

Utilization of Predispersed Solvent Extraction
for Removal and Enzymatic Degradation of Chlorinated
Solvents in Ground Water

by

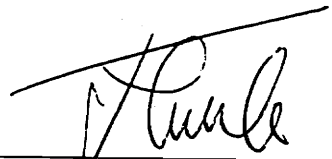
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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Master of Science
in
Environmental Engineering

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February 1996
Blacksburg, Virginia

Key words: predispersed solvent extraction, groundwater
remediation, chlorinated solvents, oil-core aprons,
microbubbles

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(ABSTRACT)

The feasibility of applying a recently developed liquid-liquid extraction method termed Predispersed Solvent Extraction (PDSE) in an *ex situ* pump-and-treat system to remove trace amounts of dissolved chlorinated solvents like perchloroethylene (PCE) and trichloroethylene (TCE) from contaminated ground water has been investigated. In PDSE, the solvent is comminuted into globules with diameters ranging from submicron to 100 microns, and stabilized by a surfactant film prior to contact with the aqueous feed. These stabilized globules, termed oil-core aphrons (OCAs), disperse readily in water since water is the continuous phase in systems where the oil-water phase ratios can be as high as 9. Due to their fine particle size and large surface area, high extraction mass-transfer rates are achieved with minimal mixing. OCA phase separation from water can be expedited with microbubble foam flotation. Experiments in this investigation focused on PDSE process development for this groundwater remediation application.

Distribution coefficients for PCE and TCE in possible OCA solvents were determined experimentally and agree with published calculated values.

Various surfactant/solvent OCA formulations using the aforementioned solvents were examined with emphasis on creating a weakly stable dispersion which would maximize extraction efficiency yet destabilize sufficiently to permit rapid flotation with minimum losses in the raffinate.

Accelerating phase separation, hence solvent recovery, through dispersion chemical destabilization with salts, coagulants, and flocculants at varied pH was examined with and without microbubble flotation.

The presence of OCAs in the aqueous phase reduced vapor phase concentrations of PCE as much as 96% and was assessed through apparent Henry's Law constants.

TCE concentrated in dodecane OCA extract was degraded with a CO-dehydrogenase enzyme complex to cis 1,2-dichloroethylene, trans 1,2-dichloroethylene, and 1,1-dichloroethylene, and vinyl chloride as a possible means of destroying TCE dissolved in the extract.

Based on the implications of these experiments, the development of a PDSE *ex situ* pump-and-treat system appears technically feasible and a conceptual process layout has been provided.

Dedication

I would like to dedicate this work to my mother, Bonnie
D. Burt.

Acknowledgments

I would like to extend my deepest gratitude to Dr. Donald Michelsen for the opportunity to work under his supervision. His unending patience, support, and friendship have always been an inspiration to me. His guidance has been invaluable to my educational experience.

I would like to thank Dr. Clifford W. Randall and Dr. John C. Little for serving on my committee.

I would like to thank Dr. Greg Ferry at Pennsylvania State University for his collaboration on the enzyme degradation phase of this work.

I would also like to thank Marilyn Grender for her assistance in troubleshooting chemical analyses, and Phil Kaiser for his helpful comments.

I extend special thanks to my family for their love and support, and to my fiancée, Amy, for her patience, love, and faith.

Table of Contents

1.0	Introduction.....	1
1.1	Research Objectives.....	6
2.0	Literature Review and Background.....	7
2.1	General Information on Target Pollutants.....	7
2.2	Competing <i>Ex Situ</i> Groundwater Treatment Technologies.....	7
2.2.1	Activated Carbon Adsorption.....	9
2.2.2	Air Stripping.....	13
2.3	Conventional Solvent Extraction.....	15
2.3.1	Predispersed Solvent Extraction.....	22
2.4	Solvent Recovery Enhancement.....	30
2.5	Vapor/Liquid Equilibrium and Henry's Law.....	34
2.6	Biodegradation of Chlorinated Solvents.....	35
2.7	Overview of Investigation.....	39
3.0	Materials and Methods.....	42
3.1	Choice of PDSE Solvents.....	42
3.2	Determination of Distribution Coefficients.....	43
3.3	Formulation Studies.....	46
3.4	Solvent Recovery Enhancement.....	47
3.4.1	Chemical Destabilization Jar Tests.....	47
3.4.2	Flocculation/Flotation Studies.....	50

3.5	Henry's Law Constant Depression.....	52
3.6	Enzymatic Degradation of TCE in PDSE Extract....	54
4.0	Results and Discussion.....	57
4.1	Determination of Distribution Coefficients.....	57
4.2	Formulation Studies.....	62
4.3	Solvent Recovery Enhancement.....	71
4.3.1	Chemical Destabilization Jar Tests.....	71
4.3.2	Flocculation/Flotation Studies.....	72
4.4	Henry's Law Constant Depression.....	77
4.5	Enzymatic Degradation of TCE in PDSE Extract....	80
4.6	Additional Extract Final Treatment Options.....	87
4.7	Design Considerations and Conceptual Flowsheet for PDSE Groundwater Application.....	88
5.0	Conclusions.....	91
6.0	Recommendations.....	93
	REFERENCES CITED.....	95
	APPENDIX A.....	102

List of Figures

Figure 1. Single Contaminant Adsorption Isotherms for Chlorinated Aliphatic Solvents.....11

Figure 2. Physical Structure of Oil-Core Aphron (OCA) and Colloidal Gas Aphron (CGA).....25

Figure 3. Time Course of Reductive Dechlorination of TCE and Product Formation by the CO-reduced CO-dehydrogenase Enzyme Complex.....38

Figure 4. Solvent Recovery Enhancement using Various Polymer Flocculants and CGA Flotation.....73

Figure 5. Solvent Recovery Enhancement using Polymer Flocculant with and without CGA Flotation.....74

Figure 6. Suppression of PCE Vapor Phase Concentration by Presence of Aqueous Phase Dodecane OCAs.....78

Figure 7. Suppression of PCE Vapor Phase Concentration by Presence of Aqueous Phase Soy Bean Oil OCAs....79

Figure 8. Conceptual Layout of PDSE Pump-and-Treat System.....89

List of Tables

Table 1. Target Contaminant Physical Property Data.....	8
Table 2a. Distribution Coefficients for Target Contaminants in Common Solvents.....	19
Table 2b. Distribution Coefficients for Target Contaminants in Common Solvents.....	20
Table 3. Results of Separatory Funnel Extraction Experiments on Ethylene Oxichlorination Process Wastewater with Kerosine and C ₁₀ -C ₁₂ Solvents.....	21
Table 4. Cationic Polymers Selected for Destabilization Tests.....	49
Table 5. Summary of CO-Dehydrogenase Enzymatic Degradation Experimental Protocol.....	57
Table 6. Experimental Distribution Coefficients for PCE in Various Oil Phases.....	60
Table 7. Experimental Distribution Coefficients for TCE in Various Oil Phases.....	61
Table 8. OCA Formulation Results with Decane/Dodecane as Solvent.....	64
Table 9. OCA Formulation Results with Soy Bean Oil as Solvent.....	66
Table 10. CO-Dehydrogenase Enzymatic Degradation of TCE Concentrated in OCAs.....	81
Table 11. CO-Dehydrogenase Enzymatic Degradation of TCE with Water as Solvent.....	82
Table 12. TCE Degradation Product Percent Distribution Based on Normalized GC Areas.....	83

1.0 Introduction

Groundwater contamination is present at greater than 85% of the 1208 sites included on the National Priority List (NPL). The Comprehensive Environmental Response, Compensation, and Liability Information System lists 30,000 other sites awaiting ranking and potential inclusion on the NPL. At more than 1700 Resource Conservation and Recovery Act facilities contaminant releases to groundwater have been evidenced. These sites, along with the large number of leaking underground storage tanks, constitute an enormous groundwater pollution problem (Olsen and Kavanaugh, 1993).

According to the Environmental Protection Agency (EPA), chlorinated solvents like perchloroethylene (PCE) and trichloroethylene (TCE) are the most common groundwater contaminants at industrial sites (U.S. EPA, 1995) These degreasing agents and common industrial solvents are known carcinogens and are released to the environment through illegal disposal, accidental spillage, and willful neglect. The extent of this groundwater contamination problem is complicated by the behavior of these contaminants in the subsurface. When released to the environment, chlorinated solvent free product, with density greater than water, can migrate to and persist below the water table as pools of Dense NonAqueous Phase Liquids (DNAPLs) in soil fractures.

Due to their low aqueous solubilities, it takes decades or even centuries for slow-moving ground water to completely dissolve subsurface accumulations of free product. Contaminant desorption from soil particles has also been a rate-limiting step in groundwater remediation (Werner and Michalski, 1995). The remediation goal is to reduce groundwater contaminant levels to or below the Safe Drinking Water Act Maximum Contaminant Levels (MCLs) shown in Table 1.

Groundwater remediation of these sites is characteristically protracted and expensive, and involves either *in situ* treatment or *ex situ* pump-and-treat technology. *In situ* remediation technologies consist primarily of *in situ* bioremediation and/or soil venting. *In situ* bioremediation involves enhancing the subsurface environment (i.e. with nutrients, electron acceptors, pH amendments, moisture, etc.) to provide an optimal growth environment for microbes to degrade target contaminants in the vadose or saturated zones. Considerable work has been focused in this area (Sims et al., 1990; Semprini et al., 1990; Hopkins et al., 1992). In soil venting, air is sparged into contaminated vadose or saturated zones to strip volatile organic compounds like TCE and PCE. A preferential flow design or vacuum induction drives extracted contaminants to recovery wells where they are treated or

exhausted (Koltuniak, 1986; Brown and Jasiulewicz, 1992). In *ex situ* pump-and-treat systems, ground water is pumped from the aquifer, appropriately treated, and reinjected into the ground or discharged to a surface water body or public works facility. *Ex situ* pump-and-treat is selected to remediate 80% of the Superfund sites with contaminated ground water (Simon, 1990/91). The current proven Best Available Treatment (BAT) technologies utilized in the remediation of ground water contaminated with chlorinated solvents in *ex situ* pump-and-treat systems are air stripping and/or activated carbon adsorption (Dyksen, 1987). Though effective in removing trace-levels of dissolved organic contaminants, activated carbon adsorption is characterized by high operation and maintenance costs. Conventional air stripping, through proper design and operation, can achieve high removal efficiencies at costs significantly lower than carbon adsorption (Amin et al., 1991). However, specific regulatory limitations on the use of air strippers, air toxics regulations, community relations, and long-term public liability necessitate air emission control to prevent pollution of ambient air. These concerns as well as the cost of emission control measures (e.g. thermal degeneration/catalytic oxidation, activated carbon adsorption), can make air stripper implementation unattractive (Cheuvront, et al., 1990).

Provisions in Section 121 of the Superfund Amendments and Reauthorization Act (SARA) of 1986 require the EPA to encourage solutions which reduce toxicity, mobility, and volume of contaminants at Superfund sites. In addition, these provisions have been interpreted to disfavor the aforementioned current conventional separation technologies which create an air pollution problem as in air stripping or solid waste problem as in activated carbon adsorption; furthermore, increased emphasis has been placed on the development of effective pollutant destruction technologies like U.V./hydrogen peroxide chemical oxidation (U.S. EPA, 1988; U. S. Congress, 1988).

The aforementioned economic and regulatory considerations warrant continuous investigation into innovative technologies which may remove dissolved chlorinated solvents from ground water and degrade them in an efficient cost-effective manner. A recently developed liquid-liquid extraction method termed predispersed solvent extraction (PDSE) represents a method for effectively concentrating trace-levels of dissolved contaminants from large quantities of water and shows promise for application in an above-ground pump-and-treat scheme. In PDSE, the solvent is comminuted into micron-sized globules and stabilized by a surfactant film prior to contact with the aqueous feed. These stabilized globules, termed oil-core

aphrons (OCAs), disperse readily in water and due to their fine particle size and large surface area, allow high extraction mass-transfer rates with minimal mixing. This contrasts the energy intensive mixing characteristic of conventional solvent extraction processing and provides an alternative for solvent extraction of dilute systems where countercurrent extraction processing with low solvent/feed ratios is impractical. The micron-sized solvent particles, after being dispersed in the feed, are floated out with a microbubble foam termed Colloidal Gas Aphrons (CGAs) leaving a raffinate denuded of solute. The surface of the raffinate is then skimmed to remove the extract concentrated with contaminants and subjected to further treatment to either recover the solvent and/or contaminants (e.g. flash distillation, steam stripping) or destroy them (e.g. hazardous waste incineration, biological degradation, U. V. peroxidation). Recent advances in the understanding of microbial metabolic pathways which degrade the pollutants of interest make biological destruction an encouraging alternative.

The purpose of this thesis was to conduct exploratory research to evaluate the feasibility of using predispersed solvent extraction as a treatment strategy in removing chlorinated solvents from contaminated ground water. Special focus was placed on solvent recovery.

1.1 Research Objectives

The work was divided into the following research objectives:

1) To screen various nonpolar solvents for favorable distribution coefficients for partitioning of dissolved PCE and TCE between the aqueous phase and the solvent (oil) phase.

2) To screen various nonpolar solvent/surfactant OCA formulations with special emphasis on the creation of a metastable or weakly stable dispersion which would maximize efficiency of extract/raffinate phase separation and increase solvent recovery.

3) To examine solvent recovery enhancement techniques including chemical destabilization with and without CGA flotation.

4) To examine PCE vapor/liquid equilibrium in a range of feed/OCA solvent ratios for possible mitigation of contaminant volatilization in *ex situ* processing due to high Henry's Law constants of chlorinated solvents.

5) To examine the potential for enzymatic degradation of TCE concentrated in OCAs by CO-dehydrogenase.

2.0 Literature Review and Background

2.1 General Information on Target Pollutants

Table 1 lists chlorinated solvents typically found in contaminated ground water at Superfund sites along with some physical property data and characteristics.

2.2 Competing Ex Situ Groundwater Treatment Technologies

Currently, the proven Best Available Technologies (BAT) most widely used for the treatment of ground water contaminated with dissolved chlorinated solvents (Table 1) in *ex situ* pump-and-treat systems are air stripping and/or activated carbon adsorption (Dyksen, 1987). U. V. peroxidation has been shown to remove up to 99% TCE for concentrations greater than 200 $\mu\text{g/L}$ and 88% PCE at concentrations exceeding 20 $\mu\text{g/L}$ in ground water applications; however, it is not state-of-practice in full-scale applications (Cheuvront et al., 1990; Amin et al., 1991).

