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COLLECTION OF PAPERS RELATED TO TREATMENT OF CONTAMINATED SOIL AND WATER

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COLLECTION OF PAPERS RELATED TO TREATMENT OF CONTAMINATED SOIL AND WATER

by

**Emergencies Engineering Division
River Road Environmental Technology Centre
Environment Canada**

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Table of Contents

Treatment of Soil Contaminated With Heavy Metals

Recent Applications of Environment Canada's Mobile Enhanced Oxidation Unit

**Efficacy of Steam Stripping in the Removal of Dichloromethane
From Groundwater**

**Selective Removal of Metal Ions From Groundwater by Polymeric
Binding and Microfiltration**

Oil Spill Sorbents: Testing Protocol and Certification Listing Program

The Separation of Stable Water-in-Oil Emulsions

**A Comparison of Steam Stripping and Air Stripping for the Removal of
Volatile Organic Compounds From Water**

**Removal of Petroleum-Derived Hydrocarbons From Contaminated
Soils by Solvent Extraction.**

**Removal of Arsenic From Groundwater Using Reagent
Binding / Membrane Separation**

RASSEMBLEMENT D'ETUDES CONCERNANT LE TRAITEMENT DES EAUX ET DES SOLS CONTAMINES

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TABLE DES MATIERES

Traitement de sol contaminés avec des métaux lourds

Applications récentes de l'unité mobile d'oxydation avancée d'Environnement Canada

Efficacité de la distillation à la vapeur afin d'extraire le dichlorométhane des eaux d'écoulement

Recouvrement sélectif d'ions métalliques des eaux d'écoulement à l'aide d'un traitement au polymère suivi d'une microfiltration

Adsorbants pour les déversement de pétrole: protocole d'étude et programme de certification

Séparation d'émulsions stable d'huile et d'eau

Comparaison de la distillation à la vapeur vs volatilsation afin de recouvrir les carbones organiques volatiles de l'eau

Recouvrement d'hydrocarbures dérivés du pétrole à partir de sols contaminés par extraction à l'aide de solvants

Recouvrement d'arsenic des eaux d'écoulement utilisant un traitement au polymère suivi d'une séparation par membrane d'ultrafiltration

**Treatment of Soil
Contaminated with Heavy Metals**

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INTRODUCTION

Soil contamination has become a serious problem and has attracted a lot of attention in North America. Treatment of contaminated soil is used extensively in Europe and has become important in North America in the recent years¹. The number of contaminated sites requiring urgent attention in Canada and United States is increasing which calls for efficient and cost effective treatment methods.

Environment Canada's Emergencies Engineering Division (EED) has recently conducted research on the methodology and the feasibility of soil remediation. The main objective of this study has been to develop and propose a process train for remediation of a soil contaminated with heavy metals and PCB's, along with the treatment of the wastewater resulting from the process. As far as PCB's are concerned, a suggestion on where the process train should include a PCB removal step has been provided. Figure 1 demonstrates the general outline of the approach adopted in this study for the treatment of contaminated soil.

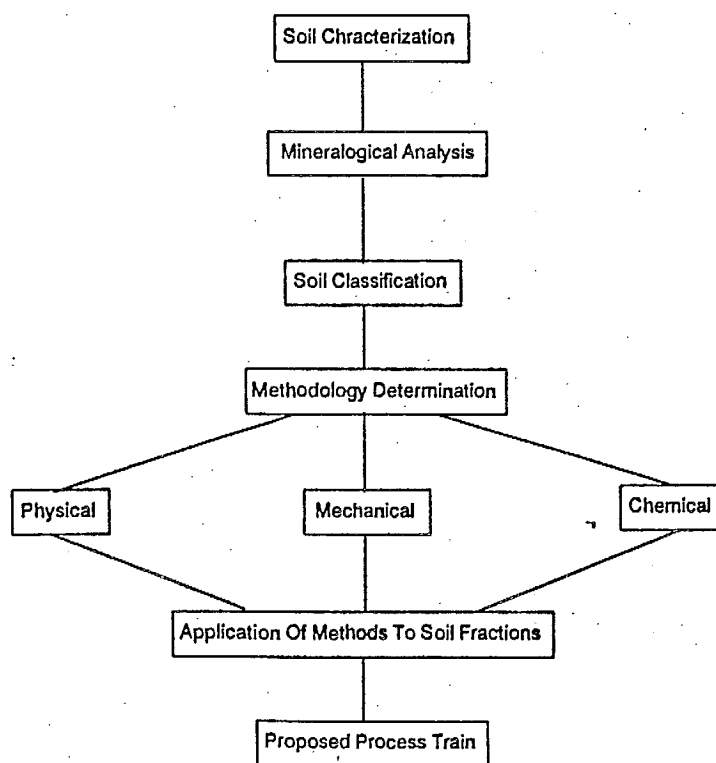


FIGURE 1. General outline of the approach adopted for soil treatment.

The site under investigation is a property of the Ministry of Transportation of New Brunswick which has been used as a scrapyard and storage for batteries and transformers. The soil is contaminated with PCB's (mainly A1260) and heavy metals such as copper (Cu), lead (Pb), zinc (Zn) and cadmium (Cd). The heavy metals are mostly in the form of metallic solids which exist in a wide range of sizes.

There are a wide variety of methods available for soil treatment. Unfortunately no specific universal method can be applied due to the diverse geological/physical characteristics of soil and nature of the contaminants contained in the soil matrix. Both the mineralogical characteristics and the metal concentration of the soil must be considered when evaluating methods for soil treatment.

The Canadian Council of Ministers of the Environment has recommended interim standards for environmental quality criteria for contaminated sites. The remediation criteria has set the acceptable concentration of metals for commercial and industrial sites at 20 ppm for cadmium, 500 ppm for copper, 1000 ppm for lead and 1500 ppm for zinc². In order to meet these standards, different methods such as physical, mechanical, chemical and their combinations have been investigated and compared. It should also be noted that due to the non-homogeneous nature of the test soil, the results and efficiency of the treatment methods were evaluated with respect to each sample tested.

Rinse waters resulting from the soil treatment process are highly contaminated with heavy metals with concentrations as high as several grams per litre. To meet environmental requirements, these metals must be removed before discharging into the environment. For this reason, any method applicable for treating waste water containing heavy metals can be used. A few established methods are reagent precipitation, ion exchange, electrodialysis and solvent extraction. Reagent precipitation (via neutralization) may be chosen for its low cost and relative simplicity.

The use of membrane technology has the potential to concentrate the final wash water produced from the soil washing (post precipitation and neutralization phase) process. The final wash waters may contain heavy metals in concentrations not acceptable for discharge. It is anticipated that the use of membranes may produce a permeate free of heavy metals which would meet discharge regulations. The concentrate from the membrane portion of the soil washing project could be reintroduced back into the process where the heavy metals could be precipitated and removed. The primary purpose of the membrane system would be to improve the efficiency of the treatment process and ensure that the large volume of water, used in the wash process, could be processed for recycle or discharge. The use of polyelectrolytes could be investigated for their ability to capture the heavy metals in a large matrix. This would enhance the rejection of the membrane and gain added volume reduction without compromising the quality of the permeate.

PROCEDURES

The details of the experimental conditions have been explained with the results. More details about the description and application of the methods listed below can be obtained from special literature in the areas of hydrometallurgy, mineral processing and wastewater treatment. The procedures and analytical methods used are as follows:

Soil Treatment

- dry classification;
- wet classification;
- attrition (wet and dry);
- acid leaching (AL);
- flotation;
- density separation (gold table/gravity table and air table);
- magnetic Separation;
- electrostatic separation;

Wastewater Treatment

- reagent precipitation;
- membrane separation.

Analytical Methods

- Scanning Electron Microscopy using Energy Dispersive X-ray Analyzer (SEM/EDX);
- digestion of the soil samples with aqua regia (1:3 v/v mixture of 70% HNO₃ and 37% HCl);
- Atomic Absorption Spectroscopy (AA).

RESULTS AND DISCUSSION

In the search for the most efficient and effective method for remediation of the test soil, several different methods were performed and compared. Tests were carried out on the raw soil (without classification) and on the fine and coarse fractions of the soil. The methods used were chemical, mechanical, physical and their combinations.

Soil Treatment

Mineralogical analysis and dry classification

A mineralogical analysis of the soil sample was carried out by Mineral Science Laboratories at the Canada Centre for Mineral and Energy Technology (CANMET). Polished sections were prepared from each fraction of the soil and mineral species were determined via ore microscopy and electron microscopy. The general phase characterization and identification of metal carriers were mainly based on SEM/EDX³. The purpose of the analysis was to determine the physical characteristics of the soil, metal carriers and the physical form in which the metals appear (eg. silicates, salts, metallic solids). Figures (2 - 5) show the nature of the metallic particles and the soil matrix. The metal contaminants of major concern were lead, copper, cadmium and zinc. These metals mostly existed in the form of metallic solids. These metallic solids, especially lead and copper were abundant in all the fractions of the soil.

According to the mineralogical analysis the average metal concentration of the soil sample was 21500 ppm Cu, 30 ppm Cd, 12600 ppm Pb and 3700 ppm Zn. Copper occurred as metallic copper (~95%), copper chloride (~2%), copper oxide, silicates and alloy. Lead was present as lead metal (~95%) covered with PbO and PbCl₂, small amount of lead chloride (~2%), oxide, sulphate, and silicates. Zinc occurred as ZnFe₂O₄, zinc metal, plus minor constituents of various complex silicate mixtures³. The analysis showed that 30% of the zinc is removable and the 70% in the form of silicates, which are already immobilized, were not considered as contaminants. It is therefore important to note that not 100% of each metal present in the soil is considered as a contaminant. The dry classification of the soil sample is presented in Figure 6 which demonstrates the size range of the soil particles in each fraction. The dry classification was performed using a sieve shaker and a set of sieves with mesh sizes of 0.038-15 mm.

