory levels, the effluent can be discharged directly to a sewer line. This will reduce the analytical requirements and facilitate system automation. In addition, an in-line analyzer could allow for rapid identification of GAC breakthrough.

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Appendix A

Design Consideration of HFM Units

As explained in Keller et al., 1998; the transfer of Volatile Organic Compounds (VOCs) from the lumen of the HFM through the micropores is driven by a concentration gradient. The concentration gradient occurs because of a constant air flow through the membrane pores, keeping the concentration of VOCs in the air phase near zero. Therefore, there is a constant diffusion of VOCs from the water to the membrane surface and into the air-filled pores. The overall mass transfer coefficient (K_L) for the contaminant is:

$$\frac{1}{K_L} = \frac{1}{K_W} + \frac{1}{Hk_M} + \frac{1}{Hk_G} \quad (\text{A-1}).$$

Where: K_W is the diffusion of contaminant through the water to the membrane surface,
 H is the Henry's law constant for the contaminant of concern
 k_M is the diffusion of contaminant through the air-filled pores
 k_G is the diffusion of contaminant from the exterior membrane surface into the bulk air

By assuming a plug flow reactor with a constant mass transfer coefficient along the length of the fiber:

$$-u_L \frac{dC_W}{dx} = K_L a (C_W - C^*) \quad (\text{A-2}).$$

Where: u_L is the water flow rate
 x is the length of a HFM unit
 a is the interfacial area of membrane per unit volume in a module
 C^* is the equilibrium concentration of contaminant in gas phase
 C_W is the location-dependent water concentration

If the vacuum pressure is sufficiently large, C^* can be assumed negligible. Equation A-2 can be solved for the effluent concentration (C):

$$C_w = C_0 e^{-K_L a \left(\frac{x}{u_L} \right)} \quad (\text{A-3}).$$

Where: C_0 is an initial concentration of the contaminant in water.

Appendix B

Design of Air Stripping Units

B.1 Physicochemical properties of MTBE

Relevant physicochemical properties of MTBE for air stripping design are:

<i>Temperature, T (°C)</i>	<i>Henry's constant, H_c (-)</i>	<i>Diffusivity in water, D_w (m²/s)</i>	<i>Diffusivity in air, D_a (m²/s)</i>
5	0.004	7.7E-10	8.89E-06
10	0.007	7.9E-10	9.19E-06
15	0.011	8.0E-10	9.51E-06
20	0.017	8.2E-10	9.82E-06
25	0.026	8.3E-10	1.01E-05
30	0.039	8.4E-10	1.05E-05
35	0.058	8.6E-10	1.08E-05
40	0.085	8.7E-10	1.11E-05

Data from Robbins et al. (1993) was used to calculate the functional relationship between Henry's constant for MTBE and temperature. Liquid-phase diffusivity of MTBE was estimated using the Wilke and Chang (AIChE J, 1955) correlation:

$$D_w = \frac{7.4 \times 10^{-8} T \sqrt{M\chi}}{\mu_w V_b^{0.6}} \quad (\text{B-1})$$

where D_w is the diffusion coefficient of the solute in water (cm²/s),
 T is the absolute temperature (K),
 M is the molecular weight of the solvent (18 g/mol),
 χ is the association parameter for the solvent (2.6 for water),
 μ_w is the viscosity of the solvent (cP)
 V_b is the molal volume of the solute (cm³/mol)

V_b is estimated using the method presented by Reid and Sherwood (1958), to be around 126 cm³/mol.

The correlation by Arnold (1930) was used to estimate the gas-phase diffusivity of MTBE, D_a :

$$D_a = \frac{0.00837T^{5/2}[(M_1 + M_2)/M_1M_2]^{1/2}}{P(V_{b1}^{1/3} + V_{b2}^{1/3})^2(T + S_{12})} \quad (B-2)$$

where D_a is the diffusion coefficient of the pollutant in air (cm^2/s),
 P is the absolute pressure (atm),
 M_1 and M_2 are the molecular weights (g/mol) of ,
 S_{12} is the Sutherland constant $= 1.47 F (T_{b1}T_{b2})^{1/2}$,
 $F = 1.016 - 0.0216 V_{b2}/V_{b1}$.