Table 1. Target Contaminant Physical Property Data and Characteristics

Chlorinated Solvent Priority Pollutants	Specific Gravity*	Aqueous Solubility (mg/L)*	Henry's Law Constant (atm, 68°F)*	Federal MCLs in Ground Water (mg/L)	Highest Ground Water Conc. Reported (mg/L)**
Carbon Tetrachloride	1.594	800	1282	0.005	0.4
1,2-dichloroethane	1.235	8690	51	0.005	NA
Methylene Chloride	1.327	20000	89	0.005	3
Tetrachloroethene (PCE)	1.623	150	1035	0.005	1.5
1,1,1-trichloroethane (TCA)	1.339	1360	390	0.2	5.44
Trichloroethene (TCE)	1.464	1100	544	0.005	27.3

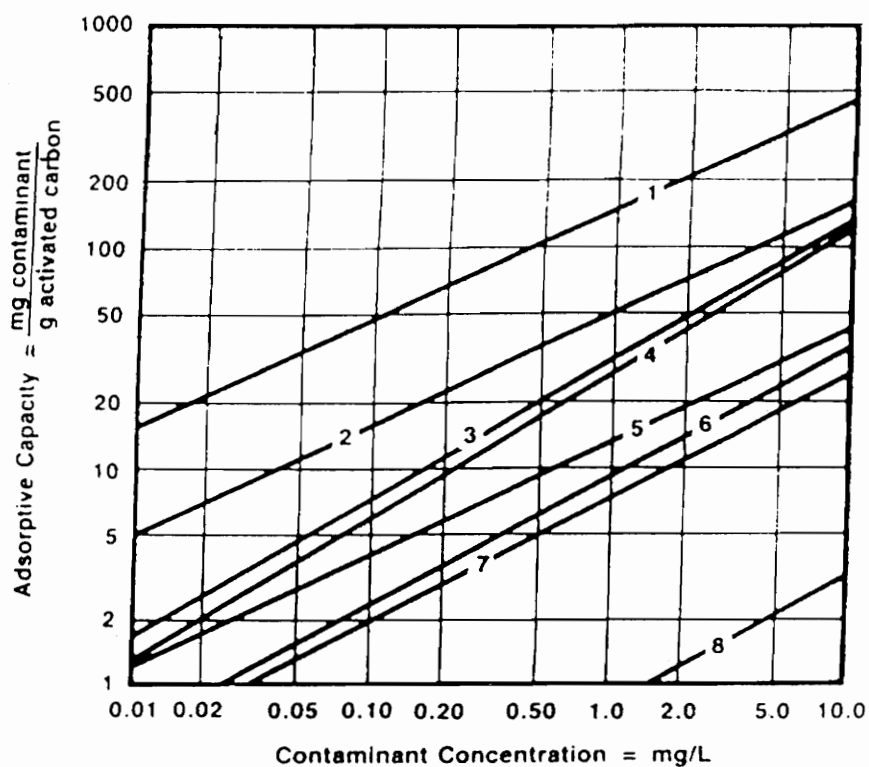
* (Nyer, 1993)

** (van der Leeden, 1990)

2.2.1 Activated Carbon Adsorption

Activated carbon adsorption removes dissolved chlorinated solvents from ground water by taking advantage of the compounds' affinity for solid-phase carbon and trapping them in the physical pore structure. Traditionally it has been used in taste and odor control applications; however, considerable research and pilot-scale studies have been conducted to evaluate the effectiveness of activated carbon processes for removing chlorinated ethenes and ethanes from ground water (O'Brien and Fisher, 1983; Shade and Sapulak, 1991; Stenzel and Merz, 1989). Activated carbon is manufactured to possess porosity as high as 80% with internal surface areas ranging from 500 to 1500 m² per gram of carbon (U.S. EPA, 1991). Typical activated carbon adsorption systems for the remediation of contaminated ground water involve fixed-bed granular activated carbon (GAC) adsorption columns operated in downflow mode and arranged in parallel or, if longer contact times are required to achieve desired effluent concentrations, in series. The fixed-bed designs are either pressure type or gravity type. Pressure type designs have higher hydraulic loading rates and save space (Stenzel and Merz, 1989). Contact time is the critical design parameter in activated carbon adsorption systems and is dependent on the types and

concentrations of contaminants. In an evaluation of 19 case studies, superficial contact times ≤ 58 minutes were necessary in 53% of the cases to reduce contaminant levels to < 1 ug/l for ground water contaminated at the mg/l level with chlorinated solvents. The superficial contact times were longer for the remaining 47%. For groundwater contaminated at the ug/l level, superficial contact times ≤ 30 minutes were sufficient in 58% of the cases surveyed for reduction to < 1 ug/l ranges of chlorinated solvents with the remaining cases being longer (O'Brien and Fisher, 1983). Other parameters considered in design and operation are type and pore size of the particle and hydraulic loading rate (Stenzel and Merz, 1989). Figure 1 presents a plot of several adsorption isotherms of the chlorinated solvents most frequently found in ground water in Table 1. From Figure 1, it is apparent that the activated carbon preferentially adsorbs compounds of increasing molecular weight. The less soluble the organic contaminants, the higher the adsorption efficiency. As the micropore structure of the carbon becomes saturated with contaminants and loses its adsorptive capacity, the effective adsorption zone moves down the column and breakthrough occurs. The column must be taken off-line and the activated carbon replaced. If the fixed-beds are operated in series, the second polishing unit assumes the lead position. The spent activated carbon can



ISOTHERM CONDITIONS:

Sample Volume = 137 ml
 Temperature = Ambient
 Agitation Time = 20 hours
 Carbon = Filtrasorb 300

ISOTHERM IDENTIFICATION

1. Tetrachloroethylene
2. Trichloroethylene
3. Carbon Tetrachloride
4. 1,1,1-Trichloroethane
5. 1,1-Dichloroethylene
6. Chloroform
7. 1,2-Dichloroethane
8. Methylene Chloride

Source: (Stenzel and Merz, 1989)

Figure 1. Single Contaminant Adsorption Isotherms for Chlorinated Aliphatic Solvents

either be regenerated thermally or chemically, or incinerated and disposed of. Thermal regeneration involves heating the spent activated carbon to temperatures ranging 1500-1700°F which volatilizes and destroys the adsorbed organics (U.S. EPA, 1991). Steam may also be applied to volatilize adsorbed organics for subsequent recovery and reuse, or treatment and disposal (U.S. EPA, 1991). Chemical regeneration requires the addition of solvent to redissolve contaminants for recovery and reuse, or treatment and disposal. With each chemical or thermal regeneration, there is an associated loss in adsorptive performance up to 15% due to pore plugging, preventing desorption and further adsorption of contaminants, as well as physical degeneration of the activated carbon (U.S. EPA, 1991). Pilot studies are usually necessary to generate performance data for any given application prior to field-scale implementation. Activated carbon adsorption is effective for removing chlorinated solvents over a broad concentration range to <1 ug/l levels. However, the application of activated carbon adsorption is characterized by high operation and maintenance costs. Regeneration typically constitutes 60-80% of the operation cost (Cheuvront, 1990). In addition, it often requires equalization for shock loading which can lead to premature column leakage and breakthrough, and water pretreatment due to intolerance of high suspended solids (greater than 50

mg/l), oil and grease concentrations (in excess of 10 mg/l), the poisoning effect of high heavy metals concentrations, and the pore fouling effect of the precipitation of inorganics at higher groundwater pH (U.S. EPA, 1991). Difficulties can also be encountered with competitive adsorption effects whereby organic compounds with higher molecular weight, like humic substances, will be adsorbed preferentially in any given matrix of contaminants (Amy et al., 1987). In addition, spent activated carbon is considered a hazardous waste under RCRA regulations (Cheuvront, 1990). For these reasons activated carbon can be economically unattractive as a primary treatment mechanism and is better suited for short-term projects, as a polishing step in a treatment train, or when the contaminant mass and hydraulic loadings are appreciably small.

2.2.2 Air Stripping

Air stripping has been effectively implemented to remove chlorinated solvents from ground water in pump-and-treat schemes (Gross and TerMaath, 1985; Byers and Morton, 1985; McKinnon and Dyksen, 1984; Kavanaugh and Trussel, 1980). Air stripping intimately contacts clean air with contaminated water removing hydrophobic compounds by driving

them, due to the concentration gradient, from the aqueous phase to the vapor phase. The volatile compounds are then carried away in the airstream leaving substantially lower contaminant concentrations in the ground water. The application of heat or steam can greatly enhance the efficiency of mass transfer. Air stripper units typically consist of a packed tower operated in countercurrent flow. Contaminated ground water flows down through the packed column and air flows upward. The water breaks into films on the packing allowing for maximum interfacial contacting area and efficient mass-transfer. Contaminants transferred to the offgas are then removed in an activated carbon bed or destroyed through catalytic oxidation or incineration. The performance of air stripping is dependent on air/water ratios, contact time, available mass-transfer area determined through the packing, temperature of the water and the air, and the physical chemistry associated with the contaminant (Perry and Chilton, 1973). Air stripping is particularly suited for removing the chlorinated solvents under consideration from ground water due to their high Henry's Law constants shown in Table 1. Under proper design and operating parameters, TCE removal rates from groundwater greater than 99.9% have been reported (Gross and TerMaath, 1985; Byers and Morton, 1985). However, air stripping may produce air pollution problems and the necessity/cost of

implementing offgas treatment to meet stringent air quality regulations could render air stripping economically unattractive. In addition, air stripping is sensitive to temperature and its application to temperatures below freezing may be cost-prohibitive. Fouling of the packing through bacterial growth and inorganics precipitation deposition (scaling) on packing can make pretreatment necessary (Dyksen, 1987).

2.3 Conventional Solvent Extraction

In conventional liquid-liquid solvent extraction, solute is transferred from one liquid-phase, the feed, to another, the solvent, with a higher chemical affinity for the solute. The solvent and feed liquid phases are characteristically immiscible. The cleaned stream is termed the raffinate whereas the solute-rich stream is termed the extract. Liquid-liquid extraction can be operated in either batch or continuous countercurrent modes. Batch liquid-liquid extraction operations involve an energy-intensive mixing stage followed by a settling stage. The mixing stage is designed to break up immiscible pregnant feed and solvent phase into tiny droplets and interdisperse them to provide sufficient interfacial contact surface area to allow

efficient solute mass-transfer and rapid approach to equilibrium. In the settling stage, the homogenized mixture of droplets coalesces and separates into two distinct phases due to density differences, and decanted for further separation processing. Single-stage mixer-settler equipment can be operated in series to achieve desired solute removals. Continuous countercurrent operations employ a variety of application specific contacting equipment where many extraction stages are incorporated in the same unit. Types of multistage equilibrium equipment include packed columns, tray columns, spray towers, and agitated contactors (Hwang, 1981; De Renzo, 1978). Internal elements may be present to achieve desired flow patterns. Spent solvent is regenerated through a second extraction or distillation and residual solvent in the raffinate is removed through air stripping, adsorption, or biological post-treatments (De Renzo, 1978). As with any liquid extraction application, solvent choice is the most important parameter aside from the design of an efficient contacting method. Perry and Chilton (1973) indicate several criteria for solvent choice. A high distribution coefficient for the equilibrium partitioning of the contaminant between solvent and aqueous phases ensures low solvent to feed ratios and relatively lower number of equilibrium stages to achieve desired contaminant removal. Solvent recovery and regenerative

potentials in the extract and raffinate directly effect operation costs. Contaminant solubility in the solvent should be high to reduce solvent requirements. Solvent solubility in the aqueous phase should be low to reduce the costs of solvent recovery, increase selectivity, and increase the range of contaminant concentrations that can be processed. A significant density difference and large interfacial tension ensure that the aqueous and solvent phases will coalesce and separate. Other criteria typically included in solvent choice are availability at a reasonable cost, toxicity and biodegradability, low corrosivity, low viscosity for high mass transfer rates, and nonflammability.

As mentioned previously, the effectiveness of solvent extraction rests on the choice of solvent, and more specifically a favorable distribution coefficient. The thermodynamic relationship representing pollutant distribution coefficient between dilute solvent and aqueous phases is defined as (Hwang, 1981)

$$K = \frac{\gamma_o^\infty}{\gamma_w^\infty}$$

where γ_o^∞ and γ_w^∞ are the infinite dilution activity coefficients of pollutant in the solvent and aqueous phases respectively. Another way of representing this is in terms of weight fraction

$$K = \frac{\text{g solute/1000 g solvent}}{\text{g solute/1000 g water}}$$

Tables 2a and 2b list calculated distribution coefficients for the partitioning of some of the pollutants of concern in various common solvents.

The application of liquid-liquid extraction for the removal of residual chlorinated ethene and ethanes in industrial waste waters has been investigated and shows promise if the economics can be justified (Earhart et al., 1976; Coco et al., 1979). Selected results for conventional separatory funnel extraction experiments conducted on a wastewater matrix from an ethylene oxichlorination process for synthesizing chlorinated solvents are listed in Table 3 (Coco et al., 1979). Kerosine and C₁₀-C₁₂ petroleum solvents were used in a solvent to wastewater ratio of 7 to 1. Based on these results, a pilot-scale Karr reciprocating plate extraction column was constructed. With kerosine as the solvent, chlorinated organic removal rates of 95% were reported with feed to solvent ratios approximating 5.5 to 1. When the C₁₀-C₁₂ solvent was used, 93.8% of the chlorinated organics were removed at feed to solvent ratios of 16.4 to 1. In addition, minimum Total Organic Carbon (TOC) residuals were noted in the raffinate with the C₁₀-C₁₂

Table 2a. Distribution Coefficients for Target Contaminants in Common Solvents

Solvent - ----- Priority Pollutant ↓	Undecane	MIBK	n-butyl acetate	Octanol	MEK	Ethyl Ether
Carbon Tetrachloride	380	930	870	436	690	1200
Trichloroethylene	170	900	900	882	1320	771
Tetrachloroethylene	1460	6300	6150	4500	13000	5500
1,2-dichloroethane	10	38	37	38	30	40
Methylene Chloride	15	50	50	72	106	45
1,1,1- trichloroethane	120	220	210	92	221	23

Source: (Hwang, 1981)

Table 2b. Distribution Coefficients for Target Contaminants
in Common Solvents

Solvent - ----- Priority Pollutant .1	Ethyl Benzene	EDC	Toluene	Xylene	Ethyl Acetate	n-hexane
Carbon Tetrachloride	1266	2329	1570	2069	668	866
Trichloroethylene	595	344	650	1030	1220	436
Tetrachloroethylene	7300	17000	8200	12000	11000	3400
1,2-dichloroethane	55	142	70	92	28	24
Methylene Chloride	59	134	68	103	89	30
1,1,1- trichloroethane	22	212	248	388	208	177

Source: (Hwang, 1981)

Table 3. Results of Separatory Funnel Extraction Experiments on Ethylene Oxichlorination Process Wastewater with Kerosine and C₁₀-C₁₂ Solvents

Chlorinated Solvent	Influent (mg/L)	Kerosine Effluent (mg/L)	C ₁₀ -C ₁₂ Hydrocarbon Effluent (mg/L)	Percent Removal with Kerosine/C ₁₀ -C ₁₂
Dichloroethylene	49	2	1	96%/98%
Trichloroethylene	24	6	5	75%/79%
Trichloroethane	75	2	3	97%/96%
Perchloroethylene	14	2	1	86%/93%
Tetrachloroethane	148	7	6	95%/96%

