



## Field demonstration of pervaporation for the separation of volatile organic compounds from a surfactant-based soil remediation fluid

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### Abstract

As part of a Department of Defense project, the US Environmental Protection Agency was responsible for designing, building and field operating a pilot-scale pervaporation unit. The field site was an active dry cleaning facility on the grounds of Marine Corps Base Camp Lejeune in Jacksonville, NC. The overall goal of the project was to remove tetrachloroethylene (PCE) from the soil beneath the dry cleaning shop using a surfactant-based soil remediation fluid and to recycle/reuse the surfactant. In order to reinject the recovered surfactant, the pervaporation unit was required to achieve an average 95% removal of contaminants from the extracted fluid over the duration of the test period. PCE removal averaged 95.8% during peak surfactant levels and exceeded 99.9% in the absence of surfactant, thereby meeting the reinjection requirement. Removal of a group of secondary contaminants at the site, termed Varsol™ compounds, was monitored via concentrations of three Varsol™ marker compounds: decane, undecane and 1,3,5-trimethylbenzene. The pervaporation system processed 100,000 gal of groundwater and surfactant solution over a period of 70 days. In order to evaluate and validate process performance, a variety of process variables and properties were monitored over the course of the demonstration. Pervaporation costs are projected to be on the order of \$20 per 1000 gal of surfactant solution treated for a moderate size system (10 gpm). Published by Elsevier Science B.V.

*Keywords:* Pervaporation; Surfactant enhanced aquifer remediation; VOC; SEAR; Microemulsion

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## 1. General overview and project description

### 1.1. General overview

The purpose of the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) is to demonstrate and validate the most promising innovative technologies that target the most urgent environmental needs and are projected to pay back the investment through cost savings and improved efficiency. The purpose of the ESTCP project entitled “Integrated demonstration of surfactant enhanced aquifer remediation with surfactant regeneration/reuse” was to validate an in situ surfactant technology for residual dense non-aqueous phase liquid (DNAPL) removal from contaminated soils and to show that an above-ground treatment system can be used to cost-effectively recycle and reuse the surfactants. The demonstration site was an active dry cleaning facility at US Marine Corps Base Camp Lejeune in Jacksonville, NC. The primary contaminant in the soil beneath the facility was tetrachloroethylene (PCE). In this project, the US Environmental Protection Agency’s (USEPA) National Risk Management Research Laboratory (NRMRL) undertook the design, assembly, testing and field operation of a pervaporation unit. This work was one component of the DoD ESTCP project. The USEPA pervaporation unit was used to remove primarily volatile DNAPL solvents from surfactant solutions, thereby enabling the reinjection of the surfactant solution into the ground. The DoD project lead, Naval Facilities Engineering Service Center, contracted with Duke Engineering and Services Inc. for subsurface characterization and treatment tasks. The University of Oklahoma was tasked to reconcentrate surfactant by micellar enhanced ultrafiltration (MEUF) after the contaminant had been removed. A schematic diagram of the integrated system is shown in Fig. 1. As depicted in the figure, an aqueous surfactant solution was prepared and injected into the subsurface via wells. Groundwater and surfactant solution were recovered via extraction

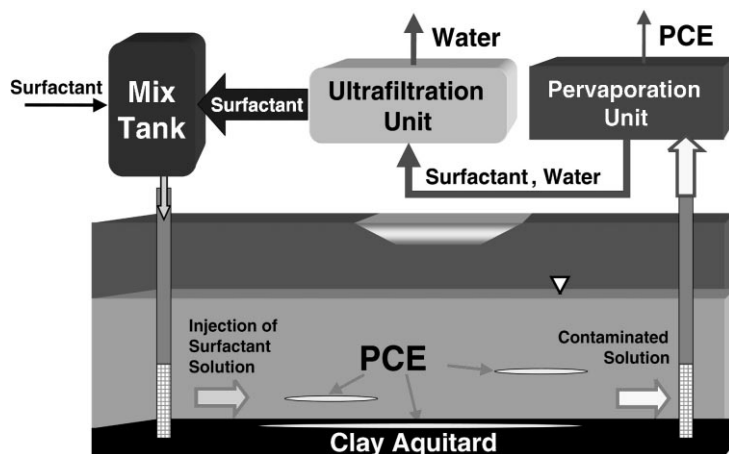


Fig. 1. Schematic diagram of integrated surfactant enhanced aquifer remediation (SEAR) and surfactant recovery processes.

wells. The hydraulic gradient established between the injection and extraction wells caused the surfactant solution to flow through the contaminated soil where contaminant mobilization and solubilization occurred. The contaminant in the solution recovered at the extraction wells was then removed using a pervaporation unit. The decontaminated surfactant solution was then reconcentrated by ultrafiltration before being mixed with fresh surfactant prior to reinjection.

The USEPA objective for the pervaporation demonstration was to achieve at least 95% single pass removal of tetrachloroethylene (PCE) and 95% averaged removal of Varsol™ components from a surfactant enhanced aquifer remediation (SEAR) fluid. Varsol™ is a hydrocarbon-based dry cleaning solvent which was used at the facility prior to PCE. Varsol™ components are present in the DNAPL at concentrations 2–4 orders of magnitude lower than PCE. Measurement of the PCE removal objective was based on weekly averages of PCE removal for the duration of the demonstration. Measurement of the Varsol™ removal objective was based on the average removals of three Varsol™ marker compounds: decane, undecane and 1,3,5-trimethylbenzene. It was expected that the Varsol™ removal objective would be met when weekly averages of Varsol™ removal exceed 95% at the end of the pervaporation treatment project as surfactant concentrations declined during the post-SEAR water flood.

*1.1.1. The process (mention of trade names, vendors, or commercial products does not constitute an endorsement or recommendation for use)*

In pervaporation, as applied in this project, a liquid stream containing VOCs is placed in contact with one side of a non-porous polymeric membrane while a vacuum or gas purge is applied to the other side. Pervaporation is pictorially represented in Fig. 2. The components in the liquid stream sorb into the membrane, permeate through the membrane and evaporate into the vapor phase (hence the word pervaporate). The vapor is then condensed. By using

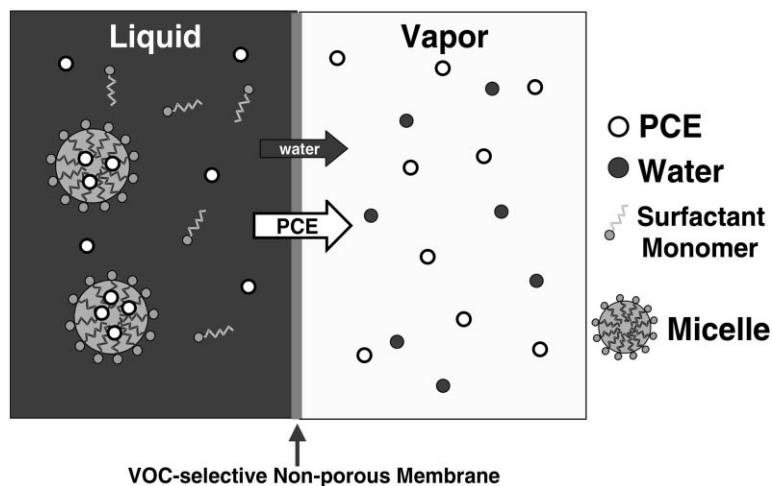


Fig. 2. Pictorial representation of the removal of VOCs from surfactant solution by pervaporation.

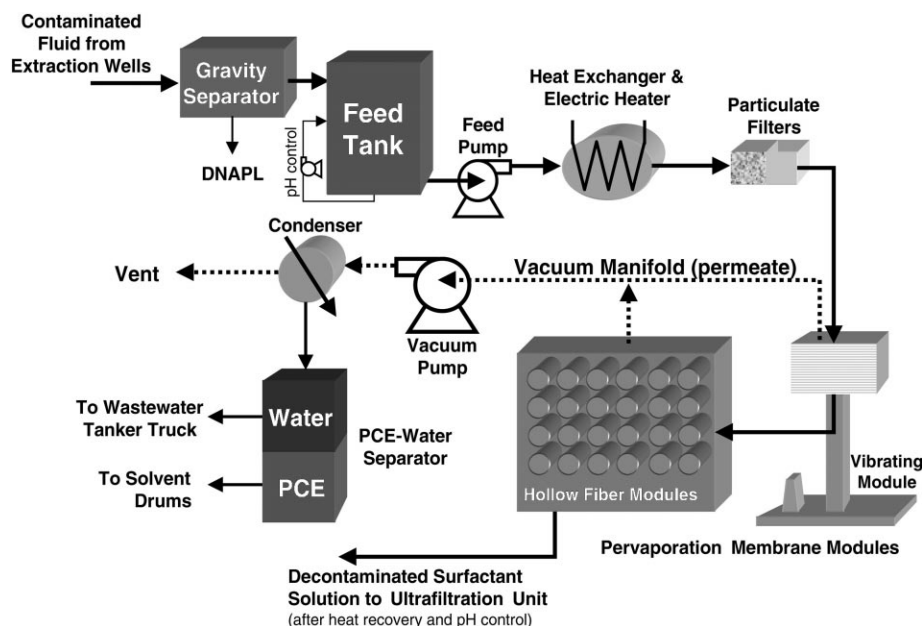


Fig. 3. Schematic diagram of USEPA pervaporation field unit at Marine Corps Base Camp Lejeune.

a membrane which is VOC-selective, the material on the vapor side of the membrane, once condensed, will contain VOCs with concentrations significantly higher than those on the liquid side of the membrane. A concentration factor of 1000 is not uncommon. Due to the low solubility of VOCs in water, a pure VOC phase and a VOC-saturated water phase are formed when the permeate vapor is condensed. If alcohols are present in the SEAR fluid formulation, a portion of those alcohols will be transported through the membrane and will partition between the water and VOC permeate phases. Since the surfactant is hydrophilic, ionic and has a low vapor pressure, it should not be a component of the permeate and thus, it will remain on the feed/liquid side of the membrane.