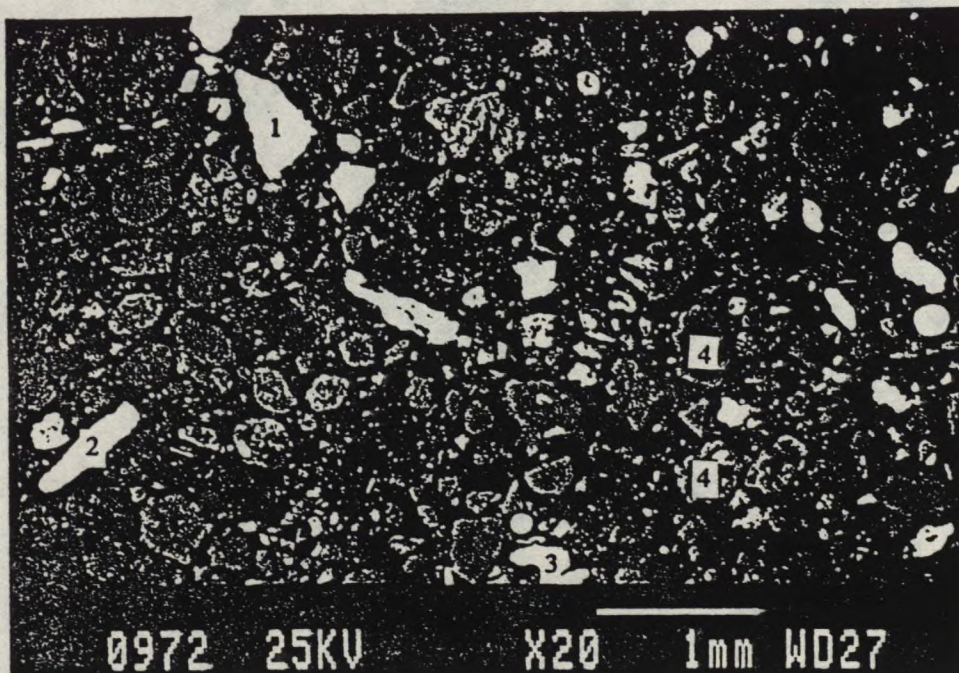


FIGURE 2. Backscattered electron micrograph showing the general mineralogy of the sample: 1- Fe_2O_3 , 2- Cu metal, 3- Pb metal, 4- silicate².

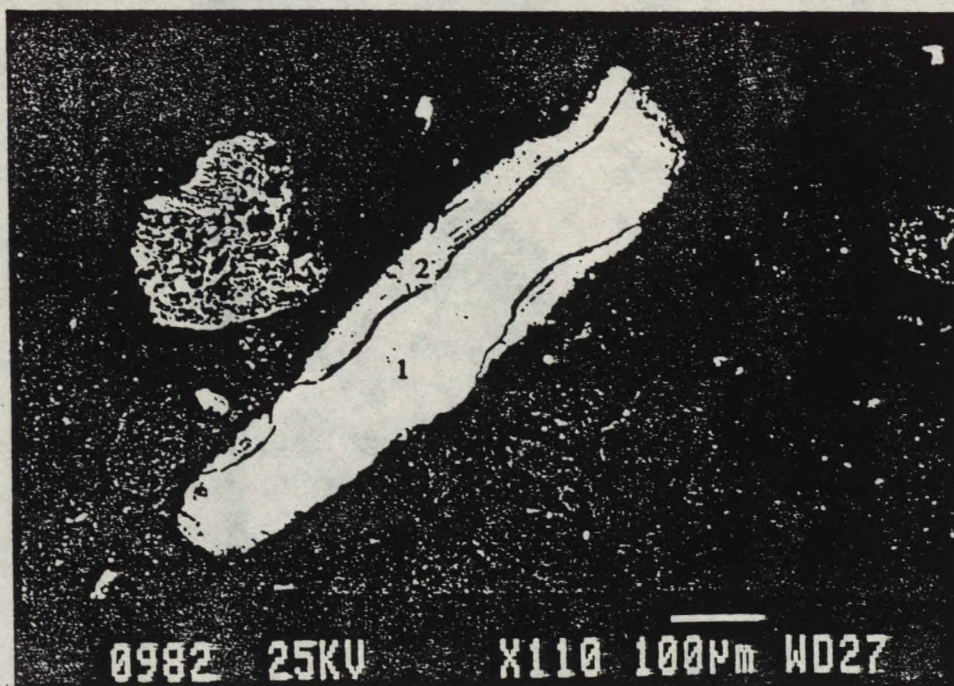


FIGURE 3. Backscattered electron micrograph showing the typical morphology of the Cu metal in the sample.
1- Cu metal, 2- Cu_2O^3 .



FIGURE 4. Backscattered electron micrograph showing the association of PbCl_2 (bright) and CuCl_2 (dark matrix).³

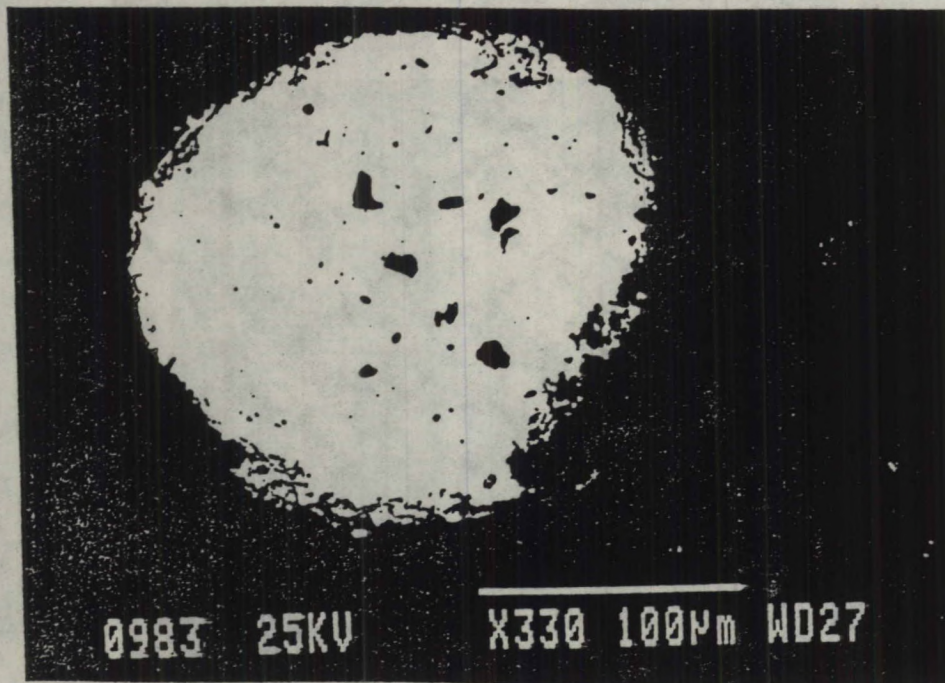


FIGURE 5. Backscattered electron micrograph showing the typical morphology of the Pb metal in the sample. The Pb metal is frequently rimmed by PbSO_4 or PbO ; quartz (sand particles) is commonly present as inclusions in the Pb metal³.

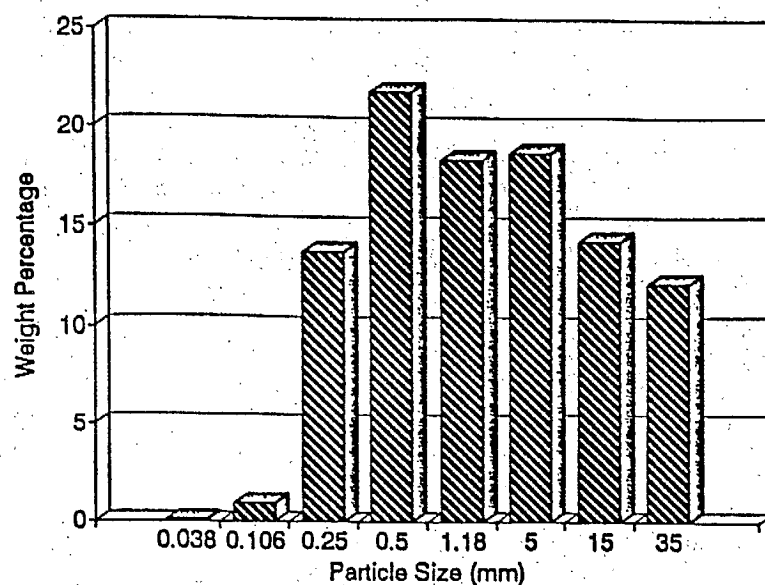


FIGURE 6 . Dry classification of the test soil.

Once the soil sample was classified into different size fractions, the metal concentration of each fraction was determined. The results of the fractional analysis of the test soil is presented in Table 1.

TABLE 1. Results of soil fraction analysis.

