Cary - 9/0402 - 23

ANL/CP--72822 DE92 005225

## Decontamination of Groundwater Using Membrane-Assisted Solvent Extraction\*

Joseph C. Hutter and George F. Vandegrift

Separation Science and Technology Section Chemical Technology Division Argonne National Laboratory 9700 S. Cass Avenue Argonne, IL 60439

#### **DISCLAIMER**

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

September 1991

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

<sup>\*</sup>Work supported by the U.S. Department of Energy, Separation Science and Technology Program, under Contract W-31-109-Eng-38.

# Decontamination of Groundwater Using Membrane-Assisted Solvent Extraction

Joseph C. Hutter and George F. Vandegrift

Separation Science and Technology Section, Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

Development of a new process to remove volatile organic compounds at dilute concentrations (VOCs) from groundwater was recently begun at Argonne. This process consists of membrane-assisted solvent extraction and membrane-assisted distillation stripping (MASX/MADS). The use of membranes in the solvent extraction and distillation stripping units improves mass transfer by increasing the interfacial surface area, thus allowing the process to be performed efficiently at high throughputs. The thermodynamics of the separation process and regions of applicability of this process are discussed.

Contamination of groundwater by dilute concentrations of VOCs has become a major problem at many Department of Energy and Department of Defense sites, as well as industrial sites nationwide. Remediation of these sites is generally difficult, energy intensive, and very expensive. Environmental regulators only allow remediation procedures which can be proven to be less damaging to the environment than the original contamination; pump-and-treat technology, such as the MASX/MADS process described here, is usually acceptable to regulators. The MASX/MADS process is also applicable to treatment of process air and water streams.

Groundwater contamination at landfills and chemical spill and dump sites can be so severe that two-phase liquid mixtures appear in the aquifer. In this situation, the organic contaminants are at their highest concentration, determined by each contaminant's equilibrium solubility. As the groundwater migrates through the aquifer, the contaminants are diluted. Often the contamination is in the ppb range only a few hundred yards from the dump site. Past practices, such as years of classifying now known carcinogens as "assorted non-toxics," have led to the decades of chemical dumping, which has caused the current environmental disaster. Over the decades, these contaminants have had time to be diluted by subsurface groundwater flows, and plumes have spread miles from the original contamination source.

Any remediation procedure must first prevent the source of contamination from adding to the problem. This means closing the dump site and eliminating the practices which led to the contamination in the first place. The near-site cleanup usually involves excavation, venting, or bioremediation to remove the high concentrations of organics in the unsaturated zone and two-

phase liquid regions and thereby prevent further subsurface contamination spreading because of groundwater flows or intermittent rainfall. The unrecovered contaminants migrate through the aquifer with the groundwater flow and are retained by the adsorptive properties of the soil. Some degradation of the contaminants can occur in the subsurface environment. The contaminated groundwater is by far the most difficult problem to remediate due to its large extent in the subsurface environment. In general, the most widely used strategy to decontaminate the groundwater is to pump it from the aquifer using a well and then air strip the contaminants from the water. The decontaminated water can then be reintroduced to the environment (1).

A groundwater contamination survey was recently completed at nine DOE sites in the United States (Morrisey, C. M., et. al., Oak Ridge National Laboratory, unpublished data). The ten most common VOC contaminants found are listed in Table I. Most of the contaminants are chlorinated hydrocarbons, and they were typically found in concentrations in the ppb range. Similar contaminants can be found at the Argonne site (2) as well as several industrial sites worldwide (3-8). The common feature at all these sites is the large distances that dilute (ppb) concentrations of contaminants have migrated. Even though the concentrations of the contaminants are low, they often exceed US EPA Drinking Water Standards as shown in Table I (9). Two of the contaminants shown in Table I, trichloroethylene and methylene chloride, we not under federal regulation, but they are usually under state or local restrictions.

Table I. Common Contaminants in Groundwater Found at DOE sites

Contaminants	Average	Maximum	US EPA
	Concentration	Concentration	Drinking Water
	(ppb)	(ppb)	Standard (ppb)
Benzene	1400	36000	5
Carbon Tetrachloride	280	10000	5
cis-1-2-Dichloroethylene	100	1600	70
trans-1-2-Dichloroethylene	160	1600	100
Trichloroethylene	310	8500	NS <sup>a</sup>
Tetrachloroethylene	150	2300	5
Methylene Chloride	220	6400	NS <sup>a</sup>
1-1-1-Trichloroethane	110	3100	200
Chloroform	30	1000	100
Vinyl Chloride	180	540	2

<sup>&</sup>lt;sup>a</sup> No US EPA Standard

#### Current Technology

Any remediation procedure must be able to reduce these low concentrations of contaminants in groundwater to the very dilute concentrations of the US EPA Standards. Solvent extraction in its conventional form is not adequate for this remediation procedure, since this technology is applicable to contaminations approaching the weight percent range and not the ppb range. The main difficulty with solvent extraction for wastewater treatment is regeneration of the solvent for recycle to the extraction section. This regeneration is usually done by conventional distillation. There are numerous literature references discussing the use of solvent extraction in wastewater treatment (10-13). The extraction step is usually relatively easy once a good solvent is found. Solvent extraction technology has led to the development of very effective solvent selection strategies based on either hydrogen bonding or Lewis acid-Lewis base concepts (14-19).