In 1995, USEPA-NRMRL initiated pilot and bench-scale tests of pervaporation for removing volatile organic compounds (VOCs) such as 1,1,1-trichloroethane (TCA) and toluene from surfactant solutions [1–4]. These experiments showed that pervaporation could effectively remove all of the studied VOCs from surfactant solutions. However, the presence of the surfactant did diminish removal efficiencies.

The pervaporation field unit was assembled by IT Corporation based on specifications provided by the USEPA. A simplified schematic diagram of the unit is provided in Fig. 3 and features of the system are detailed below. IT Corporation and USEPA engineers designed the system. The pervaporation system was designed for unattended operation. The system automatically controlled feed flow, feed pressure, vacuum pressure and emptied the permeate reservoirs. Two pervaporation membrane systems were operated in series. The first was a single vibrating membrane module containing approximately 10 m<sup>2</sup> of membrane. The second was a grid of up to 36 hollow fiber membrane modules, each containing 3 m<sup>2</sup> of

membrane area. The arrangement and number of hollow fiber modules used was modified throughout the demonstration to enhance performance.

In the field demonstration, the surfactant solution was pumped from six extraction wells by Duke Engineering to a three-way valve at the front end of the pervaporation system. Fluid from the extraction wells was blended into one stream before it arrived at the pervaporation unit. The total extraction flow rate averaged 1.0 gpm. The Camp Lejeune pervaporation field unit was designed to achieve 95% removal of PCE from this extracted fluid. The fluid contained variable amounts of surfactant (Alfoterra 145 4 PO ether sulfate (Alfoterra 145), also referred to as Isalchem 145 or IC145), isopropyl alcohol (IPA), calcium chloride ( $\text{CaCl}_2$ ) and contaminants. The alcohol was added to the SEAR fluid to reduce the viscosity of the surfactant-DNAPL microemulsion. The  $\text{CaCl}_2$  was added to reduce mobilization of soil fines that might plug the soil pores and to enhance the DNAPL solubilization behavior of the surfactant. At the onset of the remediation demonstration, water containing  $\text{CaCl}_2$  was injected. As a result, the fluid extracted initially did not contain any surfactant. As the demonstration progressed, however, the injected fluid contained 4 wt.% surfactant, 16 wt.% IPA and 0.2 wt.%  $\text{CaCl}_2$ . As a result, the concentration of Alfoterra 145 in the extracted fluid increased over time and was expected to plateau at 1.5 wt.%, with IPA rising to 6.0 wt.%. The resulting PCE concentration in the pervaporation feed stream was predicted to reach a maximum of 10,000 mg/l. Since IPA was intentionally added to the SEAR fluid, it was not considered to be a contaminant, thus, no IPA removal objective was defined for the pervaporation equipment. However, the concentration of IPA in the system was monitored to determine the level of removal achieved by the pervaporation system.

In case of an emergency shutdown of the treatment system, the three-way valve diverted flow to a waste tanker. This safety feature was only activated once during 70 days of operation, the result of a faulty flowmeter which caused an 11 h pervaporation system shutdown. In normal operation, the three-way valve allowed the surfactant solution to flow into an oil–water separator. The purpose of this separator was to remove any free-product DNAPL from the surfactant solution using gravity separation. The lower drains of this separator were connected to a 55 gal stainless steel drum for DNAPL and grit collection. The overflow from the oil–water separator gravity flowed to a 1000 gal epoxy-lined fiberglass reinforced plastic “feed” tank (Raven Industries Model DF354). The contents of this tank could be pH adjusted using a 20 gpm recirculation loop equipped with an acid addition system. The target pH of the feed solution was 4.5 to reduce the likelihood of forming carbonate precipitates and scales in the system. A nitrogen blanket was applied to both the feed tank and oil–water separator to minimize oxidation of soluble iron, thereby reducing the formation of iron precipitates. The pervaporation feed pump (Eastern Centrichem Pump Model ET7M-1725), drew fluid from the bottom of the feed tank at approximately 1 gpm. The level of fluid in the feed tank was held approximately constant, even though flow from the wells was variable, by automatically or manually adjusting the feed flow rate. Thus, the feed to the pervaporation modules was also somewhat variable but averaged 1.0 gpm. The feed solution was pumped through a heat exchanger (Vicar Inc.), an electric heater (Gaumer Co., Model C4F6N 40H4-RK-ER-X, 30 kW heater with Fenwal Series 920 Model 923 digital indicating controller with Newport Model 82 alarm unit) and a two-stage bag filtration system (Strainrite Bag Filter, Harrington Corro-Flo) with the finest filter being either 1 or 5  $\mu\text{m}$  nominal particle retention. In the heat exchanger, the influent stream

was preheated using heat recovered from the treated pervaporation residual stream. A UV system (Ideal Horizons, Model SSWE-6) located after the filters sterilized the solution to reduce biofilm growth in the MEUF system. Biofilm growth on the silicone pervaporation membranes was not expected to be a problem.

Pretreated surfactant solution was sent to a vibrating pervaporation system (New Logic International, 15 in. i-series VSEP unit) for initial PCE removal. The solution was then sent to a series of hollow fiber membrane modules (Applied Membrane Technology, Model PVCTXS1SS) for additional PCE removal. The treated surfactant solution then flowed through the recovery heat exchanger, a pH adjustment loop (to raise pH prior to MEUF) and then to an MEUF storage tank, where the solution was then processed by the University of Oklahoma. Vacuum was supplied to both pervaporation membrane systems by a multi-stage dry chemical vacuum pump with integrated vapor compression and condensation (Stokes Vacuum, CD-75 Dry Pump, 75 cfm nominal, 5 hp). A recirculating chiller (Icewagon Industries, Model DE5AC, 5 t capacity) provided coolant at 2°C to condense the permeate. The two-phase (water and organic) permeate condensate was pumped from the condenser reservoirs to a PCE/water gravity separator. The PCE phase was manually drawn off the bottom of this separator and transferred to a solvent disposal drum provided by Baker Environmental. The permeate water was transferred to a waste tanker, although, it could have been returned to the feed tank for further processing. Each liquid process stream passed through a flow totalizer in order to provide data for mass balance calculations.

### 1.2. Experimental design

Operation of the field unit followed detailed written procedures to ensure consistent performance. The system operating conditions — process temperatures, feed flowrate, residual pressures and permeate (vacuum) pressure — were maintained and monitored at least twice per day. Three times each week (usually on Monday, Wednesday, and Saturday), a set of samples was taken from the feed stream, outlet stream of the VSEP membrane system and outlet stream of the hollow fiber module system, designated Feed, Residual 1 (Resid1) and Residual 2 (Resid2), respectively. These samples were sent to USEPA facilities in Cincinnati for PCE determination by GC/FID analysis using an autosampler (Archon, Varian Corp.), purge & trap concentrator (LCS3000, Tekmar Corp.) and a Finnigan/Tremetrics 9001 GC equipped with a DB-624 megabore column and flame ionization detector (FID). Bromobutane was added to all samples by the autosampler as a surrogate to monitor the proper operation of the analytical system. Each Monday, a separate set of Feed and Resid2 samples was obtained and sent to USEPA-Cincinnati for PCE/Varsol™ determination by GC/MS (HP 6890 equipped with a HP624 column) using an autosampler (Archon, Varian Corp.) and purge & trap concentrator (LCS3000, Tekmar Corp.). The sampling method was similar for all sampling points. The needle of an airtight syringe was inserted through a septum port installed on each process line to be sampled. Since the process streams were pressurized, sample was forced into the syringe when the plunger was pulled back, thus, avoiding the creation of vacuum conditions in the syringe which might volatilize VOCs. After flushing, a slight excess of sample was drawn into the syringe. The syringe needle was then withdrawn from the septum port, excess sample expelled and the desired sample volume was injected into a volumetric flask of water (either 50 or 100 ml) which contained

3 to 6 drops of antifoam (the antifoam was prepared daily by diluting 1 g of Dow Antifoam C with 5 g water). The volumetric flask was promptly mixed by inverting and shaking at least three times, a portion of the contents was poured into a labeled 40 ml EPA vial, completely filling the vial. In general, only one dilution of each stream was performed. In some cases, two dilutions were performed to ensure that one set was within the linear calibration range of the off-site GC. The maximum dilution used was 500-fold (200  $\mu$ l in 100 ml). At the highest surfactant concentrations, a minimum of a 40:1 dilution was applied in order to reduce surfactant concentrations to minimize foam generation during purging. Each dilution was performed in triplicate, starting with acquisition of the sample by syringe. At least two of the three triplicate samples were analyzed. Permeate samples were collected at the same frequency as feed samples in undiluted form in 40 ml vials (for water or organic phases) or in 2 ml vials (only for organic phase). Later in the demonstration, the permeate organic phase which had been collected during the preceding week, was weighed and subsampled.