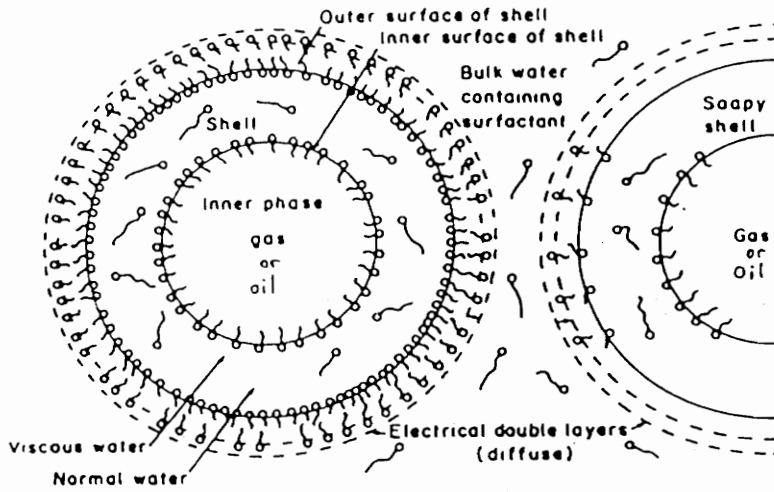
straight-chain paraffin hydrocarbon as solvent. Even with some favorable distribution coefficients evident in Table 2a and 2b and proven robust nature of the technology, conventional liquid-liquid extraction methods have traditionally not been able to compete economically or technically with activated carbon adsorption or air stripping methods in removing and treating trace levels of the contaminants of concern from ground water. At such low contaminant concentrations, the amount of solvent required is relatively small and countercurrent extraction processes become impractical. Countercurrent extraction processing is usually limited to solvent/feed ratios from 4:1 to 1:4. Operation with higher or lower ratios can result in poor phase separation and limited interfacial mass-transfer. Alternatively, a batch mixer/settler process including centrifugation may be implemented. However, at low solute concentrations, the mixing required to comminute the phases to provide sufficient interfacial mass-transfer area is high and wasteful and can result in a finely dispersed or emulsified solvent and again, poor phase separation.

2.3.1 Predispersed Solvent Extraction

A recently developed extraction procedure termed

predispersed solvent extraction (PDSE) may prove a viable method for quickly and cost-effectively extracting dilute concentrations of chlorinated solvents from large volumes of contaminated ground water. The extract with concentrated contaminants can then be subjected to any of a number of secondary treatments to either recover the solvent and contaminant (e.g. flash distillation, steam stripping) or be destroyed (e.g. hazardous waste incinerator, biodegradation, U. V. peroxidation). Predispersed solvent extraction is based on the principle that there is no need to comminute both phases. Only the solvent, the minor phase, is comminuted prior to contact with the feed by converting it into a biliquid foam (polyaphron) consisting of micron-sized solvent globules encapsulated and stabilized by an aqueous surfactant film (Sebba, 1987). These biliquid foams are typically composed of 83%-95% solvent as the dispersed phase and water as the continuous phase (Sebba, 1984). Phase Volume Ratio (PVR) is a parameter used to describe the volume ratio of dispersed oil phase to continuous aqueous phase. Properly made biliquid foams with PVRs ranging from 5 to 19 are stable and can be stored for years until required for use (Sebba, 1984). The constitutive elements in biliquid foams are termed oil-core aphrons (OCAs) and are separated by a continuous aqueous lamella. Because water is the continuous phase, these oil-core aphrons disperse readily

and homogeneously when diluted with water. The OCA aqueous structure is shown in Figure 2. OCA diameters can range from submicrometer to 100 micrometer (Sebba, 1984). Due to their fine particle size, enormous interfacial surface area is available for mass transfer to occur. For example, in a comparable quantity of solvent, OCAs with diameters of 50 microns possess 20 times the surface area of solvent particles 1 mm in diameter typically found in liquid-liquid extraction processing. OCA size, size distribution, and behavior in an aqueous system is governed by factors involved in formulation of the biliquid foam. In order to generate a biliquid foam of polyaphrons, the oil phase must be comminuted to micron sized globules and encapsulated in a surfactant film. Sebba (1984) has postulated a mechanism which involves both the spreading of the oil phase on a dilute surfactant solution and the spreading of the dilute surfactant solution on the surface of the oil phase. In order to facilitate oil-phase spreading, an oil-soluble surfactant must be present in sufficient concentration to produce a spreading pressure greater than the surface pressure of the surfactant solution. When oil containing oil-soluble surfactant is added to a dilute surfactant solution, it spreads to produce a film of varying thickness for possible hydrodynamic reasons. When the advancing edge of the film is sufficiently thin and contact angle low



Source: (Sebba, 1987)

Figure 2. Physical Structure of Oil-Core Aphron (OCA) and Colloidal Gas Aphron (CGA),

enough, the dilute surfactant solution climbs onto and spreads over the oil. Accidental perturbations at the liquid phase interface cause substrate water to break through the film inducing local retraction of the oil and the formation of oil strands which eventually break up into tiny globules encapsulated by the aqueous surfactant film. Polyaphrons are easily generated at the bench-scale using a stoppered bottle (Rodarte, 1988) or magnetic stirrer (Enzien et al., 1994). In the stoppered bottle method, a dilute surfactant solution is shaken to a foam to provide maximum surface area for the spreading of the oil. A small amount of oil is admitted to the bottle and shaken vigorously to "seed" the generation and provide additional surface area for aphrons to form. The rest of the oil is then added in small geometric increments and shaken. In the magnetic stirrer method, the surfactant solution is stirred to a foam in a beaker, "seeded", and the remainder of the oil added drop by drop from a buret at a rate of 0.6 ml/min. The stoppered bottle method provides better shearing for the production of aphrons but the magnetic stirrer method is a more reliable method for comparing various formulations and is reproducible. Continuous aphron generating equipment has also been devised (Rodarte, 1988). The nature and concentration of the oil-phase surfactant determines the size of the aphrons. The higher the concentration, the smaller the aphrons (Rodarte,

1991). Kerosine and natural oils may already contain enough surfactant. Agitation intensity has been shown to effect the size and size distribution as well, with smaller aphrons being produced at higher shearing/mixing rates (Rodarte, 1991). The aqueous phase surfactant must be present at sufficient concentration to encapsulate and stabilize the oil but at low enough concentrations such that the surface pressure at the oil-water interface does not exceed the spreading pressure produced by the oil (Sebba, 1987). Aphrons have been produced with nonionic, cationic, and anionic surfactants in the oil and aqueous phases. Since it is difficult to predict the behavior of these biliquid foam systems, stable formulations can only be determined empirically.

Due to typical micron-sized particle distribution, enormous interfacial contact area is available for rapid mass-transfer and hence rapid solute equilibrium partitioning. With rapid equilibrium partitioning of the solute between the aqueous and solvent phases, the critical processing step in the use of OCAs for extraction is separating this disperse phase from the raffinate effectively. Though less dense than the water, the oil droplets typically take a very long time to separate from the water due to their fine particle size. Flotation methods including standard dispersed-air flotation, dissolved-air-

flotation (DAF), and electrolytic flotation have been considered to expedite separation. However, these methods produce bubble diameters in ranges of 0.5-2 mm, 50-100 μ , and 5-200 μ , respectively, and OCAs with typical diameters from submicron to 25 microns remain in the liquid streamlines surrounding these quickly rising bubbles rather than contacting the bubble and being carried to the surface (Michelsen et al., 1986; Matis, 1995; Mavros et al., 1990). In addition, DAF produces volumes of air three orders of magnitude lower than conventional mechanical cells, and electrolytic flotation is relatively expensive and unconventional (Matis, 1995). Microbubble foam has been shown to be a reasonably effective flotation agent for OCAs and can be easily generated mechanically in large quantities (Sebba, 1987; Michelsen et al., 1988).

Microbubbles, also known as colloid gas aphrons (CGAs), are a dispersion of spherical gas bubbles encapsulated in a surfactant film with 95% of its bubbles not exceeding 100 μ in diameter. The aqueous structure of a CGA is shown in Figure 2. Bubble diameters typically range between 25-75 μ (Longe, 1989). The surfactant film provides a barrier to coalescence such that coalescence will not occur as long as the bubbles remain immersed in water. This allows a dispersion to be generated in one place and pumped to another. Microbubble dispersions are typically 65%-75% gas by volume

and are characterized as a wet foam. Bubble diameters and behavior are dependent upon factors including concentration and type of surfactant, generation method, and characteristics of the water (Longe, 1989). These slow rising bubbles represent a unique flotation device because of their ease of generation, size, life-time, and surface properties. Bench-scale microbubble dispersions are generated with a dilute surfactant solution and a CGA generator (Sebba, 1985). The CGA generator consists of disc connected to a vertical shaft which in turn is connected to a motor and mounted between two vertical baffles. When the disc is submerged in the dilute surfactant solution and rotated at 4000 r.p.m. or greater, waves of surfactant solution strike the baffles, reenter the water, and entrain gas which is sheared into bubbles by the disc. CGAs have been useful in several separation applications including ion and precipitate flotation, bubble-entrained floc flotation, separation of oil from sand, and removal of dispersed oil droplets from water (Sebba, 1987). A field-scale CGA generator has been constructed and tested (Michelsen et al., 1988; O' Palko et al., 1992).

The dispersion of OCAs followed by CGA flotation constitutes the process termed Predispersed Solvent Extraction (PDSE). Predispersed solvent extraction has been shown to be effective in removing dilute solutions of metals

and dissolved organics from wastewater. It has been demonstrated that with 1 ml of kerosine OCAs, oil-soluble waxoline blue dye at a concentration of 2 ppb can be removed from 2 liters of pregnant solution in one minute contact time (Sebba, 1986). In a feasibility study, extraction of 1,2-dichlorobenzene from wastewater with decane aphrons was 5 to 10 times more effective than conventional mixer/settler operations using a comparable quantity of solvent (Michelsen et al., 1986). Isobutyl heptyl ketone has been used to extract aqueous phase phenol (Sebba and Barnett, 1981). Aqueous phase copper, cadmium, uranium, and alizarin yellow dye have been extracted using kerosine OCAs with removal rates as high as 99% (Rodarte, 1988). Finally, in unpublished work, extraction of ethanol from water using aphrons made of decanol was explored (Michelsen and Wallis, 1987).

2.4 Solvent Recovery Enhancement

Clearly equilibrium partitioning of the solute into an aqueous dispersion of OCAs is very rapid due to fine particle size and large interfacial contact surface area. However, as mentioned previously, quick and effective separation of dispersed OCAs from the aqueous phase is the

critical step that determines PDSE process feasibility. In batch PDSE studies conducted in 1 liter flotation cones (500 ml of feed) with various formulations of decane OCAs and one minute 65-70 ml/min CGA injections followed by a 15 minute settling time, extract solvent recoveries were only 55%-65% (Michelsen et al., 1986). Column countercurrent PDSE phase separation studies with various formulations of decane OCAs indicate that with proper column height and operating flowrates for solvent, feed, and CGA streams, extract solvent recoveries above 90% could be achieved (Michelsen, Longe, et al., 1986). However, these recoveries were characteristically limited to low solvent feed rates and high feed/solvent flow ratios. In addition, effective extraction was limited to low throughput which may make scale-up impractical. Increases in solvent flowrate were typically followed by exponential losses to the raffinate and hence exponential decreases in solvent recovery. Attempts to counter these losses with increased CGA flowrates only resulted in increased solvent losses to the raffinate due to increased turbulence and backmixing effects and possible increased solvent solubilization due to increased aqueous surfactant concentrations. It follows that the key to better performance of PDSE and the scale-up feasibility of this technology for the purposes of treating large quantities of ground water contaminated with trace-

levels organics efficiently lies in enhancing the flotation assistance mechanism to maximize solvent and contaminant recovery with minimal losses to the raffinate.

In the flotation of colloidal and fine particle dispersions, what is floated out is often an aggregate, not a dispersed particle (Mavros et al., 1990). Flotation of negatively charged OCAs (made with sodium dodecyl benzene sulfonate) with both anionic (sodium dodecyl benzene sulfonate) CGAs and cationic (dodecyl pyridinium chloride) CGAs produces comparable solvent recoveries indicating that charge induced adsorptive tendencies between individual bubbles and particles are likely overcome by the turbulent shear effects of a CGA bubble dispersion passing through the water (Michelsen, Longe, et al., 1986). Therefore, "piggy-back" buoying of aggregates appears the primary mode of OCA flotation transport.

Dispersed OCAs are stabilized by two surface effects: steric repulsion by the surfactant adsorbed to the surface of the OCA and in the case of an ionic surfactant, additional electrostatic repulsion through the induced electrical double layer which surrounds the particle. The magnitude and sign of the electrical double layer is governed by the ionic strength of the aqueous phase, the presence of H⁺ and OH⁻ ions i.e. pH, and adsorbed charged species as in the case of an ionic surfactant (Collins and

Jameson, 1977; Tadros, 1987). Destabilizing a dispersion of OCAs and promoting the formation of aggregates should greatly enhance flotation efficiency. Electrokinetic mobility studies of wastewater oil dispersions in the presence of NaLS (sodium lauryl sulfate) and other anionic surfactants indicate that oil droplet surface charge is dominated over the entire pH range by the adsorbed surfactant negative surface charge which stabilizes the dispersion (Luthy, et al., 1977). The literature is replete with methods for chemical destabilization of colloidal and fine particle suspensions with subsequent particle aggregation (Tadros, 1987). These include the addition of polyvalent electrolyte salts (e.g. ferric sulfate, calcium chloride, aluminum sulfate) and polymeric coagulants and flocculants, and operate through charge neutralization and/or interparticle bridging. However, the application of inorganic flocculants and coagulants would make solvent recovery and/or secondary treatment difficult and economically unattractive. The application of organic polymer flocculants appears an attractive method for accelerating OCA aggregation and enhancing flotation for removal from the aqueous phase with its low dosage requirements, biodegradability, and easier separation potential in solvent recovery. By taking advantage of charge adsorption effects as well as interparticle bridging

phenomena, high molecular weight medium-high charge density cationic polymers have been shown to be effective waste oil droplet coagulants and warrant testing for this application (Luthy et al., 1977).