For groundwater applications the most common remediation procedure is air stripping followed by gas-phase activated carbon adsorption. Liquid-phase activated carbon adsorption is also used for removal of VOCs from water, but it is usually more expensive than the air stripping method. Ultraviolet (UV) radiation, catalyzed hydrogen peroxide or ozone is used to decontaminate groundwater by the destruction of the pollutants (20). Oftentimes, this technique cannot be used if the water is high in colloidal solids, which inhibit the oxidation reactions and/or foul the UV lamps. In-situ methods such as vacuum extraction or direct hydrogen peroxide injection to induce bioremediation have been applied in limited cases. In-situ bioremediation techniques are being researched, but so far have had only limited success. The major limitation of the in-situ bioremediation technologies is delivering oxygen and nutrients to the subsurface contaminants in so that the conditions required for biological activity can be maintained. In addition, the contaminants must be at concentrations high enough to support biomass. These limitations have confined bioremediation applications to very specific contaminants in highly contaminated regions, not the dilute regions of groundwater contamination usually treated by air stripping (21).

#### MASX/MADS Process

A flow diagram of the MASX/MADS process is given in Figure 1. Contaminated groundwater enters the membrane extraction module where it is contacted with a solvent that extracts the pollutants from the groundwater. The membrane material in the module is porous and is used to separate the two liquid phases and provide a large interfacial area for mass transfer. The nonvolatile solvent extracts the VOCs from the water with a distribution coefficient that is typically 100 or more. Because of this high distribution coefficient, the oil flow rate can be up to 100 times lower than the groundwater flow. The groundwater leaves the extraction unit decontaminated to a

purity as good as the drinking water standards, so that this water can be safely reintroduced to the environment. At this point, the nonvolatile solvent contains the contaminants recovered from the groundwater, and are in a concentrated form in the nonvolatile solvent. The maximum concentration of the contaminants in the nonvolatile solvent is determined from the distribution coefficient between the water and the solvent and their relative flow rates.

The solvent must be stripped of contaminants before it can be recycled to the extraction modules. This operation is carried out in the MADS unit after the solvent is heated. In this unit, the volatile contaminants are vaporized and recovered in a condenser. In addition to the contaminants, some of the solvent and residual groundwater dissolved in the solvent is recovered in the condenser. The decontaminated solvent is then recycled to the extraction modules. This process is not a conventional distillation step involving multiple stages; it is a one-stage evaporation, but stages may have to be added if higher concentrations of VOCs are required for destruction or disposal.

In the MASX/MADS process, the use of membrane modules facilitates any capacity or scaleup difficulties. Capacity is increased by adding more modules. Scaleup is easy because the well-defined interfacial area allows excellent characterization of the volumetric mass transfer rates. The modules also allow independent variation of the flow rates without flooding as in conventional solvent extraction. Density differences between the solvent and extraction feed are not required for phase separation because the membrane separates the phases (22). Unlike use of activated carbon with air stripping, the solvent is continuously regenerated and does not have to be removed to another process (steam stripping)to regenerate the adsorbent. Since this energy-intensive step is omitted, and the large volume of air required for air stripping does not have to be continuously blown through a packed column, this system should result in reduced energy consumption for operation. The contaminants are recovered in concentrated form for destruction or recycle.

Membrane Technology. Solvent extraction applications use microporous membranes with pore sizes of that range from  $0.005~\mu m$  to  $0.1~\mu m$ . This pore size range overlaps ultrafiltration and microfiltration membranes. These membranes allow mass transfer to occur by diffusion which is only inhibited by tortuous pores. Other membranes, such as those used in gas separation or reverse osmosis, rely exclusively on mass transfer by a sorption-diffusion mechanism through a dense polymer above its glass transition temperature (23). Composite membranes and have also been used in solvent extraction applications (24-26).