FRACTION SIZE (mm)	% METAL IN FRACTION			
	Cu	Cd	Zn	Pb
0.0 - 0.038	0.07	0.09	0.11	0.09
0.038 - 0.106	1.18	2.50	1.60	1.90
0.106 - 0.250	18.5	33.8	23.4	18.6
0.250 - 0.50	29.6	40.1	37.6	29.2
0.50 - 1.18	40.0	15.0	21.0	14.5
1.18 - 5	10.4	5.74	14.7	36.1
5 - 15	0.16	1.46	0.98	0.25
15 - 35	0.05	1.24	0.73	0.06

Additional analysis showed that the surfaces of the lead and copper metal pieces were coated with chlorides and oxides³. This indicates that the metallic solids in the soil were not stable under certain climatic conditions (acid rain) and would leach from the soil into the water table.

Wet Classification

A wet classification of the test soil was carried out to determine which fractions of the soil had to be treated for the maximum removal of each metal and how each fraction should be treated to obtain this goal.

The treatment consisted of attrition of the test soil for 1.5 hrs (at a propeller speed of 920 rpm and 20°C) and wet classification of the slurry. A commercial detergent was added to one of the samples to observe the effect of a surfactant on the soil structure and the metal distribution in the sample fractions. For the wet classification of the slurry, a screening and horizontal shaking was carried out using a standard shaker table. The horizontal shake was brought to a halt slowly by the reduction of the shaking speed. The process produced four fractions. Each fraction was then analyzed for its metal content.

Large copper wires and solder-like metallic solids were observed in the soil matrix. In the 1.18-4.00 mm fraction complete separation of the metallic solids was observed. In the 0.50-1.18 mm fraction an abundance of small pieces of copper wire was observed without any separation from the soil matrix. This fraction was classified into magnetic and non-magnetic subfractions by a Rare Earth Permanent Roll Magnetic Separator. Each of the subfractions were then treated with an electrostatic separator. The electrostatic separator divided each of the subfractions into conductor, middling (the term middling is used for particles having a conductivity, intermediate with respect to that of conductor and a non-conductor) and non-conductors. The various fractions obtained were analyzed for metal content and the results are presented in Table 2. The distribution of metals in the various fractions is shown in Figure 7.

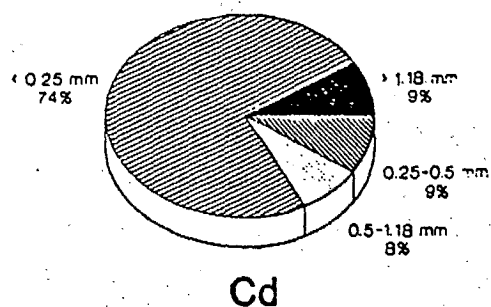
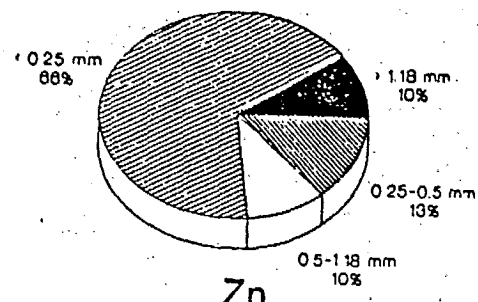
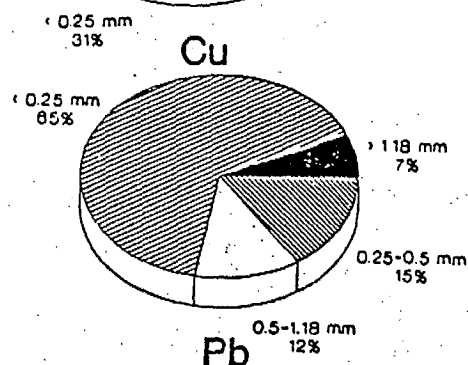
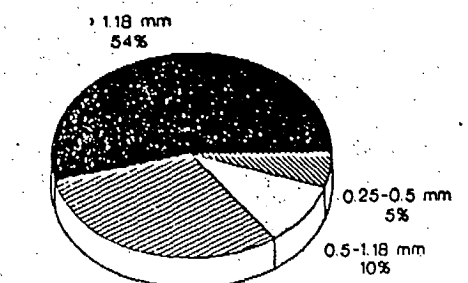
The effect of the surfactant produced an increase in the >0.50 mm fraction from 46% to 58% by weight. The surfactant weakened the forces binding the particles of all sizes together. These forces are adsorption forces, Van der Waals and London forces as well as hydrogen bonding between clay particles⁴. An increase in the removal efficiency of zinc, cadmium, copper and lead dust (in the 0.10-0.20 mm) resulted from the increase of the <0.50mm fraction obtained by using a surfactant.

Table 2 shows that the non-magnetic fraction contained 62% of total copper and 68% of total lead. The magnetic fraction contained 70% of total cadmium and 75% of total zinc. The non-magnetic fraction contained all the visible metallic solids. Therefore the electrostatic separation did not make a noticeable difference and the magnetic separation was sufficient to reduce the amount material that had to be processed.

TABLE 2. Metal distribution in the magnetic and non-magnetic sub-fractions of the 1.18-0.50 mm fraction.

FRACTION		%METAL			
		Cu	Cd	Zn	Pb
MAGNETIC	CONDUCTOR	18	20	26	37
	MIDDLING	14	34	30	7
	NON CONDUCTOR	7	17	18	12
NON MAGNETIC	CONDUCTOR	52	18	9	29
	MIDDLING	2	8	12	25
	NON CONDUCTOR	8	4	5	14

without surfactant



with surfactant

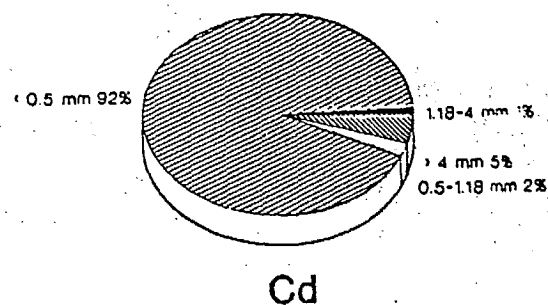
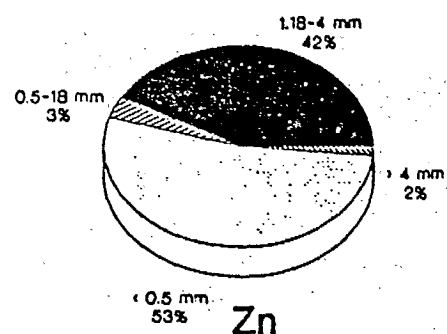
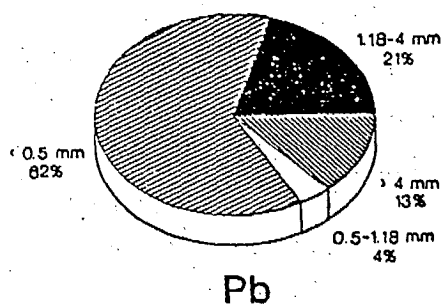
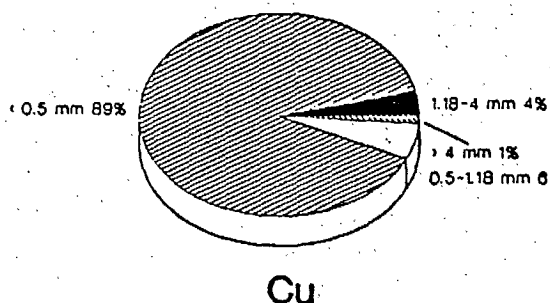


FIGURE 7. Metal distribution in the soil after wet classification, with and without the addition of surfactant.

Other Mechanical Treatment

Further mechanical separation techniques were tried on the soil sample in an effort to determine the most effective separation producing minimum waste. The soil was classified into four fractions after dry attrition. Results are presented in Table 3.

TABLE 3. Weight percentage of the soil fractions after dry attrition

FRACTION SIZE (mm)	%WT
>4.00	28
4.00 - 1.18	19
1.18 - 0.50	19
<0.50	34

The fraction >4.00 mm contained a substantial amount of solder-like metallic solids. The majority of the copper wire was observed to be in the range of 0.5-4.00 mm.

Half of the <0.50 mm fraction was subjected to wet attrition and flotation. The metallic solids in the post flotation slurry were then separated on a gold table according to density difference. The objective was to see what percentage of the sample, on the weight basis, would separate with the metallic solids. The flotation froth contained 23% of total copper, 99% of total cadmium, 18% of total lead and 45% of the total zinc which corresponded to 24% of the sample by weight.

The slurry was separated into table concentrate, table middling and table tailing using a Gold Table. These separations were based on density with table concentrate having the highest. The metallic solids were separated in the table concentrates being 18% of the total sample by weight. The table concentrate contained almost all of the metallic solids. The cylindrical shape of the copper wires interfered with the separation because the copper wires would roll down the table and separate with the middlings.

A portion of the <0.50 mm fraction was first passed through a 0.25 mm sieve. The fraction <0.25 mm had no metallic solids. The 0.25-0.50 mm fraction was then treated on an air table which also works on the principle of density difference. In the case of the air table the flow of air is upwards, unlike the gold table in which the flow of water is horizontal. Therefore the shape of the copper wires did not interfere with the separation when using the air table. The air table successfully separated the metals and concentrated them into 7% of the above fraction.

The rest of the fractions were treated in the same manner. For every fraction treated the separation with the air table was more efficient. The air table was able to separate the metallic solids by concentrating them into less than 8% (as opposed to 18% when using a Gold Table) by weight of each of the samples treated.

The >4.00 mm fraction which contained a large amount of solder like solids, was crushed down to a 4.00 mm size. As a result of the crushing all the metals were flattened and completely removed by simple screening with a 4.00 mm mesh.