2.5 Vapor/Liquid Equilibrium and Henry's Law

Henry's Law is a simple relationship which indicates the concentration of a compound in the gas phase in equilibrium with its dilute concentration in the aqueous phase, defined by a proportionality constant called Henry's Law constant. Henry's Law can be expressed as follows (Nyer, 1993):

$$P_A = H_A * X_A$$

where P_A = partial pressure of a compound in equilibrium with aqueous phase concentration (atm)

H_A = Henry's Law proportionality constant (atm)

X_A = aqueous phase concentration of compound in equilibrium with its gas phase concentration (mole/mole)

Due to the inherent hydrophobicity and hence low aqueous solubility of chlorinated solvents like trichloroethylene

and perchloroethylene, Henry's law constants are relatively high as indicated in Table 1. These values must be depressed to avoid air pollution problems during extraction and further processing in an *ex situ* pump-and-treat scenario as well as immobilize the chlorinated solvent contaminants for further treatment. The presence of OCAs in the aqueous phase may serve to lower the apparent Henry's Law constants and hence vapor phase concentrations of chlorinated solvent eliminating usual substantial losses to the vapor phase.

2.6 Biodegradation of Chlorinated Solvents

The interest in *in situ* bioremediation of ground water contaminated with chlorinated solvents (e.g. TCE, PCE) has prompted laboratory investigation into the microbial metabolic pathways which mineralize these compounds to the innocuous products of CO_2 , H_2O and Cl^- . Intimate knowledge of these pathways will provide guidance for the enhancement of subsurface conditions to induce an optimal growth environment for the microbes in the field scenario. Biomineralization of the chlorinated solvents of interest occurs in both aerobic and anaerobic bacteria.

Aerobic mineralization is catalyzed by oxygenases found in different types of bacteria. Methanotrophs, for which

methane is the sole carbon source obligate requirement, contain a nonspecific methane monooxygenase (MMO) which serves *in vivo* to fix methane oxidizing it to methanol. Methanol is then further oxidized to provide cell carbon and energy for the bacteria. MMO also initiates TCE degradation but this occurs cometabolically and fortuitously (Little et al., 1988; Tsien et al., 1989). Accordingly, microorganisms do not derive cell carbon or energy from TCE oxidation. Monooxygenase enzyme systems are also present in propane and ammonia oxidizing bacteria (PMO and AMO) although PMO has been shown to be a more efficient catalyst of TCE oxidation than either MMO or AMO (Vannelli et al., 1990; Wackett et al., 1989). Dioxygenase enzymes present in phenol and toluene oxidizing bacteria also oxidize TCE (Wackett and Gibson, 1988; Zylstra et al., 1989; Nelson et al., 1987; Folsom et al., 1990). PCE oxidation occurs through the same pathways; however, the higher the number of chlorine substituents present on the compound, the more resistant the compound to aerobic oxidation (Freedman and Gossett, 1989).

In anaerobic bacteria, chlorinated solvent degradation occurs readily through methanogenic reductive dehalogenation in a sequential manner (Freedman and Gossett, 1989). For example, PCE is initially converted to TCE, then to 1,2-dichloroethylene or 1,1-dichloroethylene, then to vinyl chloride, and finally to ethylene. As the degradation

sequence proceeds, however, dehalogenation occurs more slowly because of reduction in the redox potential of the pollutant with vinyl chloride being the most persistent (Fogel et al., 1986, Sims et al., 1990). It has been shown that reduced vitamin B₁₂ reductively dechlorinates TCE (Gantzer and Wackett, 1991) and it is suggested that corrinoids, which are present in high levels in methanogens (Gorris et al., 1988) may be responsible for the reductive dehalogenation of one carbon compounds and ethylenes (Krone et al., 1989). Recently, it was reported that a corrinoid containing CO-reduced CO-dehydrogenase enzyme complex isolated from an acetotrophic methanogen *Methanosarcina thermophila*, which synthesizes it in large quantities, reductively dechlorinated TCE to cis 1,2-dichloroethylene, trans 1,2-dichloroethylene, 1,1-dichloroethylene, vinyl chloride, and ethylene (Jablonski and Ferry, 1992). The time course of reductive dechlorination is shown in Figure 3. Apparent kinetic parameters for K_m and V_{max} were 1.7 ± 0.3 mM TCE and 26.2 ± 1.7 mol TCE dechlorinated/min/mmol Factor III. PCE could be reductively dechlorinated in a similar manner. These results have very encouraging implications for enzyme degradation as a final treatment step in the utilization of PDSE for remediating ground water contaminated with chlorinated solvents like TCE and PCE in an *ex situ* pump-and-treat scheme. Mass producing and

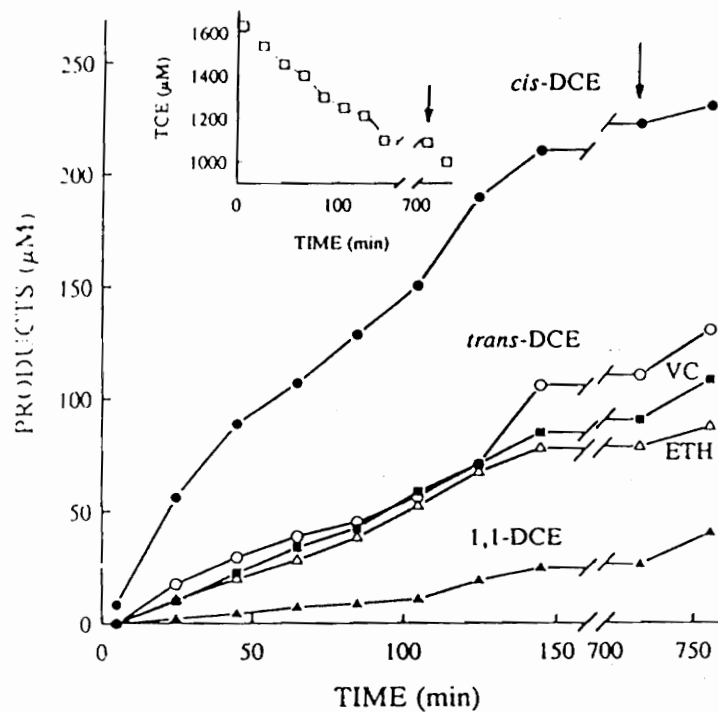


Fig. 3. Time course of reductive dechlorination of TCE and product formation by the CO-reduced CO dehydrogenase enzyme complex isolated from *Methanosarcina thermophila*. The values are the means of three replicates. The arrows indicate the point at which additional CO-dehydrogenase enzyme complex (500 μg) was added to the reaction mixture.

Figure 3. Time Course of Reductive Dechlorination of TCE and Product Formation by the CO-reduced CO-dehydrogenase Enzyme Complex

isolating an enzyme and controlling its application conditions is notably less difficult than maintaining an optimal microbial growth environment *ex situ* (e.g. fixed-film reactor) or *in situ* for the same degradative purpose. In addition, enzyme addition should compete economically with other energy-intensive pollutant destruction methods like incineration. For these reasons, the feasibility of enzymatically degrading the chlorinated solvents concentrated in PDSE extract was investigated.

2.7 Overview of Investigation

Based on the aforementioned research objectives, the work was divided into five phases.

In the first phase, an experimental method for examining the partitioning of dissolved chlorinated solvent between oil and aqueous phase was developed and used to screen eight different solvent oils for favorable distribution coefficients with PCE and TCE.

The purpose of the second phase was to optimize the extraction/flotation process, hence phase separation and solvent recovery, as a function of biliquid foam (polyaphron) formulation as well as size and size distribution of the OCAs generated. All oil phases screened

in phase one were tested in formulations. The goal was to produce a metastable or weakly stable dispersion that would be stable (i.e. resist coalescence) in its concentrated biliquid foam form but when admitted to an aqueous phase, disperse with the concentration of the OCA interface surfactant decreasing until the particle is no longer surfactant stabilized. The effects of high interfacial tension between the phases would take over, the particles would coalesce, and efficient phase separation would occur. The results from these screening tests provided guidance as to which OCA formulations might be best suited for PDSE processing for this groundwater treatment application as well as which should be considered for the final three phases of the work.

In the third phase, accelerating and enhancing the extent of solvent recovery through chemical destabilization was evaluated with and without CGA flotation. Preliminary tests using various polyvalent electrolyte salts and polymer coagulants and flocculants were performed in a jar tester followed by a final set of flocculation/CGA flotation experiments in a flotation cell.

In the fourth phase, the effect of the presence of OCAs in the aqueous phase on vapor/liquid equilibrium partitioning of chlorinated solvent (PCE) was assessed through apparent Henry's Law constants. The purpose of this

phase was to examine to what extent contaminant volatility and vapor phase contaminant concentration could be suppressed in the interest of above-ground processing.

In the last phase, TCE concentrated in PDSE extract was enzymatically degraded by CO-dehydrogenase enzyme complex to trans 1,2-dichloroethylene, cis 1,2-dichloroethylene, 1,1-dichloroethylene, and vinyl chloride.

Various critical discussions evaluating the feasibility of PDSE for this ground water remediation application are included and a process layout has been devised. Recommendations for further research have also been included.

3.0 Materials and Methods

3.1 Choice of PDSE Solvents

As with any liquid-liquid extraction application, choice of solvent is the most important parameter. Criteria for solvent choice included availability at reasonable cost, recovery/regenerative potential, biodegradability, toxicity, and the potential of chemical "compatibility" with the surface chemistry in the predispersed solvent extraction method. Of the various possible oil phases considered for solvent, the following were chosen for distribution coefficient determination and OCA formulation studies:

- Decane (Fisher Laboratory-grade)
- Dodecane (Fisher Laboratory-grade)
- Kerosine (Fuel-grade)
- Light Mineral Oil (Fisher Laboratory-grade)
- Heavy Mineral Oil (Fisher Laboratory-grade)
- Crisco Food-grade Soybean Oil
- Dow Corning 710, Polydimethylsiloxane,
(Silicone Oil, $d=1.1$ g/ml)
- Dow Corning 200, Polydimethylsiloxane,
(Silicone Oil, $d=0.9484$ g/ml)

Soybean oil represents an inexpensive easily biodegraded solvent as does decane (Enzien et al., 1994). Decane was subsequently replaced with dodecane to limit volatilization losses for later solvent recovery quantification purposes. The silicone oils were chosen because they had never been

tested to date. The silicone oil with $d=1.1$ g/ml was selected to examine whether OCAs could be formulated and settled from the aqueous phase rather than floated. The heavy and light mineral oils are simple paraffins with different Saybolt viscosities and were chosen to examine the effect of viscosity on formulation as well as for their biodegradability and availability at a reasonable cost. Kerosine has been proven in previous studies to be an effective inexpensive solvent.

3.2 Determination of Distribution Coefficients

Since neither empirically derived distribution coefficients for the solvents/contaminants of interest or method for determining them could be located in the literature, a method was developed for determining the equilibrium partitioning of chlorinated solvent between the aqueous and solvent phases. Distribution coefficients for PCE, chosen for its contaminant prevalency as well as lower toxicity, were determined experimentally in 43.5 ml (total volume) glass vials equipped with teflon septa. For each of the vials, 13 ml of the oil phase was admitted first and this was used to tare a Metler balance. A single drop of PCE was then added with a 10 μ l syringe which admitted

approximately 0.0033 g (exact values were recorded) of PCE. The remaining volume was filled with 28 ml of Milli-Q water and capped with the Teflon septa and lid leaving 2.5 ml airspace to provide a small bubble to facilitate mixing. PCE aqueous solubility at 25° C is 150 ppm and it was important that the solubility not be exceeded in these experiments because this would give false results (approximately 0.0033 g of PCE in 28 ml of water phase equates to approximately 125 ppm PCE (aq)). Three replicate vial experiments for each oil were prepared. The vials were tightly sealed and each was shaken vigorously for five minutes a day for a three day period and allowed to stand inverted so that the aqueous phase was on the bottom contacting the septa. On the third day, the vials were allowed to stand inverted and undisturbed for four more days to ensure sufficient phase separation. To examine the aqueous phase concentration of PCE and calculate distribution coefficients by mass difference, the following procedure was used. With the vials inverted as mentioned, the end of an 8 inch needle was first forced into headspace of the vial in order to allow air to enter the vial to displace the liquid drawn off the bottom. A 30 ml syringe was used to carefully pierce the septa and draw off 5 ml of the aqueous subnatant. This 5 ml of subnatant was admitted to a 9 ml Teflon sealed vial and vortexed with 1 ml of analytical grade pentane for one

minute to extract and concentrate the chlorinated solvent. After the pentane and water phases separated, a 10 μ l syringe was used to draw out 2 μ l of the pentane extract floating on the top. This was manually injected into a Hewlett Packard 5890 gas chromatograph equipped with a 30 meter J & W Scientific DB 624 6% cyanopropylphenyl-94% dimethyl polysiloxane column and an electron capture detection system sensitive only to halogenated organics. This analytical technique was adapted from EPA Method 501.2. PCE concentration was read from a seven point calibration curve with coefficient of variation 0.997. Quantifying the concentrations of PCE in the aqueous phases and oil phase, by difference, allows the calculation of distribution coefficients as the PCE weight fraction ratios of oil phase to aqueous phase. Density corrections were included. The aforementioned experimental procedure was repeated three times to ensure satisfactory results. Distribution coefficients for the partitioning of TCE into dodecane and soybean oil were also determined using the same procedure.

3.3 Formulation Studies

Formulation studies were conducted with the oil phases chosen in Section 3.1 with emphasis on generating a metastable or weakly stable dispersion as previously described. Since it is difficult to predict the behavior of OCA systems, such a metastable system could only be investigated empirically through trial-and-error formulation followed by observation. Various concentrations of different cationic, anionic, and nonionic surfactant in both the oil and aqueous phases were tested in formulations using the magnetic stirrer method. The agitation speed of the stirring mechanism was also varied. Phase Volume Ratio (PVR) was held constant at PVR=5. In order to screen a large number of formulations and note trends, a set of characterization tests was devised. A simple rating system from 1-3 indicates the stability of the biliquid foam after five minutes of standing. This is noted below:

- 1-no oil layer formed on the surface
- 2-some oil but does not flow on surface
- 3-a distinct oil layer formed which flows

In order to assess performance of flotation settling, six drops of OCA formulation, approximately 0.22 g, were admitted to a 100 ml working volume of deionized water in a

150 ml separatory funnel. The funnel was gently stirred to disperse the OCAs. After standing undisturbed for 30 minutes, a 42 ml sample was drawn from the separatory funnel, inverted three times to homogenize the dispersion, and admitted to a Monitek nephelometer to measure turbidity in ntu. In order to obtain size distribution estimates, one drop of OCA formulation was gently stirred into 20 ml of deionized water. A single drop of the suspension was examined under a microscope with a calibrated grid for size determinations. These data were taken and compiled for each formulation examined.