Due to the variety of membrane materials and solvents available, mass transfer can occur in one of several regimes. For example, steady-state concentration profile regimes for extraction of a VOC from water by an organic phase are depicted in Figure 2. Experimental data for each of these regimes and detailed expressions for the overall mass transfer coefficient are reported in the

literature (24-26). The thick solid lines in Figure 2 indicate a qualitative concentration profile. For these idealized cases, it is assumed that both the organic and aqueous liquids on each side of the membrane are in a turbulent flow regime, thus the major mass transfer resistance is confined to the liquid which is trapped in the tortuous pores. Mass transfer in the tortuous pores is due to diffusion of material through the contained liquid phase. Similar effects can be found for gasliquid systems separated by a membrane.

As depicted for the cases in Figure 2, the phase that preferentially wets the pores can be determined from free energy considerations of the system. A phase will wet a porous surface if the free energy of the wetted surface is lower than the sum of the free energies for the original liquid surface and the original porous surface. A perfectly wetted surface has a contact angle of 0°. A partially wetted material has a contact angle between 0° and 90°. If the contact angle is above 90°, the material is not wetted. The exact contact angle of the system is determined from a balance of the liquid-solid, liquid-air, and solid-air surface energies. Only the liquid-air surface energy or surface tension is easily measured experimentally, so the complex thermodynamics of this system cannot be predicted a priori. Only qualitative arguments can be made with the limited available data, and the surface tension arguments given here are based on this limited data to predict trends for wetting behavior. Even though solid-air and liquid-solid surface energies are not known exactly, some useful trends can be predicted based on estimates of their magnitudes

Figure 2a depicts a hydrophobic membrane. In this case the organic phase is in the pores, and the sum of the capillary force in the pores and the aqueous-phase hydrostatic pressure is higher than the organic-phase hydrostatic pressure; this prevents the organic phase from flowing through the pores to the aqueous side of the membrane. Since mass transfer is occurring from the aqueous phase to the organic phase in this extraction, the concentration profile is decreasing from left to right in this figure. The discontinuity in the concentration profile is due to the distribution coefficient for this system. The discontinuity results from the equilibrium condition at the immobilized interface. If the pressure on the aqueous side of the membrane exceeds a critical value, the aqueous phase will be forced into the pores. This minimum pressure to wet the pores can be estimated by a force balance for a cylindrical pore (27).

In Figure 2b the aqueous phase is in the pores in a hydrophilic membrane. This is similar to the case in Figure 2a, except that the concentration gradient is greatest in the aqueous phase in the pores. For the case depicted in Figure 2b, the hydrostatic pressure of the aqueous phase is great enough to fill the pores preferentially to the organic phase, but it is lower than the sum of the organic phase hydrostatic pressure and capillary forces, which prevents the aqueous phase in the pores from flowing through the pores into the organic phase.

The aqueous phase will preferentially wet the pores only if the free energy of the system is minimized compared to the free energy of the organic wetted surface. Hydrophilic materials such as ceramics or cellulose materials have high free surface energies, up to several thousand dynes/cm

(ergs/cm<sup>2</sup>). If the total surface energy of the aqueous wetted membrane is lower than that of the organic wetted membrane, the aqueous phase will preferentially wet the membrane. Water has a surface tension of 72 dynes/cm (or less with some impurities); thus, by wetting the hydrophilic surface the net surface energy is lowered (72 dynes/cm is less than several thousand dynes/cm). Polymer surfaces have a much lower surface energy, approaching 20 to 35 dynes/cm; thus, water will not wet many polymers since the net energy of the system will not be lowered. Wetting a low energy surface at 20 to 30 dynes/cm with a high surface energy liquid such as water at 72 dynes/cm will not lower the energy of the system. Instead, a small area of the surface will be in contact with water droplets having contact angles above 90°. Organics have surface tensions in the range of 20-30 dynes/cm; therefore, many more low energy surfaces can be wetted with organics than with water, since by wetting the porous surface with a low surface energy organic, the porous air-solid area, which has slightly higher energy, is reduced and the net energy of the system is lowered. It is also true that any surface wetted by water can be wetted by a lower surface tension organic phase as well (28).

A composite hydrophilic-hydrophobic membrane is shown in Figure 2c. The hydrophilic membrane is wetted by the aqueous phase, and the hydrophobic membrane is wetted by the organic phase. The interface is immobilized between the two membranes. The concentration profile shows an extraction in which the resistance to mass transfer in the membrane is due to the large gradient in that region.