Acid Leaching

The acid wash was carried out at 20°C and the slurry mixed at 210 rpm for 3.5 hrs. The slurry was filtered and the sludge and filtrate obtained were analyzed for their metal content.

The soil fraction of < 1.8 mm was separated and leached with three different acids HCl, H₂SO₄, and HNO₃, at a pH of 1 in order to determine the most efficient acid for the process (Table 4).

TABLE 4. Results of soil washing with HCL, HNO₃ and H₂SO₄

ACID (0.1 N)	% REMOVAL			
	Cd	Cu	Zn	Pb
HCl	54	23	80	33
HNO ₃	39	58	50	66
H ₂ SO ₄	44	35	60	0

The most effective acid was selected based mostly on the recoveries that were achieved for Cd and Zn. This was due to the fact that AL was the key method for Cd and Zn removal. Cu and Pb removal were not the deciding factor in the acid selection because ~95% of these metals were in the form of metallic solids, which were removed using mechanical treatment.

From the three acids tested, HCl was selected for its high Cd and Pb removal and relative low cost. It is important to note that a neutralization step should follow the acid leaching step and the combined effect of the AL and neutralization would result in an increase in the salinity of the soil. To reduce the problem of salinity, acid leaching should be limited to certain fractions of the soil where it would be more effective.

Mechanical Pretreatment and Acid Leaching

Once HCl had been selected, a combination of mechanical pretreatment and AL was examined. The mechanical pretreatments applied were attrition and a combination of attrition and flotation. The attrition was carried out with water at pH 7 for one sample and at pH 4.5 for another sample at 20°C and 50°C (Table 5). After each mechanical pretreatment the samples were leached with 0.1 M HCl.

TABLE 5. Results of wash at 20°C and 50°C.

TREATMENT	% REMOVAL							
	50°C				20°C			
	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb
WATER WASH pH 7 (FINE)	71	60	64	75	43	67	63	75
WATER WASH pH 4.5 (FINE)	75	54	62	50	52	70	69	50
WATER WASH FLOTATION ACT. CARBON	-	-	-	-	52	61	46	75

The results above demonstrate that temperature and pH during pre-treatment did not play an important role in the removal efficiency. It can also be seen that a substantial amount of the metals in the fine fraction has been removed. One can assume that the fine fraction (<1.18 mm) of the soil contains almost all of the zinc which can be removed by AL. Cadmium also exists mainly in the fine fraction of the soil and can be removed very effectively by AL.

Waste Water Treatment

In all the tests the wash water from attrition and the filtrate from AL had to be treated in order to be recycled or discarded. In case of discharge the interim standards set by the Canadian Council of Ministers of the Environment had to be achieved. The standards are listed in Table 6².

The wastewater treatment tests were carried out on 100 litres of solution which was based on the expected concentrations of the metals in the actual process wastewater. The samples were neutralized and the metals precipitated. The resulting liquid phase was treated with a membrane system.

Reagent Precipitation

Results of reagent precipitation are presented in Table 7. The concentration of major contaminants (Pb, Cu, Zn) dropped from several grams to several milligrams per litre. Concentration of Cd also decreased, except in the case of calcium carbonate treatment.

TABLE 6. Interim criteria for water

INORGANIC PARAMETER	PURPOSE		
	FRESHWATER/ AQUATIC LIFE (ppb)	IRRIGATION (ppb)	LIVESTOCK WATERING (ppb)
Cu	2-4	200-1000	500-5000
Cd	0.2-1.8	10	20
Zn	600	500	1500
Na	-	-	-
Ca	-	-	1000
Fe	300	5000	-
Pb	1-7	200	100

Satisfactory metal separation was not achieved for Cd (Figure 8). Iron can be separated from other components within the pH range 3-4, which produced the precipitation of approximately 90% of this metal. Copper, lead and zinc co-precipitated at pH 4-7, thus their separation from each other appeared to be impossible.

Despite the fact that the initial metal concentrations were reduced up to several orders of magnitude, the residual concentrations were higher than discharge limits. Additional treatment was therefore required. To achieve discharge limits membrane technology was used.

TABLE 7. Metals concentrations (ppm) in wastewater before and after neutralization

METAL	BEFORE TREATMENT (ppm)	AFTER NEUTRALIZATION TO pH 7 WITH (ppm):		
		NaOH	Na ₂ CO ₃	C(OH) ₂
Cu	6,540	4.81	1.13	45.0
Cd	7.44	0.30	0.35	6.20
Pb	930	1.24	3.84	12.1
Zn	1,140	16.3	11.3	-
Fe	10,970	4.52	2.32	2.13

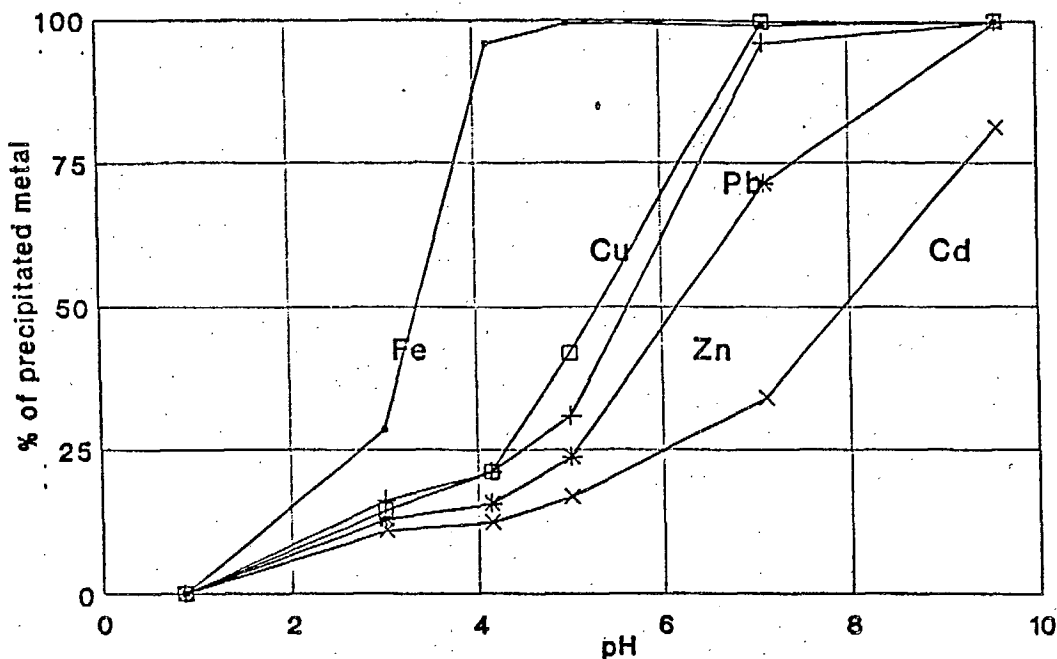


FIGURE 8. Results of the reagent precipitation of metals

Membrane Separation

The testing performed on the simulated fluid was carried out to develop a comparison of how the polyelectrolyte (polyethylene imine) affected the performance of the membrane system in its ability to separate and concentrate the heavy metals examined in this project. The membrane was arranged so that the system operated in a feed and bleed configuration and in a batch concentration mode. Both configurations were used to maximize the recovery rate while ensuring that high permeation and product quality were maintained. The test unit was loaded with a nanofiltration (NF) element. The element used was a Desal 5 2.5" x 40".

The test solution was prepared based on results obtained during the precipitation and neutralization portion of this project. From these results a 100 L solution was prepared (pH adjusted to 5.0) which contained the metals of concern. The polyelectrolyte used was polyethylene imine (MW 60000) produced by the Aceto Corp. under the name Epomine P-1000. The agent was added producing a concentration of 100 ppm in 100 L of solution at a pH of 8.5.

The solution was processed at four concentration ratios (1,2,4,8) and in a batch mode. The concentration ratio is defined as a measure of the permeate flow over the concentrate flow. Samples were taken for analysis by AA Spectroscopy to determine metal concentrations. The permeate flow was maintained as high as possible without exceeding the maximum limitation (approx. 1.6 Lpm) of the membrane.

Data from the first test indicated that the rejection values of the heavy metals ranged between 74 % to 95 %. The rejection percentage increased as the concentration increased with the maximums ranging between a ratio of 4 to 8. Rejection values for calcium and sodium are representative of the properties of the test membrane used in this project. The permeate from design would have a high sodium nitrate content due to the nature of the wash solution and the neutralization agent employed in the project. The temperature was maintained between 23° C and 25°C producing operating pressures between 180 and 260 psi for concentration ratios ranging between 1 and 8.

Data produced from the second test using Epomine 1000 gave excellent results for heavy metal rejections. The rejections ranged between 91.6 % and 99.9 % for the heavy metals at various recovery stages during the batch. The agent also affected the rejection of sodium and calcium in a negative manner. The drop in rejection was due to the agent interacting with the membrane surface and modifying its charge character. The agent has no affiliation for both these metals and thus they passed through the membrane with greater ease. The lack of pressure increase in this test verifies the passage of the salts producing a lower osmotic pressure when compared to the first test where most of the calcium and more of the sodium stayed on the concentrate side of the membrane. During this test the pressure ranged from 168 psi to 185 psi and the temperature ranged between 18.9°C to 22.2°C. Recovery rates during this test reached 95 % or a concentration factor of 20.