B.2 Physicochemical properties of water and air

T ($^{\circ}\text{C}$)	ρ_w (kg/m^3)	μ_w (Pa s)	σ_w (N/m)	ρ_a (kg/m^3)	μ_a (Pa s)
5	1001	1.46×10^{-3}	0.075	1.270	1.73×10^{-5}
10	1000	1.31×10^{-3}	0.074	1.247	1.75×10^{-5}
15	999	1.17×10^{-3}	0.074	1.226	1.77×10^{-5}
20	998	1.05×10^{-3}	0.073	1.205	1.79×10^{-5}
25	997	9.39×10^{-4}	0.072	1.184	1.81×10^{-5}
30	996	8.40×10^{-4}	0.071	1.165	1.84×10^{-5}
35	994	7.52×10^{-4}	0.070	1.146	1.86×10^{-5}
40	992	6.73×10^{-4}	0.070	1.128	1.88×10^{-5}

where ρ_w is the density of water,
 μ_w is the viscosity of water,
 σ_w is the surface tension of water,
 ρ_a is the density of air, and
 μ_a is the viscosity of air.

B.3 Pressure Drop and Tower Diameter Calculations

Conventional countercurrent air stripping towers were designed using the method outlined by Treybal (1980), Roberts et al. (1985), Ball et al. (1984) and Staudinger et al. (1990). Figure A-1 presents a mass balance around the air stripping unit, assuming that the liquid flow rate, Q_L , and the gas flow rate, Q_G , are constant through the column. The mass balance is then:

$$Q_L(C_2^L - C_1^L) = Q_G(C_2^G - C_1^G) \quad (B-3)$$

where C^L and C^G are the mass concentrations of solute in liquid and gas phases, for the influent (1) and effluent (2) streams. Equation A-3 can be rearranged to solve for C_2^G :

$$C_2^G = \frac{Q_L}{Q_G} (C_2^L - C_1^L) + C_1^G \quad (\text{B-4})$$

The influent gas stream is typically clean, such that $C_1^G = 0$. The difference between the effluent and influent liquid concentrations is given by the problem statement, where a liquid stream of known concentration must be treated to an effluent standard. Q_L is also typically provided in the problem statement, where a known liquid flowrate must be treated. Q_G is increased to obtain the desired removal from the water to the gas phase in the shortest possible column, to reduce capital expenditures and operating costs.

For a constant Q_L , the pressure drop across the column increases with increasing flow rate, until significant holdup of liquid in the packed column results in an excessive pressure drop (flooding). This upper limit in pressure drop occurs typically around 1.6 to 2.5 kPa/m (2 to 3 in. of water per foot). Packed towers are usually operated at a gas velocity corresponding to about 80% of flooding velocity, with a pressure drop in the range of 0.4 to 0.8 kPa/m (0.5 to 1 in. of water per foot). Since gas velocity is a function of tower diameter, this also places a design constraint.

For illustrative purposes, the calculation presented here is done with the following design parameter values:

<i>Parameter</i>	<i>Value</i>
Water flowrate, Q_L	0.0063 m ³ /s (100 gpm)
Influent concentration, C_1^L	500 µg/L
Effluent concentration, C_2^L	5 µg/L
Packing material	1" Intalox Saddles (ceramic)
Packing Factor, C_f	98 m ⁻¹
Packing Surface Area, a	256 m ² /m ³
Temperature, T	15 °C (59 °F)
Volumetric Air/Water Ratio, Q_G/Q_L	150:1
Mass Loading Ratio, $L_M/G_M = (Q_L/Q_G)(\rho_L/\rho_G)$	5.43

Pressure drop is estimated using Eckert's method (1970). The dimensionless parameter for the abscissa value is calculated:

$$\frac{L_M}{G_M} \left[\frac{\rho_a}{\rho_w - \rho_a} \right]^{1/2} = 0.19 \quad (\text{B-5})$$