Figure 2d shows a composite hydrophobic-dense phase membrane. An example of such a membrane is a Celgard X-20 polypropylene hollow fiber porous membrane with a 1-2 µm dense plasma polymerized disiloxane skin on the outside of the fiber. This type of membrane has been used to demonstrate the solvent extraction of contaminants from groundwater (24.29). With this membrane, the water in the lumen does not wet the hydrophobic surface, allowing the pores to be gas filled. The dense skin prevents the organic phase from contacting the water or filling the pores. The thin film allows rapid transfer of VOCs into the gas-filled pores, followed by absorption by the organic phase. Organic phase is prevented from contaminating the water, thus keeping the TOC (total organic carbon) low and meeting strict environmental regulations. For this system the major impedance to diffusion is the dense polymer, and thus the concentration gradient is in the dense phase of the membrane.

Membrane Module Technology. The earliest membrane modules were the plate-and-frame type. These modules are easy to clean if they are fouled because they can be readily disassembled, but they do not have the high surface area per unit volume of more advanced designs. The spiral-wound membrane initially used in reverse osmosis applications consisted of a membrane sock with the open end connected to a center pipe. Flow was through the sock surface, and permeate exited

in the center tube. The sock was spirally wound and placed in a pressure vessel shell. Millipore Corporation has introduced a spiral-wound crossflow module for filtration applications (30). Numerous commercial hollow fiber shell-and-tube modules give the highest surface area to unit volume ratio, but are easily fouled due to the small diameter fibers (400  $\mu$ m). Tubular membranes also have the shell-and-tube configuration. The main difference between tubular membranes and hollow fibers is that the diameters of the tubes are considerably larger (1 cm). Most solvent extraction laboratory research has been carried out with plate-and-frame modules or hollow fiber modules.

#### Conceptual Material Balance

Since the concentrations of VOCs in groundwater must be reduced, in most cases by several orders of magnitude, the extraction unit requires a solvent with a very high affinity for the VOCs. The extraction performance of a solvent is determined by the distribution coefficient:

$$D = \frac{C_{oil}}{C_{water}}$$
 (1)

Where D is dimensionless, and the liquid VOC concentrations,  $C_{\rm oil}$  and  $C_{\rm water}$ , can have units of mol/L or mass/L. Large distribution coefficients enhance the extraction performance. Usually a distribution coefficient of 100 or more will result in a very effective extraction process and achieve the EPA drinking water standard for groundwater (24). Because of the high distribution coefficient, the flow rate of the solvent can be significantly lower than the flow rate of the groundwater. The large difference in flow rates does leads to a high extraction efficiency in the membrane modules due to the good interfacial contact. This large flow rate difference would make conventional solvent extraction in a packed column or mixer-settler ineffective due to the poor stage efficiency. In addition to membranes, the Argonne-design centrifugal contactor also has a high stage efficiency at organic-to-aqueous (O/A) flow ratios as low as 1/100 (31).

Typically a VOC is found in the subsurface groundwater at a concentration of 1 ppm or less. Complete extraction of a VOC from an aqueous solution at an O/A flow ratio of one would result in a organic phase concentration of 100 ppm. If a solvent with a lower distribution coefficient <100 for the VOC is used, a higher solvent flow rate would be required to derive the same degree of extraction. The resulting VOC concentration in the solvent would also be lower.

Solvent Selection Criteria. A high distribution coefficient for extraction of a VOC makes for easy decontamination of the groundwater and difficult stripping of the nonvolatile solvent.

However, to be successful, the solvent must not only be a good extractant, but also easily regenerated. Removal of the VOC by air stripping is defined by Henry's Law defined below for an aqueous solution:

$$P y_G = H_{aq} C_{water}$$
 (2)

Where  $H_{aq}$  is Henry's Law constant for a VOC in water, atm/unit concentration in the aqueous phase; P is the total pressure, atm; and  $y_G$  is the VOC mole fraction in the gas phase. The product P  $y_G$  is the partial pressure of the VOC above the liquid phase. Henry's Law constants are specific to both the solute and the solvent. The higher the value of  $H_{aq}$ , the easier it is to remove the VOCs from the aqueous phase. In the nonvolatile solvent, the Henry's Law constant of the VOC ( $H_{oil} = H_{aq}/D$ ) is lowered relative to water due to the greater affinity of the organic solvent for the VOC due to the large distribution coefficient. Substituting Equation 1 into Equation 2 yields:

$$P y_G = H_{aq} C_{water} = H_{oil} C_{oil} = \frac{H_{aq}}{D} C_{oil}$$
 (3)

For a given concentration of VOC in the oil phase, the partial pressure of the VOC is lowered by a factor of D relative to the water case. For example, 1 ppm of chloroform in water has a partial pressure of 3.2 x 10<sup>-5</sup> atm at 20°C. Because the value of D for chloroform is 100 between water and sunflower oil, it takes 100 ppm of chloroform in sunflower oil to obtain this same partial pressure.