All field samples were stored in a refrigerator at 4°C. The samples were shipped in Styrofoam containers chilled with ice packs to Cincinnati approximately two times per week. The samples were analyzed upon receipt at USEPA-Cincinnati facilities. Unanalyzed samples were stored in a refrigerator at 4°C. The maximum storage time was 4 days. Acceptable PCE recoveries from field matrix spike samples indicated little or no decay in concentration due to storage. Organic phase samples and water samples for IPA analysis were expected to have even longer acceptable storage times of up to 14 days.

In order to evaluate the contaminant removal performance of the pervaporation system, several other process variables were measured. These non-critical parameters included surfactant concentration and IPA concentration. Surfactant analysis were provided by the University of Oklahoma based on a high performance liquid chromatography (HPLC) method. IPA analysis were performed on-site by IT Corporation using a GC/FID.

## 2. Pervaporation system design considerations

In planning for this field demonstration, USEPA engineers drew from pervaporation field demonstration experiences of outside organizations as well as their own experiences. In a 1996 field demonstration, performed by Membrane Technology and Research, Inc. (MTR), pervaporation was used to remove VOCs from groundwater at the DOE Pinellas Plant, FL. Ferrous iron in the range of 8–26 mg/l caused repeated fouling of spiral wound pervaporation modules [5]. Based on reported observations, ferrous ions were oxidizing to ferric ions when the anoxic groundwater came in contact with air in process drums. Ferric compounds have an extremely low solubility in water, thus, iron precipitates formed throughout the system. The precipitates accumulated in the pervaporation modules causing flow channel plugging which lead to increased pressure drops and reduced process efficiency.

In a 1995 field demonstration, pervaporation was used by Zenon Environmental to remove VOCs from groundwater at the Naval Air Station North Island near San Diego, CA [6]. In this demonstration, the pervaporation system consisted of hollow fiber membranes. Iron particles and carbonate scales caused module blockage. The brackish groundwater contained high concentrations of calcium (circa 200 mg/l) and magnesium ions (circa 500 mg/l) which tend to form scale precipitates in water containing carbonates, especially when heated. At this site

groundwater was heated to approximately 70°C before entering the pervaporation module which likely caused the formation of carbonate scales and precipitates. In addition, the system was operated in a multi-pass mode in which the flow rate through the module was several times higher than the groundwater flow rate. While this mode of operation yielded higher process efficiencies, it also created high retention times for precipitate nuclei, giving the nuclei more time to grow into particles which could plug the modules. The iron particles appeared to come from a carbon steel equilibration tank in which the groundwater was stored. Use of the tank was discontinued once it was identified as the source of the iron particles.

Finally, in 1996–1997 the USEPA performed a pilot-scale demonstration of pervaporation for the removal of VOCs from an actual SEAR fluid [1]. This SEAR fluid came from a demonstration conducted by the University of Texas, the Air Force Center for Environmental Excellence and Duke Engineering and Services at Hill Air Force Base Operable Unit 2 (OU-2) site. The OU-2 site had been contaminated with a degreasing solvent, primarily trichloroethylene (TCE). Due to its use, the solvent contained some oil and grease. The SEAR fluid and the degreasing solvent formed a stable microemulsion thereby enabling the hydraulic removal of the contaminant from the subsurface. However, when the solvent was removed, the residual oil was not solubilized by the SEAR fluid alone. Thus, when the pervaporation system removed the chlorinated solvent, oil was released from the fluid and became deposited on surfaces in the pervaporation module. Spiral wound modules from Hoechst Celanese Corporation were employed (similar in design to the MTR spiral wound modules). The oil coated the liquid flow spacer in the module, causing flow restrictions, increased pressure drops and reduced performance. Subsequently, experiments were performed with novel hollow fiber modules designed and produced by New Jersey Institute of Technology (NJIT) and Applied Membrane Technology (AMT) [7]. Although, oil also became deposited in the NJIT/AMT modules, the design of these modules allowed for the continuous removal of the oil through the membrane (paper in preparation). Unfortunately, the hollow fiber modules had limited temperature and pressure operating ranges. The lifetime before leakage in the modules was also suspect. No severe iron or carbonate issues were encountered with the Hill AFB SEAR fluid. However, a sandy particulate material was found to accumulate at the ends of the hollow fiber modules. It was concluded that this material was a form of heater scale which had likely flaked off the heater elements and made its way to the modules.

Throughout these experiments, it was determined that pervaporation effectively removed VOCs from groundwater and SEAR fluids. However, a variety of common groundwater and SEAR compounds had caused severe operating restrictions. The Camp Lejeune pervaporation system included several equipment and operating features designed to avoid the problems encountered in previous demonstrations. First, the feed tank was blanketed with nitrogen gas at a pressure of 2–6 in. of water. A water leg on the tank served as a pressure relief outlet. Thus, little or no oxidation of ferrous iron would occur in the pervaporation system. In addition, during normal operation, the fluid level in the tank would be held constant, thus, reducing the pressure fluctuations in the feed tank, reducing the likelihood of air being drawn into the tank and also reducing nitrogen usage. The MTR Pinellas demonstration had used surge tanks and feed tanks in which fluid from the surge tank was periodically transferred to the feed tank, thus, tank levels changed, sometimes rapidly, during the process causing reduced pressure conditions which lead to air being drawn into the



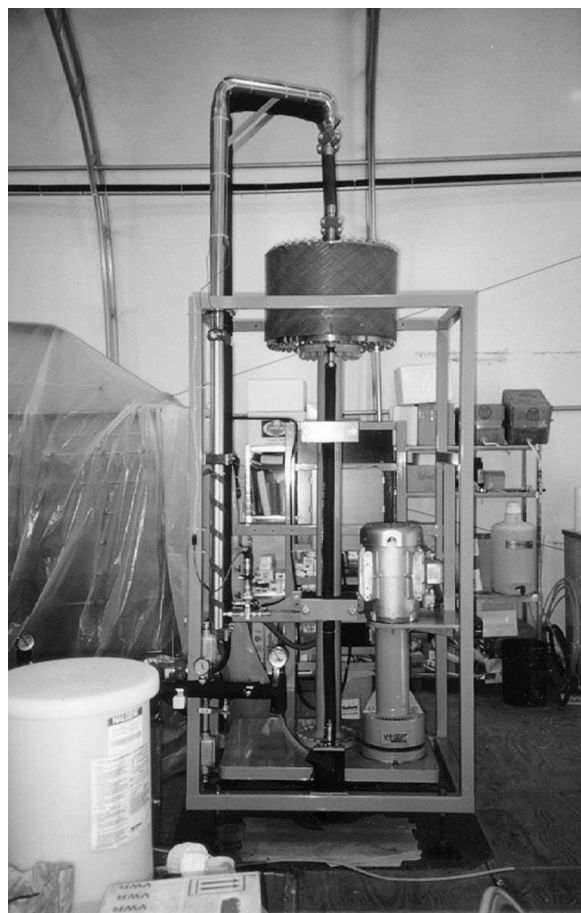
tanks. For the Camp Lejeune Unit, a pH adjustment loop was added to the feed tank so that the pH of SEAR fluid could be lowered to reduce the likelihood of carbonate precipitate formation. A solution of hydrochloric acid could be added to acidify the contents of the tank with a target pH of 4–4.5. Typical silicone pervaporation membranes are stable over a range of pH conditions, from acidic to basic, although, strongly basic conditions should be avoided. A second pH adjustment loop was located at the outlet from the pervaporation system in order to return the pH to that desired for SEAR fluid reinjection. Further, to minimize formation of scale in the electric heaters, it was recommended that a maximum heater core temperature of 50°C be employed, thus, restricting the feed temperature to the pervaporation modules to the range of 40 to 50°C. In case heater scale formed and flaked off, bag filters were located between the heater and the pervaporation modules. Filters with 25, 10, 5 and 1 µm nominal particle retention were available. Since spiral wound modules appeared to be susceptible to fouling by precipitates and oils, it was decided that this type of module would not be used for the Camp Lejeune demonstration. Instead, new pervaporation modules were designed, tested and scaled-up to deal with the problems encountered in past tests. A vibrating membrane system from New Logic International was modified to accept pervaporation membranes and operate in pervaporation mode. This system offers high efficiencies and very low fouling potential. A modified hollow fiber module design from AMT was also employed. Finally, thick membranes were used to lessen the water flux through the membranes, thereby reducing the temperature drop due to evaporation and the cooling capacity for condensation in the vacuum pump. The membranes used were thicker than desired due to production limitations for the novel membrane modules. All of these design issues and operating parameters were selected prior to field operation and before full knowledge of groundwater chemistry was available. As a result, some of them may not have been necessary and additional changes may have been advisable.