3.4 Solvent Recovery Enhancement

3.4.1 Chemical Destabilization Jar Tests

A series of OCA dispersion destabilization tests were conducted in a standard paddle-mixer jar tester, with rectangular jars, for the purposes of examining enhanced and accelerated solvent recovery. Dodecane OCAs prepared with the magnetic stirrer method with 4000 ppm NaDBS(aq) and 0.02% Tergitol 15-S-3 in the oil phase (PVR=5) were used in the testing. 3 ml of OCA biliquid foam was admitted with a syringe to 500 ml of deionized water in the jar vessel and

dispersed prior to chemical addition. Adjustments to pH were made with NaOH and H₂SO₄ and measured with a Fisher Accumet pH meter. NaCl, Al₂(SO₄)₃, FeSO₄, and CaCl₂ salts and the cationic polymers shown in Table 4 were chosen for testing as destabilization agents to promote particle aggregation and accelerate phase separation of the OCAs from the raffinate.

Specific information concerning the Betz and Nalco products listed in Table 4 was proprietary; however, these products are designed for similar industrial applications. Cationic polymers (1)-(12) were added in doses ranging from 20 ppm-2000 ppm with no pH adjustment. Initially the paddle mixing was set at 300 rpm for approximately one minute followed by mixing at 30 rpm for approximately 5 minutes. This was followed by ten minutes of quiescent settling. The behavior of the dispersion was observed carefully for this processing period for increased raffinate clarification. Cationic polymers (13)-(17) were tested in a similar manner with no pH adjustment except that the dosages ranged from 2.5 ppm-25 ppm. The salts were also tested in similar manner except that dosages ranged 50 mg/L-15 g/l over pH ranging from 3-12.

Table 4. Cationic Polymers Selected for Destabilization Tests

Cationic Polymer	Charge Density	Molecular Weight
(1) Nalcolyte 7135 polyquaterinary amine chloride	100%	100000-150000
(2) Nalcolyte 8100 polyquaterinary amine chloride	100%	50000-100000
(3) Nalcolyte 8105 polyquaterinary amine chloride	100%	<50000
(4) Nalcolyte 8108 polyquaterinary amine	100%	100000-150000
(5) Nalcolyte 8103 polyquaterinary amine	100%	50000-100000
(6) Nalcolyte 8102 polyquaterinary amine	100%	<50000
(7) Betz Entec 610	High: 70-100%	15000
(8) Betz Entec 660	Medium: 40-60%	75000-100000
(9) Betz Terrus 2220	High: 70-100%	100000-150000
(10) Betz Entec 641	High: 70-100%	150000-200000
(11) Betz Entec 962	High: 70-100%	350000
(12) Betz Entec 911	High: 70-100%	400000-600000
(13) Betz Entec 618 Acrylamide AETAC	High: 70-100%	$6-8 \cdot 10^6$
(14) Betz Entec 699	High: 70-100%	High: 10^6
(15) Betz Entec 693	Medium: 40-60%	$5-7 \cdot 10^6$
(16) Betz Entec 691	Medium: 40-60%	$5-7 \cdot 10^6$
(17) Betz Entec 648 Acrylamide Copolymer	Low: 0-30%	$6-8 \cdot 10^6$

3.4.2 Flocculation/Flotation Studies

Cationic polymers (13) - (17) in Table 4 were selected for further study in flocculation/flotation tests since they exhibited excellent dispersion destabilization and particle aggregation potential in the jar tests in Section 3.4.1.

A simple flocculation/CGA flotation cell was constructed. The apparatus consisted of a spinning-disc microbubble foam generator (Sebba, 1985), a Masterflex peristaltic pump (Tygon 16 tubing), a purge valve, and a 1 liter separatory funnel mounted on a ring stand.

Polymer solutions of 0.1% were prepared with a paddle stirrer and allowed to age for 2 hours prior to use following the advice of the manufacturer to allow the polymers to "unwind". Soybean oil OCAs with 6000 ppm NaLS in the aqueous phase and 1% isopropanol in the oil phase (PVR=5) were prepared using the magnetic stirrer method. Soybean oil was chosen as solvent because it has a low vapor pressure which would eliminate any volatile losses that might be incurred in the solvent recovery quantification procedure using another solvent like dodecane. The following procedure was used for each polymer tested. Approximately 1.80 g of biliquid foam weighed on a Metler balance (exact masses for each run were recorded) was admitted to a working volume of 700 ml deionized water (pH=6.8) in the separatory

funnel and gently swirled by hand to disperse the OCAs evenly. Polymer was added at the required dose, and the separatory funnel was stoppered and moderately shaken for 30 seconds. At 30 seconds the moderate shaking was changed to gentle swirling for an additional 3.5 minutes to allow flocculation to occur. At three minutes cumulative time the spinning-disc generator, charged with 1 liter 300 ppm NaDBS aqueous surfactant solution, was turned on (4000 rpm) and at four minutes, with the separatory funnel stopper removed, CGAs of 73% quality and stability 11 were metered into the bottom of the separatory funnel at a rate of 1.6 ml/s for 15 seconds. Quality and stability are conventional parameters for describing a microbubble foam. Quality is a measure of the amount of gas phase present in a given volume of microbubble foam and is determined in a 250 ml graduated cylinder gravimetrically. Stability is a measure of the bulk resistance of the bubbles to coalesce indicated by the volume of clear liquid at the base of a 250 ml graduated cylinder after one minute. Prior to injection, the CGAs were purged at the purge valve in the injection line until the proper foam consistency was observed. After a flotation time of 4 minutes, the supernatant liquid was drained from the separatory funnel down to the point of the oil layer/water interface. The inside of the separatory funnel was then rinsed twice with approximately 5-7 ml of acetone and

drained into a preweighed weighing boat. These were allowed to stand for 24 hours or until all of the acetone had evaporated leaving the residual soybean oil. The boats were then weighed and solvent recovery percentages were calculated. For comparison purposes, solvent recovery was examined with and without flotation for no polymer addition, as well as solvent recovery for a range of Betz 693 polymer doses without flotation. For these runs the aforementioned 8 minute protocol was followed.

3.5 Henry's Law Constant Depression

If the usefulness of predispersed solvent extraction as a treatment technology in a proposed pump-and-treat scheme is to be completely evaluated, it must address contaminant volatility and fugitive emissions problems associated with above-ground handling of ground water tainted with chlorinated solvents. Contaminant volatility can be assessed through apparent Henry's law constant and vapor/liquid equilibrium. The following experiment evaluates the effect of the presence of OCAs in the aqueous phase on vapor/liquid equilibrium partitioning of PCE.

Based on experimental distribution coefficients determined for dodecane (1262) and soybean oil (942) and an

assumed single equilibrium stage reduction in PCE concentration from 10 ppm to approximately 100 ppb (99% reduction), solvent to feed percentages ranging 2%-12% are required. Highly stable soy bean oil OCAs of PVR=5 were formulated with 7000 ppm NaLS in the aqueous phase and no oil phase surfactant with the magnetic stirrer method. Highly stable dodecane OCAs of PVR=5 prepared with 5000 ppm NaDBS in the aqueous phase and 0.015% Tergitol 15-S-3 in the oil phase were also formulated with the magnetic stirrer method. 0.5 ml, 1 ml, 2ml, and 3 ml (corresponding to 2%, 4%, 8%, and 12% solvent/feed ratio percentages) of oil-core aphrons were delivered with a syringe to 43.5 ml (total volume) vials with teflon septa. 25 ml of a 10 ppm PCE solution prepared without headspace in Milli-Q water was pipetted to each of the four vials and to another not containing OCAs. After each pipette addition, the teflon septum and cap were quickly placed. Each system was moderately shaken for 5-7 seconds to disperse the OCAs (including the control) and allowed to stand for 3 minutes. The ambient temperature throughout the experiment was 21.5 °C. 5 μ l of headspace gas from each vial was injected with a 25 μ l gas-tight syringe to the HP5890 gas chromatograph with electron capture detection. The aforementioned procedure was replicated two more times except that the vials were allowed to stand for 7 and 11 minutes under the same conditions to

ensure that vapor/liquid equilibrium had been reached. This exact procedure was used for the examination of Henry's Law constant depression with the soy bean oil system. The experiment was replicated three times for each solvent examined.

3.6 Enzymatic Degradation of TCE in PDSE Extract

As an overview of the following study, twelve identical individual extraction experiments were conducted in 43.5 ml vials equipped with Teflon septa and labeled accordingly. From each 43.5 ml extraction vial, two 0.5 ml samples of extract (0.25 ml of OCA/0.25 ml of water) were skimmed and admitted to each of 2 ml vials comprising Set A and Set B. Set B was subjected to the enzyme treatment experiments while Set A was designated initial value controls. The experiment was organized in this manner to control the extraction, close the TCE mass balance, and quantify degradative and nondegradative losses more easily.

Cells of *Methanosarcina thermophila* TM-1 were lysed in 50mM K⁺(3-[N-morpholino]propanesulfonic acid), 10% ethylene glycol, 10mM MgCl₂*6H₂O. 50mM (N-tris[hydroxymethyl]methyl-2-aminoethanesulfonate) (TES), 10% ethylene glycol, 530 mM KCl was used to elute CO-dehydrogenase from a MonoQ column.

50mM (N-tris[hydroxymethyl]methyl-2-aminoethanesulfonate), 10% ethylene glycol, 150 mM KCl was used for Superose 12 gel filtration to purify the enzyme (Ferry, 1992).

Dodecane OCAs were prepared with 5000 ppm NaDBS(aq), 0.02% Tergitol 15-S-3 in the oil phase, and PVR=5 using the magnetic stirrer method. A 10 ppm TCE solution was prepared in a 1 liter volumetric flask with no headspace. TCE was selected as the target for CODH degradation since this has already been shown to occur (Jablonski and Ferry, 1992). 1 ml of OCAs (0.91 g) were admitted to each of twelve 43.5 ml (total volume) glass vials with teflon septa. 40 ml of TCE solution was pipetted into each vial and quickly sealed. The vials were then gently shaken for 5-7 seconds to disperse the OCAs and allowed to stand "septa-side up" for 24 hours to allow phase separation. A 5ml glass syringe was used to skim 0.5 ml of extract from the top of each vial. This quantity was admitted to 2 ml vials (preweighed) which were then quickly sealed with teflon septa. Based on phase separation and weight difference in the 2 ml vials, 0.5 ml of extract corresponded to approximately 0.25 ml OCA and 0.25 ml water and exact values were recorded. Another set of twelve 2 ml vials (Set B) was prepared in the same manner. The 43.5 ml extraction vials were inverted "septa-side down", and after 24 hours for phase separation, the TCE concentration of a 5 ml sample of each raffinate, drawn off

through the septa as in the distribution coefficient experiments, was determined using the HP5890 gas chromatograph equipped with an electron capture detection system using the pentane extraction procedure as mentioned previously in Section 3.2. This step aided in tracking the TCE concentrations in the oil phases and assessing the extent of TCE extraction by the OCAs. Set B (#1B-#12B) along with four additional 2 ml vials containing 0.5 ml of 10 ppm TCE solution and no OCAs (#13-#16) was subjected to the CO-dehydrogenase tests and Set A (#1A-#12A) was left as initial value controls.

Table 5 summarizes the following experimental protocol. Vial #12B was designated a check sample to which nothing was done. The headspace of vials #1B-#11B and #13-#16 was purged with CO gas for 30 seconds at 20 psi through the septa with an injection needle and exhaust needle. For vials #1B, #5B-#9B, and #13B-#16B, 4 μ l of freshly made 0.5 M $\text{Na}_2\text{S}_2\text{O}_4$ reducing agent was injected to remove the O_2 dissolved in the TCE-OCA mixture. Vials #1B-#16B not including #12B were incubated in a shaking water bath at 45-50°C for 15 minutes to preheat the mixture before adding the enzyme which is most active in this temperature range. A CODH activity test was performed 15 minutes prior to enzyme addition to the vials and showed significant levels of CODH activity. After the 15 minutes of incubation, another 4 μ l of freshly made

Table 5. Summary of CO-Dehydrogenase Enzymatic Degradation Experiments

Vial # - ----- -	1 B	2 B	3 B	4 B	5 B	6 B	7 B	8 B	9 B	10 B	11 B	12 B	13 B	14 B	15 B	16 B
Experimental Steps ↓																
Aphrons Present	*	*	*	*	*	*	*	*	*	*	*	*				
1) CO Headspace Purge	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
2) First Addition of 4 μl 0.5 M Na ₂ S ₂ O ₄	*				*	*	*	*	*				*	*	*	*
3) Incubation at 45- 50°C for 15 minutes	*	*	*	*	*	*	*	*	*	*	*		*	*	*	*
4) Second Addition of 4 μl 0.5 M Na ₂ S ₂ O ₄	*				*	*	*	*	*				*	*	*	*
5) Addition of 0.5 ml CODH solution							*	*	*						*	*
6) Addition of 0.5 ml TES buffer	*				*	*							*	*		
7) Incubation at 45- 50°C for 120 minutes	*	*	*	*	*	*	*	*	*	*	*		*	*	*	*

0.5 M $\text{Na}_2\text{S}_2\text{O}_4$ was injected into vials #1B, #5B-#9B, and #13-#16, followed by the injection of 0.5 ml enzyme solution (vials #7B-#9B and #15B-#16B) or the TES buffer (vial #1B, #5B-#6B, and #13-#14). The purpose of the second $\text{Na}_2\text{S}_2\text{O}_4$ addition was to remove dissolved O_2 in the CODH preparation and maintain consistency in the controls with the buffer addition. The vials, except #12B, were incubated in the shaking water bath at 45-50°C for two hours and then allowed to cool to room temperature. 1 ml of pentane was added to all the vials in Set A and Set B to extract the remaining TCE and possible degradation products. In order to approximate TCE concentration in the oil phase for the enzyme test samples, pure dodecane standards with known concentration of TCE were pentane extracted in the same way. Each of the vials was vortexed for one minute to adequately mix the samples. The contents in the vials treated with CODH assumed a gelatinous consistency which required centrifugation until the pentane phase had clearly separated. The pentane supernatant was drawn off and analyzed for TCE and degradation products with the HP5890 using the autosampler.