For the intended application of MASX/MADS, ther are numerous candidates for solvents, as well as a range of possible contaminants in the groundwater. Table II gives the distribution ratios and Henry's Law constants for three selected contaminants treated with a water-sunflower oil system at 20°C. This table was generated from published data.(24)

Table II- Distribution Ratios and Henry's Law Constants for the Water-Sunflower Oil System at 20°C

Compound	D	H <sub>water</sub> (atm/mol/l)	H <sub>oil</sub> (atm/mol/l)
Chloroform	100	3.82	0.0382
Carbon Tetrachloride	867	30.2	0.0349
Tetrachloroethylene	2567	18.0	0.0070

As shown in Table II, chloroform and carbon tetrachloride have about the same Henry's Law constant above oil, even though carbon tetrachloride is considerably more volatile above water than chloroform. The high distribution coefficient for carbon tetrachloride significantly reduces the Henry's Law constant for the oil phase. The relatively high partial pressure of tetrachloroethylene above water is significantly reduced in oil due to the large distribution coefficient.

#### Regeneration of the Solvent, Ideal Inert Stripping-Gas Case

One way to regenerate the solvent is to strip the VOC contaminants using an inert stripping gas. The temperature and pressure in the stripping unit determine the gas flow rate, since Henry's Law determines the maximum VOC composition exiting in the strip gas. The partial pressures of 100 ppm for the three contaminants above sunflower oil at 20°C are given in Table III.

Table III- Partial Pressures of Three Candidate Contaminants (each at 100 ppm) above Sunflower Oil at 20°C and a total pressure of 1 atm

Compound	Partial Pressure, Py <sub>G</sub>	
-	(atm)	
Chloroform	3.2 x 10 <sup>-5</sup>	
Carbon Tetrachloride	$2.9 \times 10^{-5}$	
Tetrachloroethylene	$0.43 \times 10^{-5}$	

In situations where a combination of contaminants is involved, the least volatile component (in the case of Table III, tetrachloroethylene) controls the design of the stripper. Once the operating temperature and pressure is set, the exiting mole fraction of tetrachloroethylene is determined from its partial pressure. The mole fraction of the strip gas and its minimum flow rate can then be calculated.

For equal concentrations in water of the three contaminants listed in Table II, the extraction unit design for identical removals of each contaminant is controlled by the most difficult component to extract. In this case, that component is chloroform, because it has the smallest distribution coefficient. The minimum flow rate of solvent is set by this component, and for the equilibrium case, an O/A ratio of 1/100 is adequate. The other components are more easily extracted; an O/A

ratio of 1/867 or 1/2567 is required for carbon tetrachloride and tetrachloroethylene, respectively, based on the data in Table II. The excess solvent for the components other than chloroform will improve the extraction removal efficiency of these components. The regeneration of the nonvolatile solvent is controlled by the VOC with the lowest partial pressure above the oil phase. The most difficult component to extract does not necessarily have to be the most difficult component to strip from the oil. The data in Table II indicate that at 20°C tetrachloroethylene will be the most difficult component to remove from the oil due to its low Henry's Law constant in the oil. Therefore, although a substantial amount of tetrachloroethylene can accumulate in the recycled nonvolatile solvent before the extraction performance exceeds its design value, the stripper must continuously remove enough tetrachloroethylene from the solvent with each pass so that the solvent can be recycled. These factors must be accounted for in the final design.

The economics of operating an air stripper to remove VOCs from water is controlled by the costs to run the blowers to deliver the air stream to the packed column stripper (32). The air requirement for removing VOCs from a nonvolatile solvent or water is set by Henry's Law and is the same whether a packed column or membrane module is used. Using membrane modules instead of packed columns for air stripping increases the compression power cost significantly since the modules are much smaller than the packed column and the gas phase pressure drop is increased. However, instead of using large gas volumes and compressor power, heat energy can be introduced to remove the VOCs from the nonvolatile solvent. At higher temperatures, the air volume requirement is significantly reduced because the volatility of the VOCs is increased. It is not practical to heat large volumes of water, but it may be practical to heat smaller volumes of nonvolatile solvents with much lower specific heat capacities compared to water.

Recovery of the VOC Components in the Condenser. To recover a VOC component in the condenser, the partial pressure of the VOC in the strip gas must exceed the vapor pressure of the condensed phase:

$$P y_i > P^{vap}$$
 to Condense (4)

In the idealized stripping-gas case, only the VOCs are in the gas phase and should condense since the solvent is considered nonvolatile compared to the VOCs. For a 100 ppm chloroform concentration in sunflower oil at 20°C, the partial pressure of the chloroform (3.2 x 10<sup>-5</sup> atm) does not exceed its vapor pressure at -60°C, so the chloroform will not condense, as indicated by the data in Table IV.