TABLE 8. Rejection data using polyelectrolyte

REJECTION VALUES OBTAINED FOR TEST METALS						
METAL	INITIAL CONC. (ppm)	RECOVERY %	50	75	90	95
Pb	4.97		97.8	98.4	99.1	99.2
Na	11790			0		0
Ca	563			80.5		83
Zn	3.61		99.6	99.7	99.9	99.9
Cu	1.19		91.6	99	99.5	99.7
Cd	1.2		97.9	98.6	99.3	99.5
Fe	1.12		91.4	91.4	94.2	95.4

TABLE 9. Rejection data using no polyelectrolyte

REJECTION VALUES OBTAINED FOR TEST METALS						
METAL	INITIAL CONC. (ppm)	RECOVERY%	50	67	75	86
Pb	3.83		98.5	98.5	98.5	98.5
Na	12000		9.5	26	10.4	8.2
Ca	1660		99.9	99.9	99.8	99.8
Zn	3.87		90	92	91	89
Cu	0.88		74	82	83	84
Cd	0.91		83	85	86	85
Fe	0.5		80	93	95	94

NOTE: Pb results were obtained during an independent test

Proposed Process

The following diagram shows the proposed process for removal of heavy metals and PCB's from the contaminated soil:

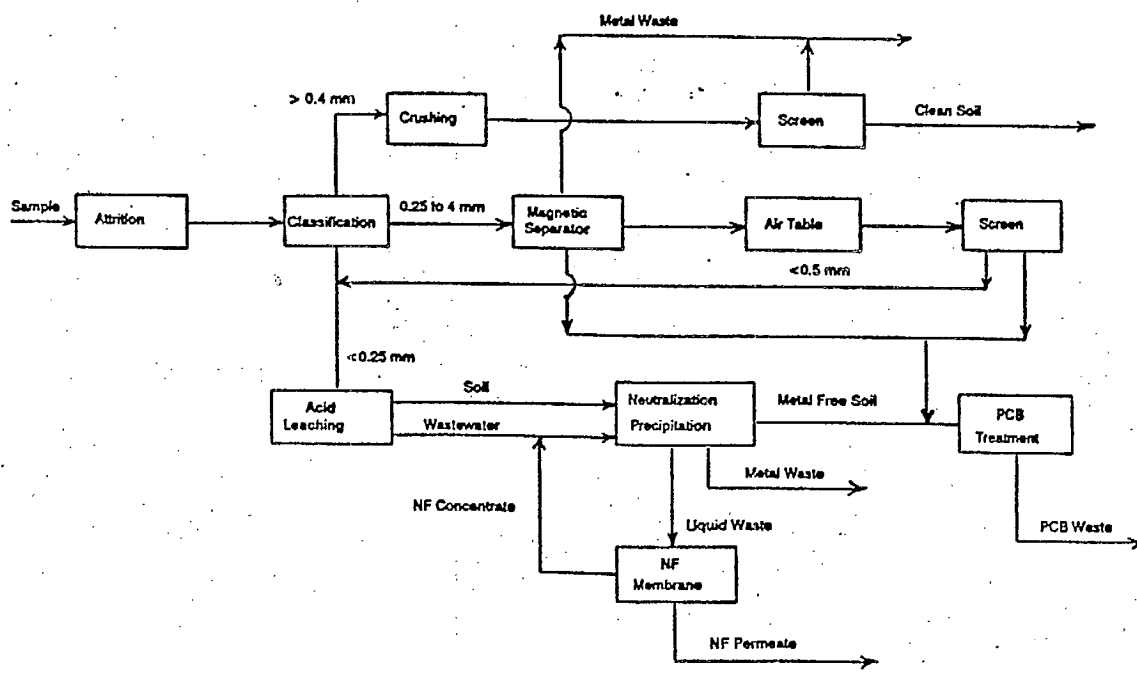


FIGURE 9. Proposed process flow sheet for remediation of soil contaminated with heavy metals and PCB's.

CONCLUSIONS

1. A process train was developed for the removal of the heavy metals from the contaminated soil. It consists of mechanical, physical and chemical treatment methods.
2. The majority of metals were removed by crushing, screening and the use of an air table.
3. Magnetic separation improved the efficiency of the process by reducing the amount of material that had to be processed.
4. Acid leaching was required to remove the heavy metals from the soil fractions less than 0.50 mm in size. When acid leaching was integrated with the mechanical and physical processes, the separation efficiency was enhanced.
5. Reagent precipitation reduced the concentration of heavy metals by several orders of magnitude.
6. Employing nanofiltration on the wastewater produced good results. High volume reduction in conjunction with good permeate quality containing acceptable levels of heavy metals, was obtained during the test.
7. The potential process train resulting from this project would incorporate the following steps:
 - attrition of raw soil;
 - dry classification;
 - mechanical and physical separation of the metals;
 - acid leaching;
 - treatment of wastewater;
 - removal of PCB's.

ACKNOWLEDGEMENTS

Special thanks to Mr. M. Raicevic from CANMET Mineral Processing Laboratory for his input in this study. The authors express their thanks to Mr. H. Whittaker, Chief of Emergencies Engineering Division, who helped organize this work and to Ms. L. Keller, also from Emergencies Engineering Division, for her valued comments.

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**Recent Applications of Environment Canada's
Mobile Enhanced Oxidation Unit**

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INTRODUCTION

The Emergencies Engineering Division of Environment Canada (EED) has a mandate to evaluate and demonstrate new and existing technologies for the clean-up of chemical spills. Most of the technologies studied are in the form of mobile systems, which can be considered as alternatives to the conventional treatment techniques frequently applied to contaminated groundwater and industrial waste streams. As regulations on environmental protection emerge and standards (The Canadian Environmental Protection Act, CEPA) are set to manage toxic substances, government agencies are encouraging treatment technologies which meet both water and air emission discharge limits. CEPA became law on June 30, 1988 and focuses directly on pollution problems on land, in water, oceans and through all layers of the atmosphere. This new legislation gives the federal government broad powers to define national standards for any substance that threatens to harm the health and/or environment of Canada and its citizens. (Jacob, 1990)

Advanced oxidation processes (AOP's) are a family of related reaction processes that result in the oxidation of organic compounds. They are quickly becoming recognized as feasible, environmentally acceptable treatment technologies for destroying harmful organic compounds in water. These technologies have been developed to the point where they have become, in many cases, more technically viable, reliable and economical than the more traditional technologies such as carbon adsorption, air stripping and biological activated sludge, which have been shown to:

- 1) Be selective in their treatment of organic compounds,
- 2) Transfer contaminants from one medium to another and/or,
- 3) Require secondary disposal of contaminants (Gossett, 1990).

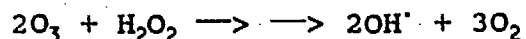
The oxidation of organic pollutants in water is an attractive method of treatment due to its ability to convert the compound to innocuous materials, such as carbon dioxide and water when carried to completion. If not carried to completion, however, partial oxidation usually results in products with enhanced biodegradability (Carey, 1990), an example being chlorinated hydrocarbons. The most common full-scale, commercially applied, enhanced oxidation processes, at this time, are those which involve the generation of the most highly oxidized species available, the hydroxyl radical (OH), as an intermediate product (Gossett, 1990). This very powerful oxidizing agent reacts with virtually all organic compounds; and therefore, greatly increases the rate of oxidation when compared to traditional oxidation processes involving oxidants such as molecular ozone, hydrogen peroxide or

hypochlorite. The rate of attack by hydroxyl radicals is typically one million (10^6) to one billion (10^9) times faster than the corresponding attack with molecular ozone. (Cater et al. 1990) The reaction mechanisms and chain reactions leading to the generation of the $\cdot\text{OH}$ radical from ozone, H_2O_2 and UV light has been described by several authors⁵⁻⁸. The three most common pathways are described by the following simplified chemical equations:

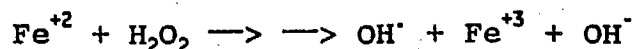
1) PHOTOLYSIS OF H_2O_2 WITH UV LIGHT



2) THE REACTION BETWEEN OZONE AND H_2O_2



3) FENTON'S EQUATION



The further reaction of the OH radical with the organic compounds in question is largely dependant on the rate constant for that reaction as listed in Table I (Glaze and Kang, 1990)

TABLE I. Rate constants for the hydroxyl radical

COMPOUND, M	$k_{m,OH}$ ($10^{+9} m^{-1} s^{-1}$)
BENZENE	7.8
HYDROPEROXIDE ION	7.5
VINYL CHLORIDE	7.1
CHLOROBENZENE	4.5
1-BUTANOL	4.2
TRICHLOROETHANE	4.0
NITROBENZENE	3.9
PYRIDINE	3.8
TOLUENE	3.0
TETRACHLOROETHENE	2.3
CARBONATE ION	0.39
DICHLOROMETHANE	0.058
BICARBONATE	0.0085
CHLOROFORM	0.005
CARBON TETRACHLORIDE	NR

Table I demonstrates that hydroxyl radicals are not very reactive towards chlorinated methane compounds. In fact, saturated aliphatics in general are quite unreactive towards the hydroxyl radical. This table also displays evidence that the carbonate and bicarbonate ions act as scavengers of the hydroxyl. (Scavenger is a term used for reactions of substances with OH radicals that do not yield species that propagate the chain reaction.)