### 3. Pervaporation system performance

#### 3.1. Timeline of pervaporation field activities

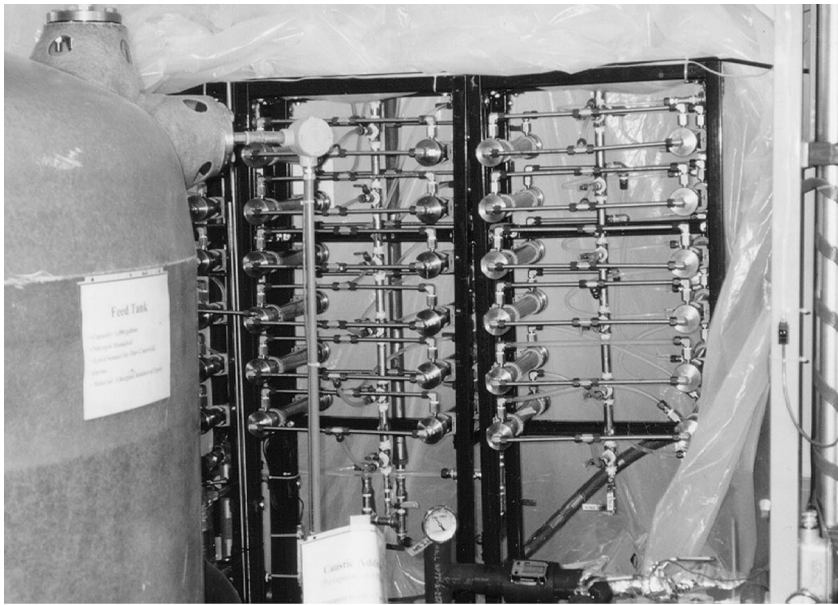
The field pervaporation system was delivered to the Camp Lejeune site on Wednesday, 17 March 1999. A field tent was used as weather protection for the system. The floor of the tent consisted of a double layer of polypropylene sheeting covered with plywood. A berm around the inside edge of the tent provided secondary containment for any accidental spills. Pictures of the membrane systems and of the inside of the tent are provided in Fig. 4. Installation and start-up testing of the pervaporation system was completed on Friday, 19 March 1999. The system was then operated in recirculation mode (treated residual was returned to the feed tank) using tap water as the feed liquid. The pervaporation system operated in this mode until Monday, 29 March 1999 at 14:30 h (day 0), when the system began accepting groundwater from the six extraction wells. On day 0, the pervaporation system was switched to single pass mode in which extracted water was withdrawn from the feed tank, processed through the pervaporation modules, then sent either to a waste tanker or to the MEUF feed tanks. Treated fluid was sent to the waste tanker until 18:30 h, 15 April 1999 (day 17) when it was directed to the MEUF feed tank. Prior to day 17, surfactant concentrations were too low to make

ultrafiltration practical. Surfactant injection into the subsurface was halted on the afternoon of Thursday, 3 June 1999 (day 66). The pervaporation system accepted extracted fluid until the morning of Monday, 7 June 1999 (day 70). At this time, USEPA staff performed a 50% dilution of material in the feed tank to determine the effect of diluting the surfactant on PCE removal. After approximately 24 h of flushing with tap water, the pervaporation system was shut down on Tuesday, 8 June 1999. Originally, the pervaporation system was to be operated until surfactant concentrations dropped to approximately 0.1 wt.% during the post-SEAR water flood. Due to a 2-week extension in the SEAR flood and scheduling conflicts, it was not possible to operate the pervaporation system past day 70. The pervaporation system was disassembled and returned to the USEPA's Test and Evaluation Facility in Cincinnati, OH during the week of 28 June 1999.



(a)

Fig. 4. Pictures of (a) vibrating pervaporation unit (b) hollow fiber pervaporation modules and (c) Camp Lejeune pervaporation field system.



(b)



(c)

Fig. 4. (Continued).

### 3.2. Process parameters and measurements

#### 3.2.1. Iron, calcium, pH

During the Camp Lejeune demonstration, influent ferrous iron concentrations ranged from 8 to 19 mg/l, averaging 14 mg/l, similar to concentrations which caused problems in the Pinellas pervaporation demonstration. The concentration of ferrous iron leaving the pervaporation system was 13 mg/l, the same as the influent concentration considering sampling and analytical errors/variability. No iron precipitates were observed in the system. Thus, it appears that the nitrogen blanketing system worked effectively. The average pH of the extracted water was 4.3, within the target range for the feed tank, thus, no pH adjustment was necessary. The calcium concentration was on the order of 300 mg/l due to the addition of CaCl<sub>2</sub> to the SEAR fluid. No calcium or carbonate precipitate was observed in the filters or membrane modules. Initially, filters of 25 and 5 μm retention were used in series. These were removed once to determine their condition and replaced with 5 and 1 μm filters. A pressure drop increase across the filters was never observed. A fine grey colored particle was seen in the filter, although, no accumulation on the filter surface was apparent. The grey particles were likely clay fines from the soil. Aside from the grey color, the original filters appeared to be in good shape.

#### 3.2.2. Temperature

The target feed temperature into the first membrane unit of the Camp Lejeune pervaporation system was 40°C. Due to heat losses from hoses, filters and piping, the temperature of the fluid entering the first pervaporation module was 5 to 6° below the heater set point. Temperatures at the second pervaporation system were 8 or 9° below the heater set point. Since system performance is a function of temperature, the reduced temperatures in the pervaporation systems were resulting in lower PCE removal performance. In addition, because the temperature of the residual fluid was low, limited heat could be recovered to pre-heat the feed. Thus, the heater was required to make up for the heat losses, resulting in heater core temperatures greater than the 50°C desired maximum. Mid-way through the demonstration, insulation was installed on process hoses and equipment to reduce temperature losses. Foam insulation was installed on hoses while plastic sheeting was draped over the hollow fiber module grid. In addition, the heater set point was raised so that the temperature of fluid entering the first pervaporation module approached 40°C. These changes yielded fairly stable operating temperatures during the second half of the demonstration. The temporal variation of the average temperature in the pervaporation modules is shown in Fig. 5.

#### 3.2.3. Flow rate

The target flow rate for the combined extraction wells was 1.0 gpm. Due to calibration difficulties, filter plugging and extraction pump malfunctions during the first several weeks of the SEAR demonstration, the flow rate from the extraction wells to the pervaporation system was somewhat variable. Eventually, the extraction rates were better behaved and pervaporation flow rate stabilized. The average feed flow rate to the pervaporation system was 0.99 gpm. On a few occasions, a high or low flow rate was required to keep up with the pumping rate for the extraction wells. The minimum and maximum pervaporation

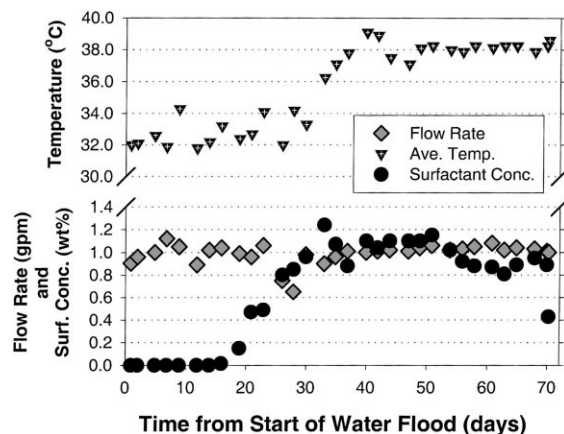


Fig. 5. Time variation of flow rate, surfactant concentration and average temperature during USEPA Camp Lejeune pervaporation field demonstration.

feed flow rates observed were 0.65 and 1.16 gpm, respectively (the minimum and maximum conditions during sampling events were 0.65 and 1.12 gpm, respectively). A plot of pervaporation flow rates measured during sampling events versus time is provided in Fig. 5.

#### 3.2.4. Module configuration and operating parameters

The configuration of the VSEP i-series unit was fixed. The unit consisted of only one membrane module, a 15 in. tall stack, the smallest produced by the vendor. The membrane stack contained approximately 10 m<sup>2</sup> of silicone rubber membrane (Nott 1010, 250 μm thick fiberglass reinforced silicone-coated fabric). The only operating variable for the VSEP system was the vibration frequency which also determines the amplitude of vibration, termed the “travel distance”. The target travel distance was 0.5 in. and this amplitude was maintained until day 33 when it was reduced to 0.25 in. The corresponding vibration frequencies were 48.2 and 47.5 Hz, respectively. The amplitude was reduced to minimize a minor liquid leak which developed around one of the fittings on the module. This leak was later traced to a cracked plastic pressure plate in the module, which was replaced after the demonstration had been completed. Vibration amplitude is linked to VOC removal performance, although, the difference between 0.25 and 0.5 in. in the presence of surfactant is not expected to be very significant. In controlled experiments, it has been observed that the biggest gains are obtained in the transition from no vibration to 0.25 in. vibration with incremental gains thereafter [4].