The ordinate at 0.8 kPa/m of packing is obtained from Eckert's correlation:

$$\frac{G_M^2 \mu_w^{0.1} C_f}{\rho_a (\rho_w - \rho_a)} = 0.085 \quad (\text{B-6}).$$

The gas mass loading rate, G_M is then calculated from Equation B-6:

$$G_M = \left[0.085 \rho_a (\rho_w - \rho_a) / C_f \mu_w^{0.1} \right]^{1/2} = 1.44 \text{ kg/m}^2 \text{ s} \quad (\text{B-7}).$$

The tower diameter is then calculated:

$$D = \sqrt{\frac{4 (Q_G/Q_L) Q_L \rho_a}{\pi G_M}} = 1.01 \text{ m} \quad (\text{B-8}).$$

B.4 Mass Transfer Coefficients

The Onda model (Onda et al., 1968) is used to estimate the mass transfer coefficients. For the liquid phase mass transfer coefficient, k_L :

$$k_L = 0.0051 \left(\frac{L_M}{a_W \mu_w} \right)^{2/3} \left(\frac{\mu_w}{\rho_w D_w} \right)^{-1/2} \left(\frac{\rho_w}{\mu_w g} \right)^{-1/3} (a_t d_p)^{2/5} \quad (\text{B-9})$$

where a_W = wetted surface area of packing, (m^2),
 g = gravitational acceleration constant, (m/s^2)
 a_t = total specific surface area of packing (m^{-1}),
 d_p = nominal packing size, (m).

The wetted surface area of the packing can be estimated using:

$$a_W = a_t \left[1 - \exp \left\{ -1.45 \left(\frac{\sigma_C}{\sigma_w} \right)^{0.75} \left(\frac{L_M}{a_t \mu_w} \right)^{0.1} \left(\frac{L_M^2 a_t}{\rho_a^2 g} \right)^{-0.05} \left(\frac{L_M^2}{\rho_L \sigma_w a_t} \right)^{0.2} \right\} \right] \quad (\text{B-10})$$

where σ_c = critical surface tension for packing material = 0.033 N/m.

The gas phase mass transfer coefficient, k_G , is estimated according to:

$$k_G = 5.23 C_f D_G \left(\frac{G_M}{a_t \mu_a} \right)^{0.7} \left(\frac{\mu_a}{\rho_a D_G} \right)^{1/3} (a_t d_p)^{-2} \quad (\text{B-11}).$$

where C_f = correction factor for packing = 98 for 25 mm ceramic Intalox Saddles.

Equations B-9 to A-11 are empirical correlations which have been verified for the following ranges:

$$1 < L_M < 15 \text{ kg/m}^2 \text{ s}$$

$$0.017 < G_M < 1.7 \text{ kg/m}^2 \text{ s}$$

The overall mass transfer coefficient, $K_L a_w$ is calculated using:

$$K_L a_w = \left[(k_L a_w)^{-1} + (k_G a_w H_c)^{-1} \right]^{-1} \quad (\text{B-12})$$

Mass transfer coefficients were estimated using equations B-9 to B-12 at various temperatures:

T (°C)	$k_L a$ (m/s)	$k_G a$ (m/s)	$K_L a$ (s-1)
5	8.48×10^{-5}	2.18×10^{-2}	4.12×10^{-3}
10	9.28×10^{-5}	2.21×10^{-2}	5.42×10^{-3}
15	1.02×10^{-4}	2.23×10^{-2}	6.83×10^{-3}
20	1.11×10^{-4}	2.26×10^{-2}	8.34×10^{-3}
25	1.21×10^{-4}	2.28×10^{-2}	9.93×10^{-3}
30	1.33×10^{-4}	2.31×10^{-2}	1.16×10^{-2}
35	1.45×10^{-4}	2.34×10^{-2}	1.34×10^{-2}
40	1.59×10^{-4}	2.37×10^{-2}	1.52×10^{-2}

B.5 Calculation of Packing Height

The total packed height, H_t , can be estimated using:

$$H_t = \frac{u_o^L}{K_L a_w} \frac{C_2^L}{C_1^L} \int_{C_1^L}^{C_2^L} \frac{dC^L}{(C^L - C^{L*})} = HTU_x NTU \quad (\text{B-13})$$

where u_o^L = superficial liquid velocity = L_M / ρ_w , ($\text{m}^3 / \text{m}^2 \text{ s}$)

HTU = height of a transfer unit, (m)

NTU = number of transfer units.