EED's MOBILE UNIT

In 1988, EED decided to have a transportable demonstration unit designed and built for chemical spill clean-up. The unit (Figures 1 & 2), was originally designed to fit into the back of a 16ft cube van while having a maximum treatment flowthrough capacity of 2000 L/h. The system is equipped with three vertical cylindrical stainless steel reactors, each containing a 6kW high

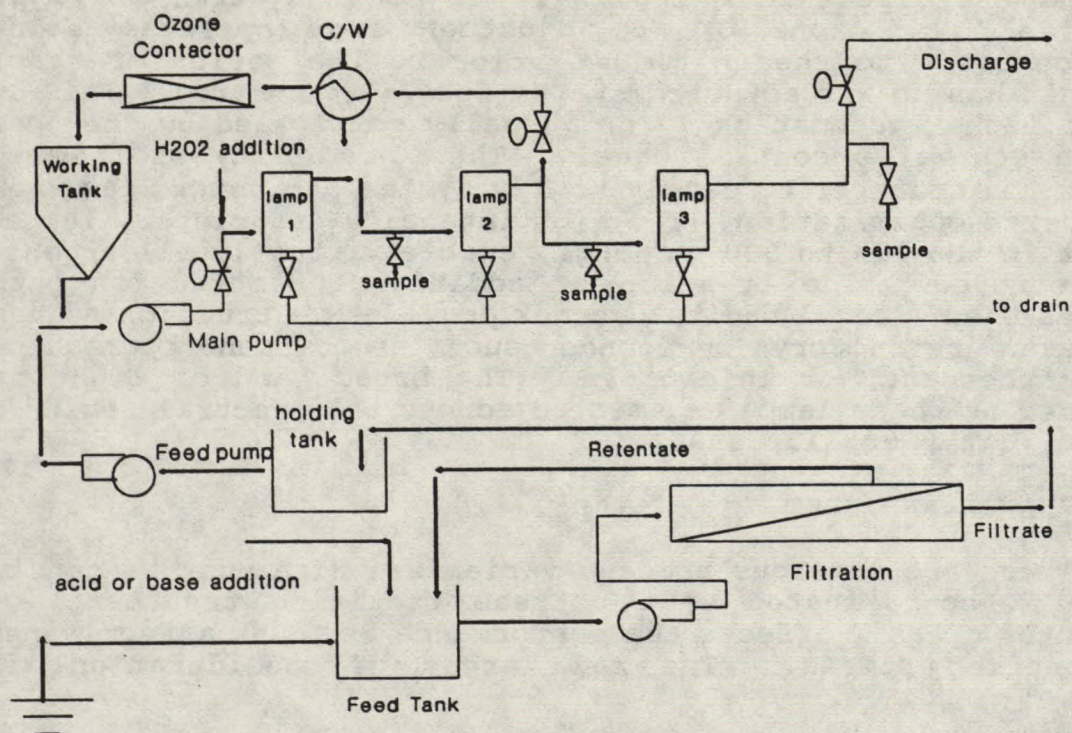


Figure 1. Process flow diagram

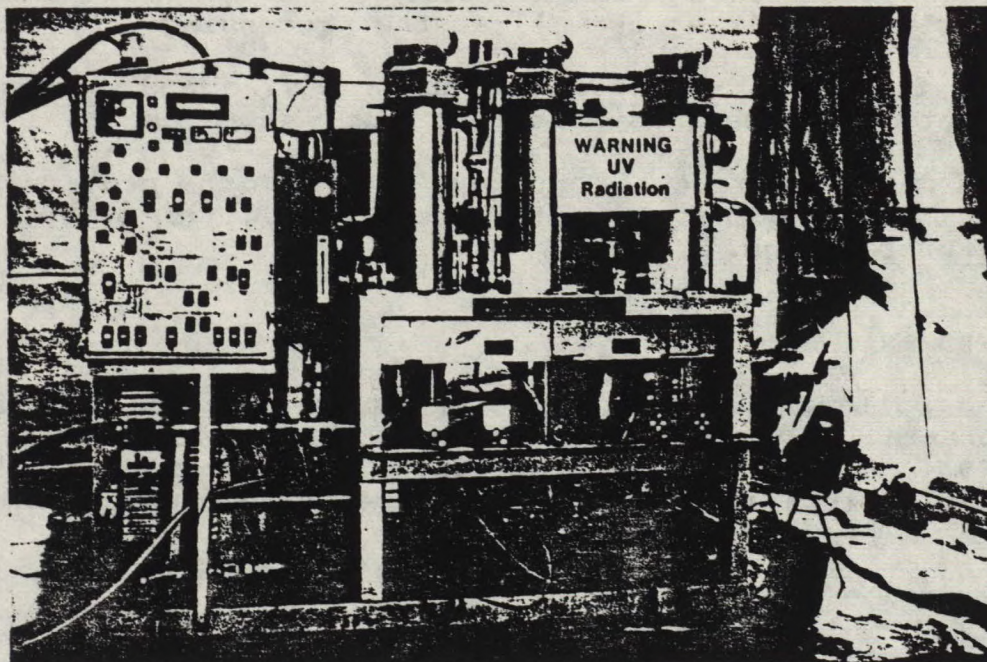


Figure 2. EED'S mobile enhanced oxidation unit

power lamp, a quartz sleeve and a transmittance controller to prevent the sleeve from fouling. Injector systems for hydrogen peroxide (H_2O_2), ozone (O_3), pH adjustment and proprietary solutions are connected to the unit just prior to the series of reactors. The unit has an air actuated system for valve control. This system can be either automatically or manually controlled by the operator from a schematic control panel. The flexibility of this system allows the operator to easily modify system parameters as required for system optimization. The high intensity proprietary lamps with output in the 195 to 300 nm range, enable virtually all organics to be destroyed. The creation of additional destruction pathways besides the hydroxyl radical attack provides destruction mechanisms for even refractory compounds such as carbon tetrachloride, trichloroethane, or chloroform. The broad band of light source provided by these lamps is emitted across the spectral region below 300 nm (Cater et al., 1990).

PERFORMANCE AND COST

There are numerous process variables which must be considered for each contaminated waste stream requiring treatment. Each parameter greatly affects the performance and cost effectiveness of the entire process. The main areas of consideration are as follows:

- 1) The nature of the contaminant - affects the choice of oxidant and catalysts; as well as, the type of UV light required.
- 2) The initial concentration - affects the amount of oxidant and catalyst required; as well as the processing time.
- 3) The flow rate - affects the number, size and design of the reactors; as well as, the lamp power to be used
- 4) The degree of removal required - affects the processing time, the number and nature of the treatment stages; as well as, the reactor design.

CASE STUDIES

The following sections of the report describe several pilot scale treatability studies carried out by EED's mobile unit between 1989-1990. Due to the confidential nature of the case studies, several site locations and company names have been omitted.

Case Study 1

This study involved a six week trial to demonstrate the use of enhanced oxidation for the treatment of groundwater and an

industrial waste stream contaminated with 1,4 dioxane at a concentration ranging between 20 and 110ppm.

The objectives of the study were as follows:

- 1) To confirm previous laboratory treatability study data for reducing dioxane concentrations in the groundwater
- 2) To evaluate both the UV/Ozone and UV/peroxide based treatment options for treating both raw and de-ionized water with each option.
- 3) To show that this technology was capable of destroying dioxane reliably and consistently.
- 4) To reduce the dioxane concentration to less than 3ppm for sewer discharge during a 24 hour pump test.

The groundwater feed to the unit was pumped both directly (raw) and via a deionization unit which removed iron and dissolved inorganic matter prior to destruction. In continuous mode the unit was operated between 19 and 114 L/min (5 and 30USgpm). During the test period, operating conditions were varied until the system was optimized. Various test configurations were examined. They involved the use of UV, Enox 450, ozone, and Enox 510 in batch and continuous mode of operation. (Enox 450 is a hydrogen peroxide based additive and Enox 510 is a water soluble rate enhancing additive which leaves no harmful residue.)

Results. Pump Test - Figure 3 illustrates the results achieved in the 24-hr pump test where the unit, operated at 75 L/min (20USgpm), reduced the dioxane level to below the target 2ppm. The three higher points were a result of the optimization process used during the tests.

Raw versus de-ionized water - The presence of iron and other dissolved inorganic matter in the raw feed resulted in lower destruction of the Dioxane in one of the wells Figure 4. These compounds absorb some of the UV light, thus inhibiting the photolysis of peroxide to produce hydroxyl radicals as well as providing competition for dioxane in the reaction with hydroxyl radicals.

Enox 510 - Figure 5 provides a comparison of two runs with and without the rate enhancing additive (Enox 510). Since the treatment objective was 0.3ppm, the small benefit was not sufficient to justify it's use.

Ozone - Unlike the non-ozone based treatment, efficiency of dioxane destruction in deionized water did not improve over that

obtained with the raw water. This is displayed in Figure 6.

Other Findings.

- 1) The system was able to reduce dioxane in either raw or de-ionized water consistently from 100ppm to <2ppm.
- 2) UV/PEROXIDE based system was a viable alternative to the ozone system with considerably lower capital costs and somewhat higher operating cost.

Recommended Unit. A UV/H₂O₂ configuration provided the best performance /cost ratio. The recommended system was designed to treat the raw feed at 760 L/min (200USgpm) from 50 to 0.3ppm and also higher concentrations at lower flow. This unit was preferred over the ozone configuration. Although the ozone system of the same

design had a slightly lower operating cost, the capital cost was higher and off-gases (ozone or possible VOCs.) would have to be treated prior to discharge.

Case Study 2

Another six week trial was carried out in February 1990 to investigate the feasibility of enhanced oxidation technology for the treatment on industrial wells contaminated with medium to high ppb concentrations of chlorinated aliphatic hydrocarbons.