In contrast to the VSEP unit, the configuration of the hollow fiber module system was highly variable. A total of 36 individual modules were available during the demonstration. Initially, only 32 of the modules were used as a 16 × 2 grid in which each module was exposed to only half of the total flow. Later, the remaining four modules were added in series with the other modules as a 4 × 1 grid in which each module was exposed to the entire liquid flow. In these modules, a higher flow rate will increase the VOC mass

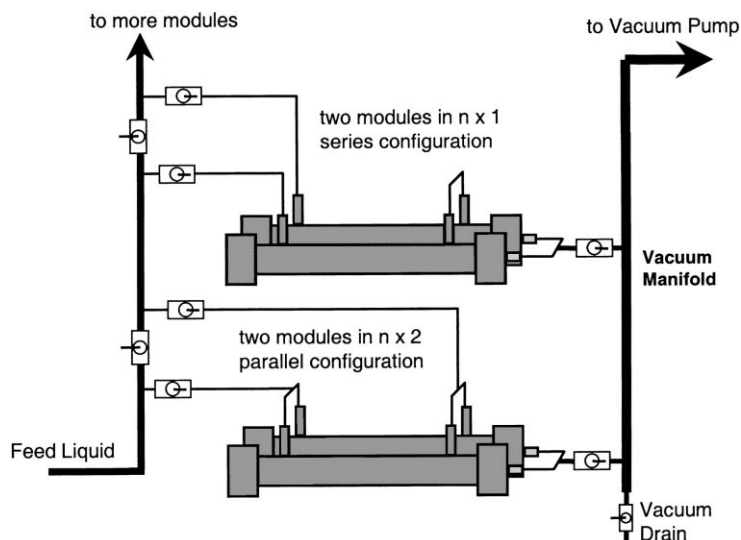


Fig. 6. Schematic diagram of the hollow fiber module configurations used during the demonstration. The lower two modules are shown connected in parallel ( $n \times 2$ ) and the upper two modules are shown connected in series ( $n \times 1$ ). The two sets are connected in series with regard to liquid flow but in parallel with regard to the vacuum.

transport efficiency. Thus, a  $24 \times 1$  grid will be more efficient than a  $12 \times 2$  grid although, the same number of modules are used. The main negative effect of an  $n \times 1$  grid is a higher pressure drop. Since higher flow rates and pressures can cause module failures due to fiber leaks, there is a tradeoff between improved VOC removal efficiency and possible damage to the modules. By the end of the demonstration, 24 of the modules were operated as a  $24 \times 1$  grid in order to achieve the desired levels of PCE removal. The remaining modules were operated in a  $5 \times 2$  or  $6 \times 2$  grid. A schematic diagram showing the difference between the  $n \times 1$  and  $n \times 2$  module configurations is provided in Fig. 6.

### 3.2.5. Surfactant and alcohol

As mentioned previously, the surfactant concentration was expected to change significantly over the course of the demonstration, starting with no surfactant, rising to a plateau of 1.5 wt.%, then dropping during the post-SEAR water flood. A temporal plot of surfactant concentration is also provided in Fig. 5. Surfactant injection commenced on 6 April 1999 (day 8) and due to the retention time of the test plot, quantifiable levels of surfactant were not observed until 14 April 1999 (day 16). Due to higher than expected subsurface dilution, the surfactant concentration in the fluid from the six extraction wells never reached the expected peak of 1.5 wt.%. The highest observed surfactant concentration was 1.2 wt.% on day 33. The average surfactant concentration during the plateau region was 1.0 wt.%. During this same time, the IPA concentration rose from 0 to a plateau average of 4.1 wt.%, or roughly four times the surfactant concentration — the same ratio as for the injection fluid (4 wt.% surfactant and 16 wt.% IPA). The pervaporation system removed about 5% of the

IPA resulting in an average concentration in the residual stream of 3.8 wt.%. Significantly more IPA would have been removed if thinner membranes had been utilized. The permeate water condensed in the vacuum pump contained up to 30 wt.% IPA due to the selectivity of the silicone membrane for IPA relative to water.

### 3.2.6. PCE concentrations and removal

Preliminary modeling of the subsurface extraction system performed by the University of Texas at Austin predicted that PCE concentrations in the mixed extracted fluid would start at about 70 mg/l during the pre-SEAR water flood, rise to a maximum of 10,000 mg/l during the SEAR and decline to 40 mg/l during the post-SEAR water flood. Concentrations in excess of 1000 mg/l were predicted for a period of approximately 40 days. PCE concentrations actually observed in the pervaporation feed and final residual (effluent) streams are displayed in Fig. 7. PCE concentrations started at 35 mg/l. After only 5 days, feed concentrations approached the PCE water solubility limit of 240 mg/l, likely due to the presence of DNAPL in the process lines and oil/water separator. PCE concentrations remained below the water solubility of PCE until surfactant appeared in the extraction fluid. However, as shown in the figure, PCE concentrations in the pervaporation system never exceeded 1000 mg/l, reaching a maximum of 890 mg/l. It was later observed that the input parameters for the subsurface modeling program overestimated the level and extent of contamination. The PCE concentration in the final Residual (Resid2) stream ranged from below detection limits (<0.05 mg/l) to 61 mg/l. These concentrations translate to PCE removal efficiencies ranging from 93.1 to 99.96% PCE removed. The fraction of PCE removed in the VSEP membrane system ( $X_{VSEP}$ ) was calculated according to the following relationship:

$$X_{VSEP} = \frac{(C_F - C_{R1})}{C_F} \quad (1)$$

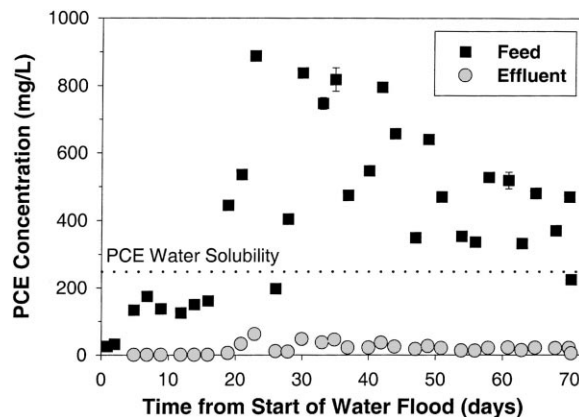


Fig. 7. Feed and effluent (Resid2) PCE concentrations measured during Camp Lejeune pervaporation field demonstration, note: error bars represent the standard deviation of duplicate analysis, error bars are generally smaller than the size of the symbols.

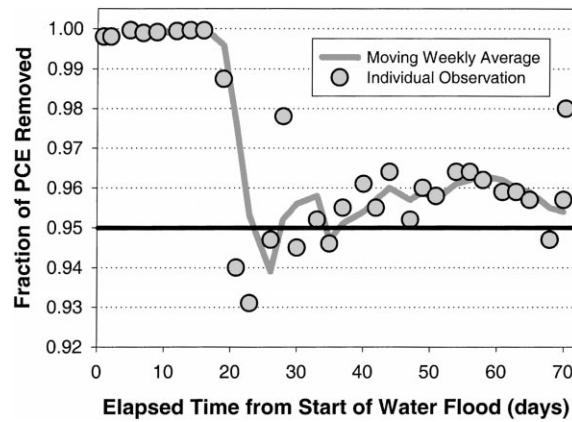


Fig. 8. Variation of the overall fraction of PCE removed by pervaporation field unit for each sampling event (symbols) and the moving weekly average removal (line) with elapsed time. Overall removal calculated from data in Fig. 6. Note: size of error bars is smaller than the size of the symbols.

The fraction removed in the hollow fiber membrane system ( $X_{HF}$ ) is

$$X_{HF} = \frac{(C_{R1} - C_{R2})}{C_{R1}} \quad (2)$$

The total fraction of PCE removed by the process ( $X_T$ ) was determined by

$$X_T = \frac{(C_F - C_{R2})}{C_F} \quad (3)$$

where  $C_F$  is Feed concentration (mg/l);  $C_{R1}$  intermediate Residual (Resid1) concentration (mg/l);  $C_{R2}$  final Residual (Resid2) concentration (mg/l).

The overall fraction of PCE removed, determined for each sampling event, is plotted in Fig. 8. The moving weekly average (average of three successive measurements) is also displayed in Fig. 8. As seen in the figure, the moving average only dropped below the target of 95% removal on two occasions and never dropped below 94%. It should be noted that relative PCE removal was not a function of PCE feed concentration, at least not for the concentrations encountered in this project. In other words, a system which removes 95% of PCE from a solution containing 50 mg/l will remove 95% from the same solution containing 1000 mg/l. The residual solutions will have significantly different levels of PCE (2.5 versus 50 mg/l), but the fraction of PCE removed will be the same.