4.0 Results and Discussion

4.1 Determination of Distribution Coefficients

The results from the distribution coefficient determinations are shown in Tables 6 and 7. Error indicated represents 95% confidence interval. Experimental values determined for PCE/decane, 1524 ± 70 , and PCE/dodecane, 1262 ± 42 , agree with expected values based on published calculated distribution coefficients for undecane of 1460 and tridecane of 1100 (Hwang, 1981). The experimental value for TCE/dodecane of 248 ± 20 also agrees with published calculated values of 170 for undecane and 306 for tridecane (Hwang, 1981). This lends credence to the method devised. Though no emulsified oil was observed in the aqueous phase prior to analysis, any emulsified oil would serve to lower apparent distribution coefficients because of the increased solubilized PCE in the aqueous phase. Though these solvent distribution coefficient values are not as high as might be desired for solvents in a field-scale pump-and-treat system, their biodegradability, low toxicity, heating values, low water solubility, and availability at a low cost are distinct advantages over common solvents like MEK, benzene, and ethyl acetate. In Table 2b, ethyl benzene with

Table 6. Experimental Distribution Coefficients for PCE in Various Oil Phases

Solvent Phase	Solvent/Water Distribution Coefficient (PCE), T = 21.5° C
Fisher Laboratory-grade Decane	1524 ± 70
Undecane (Hwang, 1981)	1460
Fisher Laboratory-grade Dodecane	1262 ± 42
Tridecane (Hwang, 1981)	1100
Fuel-grade Kerosine	1369 ± 28
Fisher Laboratory-grade Light Mineral Oil	1116 ± 111
Fisher Laboratory-grade Heavy Mineral Oil	945 ± 51
Crisco Food-grade Vegetable Oil (Soybean Oil)	942 ± 74
Dow Corning 710 Polydimethylsiloxane (Silicone Oil, d=1.1 g/ml)	639 ± 62
Dow Corning 200 Polydimethylsiloxane (Silicone Oil, d=0.9484 g/ml)	467 ± 34

Table 7. Experimental Distribution Coefficients for TCE in Various Oil Phases

Solvent Phase	Solvent/Water Distribution Coefficient (TCE), T=21.5°C
Crisco Food-grade Vegetable Oil (Soybean Oil)	249 ± 18
Undecane (Hwang, 1981)	170
Fisher Laboratory-grade Dodecane	248 ± 20
Tridecane (Hwang, 1981)	306

distribution coefficient 7300 for perchloroethylene and 595 for trichloroethylene looks promising for use as solvent; however, its increased solubility compared to straight chain hydrocarbons may incur undesirably higher losses to the raffinate. Similarly, Xylene with published calculated distribution coefficient of 12000 for perchloroethylene and 1030 for trichloroethylene in Table 2b could serve as a viable solvent candidate.

4.2 Formulation Studies

Distribution coefficient data in Figures 2a and 2b were not discovered in the literature until later in this investigation. Formulation studies would have included some of the solvent phases with higher distribution coefficients like xylene and ethyl benzene had this data been discovered earlier. Since all oil phases screened in Section 3.2 showed favorable distribution coefficients with the contaminants of interest, all were tested in formulations. Stable biliquid foams could not be formulated with either of the silicone oils tested though NaLS (sodium lauryl sulfates), NaDBS (sodium dodecyl benzene sulfonate), and DPC (dodecyl pyridinium chloride), were used in a aqueous phase concentrations up to 15000 ppm with Tergitol 15-S-3 oil-

phase concentrations as high as 3% and PVR=5. The mineral oils examined produced equally poor results in common formulation ranges, disappearing upon standing though remaining as a biliquid foam for longer than the silicone oils. The mineral oils were $\geq C_{16}$ paraffins which have an Hydrophilic-Lipophilic Balance (HLB) of zero. This indicates that they may be difficult to comminute and stabilize in an aqueous environment. A common reason may be supplied for the silicone oils. Stable kerosine OCA biliquid foams could easily be produced with the absence of oil-phase surfactants and aqueous surfactant concentrations ranging 4000-5000 ppm (NaDBS, NaLS, DPC); however, kerosine OCAs dispersed in water were typically in <5 micrometer size range and exceeded the turbidity limit on the nephelometer consistently in the flotation studies. In addition, kerosine varies in composition of aromatics, paraffins, and naphthas from source to source making experimental reproducibility difficult. Hence, kerosine OCA formulations were discontinued after initial experimentation. Decane/Dodecane and soy bean oil aphrons produced favorable formulations; therefore, the remainder of the formulation studies focused on the creation of metastable formulations with these solvents. Tables 8 and 9 represent only a sampling of encouraging formulations based on the criteria defined. The upper limit of the range of the nephelometer was 200 ntu;

Table 8. OCA Formulation Results with Decane/Dodecane as Solvent

Water Phase	Oil Phase	Biliquid Foam Stability	Residual Turbidity (ntu)	Estimated Size Dist. (μ)
4000 ppm NaDBS	(none) (decane)	3	13	20-84
4000 ppm NaDBS	0.1% Tergitol 15-S-3 (nonionic) (decane)	2	27	6-30
4000 ppm NaDBS (LA)	0.1% Tergitol 15-S-3 (decane)	2	6	40-65
4000 ppm NaDBS	0.01% Tergitol 15-S-3 (decane)	2	11	15-42
4000 ppm NaDBS	0.1% Macol 35 (nonionic) (dodecane)	2	57	1-20
4000 ppm NaDBS	0.2% Ethofat (nonionic) (dodecane)	1	25	8-20
4000 ppm NaDBS	0.1% Merpol A (nonionic) (dodecane)	1	22	<15
4000 ppm NaDBS	0.02% TMAZ-85 (HLB=11.1) (decane)	2	13	20-40
4000 ppm NaDBS	0.1% TMAZ-80 (HLB=15) (decane)	1	31	1-18
4000 ppm NaDBS	0.1% Armak 1689 (anionic) (dodecane)	2	71	8-32
4000 ppm NaDBS	0.2% Durfax 80K (nonionic) (dodecane)	1	22	5-30

Table 8 (continued)

Water Phase	Oil Phase	Biliquid Foam Stability	Residual Turbidity (ntu)	Estimated Size Dist. (μ)
4000 ppm NaDBS	0.1% Armeen C (cationic) (dodecane)	2	19	10-64
4000 ppm NaDBS	0.1% Poly-Step A7 (anionic) (dodecane)	1	53	3-28
5500 ppm DPC	(none) (aphrons did not form)	NA	NA	NA
5500 ppm DPC	0.1% Ethofat (dodecane)	1	56	5-40
5500 ppm DPC	0.1% Merpol A (dodecane)	2	36	<15
5500 ppm DPC (LA)	0.1% Tergitol 15-S-3 (decane)	2	3	45-73
5500 ppm DPC	0.1% Poly-Step A7 (dodecane)	3	41	10-50
5000 ppm NaLS	(none) (decane)	3	10	40-100
5000 ppm NaLS	0.1% Tergitol 15-S-3 (decane)	2	35	15-67
5000 ppm NaLS	0.05% Ethofat (dodecane)	1	87	2-25
5000 ppm NaLS	.1% Armeen C (dodecane)	3	49	15-50

(LA): Low Agitation

Table 9. OCA Formulation Results with Soy Bean Oil as Solvent

Water Phase	Oil Phase	Biliquid Foam Stability	Residual Turbidity (ntu)	Estimated Size Dist. (μ)
5000 ppm NaLS	(none)	1	36	8-65
5000 ppm NaLS (LA)	(none)	3	22	55-98
5000 ppm NaLS (LA)	0.1% T-MAZ 80 (HLB=15)	1	115	<28
5000 ppm NaLS (LA)	0.01% T-MAZ 80 (HLB=15)	1	53	10-34
5000 ppm NaLS	1% Isopropanol	1	11	33-74
5000 ppm NaLS	0.01% Tergitol 15-S-3	2	40	20-48
5000 ppm NaLS	0.1% Durfax	1	71	2-55
5000 ppm NaLS	0.1% DPC	3	32	12-63
5000 ppm NaLS	0.1% Polystep A-7	2	61	10-45
5000 ppm NaLS	0.01% Armeen C	2	89	5-50
5000 ppm NaLS	0.01% NaDBS	3	45	19-70

(LA): Low Agitation

hence, formulations for which the turbidity measurement exceeded this limit were not considered for further study or included in the tables. Decane and dodecane OCAs produced more stable biliquid foams which exhibited better phase separation than soy bean oil. Soy bean oil formulations characteristically had a larger size distribution but tended to emulsify as well. The previously described "metastable" formulation could not necessarily be achieved, but only approached on a relative scale. Some general trends could be noted however.

Since the oil-phase surfactant type and concentration has been shown to influence size and size distribution of oil-core aphrons produced whereas the aqueous phase surfactant serves as a stabilization mechanism, surfactant manufacturers were consulted concerning this application and many surfactants were obtained for testing. This was the only way to approach the task since any encouraging formulations could only be empirically derived. Appendix A includes product information for the surfactants tested.

Lowering the aqueous phase surfactant concentrations in an effort to suppress the effects of the surface forces stabilizing the OCAs was met with undesirable results regardless of oil-phase surfactant concentration and type, and intensity of mechanical agitation. From the formulation studies it appears that there is a critical point in aqueous

phase surfactant concentration below which a stable biliquid foam cannot be formed. Below this point, significant quantities of free phase oil are evident even moments after formulation even though some stable biliquid foam may remain in the formulation for a limited period of time. This critical point occurs at aqueous phase concentrations of approximately 4000 ppm for NaDBS/decane/dodecane formulations, 5000 ppm for NaLS/decane/dodecane/soy bean oil formulations, and 5500 ppm for DPC/decane/dodecane/soy bean oil formulations. Formulations prepared with nonionic surfactants like Tergitol 15-S-12 in the aqueous phase produced a significant number of aphrons in the <10 micron range which emulsified and phase separated poorly. Testing with nonionics was therefore discontinued.

From Tables 8 and 9 it is apparent that the oil-phase surfactant concentration and type significantly influences the size and size distribution of the aphrons. Heuristically, the higher the concentration, the smaller the size and size distribution; in addition, the longer the hydrophobic substituent group, the smaller the aphrons. The smaller the size and size distribution of aphrons, the slower the flotation. Comparisons of the effects of nonionic, anionic, and cationic surfactants in the oil-phase were inconclusive. One approach to formulation was to affect the oil-phase HLB with sorbitan monoleate and trioleate

esters (PPG S-MAZ and T-MAZ series) which could be combined in certain ratios to achieve an oil phase HLB, which, if matched to the HLB of the oil phase, produced a stable emulsion. These were originally designed as emulsifying agents but can also be used to induce emulsion "instability" if properly added to increase hydrophobicity or instability. Early microscopy studies of OCAs formulated with these products indicated very narrow size distributions though typically in the <10 micron range. Based on these observations, both dodecane/decane and soy bean oil (HLB=6) OCAs were formulated over a range of "induced" oil phase HLBs, oil-phase concentrations, and agitation speeds, with aqueous surfactant concentrations of NaDBS, DPC, and NaLS as low as 2000 ppm. A synergistic effect was observed between the S-MAZ and T-MAZ products such that stable biliquid foams could be produced with low aqueous phase surfactant concentrations. This technique of creating an "unstable" biliquid foam exhibited favorable phase separation as well as larger aphrons at lower mixing intensities and lower concentrations of emulsifying agents. However, the <5 micron size range still occupied a significant percentage of the aphron size distribution and these did not float from the raffinate as readily as larger sizes.

At lower agitation intensities, approximately three-fifths mixing speed, OCAs generated were characteristically

larger and provided better phase separation upon dispersion in water, but the biliquid foams were less stable. More free phase oil was evident on the surface of the biliquid foam moments after formulations than identical formulations with the higher mixing speeds. It is apparent that a critical amount of energy or shear must be imparted to the biliquid foam during the formulation to provide sufficient stabilization (due to surface forces) as a function of particle size. In addition, mixing intensity was significantly impaired by increased viscosity as PVR=5 was reached in the formulations. This implicates obvious effects on size and size distribution in formulations.

Apparently, the key to PDSE processibility is to control the size distribution of the aphrons generated. This is primarily a function of the method of mechanical generation and less on the chemistries involved. Since OCAs can be formulated from a variety of aqueous phase and oil-phase surfactants, OCA formulation surfactant choices, for scale-up purposes, may be more a function of cost and toxicity. OCAs resulting from stable biliquid foam formulations which exhibited promising phase separation were typically in the >40 micron size range with a minimal number of OCAs in the lower size distribution range. It became clear, during the formulation studies, that if PDSE is to perform as a method for effectively extracting trace-

dissolved contaminants from ground water, solvent recovery must be enhanced and accelerated to hold solvent losses to a minimum in the raffinate, and provide reasonable feed throughput. This conclusion warranted testing of chemical destabilization methods for this purpose. This is covered in the Section 4.3

4.3 Solvent Recovery Enhancement

4.3.1 Chemical Destabilization Jar Tests

Results of the chemical destabilization studies were marked by a general difficulty in overcoming the steric and surface charge effects stabilizing the OCAs. Of the salts examined over the pH range defined, only $\text{Al}_2(\text{SO}_4)_3$ and FeSO_4 showed any promise of removing the OCAs from the raffinate through enmeshment in precipitate at pH of 5 and 4 and minimal concentrations 650 mg/l and 950 mg/l, respectively. CaCl_2 showed a tendency to destabilize the OCA suspension reasonably at pH 4-6 and concentration 7.3 g/l. This may be due to precipitation of the surfactant. However, a colloidal haze was still evident in the raffinate. Cationic polymers (1) - (12) in Table 4 designed for this application did not

produce promising results over the concentration range examined. The Terrus 2220 and Entec 660 polymers were self-precipitating agents which produced pin-floc at concentrations in excess of 500 ppm but not in appreciable quantities to warrant further testing. Cationic polymers (13) - (17) in Table 4 showed excellent particle aggregation effects at low concentrations due possibly to interparticle bridging associated with higher molecular weight, and warranted further study in CGA flocculation/flotation studies discussed in Section 4.3.2.