The main objective of this trial was to determine the most cost effective approach to reducing the VOC concentrations to less than 5ppb at a flowrate of 23 L/min (6USgpm). The VOCs of concern and their average feed concentrations were as follows:

Compound	Concentration (ppb)
methylene chloride (MeCl, CH ₂ Cl ₂)	130-730
trichloroethylene (TCE, CHCl=CCl ₂)	9700-19900
1,2 trans-dichloroethylene (DCE, C ₂ H ₄ Cl ₂)	6000-12500
vinyl chloride (VC, H ₂ C=CHCl)	10-1010
chloroethane (EtCl, C ₂ H ₅ Cl)	10

The testing was conducted in continuous mode of operation in all cases. A steady flow through rate of 20 L/min (5USgpm) was maintained during the trial period. As described in the first case study, process parameters were varied during the testing, however, high iron concentrations and the nature of the contaminants affected several of the system parameters. By maintaining a constant pH of 3, the precipitation of iron was prevented and the system was optimized. Ozone was not included as a test parameter

Figure 3 24 HOUR PUMP TEST
JAN 31 - FEB 1

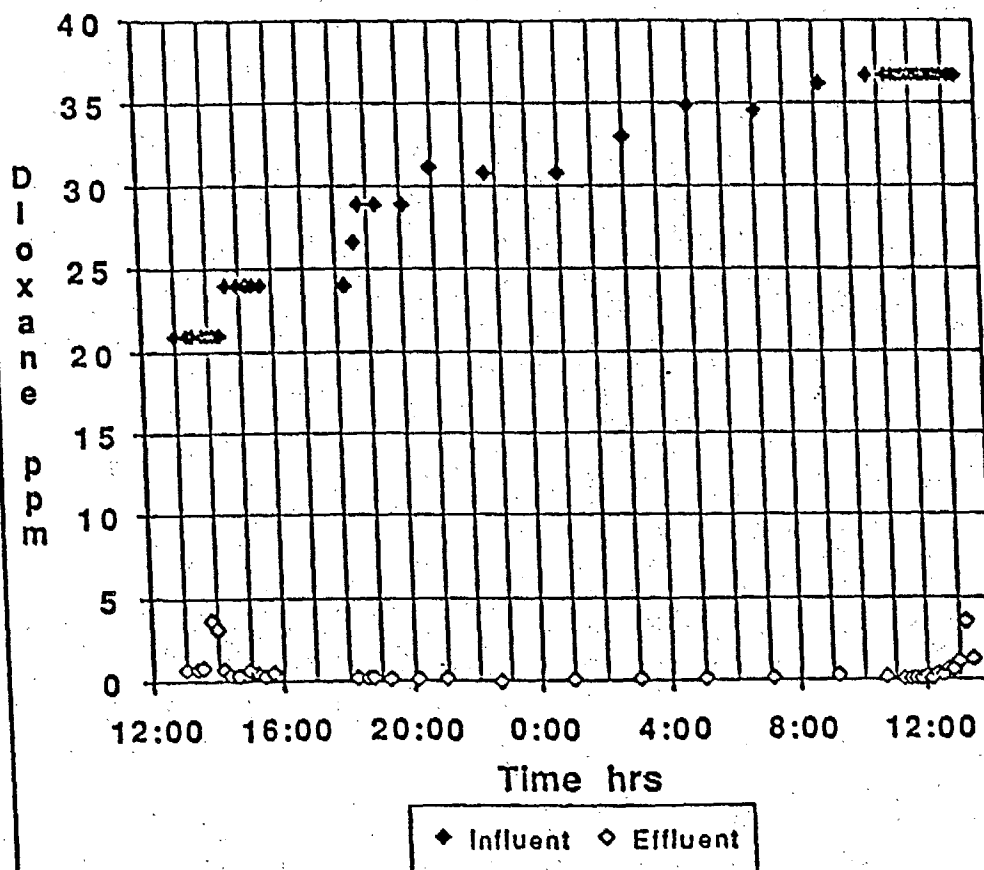


Figure 4 Comparison of Treating Raw and De-Ionized Water

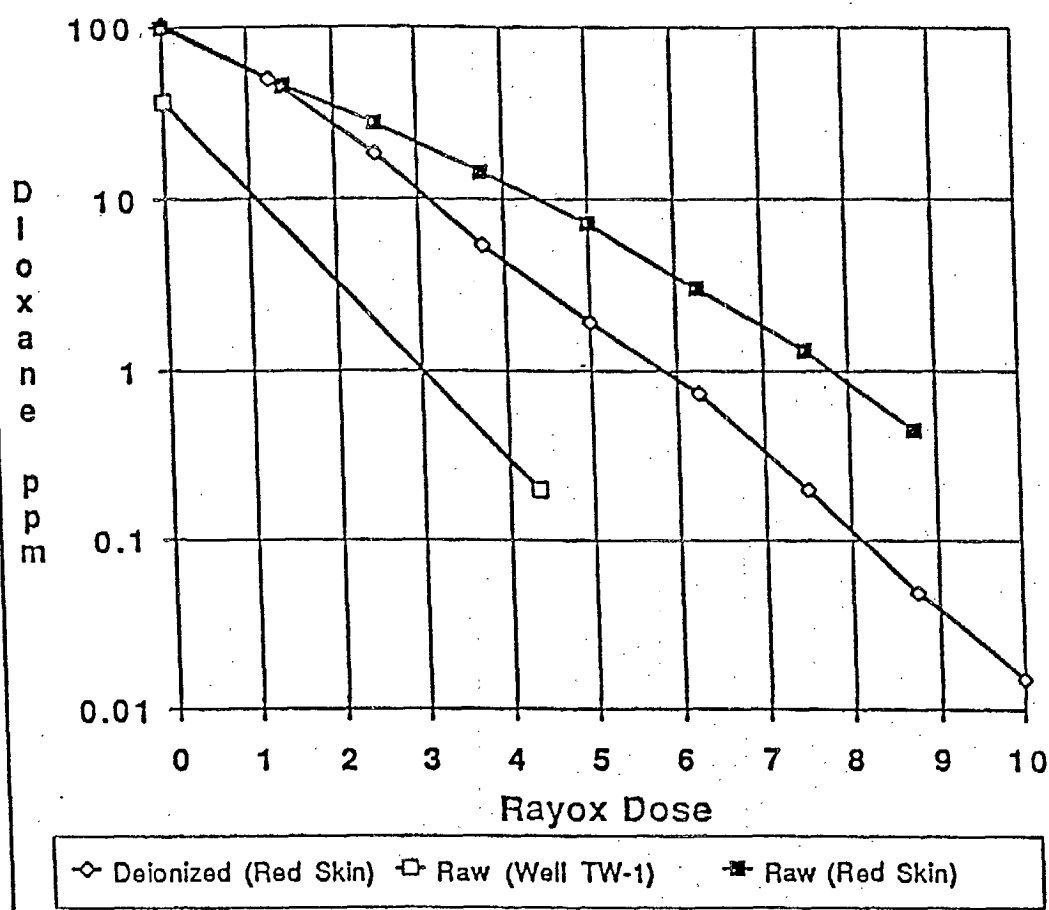


Figure 5 Effect of Enox 510 on UV/Enox 450 Treatment

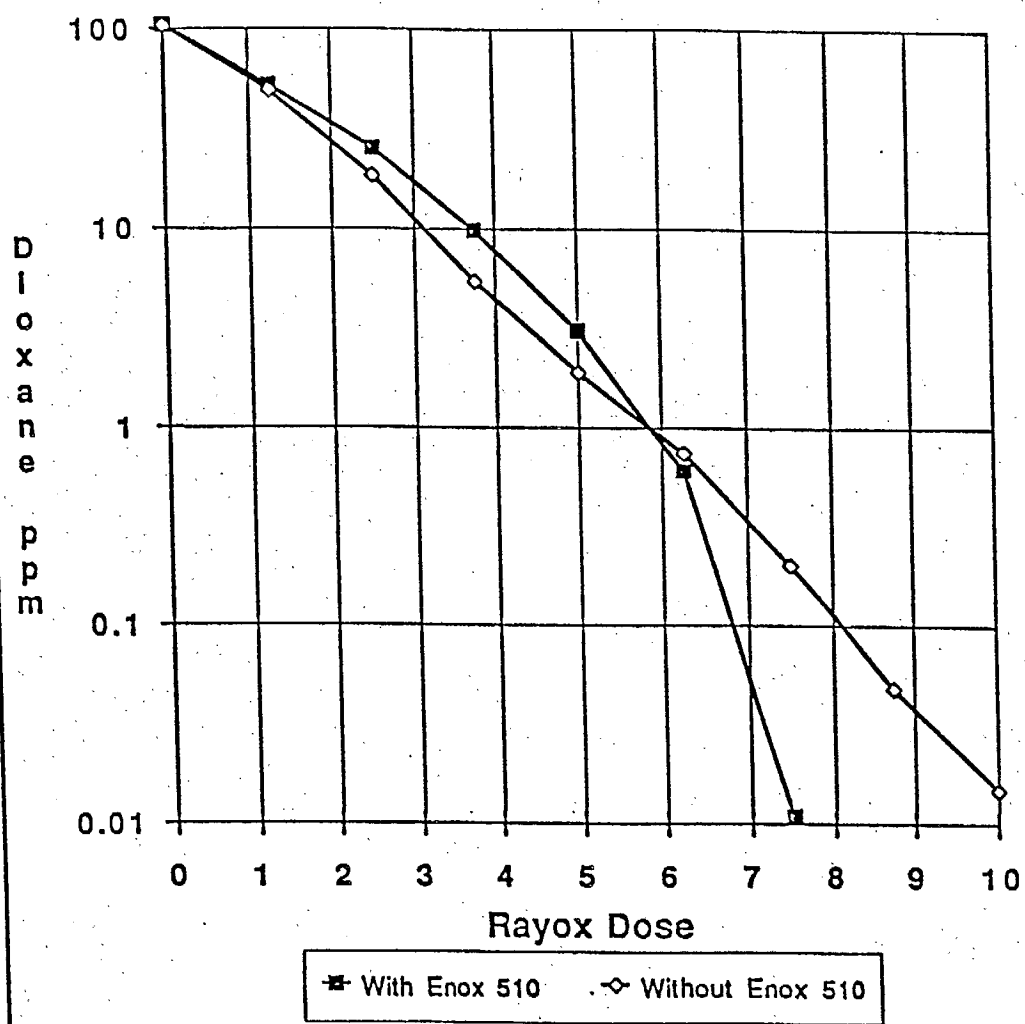
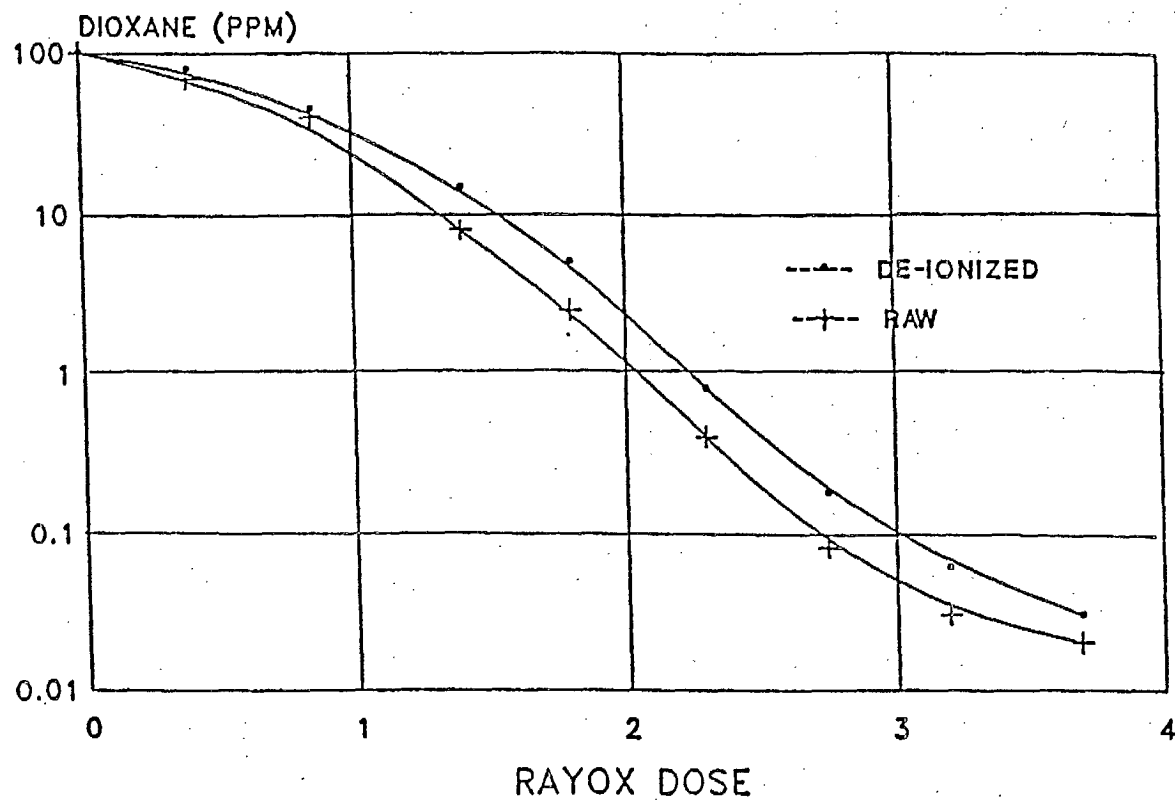


Figure 6 OPTIMUM OZONE BASED TREATMENT



due to the volatile nature of the components. Air stripping of the VOCs in an ozone /air stream would have simply transferred the contaminant from one medium to another, without destroying it.

Results. A discharge level of <5 ppb for total VOCs was achieved with the mobile unit at a continuous flow rate of 19 L/min. The individual effluent concentrations of each compound are as follows:

COMPOUND	EFFLUENT (ppb)
MeCl	3.1
TCE	0.4
DCE	<0.1
VC	0.5
EtCl	<0.3

Recommended Unit. A 40 L/min UV/H₂O₂ system operated at a pH of 3 was recommended for this groundwater stream. A baffled holding tank, with a residence time of approximately 20 minutes, was also included in the final design.

Case Study 3

The third demonstration took place during the months of May and June of 1990. This 6-week trial involved the treatment of a variety of nitrate esters (explosives) in three wastewater streams.

The main objective of this trial was to determine the most cost effective approach to reducing the concentrations of each of the compounds to <1ppm. The four compounds of interest and their influent concentrations are listed in Table II.

Table II. Influent concentrations of explosive compounds in case study 3

COMPOUND	SITE 1 INFLUENT CONC. (PPM)	SITE 2 INFLUENT CONC. (PPM)	SITE 3 INFLUENT CONC. (PPM)
NG	952-1009	N/A	1186-1212
TEGDN	N/A	3566-4630	N/A
TMETN	N/A	113-252	N/A
PGDN	N/A	N/A	277-2064

Site 1. Five runs were conducted on this water stream with various UV/H₂O₂ doses, as well as three runs with UV alone. The pH was maintained at a neutral level and the flowrates were averaged at 15 L/min (4 USgpm).