PCE removal will, however, be a function of surfactant concentration, flow rate, temperature and membrane module configuration. Surfactant reduces process efficiency because of the partitioning of the VOC into the surfactant micelles, thereby reducing the availability, or activity, of the VOC [2,3,8,9]. Increasing surfactant levels will reduce VOC removal for a pervaporation system. In simplistic terms, flow rate effects removal as follows:

$$\frac{C_R}{C_F} = \exp\left(\frac{-kA}{Q}\right) \quad (4)$$



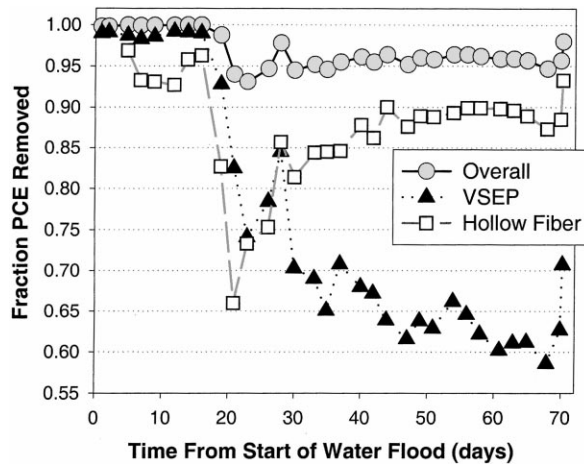


Fig. 9. Time variation of the fraction of PCE removed in the vibrating VSEP and hollow fiber pervaporation systems and the overall PCE removed by the Camp Lejeune pervaporation unit.

where  $C_R$  is the Residual VOC concentration,  $C_F$  is the Feed VOC concentration,  $k$  is the overall lumped mass transport coefficient,  $A$  is membrane area and  $Q$  is the flow rate. Thus, all other variables being equal, VOC removal is an exponential function of flow rate. However, the removal of VOCs from water is typically controlled by diffusion through the liquid boundary layer next to the membrane, a situation referred to as “concentration polarization”. In these cases,  $k$  is also a function of  $Q$ , so the relationship between removal and flow rate can be quite complex.

All things considered, changes in surfactant concentration will dominate PCE removal performance while temperature, flow rate, and module configuration will have secondary effects. Therefore, it was expected that PCE removal would be high initially, then drop when surfactant appeared in the extracted fluid. This is the general trend observed in Fig. 8. Overlaid on this general trend, changes in the other process parameters caused day to day variations in PCE removal. This relationship can be observed by comparing the process variables in Fig. 5 to the PCE removal performance in Fig. 8. A spike in PCE removal on day 28 corresponds to the lowest flow rate encountered during the demonstration. Although, the overall PCE removal was of importance for meeting regulatory reinjection requirements, the individual performance of the two pervaporation systems was of interest for understanding the behavior of these systems. The performance of each system is shown in Fig. 9. In this figure, the fraction of PCE removed by each system, of the PCE entering that particular system, is displayed. For systems operated in series, the overall fraction removed ( $X_T$ ) is calculated from the individual fraction removals ( $X_{VSEP}$  and  $X_{HF}$ ) as follows:

$$(1 - X_T) = (1 - X_{VSEP})(1 - X_{HF}) \quad (5)$$

or, in terms of the fraction remaining,  $Y_i$ :

$$Y_T = Y_{VSEP} Y_{HF} \quad (6)$$

where  $Y_i = 1 - X_i$ .

Table 1  
PCE removal performance for each pervaporation subsystem and the overall system in the presence and absence of surfactant

Pervaporation system	Fraction of PCE removed <sup>a</sup>	
	No surfactant (days 5–16)	Surfactant plateau region (days 28–70)
VSEP system	0.9887 ± 0.0019	0.655 ± 0.026
Hollow fiber system	0.947 ± 0.015	0.875 ± 0.024
Overall pervaporation system	0.99936 ± 0.00025	0.9576 ± 0.0035

<sup>a</sup> Average and 95% confidence limits provided.

Performance of the VSEP system declined with increasing surfactant concentration and only showed variation with flow rate while temperature effects were minor for the range of temperatures experienced in this project. Performance of the hollow fiber system also declined with increasing surfactant concentrations, but rebounded as process temperatures were raised and more modules were brought on-line (on day 28). In addition, the configuration of the modules was modified as the project progressed in order to improve efficiency. As noted previously, an experiment was performed on the final day of operation, in which the contents of the feed tank were diluted 50% to observe the effect on PCE removal. As seen on day 70 in the figures, PCE removal increased for both pervaporation systems as the surfactant was diluted from 0.89 to 0.43 wt.%. The performances of each pervaporation system, in the presence and absence of surfactant, are detailed in Table 1.

As seen from this data, the pervaporation system achieved a very high removal of PCE in the absence of surfactant (>99.9%) and exceeded the project objective of 95% PCE removal in the presence of surfactant, achieving an average PCE removal of 95.8% during the surfactant plateau region. Although, the hollow fiber system exhibited a higher PCE removal performance than the VSEP system in the presence of surfactant, the VSEP system was more efficient considering the amount of membrane area involved — the hollow fiber system contained 10 times more membrane area than the VSEP. The VSEP delivered a PCE removal performance equivalent to a hollow fiber system containing five times as much membrane area.

### 3.2.7. PCE mass balance and permeate water

Mass balance calculations were made by comparing the mass of PCE which was removed (based on feed flow rate and Feed/Residual sample data) to the mass of PCE which was collected as permeate (based on permeate flows and concentrations). The mass of PCE in the feed should be equal to the sum of the PCE (1) remaining in the final Residual, (2) dissolved in the permeate water, (3) present in the permeate organic and (4) escaping with incondensable gases from the vacuum pump. The mass of PCE removed by the membrane system and recovered as permeate were calculated according to the following expressions:

$$M_{\text{removed}} = Qt(C_F - C_{R2}) \times 10^{-6} \quad (7)$$

$$M_{\text{recovered}} = M_{\text{porg}}w_{\text{porg}} + M_{\text{pw}}w_{\text{pw}} = (V_{\text{porg}}C_{\text{porg}} + V_{\text{pw}}C_{\text{pw}}) \times 10^{-6} \quad (8)$$

where  $M_{\text{removed}}$  is mass of PCE removed by the membrane (kg),  $Q$  volumetric feed flow rate (l/min),  $t$  elapsed time (min),  $M_{\text{recovered}}$  mass of PCE recovered in permeate (kg),  $M_{\text{porg}}$  mass of permeate organic phase collected in time  $t$  (kg),  $M_{\text{pw}}$  mass of permeate water phase collected in time  $t$  (kg),  $V_{\text{porg}}$  volume of permeate organic phase collected in time  $t$  (l),  $V_{\text{pw}}$  volume of permeate water phase collected in time  $t$  (l),  $w_{\text{porg}}$  mass concentration of PCE in permeate organic phase (kg-PCE/kg-organic),  $w_{\text{pw}}$  mass concentration of PCE in permeate water phase (kg-PCE/kg-water phase),  $C_{\text{porg}}$  concentration of PCE in permeate organic phase (mg/l),  $C_{\text{pw}}$  concentration of PCE in permeate water phase (mg/l).

According to the quality assurance project plan, mass balance closure was to be indicated when the mass recovered was between 60 and 130% of the mass removed. Weekly mass balances were performed over four successive weeks (from 5/8/99 to 6/5/99) and yielded closures of 111.7, 95.2, 98.5 and 100.6%. Over these 4 weeks, 73.34 kg of PCE were recovered in the permeate and 72.17 kg were calculated to have been removed from the feed solution yielding an overall closure of 101.6% with a 95% confidence interval of  $\pm 7.0\%$ . Thus, mass balance was achieved.

Over the course of the 70 day operation, approximately 2200 l of permeate water phase were collected. The rate of collection was reasonably constant. Due to the variation in IPA feed concentration, the concentration of IPA in the permeate water phase ranged from 0 wt.% at the outset to as high as 30 wt.% during peak IPA concentrations. The cumulative permeate water phase was estimated to contain 1700 kg of water. Water and IPA fluxes were not calculated due to the variations in IPA concentration, membrane area, and process temperatures as well as the fact that the permeate water values represent the combined permeate from two types of very different modules.

### 3.2.8. Varsol<sup>TM</sup> removal

As stated in the objectives section, measurement of the Varsol<sup>TM</sup> removal objective was to be based on the average removal of three Varsol<sup>TM</sup> marker compounds: decane, undecane and 1,3,5-trimethylbenzene (commonly called mesitylene). The Varsol<sup>TM</sup> removal objective would be met when weekly averages of Varsol<sup>TM</sup> removal exceeded 95% at the end of the pervaporation treatment project as surfactant concentrations declined during the post-SEAR water flood. Based on the surfactant partitioning behavior of these compounds, it was expected that they would be harder to remove than PCE from a surfactant solution and the removal would decrease according to the following series: 1,3,5-trimethylbenzene > decane > undecane. Prior to surfactant breakthrough, concentrations of all three Varsol<sup>TM</sup> markers were below the 0.005 mg/l threshold reporting value of the GC/MS method employed. During the surfactant plateau region (days 28–70), concentrations ranged from 0.8 to 1.8 mg/l for decane and 0.5 to 1.4 mg/l for undecane — two to three orders of magnitude lower than PCE concentrations. Concentrations of 1,3,5-trimethylbenzene never exceeded the 0.5 mg/l threshold reporting value established for the GC/MS method with surfactant solutions. As with PCE concentrations, Varsol<sup>TM</sup> concentrations were up to 10 times lower than had been expected based on model predictions. Since concentrations of Varsol<sup>TM</sup> marker compounds were always near the threshold reporting value of the analytical method, calculations of Varsol<sup>TM</sup> removal are less accurate and less precise than those for PCE. During the surfactant plateau region, decane removal averaged 56% and undecane removal averaged 33%. Based on the surfactant partitioning behavior of the Varsol<sup>TM</sup> marker com-

pounds (measured separately by headspace chromatography at USEPA facilities), it is estimated that removal of 1,3,5-trimethylbenzene was likely around 70%. Average Varsol™ removal would certainly have exceeded 95% in the absence of surfactant due to the high vapor–liquid partitioning coefficients (Henry’s law constant) observed for the Varsol™ markers. Based on this vapor–liquid partitioning information, Varsol™ removal from water should exceed even that of PCE. Unfortunately, concentrations of the compounds were too low to quantify when no surfactant was present. Although, the Varsol™ removal objective was likely met, it could not be quantified due to the low Varsol™ concentrations encountered.