4.3.2 Flocculation/Flotation Studies

Results from the flocculation/flotation tests are shown in Figures 4 and 5. Values shown are within $\pm 4\%$ error. Figure 4 displays solvent recovery percentages with CGA flotation with respect to polymer dosages for the polymers examined. Figure 5 displays solvent recovery curves for Betz 693 flocculation with and without CGA flotation. Only 20% of the soybean oil solvent was recovered over the eight minute period with simple settling (without the addition of polymer flocculant and without flotation). With microbubble (CGA) foam flotation and no polymer addition, 31% of the soybean oil solvent was recovered. Polymer performance appeared to

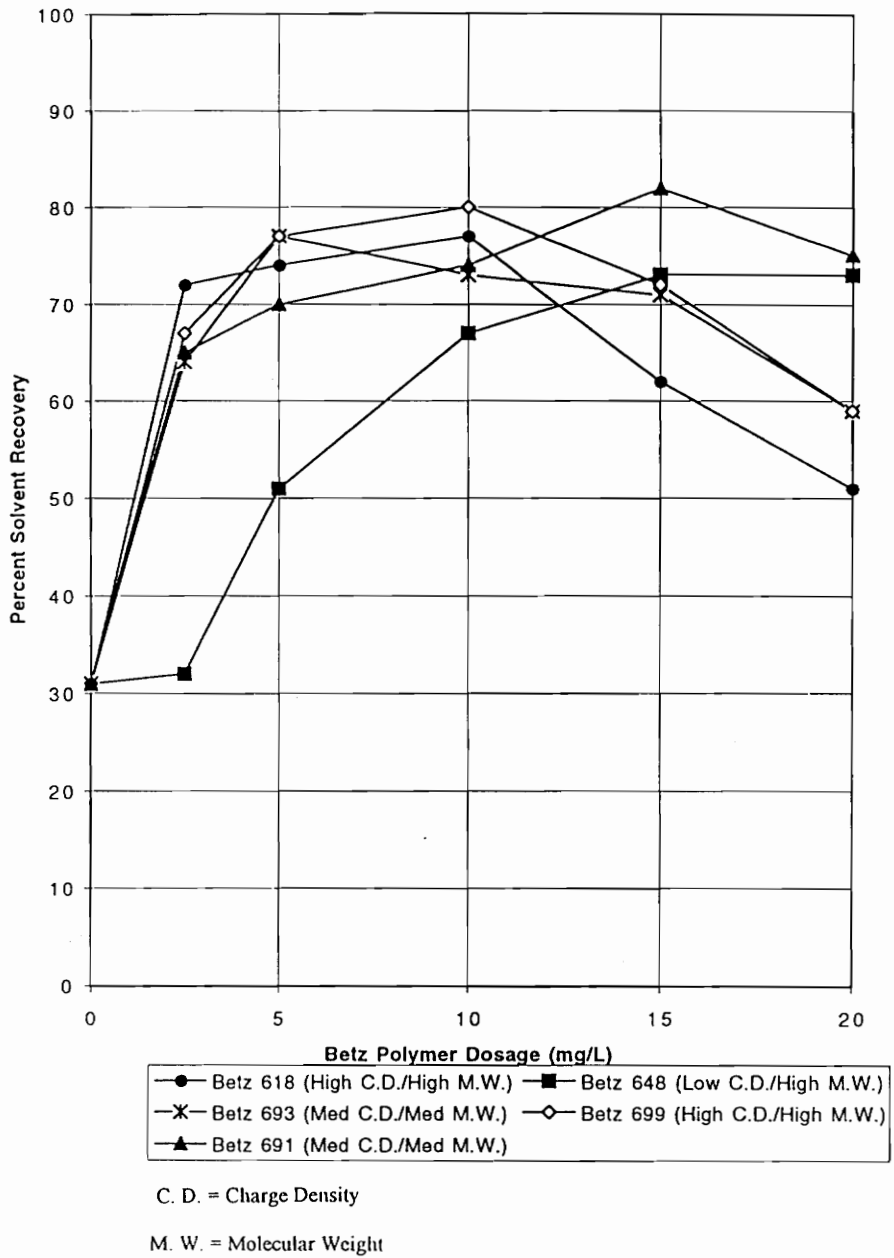


Figure 4. Solvent Recovery Enhancement using Various Polymer Flocculants and CGA Flotation

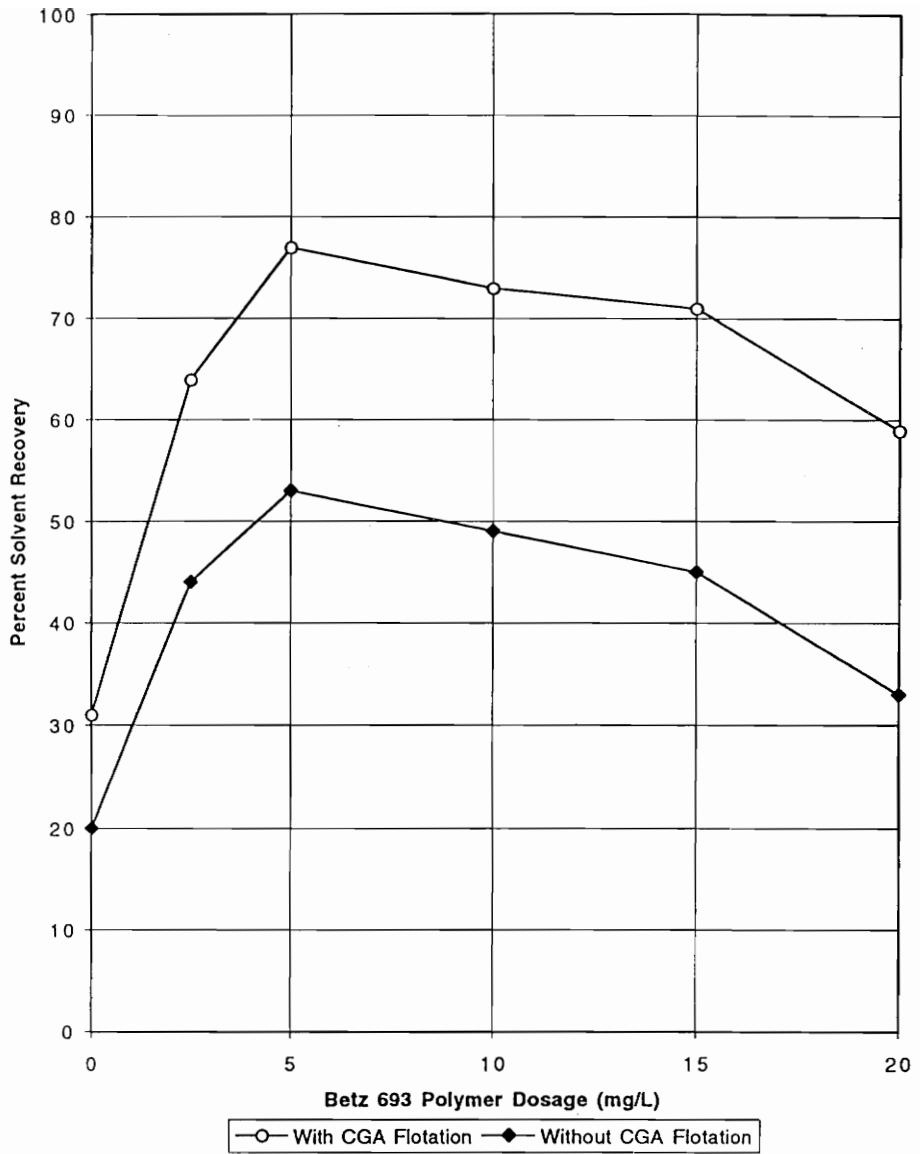


Figure 5. Solvent Recovery Enhancement using Polymer Flocculant with and without CGA Flotation

be linked to charge density for the system studied. In Figure 4, high doses of low charge density polymer Betz 648 were required to achieve solvent recoveries comparable to the higher charge density polymers. This may be due to insufficient charge neutralization or double layer compression at the interfaces of the stabilized oil droplets to allow them to coalesce. Preliminary jar tests in Section 4.3.1 support this assertion. Any apparent oil coalescence in the jar tests, though minimal, was observed to occur at high ionic strengths. All curves in Figure 4 indicate a maximum solvent recovery, the point past which some restabilization of the suspension or flocculation inhibitory effect may occur, hence limiting particle aggregation. That point of inflection may represent a surface charge reversal or steric interaction from excess adsorbed polymer and hence partial restabilization of the suspension, or the point at which any increase in higher charged polymers causes portions of the same polymer to adsorb to the same droplet limiting interdroplet bridging and particle aggregation. Polymer doses as low as 2.5 mg/L increased solvent recovery as much as 41% over simple CGA flotation on the observed time-scale. Increases in solvent recovery as high as 51% over simple CGA flotation were noted at higher polymer doses on the observed time-scale. In Figure 5 the advantage of using CGA flotation is obvious. Increases in solvent

recoveries ranging 20-28% are attributed to CGA flotation coupled with flocculation compared to flocculation/settling alone. Interparticle bridging between bubbles and flocculated material as well as "piggy-back" flotation may be occurring. In addition to accelerating solvent recovery, the presence of cationic polymer in the aqueous phase eliminated voluminous foaming at the air water interface normally encountered with the negatively charged microbubble foam generated with NaDBS surfactant. This "contrafoam" or opposing charge effect has been noted experimentally (Sebba, 1987). Though solvent recovery was greatly enhanced, a slight haze was still evident in the raffinate. Evaluations of size distribution of these remaining OCAs under a microscope revealed that these particle sizes were characteristically in the submicrometer to 3 micron range. Since flotation and flocculation efficiency is dependent on size and size distribution of the particles, *inter alia*, there are distinct advantages to controlling the size distribution of the OCAs undergoing flocculation and eliminating this particle size range in biliquid foam formulation with proper selection of agitation, surfactants, and surfactant concentrations. This would ensure higher solvent recovery. It is conceivable that under proper operating conditions in an extraction system coupled with flocculation, extraction and nearly complete efficient

solvent recovery could be achieved.

4.4 Henry's Law Constant Depression

The results for Henry's Law constant depression experiments with the soy bean oil and dodecane OCAs are shown in Figures 6 and 7 respectively. Values shown are within $\pm 5\%$ error. PCE gas phase concentration in the control vial was calculated using an empirical relationship at $T=21.5\text{ }^{\circ}\text{C}$, $P=1\text{ atm}$, and 10 ppm PCE (aq) (Cummings, 1987) and matched to the control area received from the GC analysis. It was assumed the PCE gas phase concentration would decrease linearly with each volume unit OCA addition, and based on this assumption, the remainder of the gas phase concentrations were calculated using areas received from the GC analysis. From Figures 6 and 7, it is apparent the PCE gas phase concentration and hence Henry's Law constant are reduced by 96% and 94% at solvent/feed percentages as low as 2%. Solvent/feed percentages were not examined below this value because it represents a practical lower operating limit with the given distribution coefficients. The PCE gas phase concentrations decrease slightly after the initial dramatic decrease. PCE gas phase concentrations at 3, 7, and 11 minutes were within $\pm 5\%$ indicating that equilibrium was

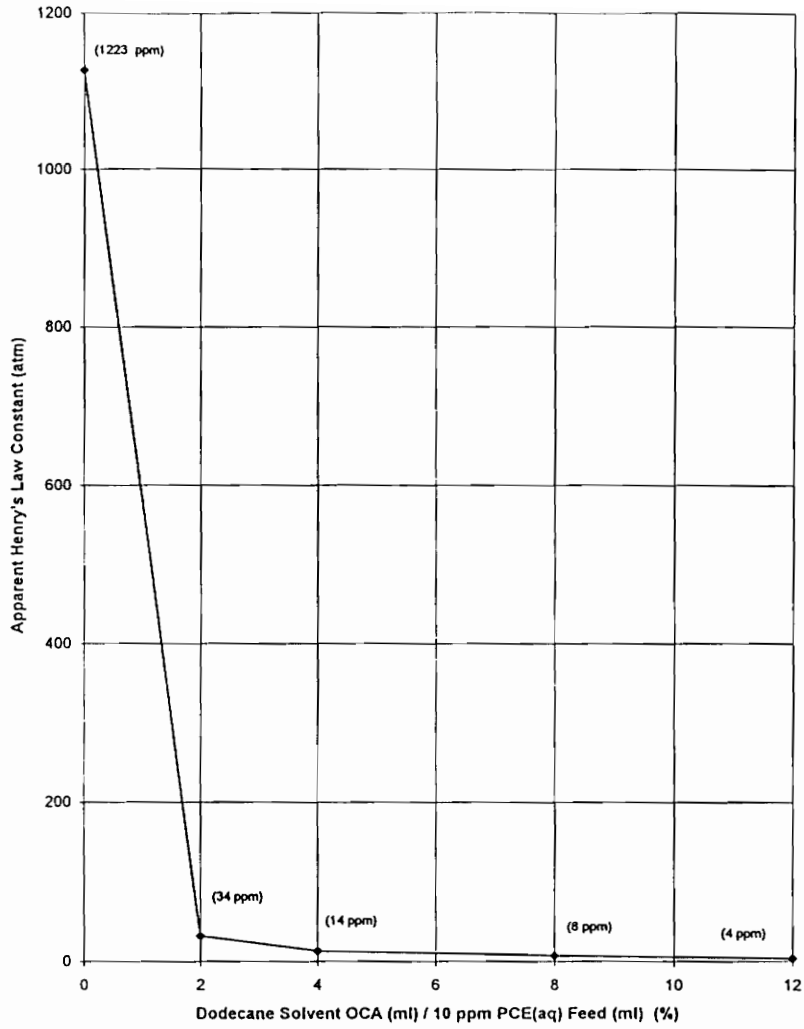


Figure 6. Suppression of PCE Vapor Phase Concentration by Presence of Aqueous Phase Dodecane OCAs

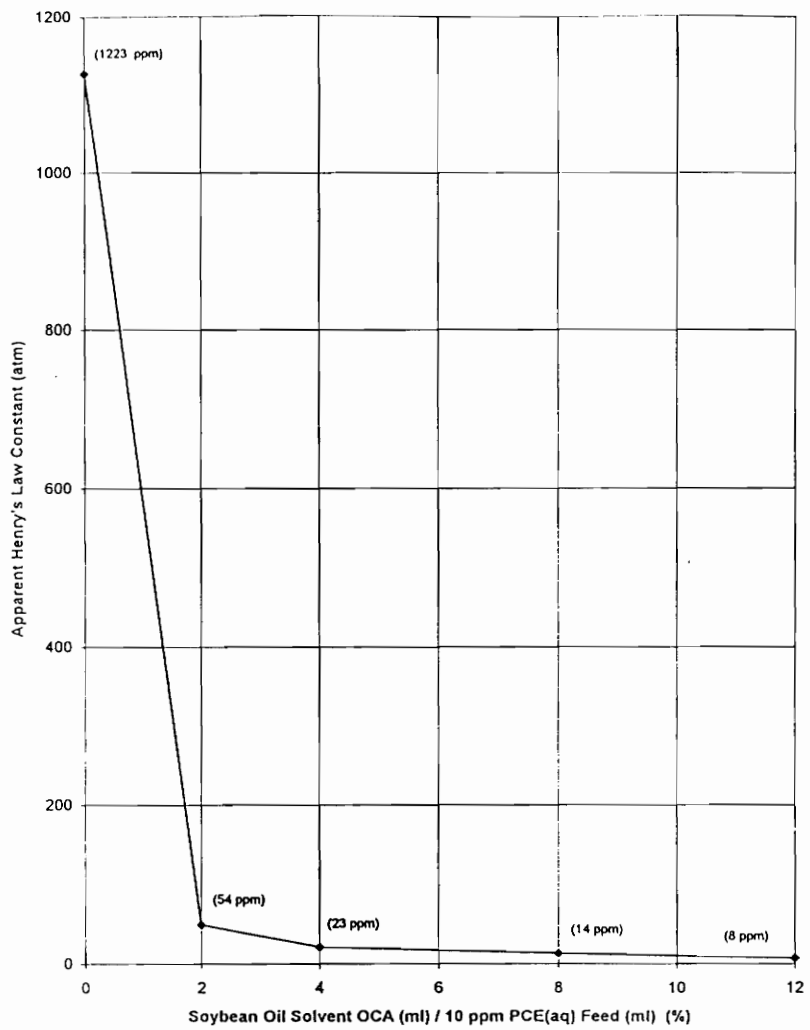


Figure 7. Suppression of PCE Vapor Phase Concentration by Presence of Aqueous Phase Soy Bean Oil OCAs

reached within the first 3 minutes. There were two primary reasons depressing the Henry's Law equilibrium constant. The first was that OCAs removed contaminants from the aqueous phase making less of the hydrophobic contaminants available to leave through the aqueous phase. The second is that OCAs that have "gravity settled" out occupy significant surface area at the gas/liquid interface mixed in with the continuous aqueous phase. Since disperse phase as well as continuous phase occupy the interface, the gas phase PCE is in equilibrium with both the oil and water phase markedly decreasing its vapor phase concentration below the control. The results of this experiment have important and encouraging implications from the standpoint of above-ground groundwater treatment process design.