Temperature	P <sup>vap</sup>	
(°C)	(atm)	
20	2.6 x 10 <sup>-1</sup>	
0	$8.0 \times 10^{-2}$	
-20	2.6 x 10 <sup>-2</sup>	
-40	$6.2 \times 10^{-3}$	
-60	25 × 10-4	

Table IV- Vapor Pressures of Chloroform in the Condenser<sup>a</sup>

By stripping the solvent at elevated temperatures, the VOCs partial pressure will increase and it should be possible to recover them in a condenser. However, the stripping is controlled by the least volatile contaminant, and the other contaminants will be diluted in the strip gas, making them even more difficult to recover for this idealized case.

#### Regeneration of the Solvent, Distillation Case

In the usual application of solvent extraction for the recovery of dilute VOCs from water, the solvent is regenerated by conventional distillation. This process is applied to aqueous systems which have much higher concentrations of contaminants than the ppb concentrations found in groundwater. The distillation procedure requires collection of vapor-liquid equilibrium (VLE) data for the VOC-solvent system before the distillation system can be designed. Typical vapor-liquid equilibrium curves for these VOC-solvent systems are given in Figure 3. This represents the VLE behavior expected for the natural oils and contaminants planned for use in the MASX/MADS process.

The extremely dilute VOC region in Figure 3 is of interest for the MASX/MADS process. As seen from the data, the vapor and liquid compositions converge as the VOC becomes more and more dilute. Thus, as the VOC concentration decreases, producing a high purity VOC product becomes increasingly difficult. Generating a high purity VOC product from a conventional distillation column would require operation at nearly total reflux and be very energy intensive. This problem has limited conventional solvent extraction to much higher concentrated streams, where the recovered solvent is contaminated enough to be regenerated by conventional distillation, and a highly concentrated impurity product is produced as well. In the ppm or ppb region encountered for the MADS, the solvent vapor partial pressure is much higher than the VOC partial pressure. Because of this, by vaporizing and condensing some of the solvent along with the VOC,

<sup>&</sup>lt;sup>a</sup> Partial pressure of chloroform in the stripping gas is 3.2 x 10<sup>-5</sup> atm at 20°C.

it should be possible to recover an enriched solution of the VOC in the solvent. The remaining solvent will have a substantially lower VOC concentration and can then be recycled to the extraction unit. Condensing the VOC-solvent vapor will be much easier since its dew point will be much higher than the required temperature to recover the VOCs directly from an inert strip gas, as discussed previously. Enriching the VOC vapor that is condensed to a greater extent will require additional stages, with each MADS stage smaller than the previous one due to the lower liquid flow rate obtained with each enriching step.

Advantages of Membranes. The mass transfer rate for this type of separation process is given by

$$J = K_L a (C^* - C)$$
 (5)

Where  $K_L$ a is the mass transfer coefficient,  $C^*$  is the VOC concentration in the solvent in equilibrium with the vapor phase, C is the actual solvent VOC concentration, and J is the flux of the VOC. For the dilute VOC in the solvent,  $C^*$  and C, approach each other due to the VLE data convergence, so that the flux approaches zero and separation does not occur. By using membranes, the mass transfer coefficient can be increased by a factor of a thousand or more compared to a conventional packed column (33). This increase in  $K_L$ a will enhance even small differences in  $C^*$  and C due to the VLE data convergence, thus making the separation more feasible.

The VLE data needed to evaluate the MASX/MADS process are currently being collected. It is expected that this process will perform well.

#### Conclusions

Membrane-assisted solvent extraction of dilute VOCs from groundwater is technically feasible. The regeneration of the solvent is the difficult step in the development of the process. It is not feasible to air strip the solvent at ambient conditions due to the low partial pressures of the VOCs above the solvent. These low partial pressures in the strip gas make the VOCs impossible to recover with a condenser. However, by using a membrane-assisted vaporization procedure, the VOCs can be recovered from the organic phase. Some vaporization of the solvent will occur, and this two-phase system will condense at a dew point much higher than the required temperature to recover the VOCs directly from an inert strip gas.