### 3.2.9. *Quality assurance/quality control*

In order to ensure an adequate quality level for the pervaporation demonstration, a quality assurance project plan was prepared, reviewed, approved and followed. One field QA audit and two analytical laboratory QA audits were performed to ensure adherence to the approved QAPP. With regard to GC/FID PCE measurements, the relative percent difference between duplicate analysis were generally within 2% and very rarely exceeded 5%. PCE matrix spike recoveries (both Resid2 and field blank spikes) ranged from 80 to 110%, with most in the 95 to 105% range. The rotameter used to determine flow rate for mass balance calculations was accurate to within 3%, based on periodic bucket tests.

### 3.3. *Accomplishments of the pervaporation demonstration*

The USEPA pervaporation field demonstration at Camp Lejeune yielded a number of accomplishments. Most importantly, the pervaporation field unit was able to meet the 95% PCE removal requirement for reinjection of the recovered SEAR fluid, thus, enabling reuse of the surfactant. Reinjection of the first batch of recycled surfactant commenced on 13 May 1999 (day 45). Secondly, the pervaporation system operated continuously for 70 days with only one short duration shutdown. During these 70 days, 100,000 gal of groundwater and SEAR fluid were processed. Previously reported field demonstrations were unable to operate for more than a few days without encountering shutdown events. Thirdly, fouling of the pervaporation modules by iron precipitation, carbonate scale, or oil was not observed despite the presence of ferrous iron, calcium ions, and “free oil” from the surfactant in the feed solution. Successful avoidance of fouling was achieved by process design and module selection decisions. A fourth accomplishment was the achievement of 102% PCE mass balance closure over 4 weeks of operation. Finally, this field demonstration marked the first full-scale implementation of the VSEP vibrating membrane system for pervaporation. In fact, over the course of this project, the use of the vibrating system for pervaporation was taken from concept, through bench-scale testing, pilot-scale evaluation, to full-scale implementation.

### 3.4. *Lessons learned and problems encountered*

Several problems were encountered during the course of the field work. In addition, a number of process design changes can be recommended after the field experience. A description of these issues is included here to assist future practitioners, just as past experiences from other field demonstrations strengthened the design of the Camp Lejeune pervaporation

system. It should be noted that all of these problems were resolved or, for minor problems, tolerated with no detrimental effect on the project.

A hairline crack in a plastic pressure plate inside the VSEP module allowed surfactant solution to drip slowly out of the bottom of membrane stack and to come in contact with a gland seal O-ring separating the vacuum chamber from the pressure plate. The vacuum chamber of the membrane module was inspected several times during the demonstration and surfactant was observed to have accumulated in that location. In addition, an oily substance was found in the chamber. It is likely that the fluid leaking from the plate crack also leaked past the gland seal O-ring. Once exposed to vacuum, the water, VOC and IPA evaporated from the solution, leaving behind surfactant and oil. The oil apparently originated from the manufacture of the surfactant. The surfactant vendor indicated that the active surfactant contained approximately 1% “free oil”, likely polypropylene glycol oligomers and polymers. The free oil is not water soluble although, it does dissolve in IPA or in a surfactant solution. The presence of the surfactant and free oil in the vacuum chamber could have caused partial blockage of permeate drainage cloths in the membrane trays, resulting in reduced VSEP performance. After the demonstration was completed, the cracked plate was replaced with a new plate. It was found that the free oil and surfactant could be removed from the permeate zone using IPA and water, respectively. PCE removal efficiencies equivalent to those observed during the start of the field demonstration were achieved in post-demonstration testing indicating that no irreversible performance reductions resulted from surfactant and free oil accumulation in the permeate chamber.

Leakage of surfactant solution also occurred in the hollow fiber modules. Of the 36 modules, only one displayed substantial leakage. Approximately 11 others displayed leakage at levels low enough for the evaporation of the water to keep up with the leak. Thus, leaky fibers became filled with surfactant and free oil over time, but the leaks did not appear to greatly impact performance. The majority of the leaking modules were located at the front end of the hollow fiber grid, experiencing the greatest liquid pressures, up to 32 psig. Pressures on the order of 15 psig did not appear to negatively impact the modules. Thus, it can be concluded that these particular modules should not be operated at pressures above about 15 psig for extended periods of time.

Transfer of condensate from the second permeate condensate reservoir to the PCE/water separator was problematic. In this case, a two-phase fluid (DNAPL and water) at atmospheric pressure must be pumped from a reservoir elevated approximately 12 in. above the pump inlet to a tank situated 48 in. above the pump outlet. A centrifugal pump and two gear pumps each failed. The second gear pump was replaced with a Teflon-diaphragm pump which effectively handled the two-phase condensate for the last few weeks of the field work. The effect of solvents on pump operation, whether due to seal damage or cavitation, etc. and pump suction head requirements should be given due consideration.

Since temperature plays a significant role in PCE removal performance as well as in fouling avoidance, control of temperature is a critical process issue. The main obstacle to temperature control during the field demonstration was heat loss from Teflon-lined rubber hoses, stainless steel piping and fittings and the hollow fiber modules. Foam insulation was installed on process hoses and pipes. A 0.006 in. thick polypropylene tarp was draped over the entire hollow fiber module assembly to stop convective heat losses due to air flow in the tent.

### 3.5. Pervaporation process costs

The cost of pervaporation treatment is a function of many variables. The variables with the largest impact are the flow rate to be treated, desired treatment level, surfactant concentration and type of surfactant, VOCs to be removed and micellar partitioning behavior of the VOCs. As discussed previously, the fraction of VOC removed is relatively independent of the feed concentration — a system designed to remove 99% VOC from a stream containing 100 mg/l VOC will likely also remove 99% VOC from a stream containing only 1 mg/l of the same VOC. However, the concentration of VOC remaining in these two cases will be very different (1 versus 0.01 mg/l). VOC concentrations can vary significantly during a surfactant remediation, but surfactant concentrations (and therefore, relative removal efficiency) will likely stay within pre-determined bounds. Thus, a relative % VOC removal target is generally preferred over absolute concentration targets from a standpoint of system design. At Camp Lejeune, 95% relative VOC removal was required.

Regarding energy usage, the Camp Lejeune pervaporation system drew 27 A of three phase, 480 V electrical service, or about 13 kW which translates to approximately \$30 per day at residential rates (\$0.10/kWh) and \$15 per day at reduced commercial rates (\$0.05/kWh). The heater and chillers required the bulk of the energy.

As shown in Eq. (4), the amount of membrane area required to achieve a desired % VOC removal is proportional to the flow rate to be treated. However, the processing cost per unit volume of liquid treated, decreases due to economies of scale achieved. The effect of micellar partitioning of the VOC on treatment cost is a complicated relationship. Based on pilot-scale observations and micellar partitioning studies with several surfactants and VOCs, the effect of surfactant on processing cost can be estimated. In brief, the observed mass transport coefficient,  $k$ , in Eq. (4) appears to vary with the extracellular fraction of VOC ( $f_{ex}$ ) to the 0.5 power. For example, if  $f_{ex} = 0.33$  (meaning that (1/3) of VOC molecules are outside surfactant micelles while (2/3) have partitioned inside the micelles), then the observed mass transport coefficient will be 0.57 times  $k$  in the absence of surfactant. Thus, the membrane area will have to be increased by a factor of 1/0.57, or 1.74 times, in order to achieve the same relative % VOC removal. Treatment costs for a variety of scenarios are provided in Table 2. Following the convention established for comparing pump and treat systems, costs are calculated per 1000 gal of liquid treated. As in all cost estimates, the assumptions which form the basis for the estimates and the items included/excluded are required in order to compare costs of competing technologies. The assumptions used in preparing Table 2 are provided as footnotes to the table.