The integral in Equation B-13 can be solved for cases where a dilute solution is considered, and under isothermal conditions:

$$NTU = \frac{S}{S-1} \ln \left[\frac{(C_2^L / C_1^L)(S-1) + 1}{S} \right] \quad (\text{B-14})$$

where S = stripping factor = $H_c (Q_G / Q_L)$.

The following table presents the calculated stripping factor and total tower height for the conditions outlined above:

T (°C)	HTU (m)	NTU	S	H_t (m)
5	1.70	-	0.87	-
10	1.29	11.89	1.40	15.4
15	1.02	7.35	2.20	7.5
20	0.84	6.03	3.40	5.0
25	0.70	5.44	5.20	3.8
30	0.60	5.12	7.83	3.1
35	0.52	4.94	11.64	2.6
40	0.46	4.83	17.09	2.2

As indicated in the table, it is not possible to obtain the prescribed removal efficiency at 5°C, since the equilibrium concentrations of MTBE in the water and air phases limit the stripping process.

B.6 Pumping and Air Blower requirements

The power required to pump the water to the top of the column is given by:

$$P_w = Q_L \rho_w g H_t \quad (\text{B-15})$$

Based on the pressure drop in the air phase calculated in section B-3, the power required to blow the air through the packed tower is:

$$P_a = Q_G \Delta p H_t \quad (\text{B-16}).$$

A safety factor of 30% additional power is added to these calculations. From section B-3, the pressure drop, $\Delta p = 800 \text{ N/m}^2$. The power requirements for these conditions are:

T (°C)	P_w (kW)	P_a (kW)
10	1.4	20.1
15	0.70	9.9
20	0.47	6.6
25	0.35	5.0
30	0.29	4.0
35	0.24	3.4
40	0.20	2.9

B.7 Influent water heating requirements

To improve the removal efficiency of the air stripping unit, it may be necessary to heat the influent water. Influent water is considered to be at 15°C, and three process temperatures are considered: 25, 30 and 35°C. The following equation is used to estimate the influent water heating requirement, h_w , considering an average heat capacity for water, C_w^p , of 4.18 kJ/kg °C:

$$h_w = Q_L \rho_w C_w^p \Delta T \quad (\text{B-17}).$$

For the current case, the required power to heat the water would be 264, 396 and 528 kW for the three temperature differentials considered.

B.8 Requirements for thermal treatment of gas stream

One option for the treatment of the exhaust gas from the air stripping unit is thermal treatment. This requires heating the gas from nearly ambient conditions to around 750 °C. The following equation is used to estimate the influent water heating requirement, h_a , considering an average heat capacity for water, C_a^p , of 0.25 kJ/kg °C:

$$h_a = Q_G \rho_a C_a^p \Delta T \quad (\text{B-18}).$$

For the current case, considering and Air:Water volumetric ratio of 200, the heating requirements are 1,286 kW. It is assumed that if thermal treatment is used to oxidize the MTBE vapors in the exhaust, the heat required for the thermal oxidizer can be recovered through a heat exchanger to preheat the water, since the power requirements are lower for preheating the water influent.