#### Literature Cited

- <sup>1</sup>Brown, R. A., Sullivan, K. Poll. Eng. 1991, 23, 62-68.
- <sup>2</sup>Moos, L. P., Duffy, T. L. 1990 Annual Site Environmental Report:; ANL-90/8, Argonne National Laboratory, Argonne, IL, 1990.
- <sup>3</sup>Goodrich, J. A., Lykins, B. W., Clark, R. M., Oppelt, E. T. J. AWWA March 1991, 55-62.
- <sup>4</sup>DeWalle, F. P., Chian, E. S. K. J. AWWA April 1981, 206-211.
- <sup>5</sup>Stuermer, D. H., Ng, D. J., Morris, C. J., Env. Sci. Tech. 1982, 16, 582-587.
- <sup>6</sup>Reinhard, M., Goodman, N. L., Barker, J. F. Env. Sci. Tech. 1984, 18, 953-961.
- <sup>7</sup>Roberts, A. J., Thomas, T. C. Env. Tox. Chem. 1986, 5, 3-11.
- <sup>8</sup>Forst, C., Roth, W., Kuhnmunch, S. Int. J. Env. Anal. Chem. 1989, 37, 287-293.
- <sup>9</sup>U. S. Environmental Protection Agency, *Drinking Water Regulations and Health Advisories*, April 1990.
- <sup>10</sup>Sandall, O. C., Shiao, S. Y., Myers, J. E. AIChE Sym. Ser. 1975, 70, 24-30.
- <sup>11</sup>Hwang, S. T. AIChE Sym. Ser. 1981, 77, 304-315.
- <sup>12</sup>Ricker, N. L., King, C. J. AIChE Sym. Ser. 1978, 74, 204-209.
- 13 Hewes, C. G., Smith, W. H., Davis, R. R. AIChE Sym. Ser. 1975, 70, 54-60.
- <sup>14</sup>Earhart, J. P., Won, K. W., Wong, H. Y., Prausnitz, J. M., King, C. J. CEP May 1977, 67-73.
- 15 Ewell, R. H., Harrison, J. M., Berg, L. Ind. Eng. Chem. 1944, 36, 871-875.
- <sup>16</sup>Joshi, D. K., Senetar, J. J., King, C. J., Ind. Eng. Chem. Proc. Des. Dev. 1984, 23, 748 -754.
- <sup>17</sup>Barbari, T. A., King, C. J. Env. Sci. Tech. 1982, 16, 624-627.
- <sup>18</sup>King, C. J., Barbari, T. A., Joshi, D. K., Bell, N. E., Senetar, J. J. Equilibrium Distribution Coefficients for Extraction of Chlorinated Organic Priority Pollutants from Water -1 EPA-600/2-84-060a; U. S. Dept. of Commerce, National Technical Information Service: Springfield, VA, 1984.
- 19 King, C. J., Barbari, T. A., Joshi, D. K., Bell, N. E., Senetar, J. J. Equilibrium Distribution Coefficients for Extraction of Chlorinated Organic Priority Pollutants from Water -2 EPA-600/2-84-060b; U. S. Dept. of Commerce, National Technical Information Service: Springfield, VA, 1984.
- <sup>20</sup>Hager, D. G., *Physical/Chemical Processes Innovative Hazardous Waste Treatment Technology Series*; Freeman, H. M., Ed., Innovative Hazardous Waste Treatment Technology Series-Volume 2; Technomic: Lancaster, PA, 1990, 143-154.
- <sup>21</sup>Roulier, M., Ryan, J., Houthoofd, J., Pahren, H., Custer, F., *Physical/Chemical Processes Innovative Hazardous Waste Treatment Technology Series*; Freeman, H. M., Ed., Innovative Hazardous Waste Treatment Technology Series-Volume 2; Technomic: Lancaster, PA, 1990, 199-204.
- <sup>22</sup>Prasad, R., Sirkar, K. K. AIChE J. 1987, 33, 1057-1066.
- <sup>23</sup>Chemical Engineers Handbook, Perry, R. H., Green, D. W., Eds., McGraw-Hill: Highstown, NJ, 1989, 17-14 17-34.
- <sup>24</sup>Zander, A. K., Qin, R., Semmens, M. J. J. Env. Eng. 1989, 115, 768-784.
- <sup>25</sup>Prasad, R., Sirkar, K. K. Sep. Sci. Eng. 1987, 22, 619-640.

- <sup>26</sup>Prasad, R., Frank, G. T., Sirkar, K. K. AIChE Symp. Ser. 1988, 84, 42-53.
- <sup>27</sup>Callahan, R. W. AIChE Symp. Ser. 1988, 84, 54-63.
- <sup>28</sup>Rosen, M. J., Surfactants and Intertacial Phenomena, John Wiley & Sons, Inc.: New York, NY, 1978, 174-184.
- <sup>29</sup>Semmens, M. J., Method of Removing Organic Volatile and Semivolatile Contaminants from Water, U. S. Patent # 4960520, 1990.
- <sup>30</sup>Millipore, Analysis, Purification, Monitoring, Quality Control, 1990 Catalog.
- <sup>31</sup>Leonard, R. A., Chemical Technology Division Annual Report, 1989, ANL-90/11, Argonne National Laboratory, Argonne, IL, 1990.
- 32Byers, W. D., *Physical/Chemical Processes Innovative Hazardous Waste Treatment Technology Series*; Freeman, H. M., Ed., Innovative Hazardous Waste Treatment Technology Series-Volume 2; Technomic: Lancaster, PA, 1990, 19-29.
- <sup>33</sup>Zander, A. K., Semmens, M. J., Narbaitz, R. M. J. AWWA 1989, 81, 76-81.