4.5 Enzymatic Degradation of TCE in PDSE Extract

Results from CODH degradation tests are shown in Tables 10, 11, and 12. Set A indicates the initial value controls whereas Set B indicates the enzyme treated samples. Analysis of the raffinate in each of the twelve extraction vials revealed that consistently 98-99% of the TCE was removed by the OCA extraction. CODH degradation of TCE was interpreted through three key parameters: TCE nondegradative losses,

Table 10. CO-Dehydrogenase Enzymatic Degradation of TCE Concentrated in OCAs

Extraction Test	Set A: Initial TCE Conc. (mg/L solvent)	Set B: Final TCE Conc. (mg/L solvent)	TCE Loss (%)
1	100.1 (1A)	9.0 (1B)	91.0
2	103.5 (2A)	38.2 (2B)	63.1
3	107.9 (3A)	17.7 (3B)	83.6
4	152.5 (4A)	64.8 (4B)	57.5
5	126.5 (5A)	9.4 (5B)	92.6
6	135.8 (6A)	10.6 (6B)	92.2
7	124.2 (7A)	0.3 (7B)	99.8
8	167.4 (8A)	1.4 (8B)	99.2
9	154.8 (9A)	0.2 (9B)	99.9
10	163.0 (10A)	19.2 (10B)	88.2
11	135.1 (11A)	47.6 (11B)	64.8
12	149.6 (12A)	147.6 (12B)	1.3

Table 11. CO-Dehydrogenase Enzymatic Degradation of TCE with Water as Solvent

Extraction Test	Initial TCE Conc. (mg/L solvent)	Final TCE Conc. (mg/L solvent)	TCE Loss (%)
13	10	0.006	99.9
14	10	0.003	99.9
15	10	0	100.0
16	10	0.013	99.9

Table 12. Degradation Product Percent Distribution Based on Normalized GC Area

Chlorinated Species - ----- Sample #	TCE (%)	cis 1,2-DCE (%)	trans 1,2-DCE (%)	1,1-DCE (%)	vinyl chloride (%)
7A	6.4	11.6	0.7	14.9	66.4
8A	16.9	8.3	3.4	16.2	55.2
9A	4.7	15.6	7.2	14.9	57.6
15	0	10.1	9.0	19.5	61.4
16	100	0	0	0	0

overall TCE losses, and the presence of TCE degradation products in the vials to which enzyme had been added. Despite attempts to minimize experimental nondegradative volatile losses, OCA experimental controls #10B, #11B, and #1B-#6B indicate losses ranging from 57.5% to 92.6% of original oil phase TCE concentration. Nondegradative losses in controls #13 and #14 of the CODH degradation tests without OCAs were 99.9%. These losses are due to the CO headspace purging step designed to reduce the enzyme as well as any experimental step involving the breaking of the Teflon septa. Check sample #12 to which nothing was done indicated nondegradative losses of only 1.3%. In vials #7B, #8B, and #9B to which CODH enzyme was added to OCA extract, overall losses ranged from 99.2% to 99.9%. In vials #15 and #16 where enzyme was added to only a 10 ppm solution, overall losses reached 100% and 99% respectively. In vials #7B-#9B and #15 where enzyme activity was noted to occur, differences between overall and nondegradative losses may be attributable to enzymatic degradation. In order to detect the presence of TCE degradation products in the enzyme treated samples, individual 5 ml samples of pentane were spiked with cis 1,2-dichloroethylene, trans 1,2-dichloroethylene, and 1,1-dichloroethylene to determine GC column retention times. Vinyl chloride was not included because it was not available. The "standardized" retention

times characteristically preceded TCE retention time. Degradation products were noted in all enzyme treated samples except for #16 which showed no enzyme activity despite the application of the enzyme degradation protocol. All the chromatograms of the enzyme treated samples revealed a large peak at a retention time, shorter than retention times of the degradation products previously identified, that was not present in the samples containing no enzyme addition or indicating no enzyme activity (i.e. vial #16). Careful examination of all steps involved in the experimental protocol including enzyme preparation could not identify a halogenated species which would produce this peak. After consulting a J & W Scientific catalog, noting relative retention times for chlorinated ethylenes in consideration for a similar GC analytical configuration, and noting the persistence of vinyl chloride in the time course of enzymatic degradation in the literature in Figure 3, it was deduced that this peak corresponded to vinyl chloride. In addition, enzyme treatment chromatograms revealed a significantly large peak occurring at retention times approximately two minutes after TCE. The experimental protocol and analytical techniques were reviewed but a halogenated species that could produce this peak could not be identified. Percent distribution of the TCE degradation products based on GC areas are shown in Table 12. This table

agrees with the time course of TCE degradation products shown in Figure 3. Vinyl chloride is indeed the persistent species and represents the largest percentage of the products in all enzyme treatments except vial #16 where enzyme activity did not occur. Greater quantities of cis 1,2-dichloroethylene were formed in the active enzyme treatments than the trans 1,2-dichloroethylene isomer. However, disproportionately larger amounts of 1,1-dichloroethylene were formed than evident in Figure 3 and it is unknown why this was necessarily the case.

The dodecane OCAs were heat stable and maintained their structural integrity throughout the incubation periods. Heat is an effective method of altering chemical equilibrium and driving the TCE out of the oil phase and into the aqueous phase making it available for enzymatic degradation. Maintaining the structural integrity of the OCAs ensures high interfacial mass transfer surface area and hence high chlorinated solvent degradation rates. It is also apparent that the solvent, dodecane, as well as the other surfactants did not interfere enzyme activity although it would be important to know to what degree, if any, these are inhibitory. The enzyme is sensitive to ionic strength greater than 0.3 M and the aqueous environment from a process and groundwater remediation standpoint would need to reflect this limitation. Vinyl chloride, the most persistent

degradation product due to low redox potential, is highly toxic and would require further reduction to ethylene if this treatment is to be an effective contaminant destruction technique. If enzyme treatment is the final step, it will be necessary to examine if the presence of polymer adversely affects enzyme activity. Though process feasibility can only be addressed through further experimental work, it appears that PDSE with CODH enzyme addition as a final chlorinated solvent degradation step is a viable technique for concentrating trace-dissolved chlorinated solvents from ground water and enzymatically degrading the contaminants in the extract in an *ex situ* pump-and-treat scheme.

4.6 Additional Extract Final Treatment Options

Secondary treatment technology to degrade the chlorinated solvent contaminants concentrated in the extract is not limited to enzymatic treatment. The solvent may be regenerated through flash distillation or steam stripping and contaminants recovered for reuse or destruction. Heat coupled with U.V. peroxidation could be used to drive the contaminants out of the solvent phase and into the aqueous phase where they can be chemically oxidized. Alternatively, the extract could be completely destroyed in a hazardous

waste incinerator. These represent only a few viable options.

4.7 Design Considerations and Conceptual Flowsheet for PDSE Groundwater Application

A conceptual layout of an *ex situ* process for treating ground water contaminated with dissolved chlorinated solvents with PDSE is shown in Figure 8. Pretreatment may not be necessary since there is no need to avoid high suspended solids concentrations; in addition, the stability of OCA dispersions has experimentally been shown to be resilient to high electrolyte concentrations so their removal may not be necessary either. The flowsheet was derived with a different feed/solvent contacting method than a column countercurrent extraction arrangement since low dose polymer addition is being considered to enhance solvent recovery. The process is comprised of a "two stage" flocculation/flotation arrangement where the second unit may serve as a polishing step. The raffinate from the first tank is sent for a second extraction to reduce the concentrations of contaminants even further if necessary. The

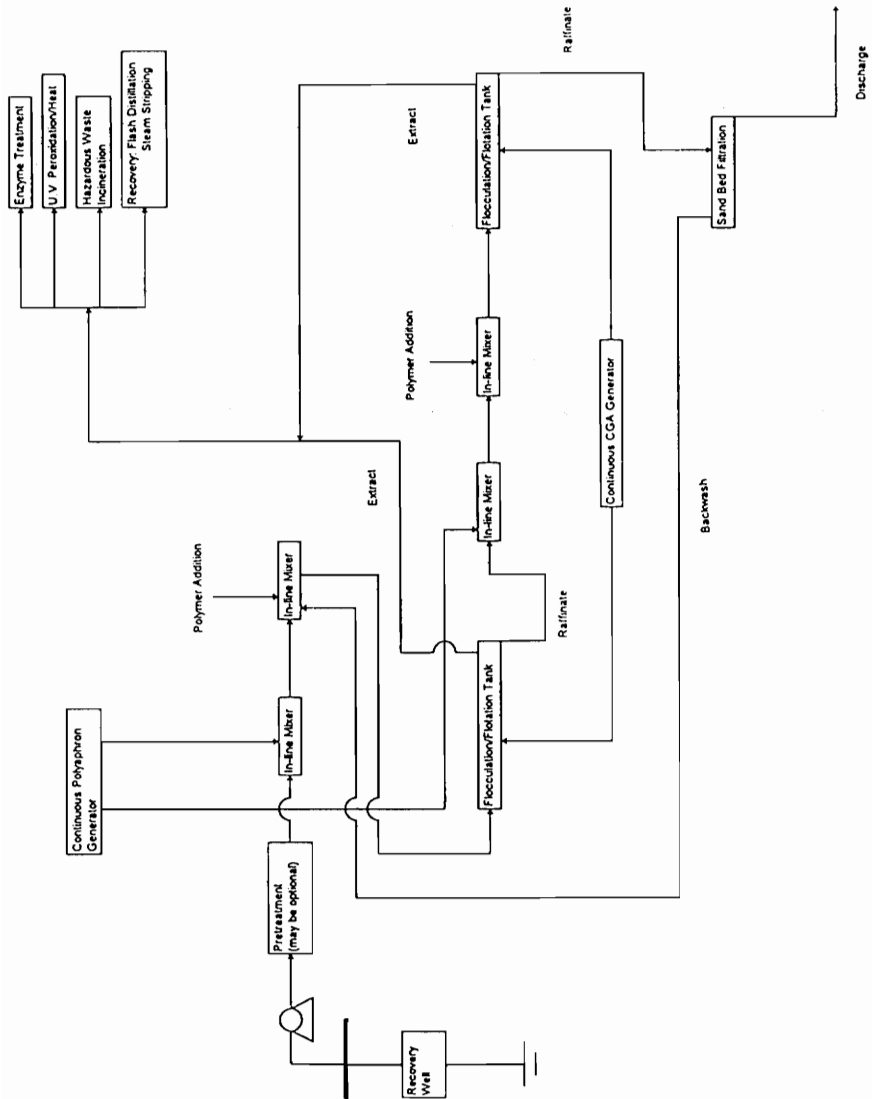


Figure 8. Conceptual Layout of PDSE Pump-and-Treat System

flocculation/flotation tanks should be low mix high residence time units equipped with an arrangement of perforated distribution plates from which CGA foam can be sparged. The solvent layer is skimmed from each tank and sent to secondary treatment involving destruction or recovery. Sand bed filtration has been shown to be an effective method for removing residual OCAs from the raffinate (Michelsen et al., 1984). Choice of solvent used in the PDSE process should emphasize low aqueous solubility to minimize losses in the raffinate. In addition, coalesced recovered oil could be reconstituted into aphrons to provide the necessary mass transfer properties.

5.0 Conclusions

The application of predispersed solvent extraction for the removal of trace-dissolved chlorinated solvents from large quantities of ground water appears technically feasible based on the results of exploratory research presented here. The following conclusions seem warranted:

- A reliable experimental method for the distribution coefficient determination of chlorinated organics in organic solvent/aqueous systems has been developed. PCE and TCE among other chlorinated contaminants of concern exhibit favorable distribution coefficients in a variety organic solvents including environmentally friendly decane and soy bean oil solvents making extraction a feasible alternative.
- Soy bean oil and decane/dodecane solvents can be used with a variety of surfactant chemistries to formulate OCAs which exhibit fair phase separation qualities although a "metastable" OCA formulation could not necessarily be achieved.
- Developing an OCA dispersion that phase separates efficiently is dependent on elimination of the <15

micron size range and generation of a larger number of sizes in the >40 micron range. This is determined by agitation (shear) properties during generation as well as the concentrations and types of surfactants used in formulation.

- Dispersion destabilization for accelerated and enhanced solvent recovery purposes can be achieved with very low doses of high molecular weight, medium-high charge density cationic polymers. Chemical addition with CGA flotation increases phase separation performance over (1) simple flotation settling with and without CGA flotation assist and (2) flocculation/settling alone.
- The presence of OCAs in the aqueous phase suppresses volatilization losses and toxic nature of contaminants, concentrating and immobilizing them in the oil phase for further treatment in above-ground handling.
- Chlorinated solvents concentrated in PDSE extract can successfully be degraded with CO-Dehydrogenase. This technique may compete with other energy-intensive degradation treatments like hazardous waste incineration.

6.0 Recommendations

Further PDSE process development studies should be conducted to ensure process feasibility for this groundwater application. These should focus on the following:

- formulation testing and phase separation studies with other solvents with higher contaminant distribution coefficients and low aqueous solubility to minimize the solvent requirement and subsequent losses to raffinate
- development of a mechanical OCA generation method exerting tighter control on the shear field to eliminate the <15 micron size range thus ensuring better phase separation and flocculation
- a better understanding of how various surfactant chemistries affect formulation to enable the creation of OCA dispersions which exhibit better phase separation characteristics
- development of a better experimental protocol to examine the process feasibility of and to what extent enzyme treatment can be used as a final treatment step and to control nondegradative losses

- experimentation with heterogeneous formulations of OCAs with different solvent phases targeted to specific contaminants in a complex waste matrix for efficient removal of all these contaminants
- pilot-scale studies of the conceptual process layout to examine the continuous extraction contacting/processing method as well as process feasibility for scale-up
- completion of an economic analysis to evaluate competitiveness with conventional ground water treatment processes for the same applications

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Appendix A.

Surfactants and corresponding manufacturers of surfactants used in the formulation studies.

- NaDBS (D-40), Biosoft
- Tergitol, Union Carbide
- Macol 35, PPG Industries Inc.
- Ethofat, Akzo Nobel Chemicals Inc.
- Merpol A, DuPont
- SMAZ/TMAZ series, PPG Industries Inc.
- Armak 1689, Akzo Nobel Chemicals Inc.
- Dufax, Durkee
- Armeen C, Akzo Nobel Chemicals Inc.
- Poly-Step A7, Stepan Company