Appendix C

SAVE System

The SAVE system used in this demonstration was “Modular SAVE II” manufactured by Remediation Service Int’l (RSI). The major system components are:

- Eight-cylinder internal combustion engine(ICE): power source/compressive thermal oxidizer
- Automotive catalytic converter(s): for the engine exhaust
- Engine Air/Fuel Controller: control air to fuel ratio, vacuum and operate the aeration tank.
- Noise abatement, lockable cabinet
- Moisture knockout tank(s) with high level shut off switch and air particulate filters
- Spray aeration tank
- Skid or trailer mounted

Operating assumptions according to RSI:

- BTU value of weathered gasoline is 19,000 BTU/lb.
- Maximum inlet concentration into a engine is 16,000 to 40,000 ppmv after dilution air
- The engine is operating as a power source and an abatement device.
- Inert gases such as CO₂ are not present in the well flow and oxygen exceeds 15 percent.
- A molecular weight of 86 (hexane) is used for VOC removal calculations.
- All flow rates are in standard cubic feet per minute assuming temperature = 60 °F and atmospheric pressure = 14.7 psig.
- Natural gas averages \$0.72/therm. One therm is equal to 100,000 BTUs.
- One month is computed at 720 hours.

The ICE has an average flow capacity of 75 standard cubic feet per minute (scfm) at an average 20 lbs/hr destruction rate capacity of volatile organic compounds (VOC) and capable of vacuums up to 9.80 psi (20 inHg) at 2000 RPM @ 20 inches Hg. The engine operating parameters are as follow:

Average soil vapor abatement	75 scfm @ 16,000 to 40,000 ppmv
Average BTU/hour destruction rate	380,000 BTU/hr
Average lbs per hour destruction rate	25 lbs/hr

Average Supplementary Fuel demand At Zero hydrocarbon loading with Oxidation abatement	380,000 BTU/hr
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Minimum Supplementary Fuel Demand At 100% hydrocarbon loading with Oxidation abatement	2,500 BTU/hr
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Range of Natural gas cost per month at 100% runtime at various BTU loading	0 to \$1,970/mo
Electrical cost per month at 100% runtime	-0-/mo

Maximum Supplementary Fuel demand At Zero hydrocarbon loading with engine As power source (operated at 1200 rpm) and Carbon Adsorption used for abatement Maximum energy usage	126,500 BTU/hr
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Maximum Natural gas cost per month at 100% runtime	0 to \$656/mo
Electrical cost per month at 100% runtime	-0-/mo

Appendix D

Complete List of the Analytical Results

Compound	Concentration Before Water Softeners	Concentration After Water Softeners	Units
<u>General Minerals</u>			
Alkalinity	450-530	480-540	mg/L
pH	7.3-7.4	7.4-7.8	
Total Hardness	960-1060	N.D. (10)-170	mg/L
Conductivity	1870-11600	2370-11900	uMHOs/cm
T.D.S.	1730-1860	1760-1840	mg/L
Turbidity	40-58	0.77-8.5	NTUs
Calcium	330-350	N.D. (2)-47	mg/L
Bicarbonate	450-490	N.D. (10)	mg/L
Carbonate	N.D.(10)	N.D. (10)	mg/L
Hydroxide	N.D.(10)	N.D.(10)	mg/L
Chloride	78-110	N.D.(10)	mg/L
Fluoride	0.95-1.2	N.D.(0.1)	mg/L
Nitrate as N	N.D. (0.1)	N.D.(0.1)	mg/L
Sulfate	660-760	N.D.(1)	mg/L
Color	N.D.(5)-8	N.D.(5)	Color
Copper	N.D.(0.03)	N.D.(0.03)	mg/L
Manganese	N.D.(0.1)-0.9	N.D.(0.1)	mg/L
Potassium	6.3-5.7	N.D.(4)-4	mg/L
Zinc	N.D.(0.06)-0.52	N.D.(0.06)-0.06	mg/L
Magnesium	80-83	N.D. (1)-11	mg/L
Iron	2.0-5.4	0.08-0.81	mg/L
Sodium	170-210	530-820	mg/L
<u>VOC's</u>			
MTBE	260-8,090	N.D. (5)-700	ppb
Benzene	N.D. (5)-47,300	N.D. (5)-64	ppb
Toluene	N.D. (5)-12,200	N.D. (5)	ppb

TDS: Total dissolved solids

VOC's: Volatile organic compounds

ND: Not detected

uMHOs/cm: micromhos/cm

NTUs: Nephelometric turbidity units