#### Figure Captions

- Figure 1. Flow diagram for the MASX/MADS process.
- Figure 2. Concentration profiles in hydrophobic and hydrophilic and composite membranes used in solvent extraction.
- Figure 3. Vapor-liquid equilibrium for the VOC-solvent system.

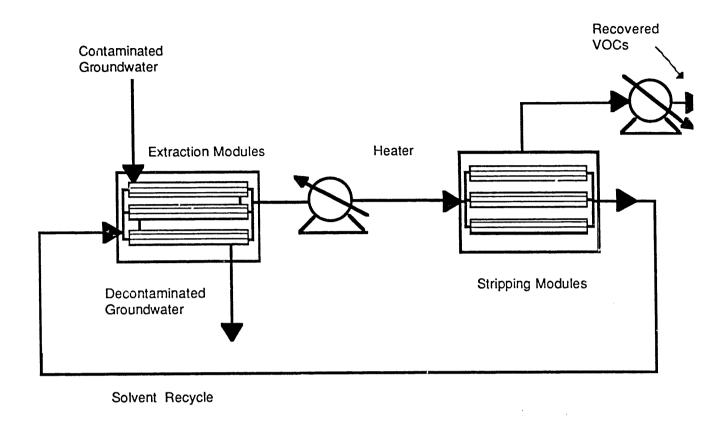
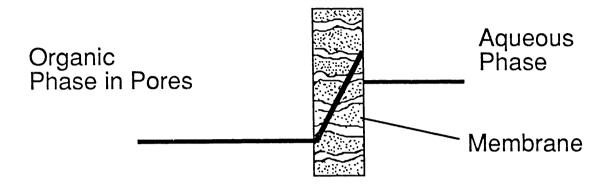


Figure 1

### a.) Hydrophobic Membrane



## b.) Hydrophilic Membrane

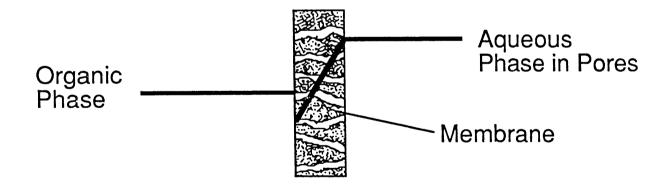
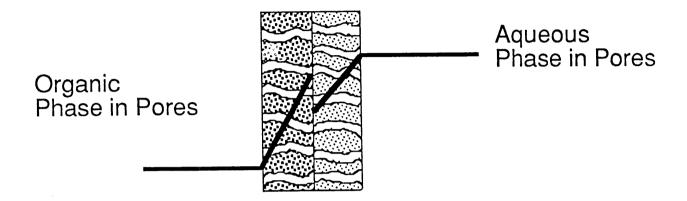


Figure 2

## c.) Composite Hydrophilic-Hydrophobic Membrane



## d.) Composite Hydrophobic-Dense Membrane

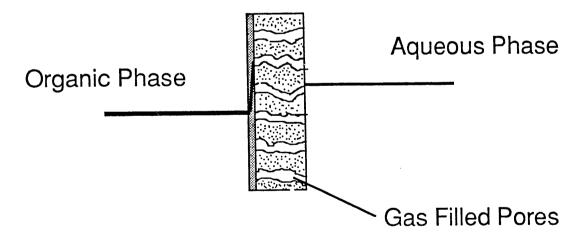


Figure 2

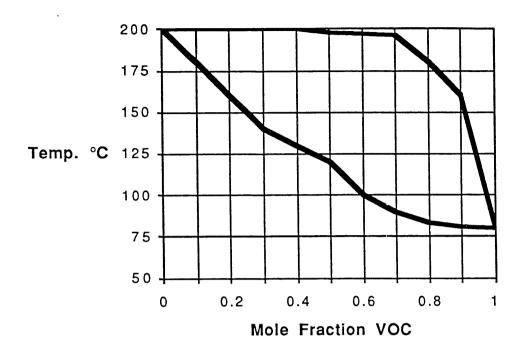


Figure 3

# DATE FILMED 312192

I