As shown in Table 2, pervaporation treatment costs decline significantly as the capacity of the system increases. This decline is a result of economies of scale which can be achieved with chemical process equipment. However, capital costs of membrane modules and housings, alone, typically do not benefit from economies of scale as do column type separation technologies like distillation, steam stripping and air stripping. In membrane systems, the maximum amount of area available in a single module is generally much smaller than the typical amount of membrane required to achieve the desired separation. Thus, the needed area is obtained by linking several of the smaller units together which yields a cost scaling factor near unity as opposed to 0.4–0.6 for other process equipment. In contrast to typical pervaporation systems, the VSEP pervaporation system introduced in this project exhibits

Table 2  
Estimated pervaporation treatment costs as a function of system capacity, surfactant

Scenario	Flow rate (gpm)	% VOC removal	VOC	Alfoterra 145 surfactant concentration (wt.%) and resulting VOC partitioning constant	Pervaporation treatment cost <sup>a</sup> (\$/1000 gal)
Actual Camp Lejeune Unit	1.0	95	PCE	~1.0 ( $f_{ex} = 0.15$ )	275
Optimized Camp Lejeune Unit	1.0	95	PCE	~1.0 ( $f_{ex} = 0.15$ )	100
Medium flow, no surfactant, high VOC removal	10	99.99	PCE	0 ( $f_{ex} = 1.0$ )	19
High flow, no surfactant, high VOC removal	30	99.99	PCE	0 ( $f_{ex} = 1.0$ )	14
Medium flow, no surfactant, medium VOC removal	10	99	PCE	0 ( $f_{ex} = 1.0$ )	17
Medium flow, medium surfactant, medium VOC removal	10	99	PCE	0.4 ( $f_{ex} = 0.33$ )	20
Medium flow, high surfactant, medium VOC removal	10	99	TCE	1.4 ( $f_{ex} = 0.33$ )	20
Medium flow, high surfactant, medium VOC removal	10	99	PCE	1.4 ( $f_{ex} = 0.1$ )	24

<sup>a</sup> Note: the treatment costs provided are believed to have an accuracy of +50% or –25%. Assumptions for the pervaporation cost table are listed below (excluding the Actual Camp Lejeune scenario which was based on the system actually operated in the field): (1) VOC mass transport coefficient ( $k$ ) assumed to be  $5 \times 10^{-3}$  cm/s in absence of surfactant; (2)  $k \propto f_{ex}^{0.5}$ -based on experiments with surrogate solutions; (3) system based on “VSEP” technology (cost estimates for spiral wound systems were similar to the VSEP costs, while hollow fiber modules were significantly higher); (4) groundwater used to condense majority of permeate in condenser prior to liquid ring vacuum pump, thus, reducing size and energy requirement for pump chiller; (5) low water flux through membrane (0.1 kg/m<sup>2</sup> h) — reduces vacuum, heater and chiller requirements. Use of membranes with a 5–10 times higher water flux would add \$5–\$10 per 1000 gal treated; (6) electricity cost of \$0.10/kWh (7) 8 h of labor required each week for maintenance, loaded labor cost of \$20/hr; (8) installed system cost is 3.5 times non-VSEP component cost plus cost of VSEP system; (9) 10 year capital depreciation; (10) annual maintenance cost is equal to 5% of the installed capital cost. Membrane module life of 3 years (module replacement separate line item from other maintenance); (11) annual treatment cost is the sum of annual capital depreciation, annual membrane replacement, annual energy usage, annual maintenance; (12) siting costs and disposal costs not included.

attractive economies of scale. The VSEP system does not reach the area “replication” point until approximately 200 m<sup>2</sup> — significantly higher than for hollow fiber modules (3–10 m<sup>2</sup>) or spiral wound modules (15 m<sup>2</sup>). Future generations of the VSEP technology are expected to allow even higher maximum module areas.

The treatment cost for the actual pervaporation system used at Camp Lejeune was estimated to be \$275 per 1000 gal. An optimized 1 gpm system for the same application would yield a treatment cost of \$100 per 1000 gal. For 10 gpm systems achieving 99% removal of chlorinated VOC from surfactant solutions estimated treatment costs range from \$17 to \$24 per 1000 gal or \$245 to \$345 per day of operation. Treatment costs for pervaporation systems based on spiral wound modules were found to be somewhat higher than those for the VSEP system. The lower cost of the VSEP system, better economies of scale and concerns regarding fouling with spiral wound modules led to the use of the VSEP system in the cost analysis. Systems based on hollow fiber modules were not cost-competitive with the VSEP system. Improvements in mass transport and reductions in cost for the hollow fiber modules would make them more cost competitive, but they would still not have the economy of scale advantage of the VSEP.

### 3.6. IPA recovery

Just as pervaporation can remove chlorinated VOCs from water, so too, can it remove IPA from water. However, the pervaporation unit which was designed for PCE removal at Camp Lejeune was not designed for IPA recovery, the membranes were too thick to provide for sufficient IPA fluxes. A second pervaporation system, loaned to the USEPA by MTR was utilized to demonstrate the recovery of IPA from the SEAR fluid (actually, the MEUF permeate was used as the feed material for the IPA recovery system). The results of the IPA recovery investigation will be reported in a separate publication. Process design scenarios which allow for the removal of VOC and recovery of IPA using the same pervaporation modules are under consideration, thus, making the economics very attractive.

## 4. Conclusions and recommendations

The USEPA pervaporation field unit met the PCE removal requirement for reinjection of surfactant during the ESTCP SEAR demonstration project at Marine Corps Base Camp Lejeune. The unit processed 100,000 gal of groundwater and SEAR fluid in continuous operation over 70 days. PCE removal averaged 95.8% during the surfactant plateau region and exceeded 99.9% when treating groundwater containing no surfactant. The average flow rate through the system was 0.99 gpm. PCE concentrations ranged from 35 to 890 mg/l while surfactant concentrations ranged from 0 to 1.2 wt.%. Concentrations of hydrocarbon secondary contaminants (Varsol<sup>TM</sup> compounds) were significantly lower than PCE concentrations at all times. Varsol<sup>TM</sup> marker concentrations in all samples were below detection limits in the absence of surfactant, thus making quantification of removal impossible. In the presence of surfactant, removal averaged 33% for undecane and 56% for decane, although, concentrations were generally near or below the method detection limits. Due to low concentrations of 1,3,5-trimethylbenzene observed even in the presence of surfactant, removal of this com-



pound could not be quantified, but would likely have been around 70% based on micellar partitioning behavior observed in laboratory tests. Likewise, in the absence of surfactant, Varsol™ removal should have exceeded that of PCE, but was not quantifiable. As a result, whether the average 95% removal criteria was met for Varsol™ could not be determined. A pervaporation system with four to five times the membrane area of the Camp Lejeune pervaporation unit would be needed to achieve 95% Varsol™ removal during peak surfactant concentrations. Such a system, however, would remove more than 99.999% PCE from the same surfactant solution. Reasonable risk-based contaminant removal criteria must be established for each site so that a practical treatment system can be designed for the economical recovery and reuse of surfactants while still meeting the risk management needs of the site and its neighbors. Relative contaminant removal requirements (such as 95% removal) are preferred to fixed concentration objectives for pervaporation system design since pervaporation systems typically remove the same relative amount of VOC, independent of feed concentration.

Fouling problems encountered in previous pervaporation demonstrations were not experienced in the Camp Lejeune demonstration, a result of the prudent design and operation of the system, despite conditions which would favor fouling. For example, high concentrations of iron (14 mg/l  $\text{Fe}^{2+}$ ) and calcium (300 mg/l  $\text{Ca}^{2+}$ ) were present as well as free oils from the surfactant production process. No chemical additives, other than nitrogen gas, were required to avoid fouling. The main problem associated with the membrane modules was the presence of small leaks of liquid into the permeate regions of the module, most of which did not appreciably affect performance. The estimated cost of the pervaporation separation was \$275 per 1000 gal treated for the Camp Lejeune field system. An optimized unit for the Camp Lejeune demonstration would cost \$100 per 1000 gal treated. Significant cost reductions are possible for larger systems with a best-design 10 gpm system costing only \$17–24 per 1000 gal treated for 99% PCE removal. In comparison, each 1000 gal of surfactant solution during the surfactant plateau region contains \$500–\$600 worth of surfactant (assuming 1.2 wt.% of \$5/lb high-activity surfactant or 4.8 wt.% of \$1.5/lb moderate-activity surfactant). Thus, the value of recovered surfactant more than covers the cost of the pervaporation system. Costs for removing less-hydrophobic VOCs, such as TCE, TCA and toluene, from surfactants would be lower than for PCE while removal costs for more hydrophobic VOCs, such as the Varsol™ hydrocarbons, would be higher. Since pervaporation involves the volatilization of the contaminant, the technology is generally not suitable for treatment of streams containing semi-volatile and non-volatile contaminants. However, pervaporation has an added advantage over competing VOC removal technologies in that the system could be designed to recover alcohols for reuse at the same time it removes VOCs. Alternatively, a pervaporation system could be installed to remove alcohol from the MEUF permeate stream, thereby reducing disposal costs and enabling the reuse of the alcohol.

Finally, the vibrating pervaporation system introduced during the Camp Lejeune demonstration has the potential to dramatically reduce pervaporation costs for a variety of separations as well as the ability to handle solutions with a high fouling potential. Although, pervaporation costs may not approach those required for drinking water treatment, they may be competitive for more contaminated streams such as those encountered by traditional pump and treat systems. Treatment costs for 100 gpm pervaporation systems (99.99% VOC removal from groundwater) are projected to be below \$10 per 1000 gal treated, with no fugitive emissions and the ability to handle solutions with high concentrations

of iron and scale-forming compounds. Specifically, a project to evaluate pervaporation for methyl-*t*-butylether (MTBE) removal from groundwater has been proposed. In addition, work is on-going (as of December 1999) to construct a VSEP membrane module out of traditional pervaporation membrane rather than the non-traditional material used for the Camp Lejeune VSEP module. This change should result in an increased VOC removal efficiency. Thus, the new vibrating pervaporation system holds a great deal of promise, largely untapped at the present time.

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