Site 2. Five waste streams were treated at this site. All streams of with compounds TEGDN and TMETN, contained high concentrations of carbonates (scavengers of the hydroxyl radical), except one. Bench-scale studies demonstrated that the carbonate could be precipitated with the use of lime. In this on-site study, however, the lime was not effective. Although UV photolysis successfully treated this stream, a more cost efficient design was investigated. This alternative involved proprietary pretreatment system to remove the carbonate without the use of lime.

Site 3. At this site, the two composite streams containing separate compounds, both contained the UV blocking carbonates and nitrates, while the two recycle streams did not. As a result, the studies were separated. The runs on the composite streams involved four different treatment process methods. A straight UV photolysis run proved effective, but uneconomical. The proprietary pretreatment/ UV/peroxide system, similar to the one studied in site 2, destroyed the compounds, but because the stream contained a higher concentration of UV blocking nitrates, it also proved to be very costly. Three runs were completed using the combination of lime/ozone, which was the recommended system from the previous treatability study. As before, lime was used to remove the carbonate as limestone precipitate. This sludge was left in the water, which had a milky colour, until after treatment of PGDN to less than 1 ppm. Thereafter, the sludge could be separated as a non-hazardous waste. These runs also involved the recycling of unused ozone from the main reaction tank into a second tank, where it could be used further.

A total of six runs were completed on the two recycle streams. A run using straight ozone was unsuccessful, while straight UV photolysis provided the required destruction at a more economical cost than with the composite streams. The runs involving the use of both UV and hydrogen peroxide, proved to be successful, as well as more economical than the straight photolysis.

Results. The discharge objective of <1 ppm was achievable with all streams tested. Figures 7-13 present the graphical results of the three site studies at their optimum operating conditions.

Recommended Unit. Table III summarizes the recommended systems and states whether or not scavengers were present in the various streams.

Table III. Recommended systems for case study 3

SITE	STREAM	RECOMMENDED SYSTEM	SCAVENGERS	pH
1-NG	----	UV/H ₂ O ₂	NO	7
2-TEGND, TNETN	composite	Proprietary pretreat./ UV/H ₂ O ₂	YES	3
	recycle	UV/H ₂ O ₂	NO	7
3-PGDN	composite	lime/ozone	YES	7
	recycle	UV/H ₂ O ₂	NO	7

OTHER CASE STUDIES

Table IV briefly summarizes several other case studies which have been carried out using EED's mobile unit. More detailed information on each of these sites is available through EED or Solarchem Environmental Systems.

Table IV. Other cases investigated with enhanced oxidation

LOCATION	COMPOUNDS	INFL. CONC. (PPM)	EFFL. CONC. (PPM)	RECOMM'D SYSTEM
GLOUCESTER ONTARIO GROUND- WATER	TCE	1.551	0.0	pH ₂ adjust/ MF/UV/H ₂ O ₂
	BENZENE	0.228	0.0	
	CHLOROFORM	0.081	0.037	
	CHLOROBENZ	0.054	0.0	
	1,2 DCA	0.012	0.0	
NEW BRUNSWICK GROUND- WATER	BENZENE	36	0.63	MF/RO UV/H ₂ O ₂ (ON CONC.)
	TOLUENE	54	0.03	
	XYLENE	28	ND	
QUEBEC, INDUSTRIAL WASTE STREAM	CN ⁻	6	2	UV/H ₂ O ₂
US SUPERFUND SITE	DCE	0.5	ND	UV/H ₂ O ₂ / ENOX 510
	DCA	5	ND	
	BENZENE	3	0.009	

* MF/RO Refers to the two membrane technologies, microfiltration

Figure 7 DESTRUCTION OF NG WITH
UV/H2O2 BASED RAYOX

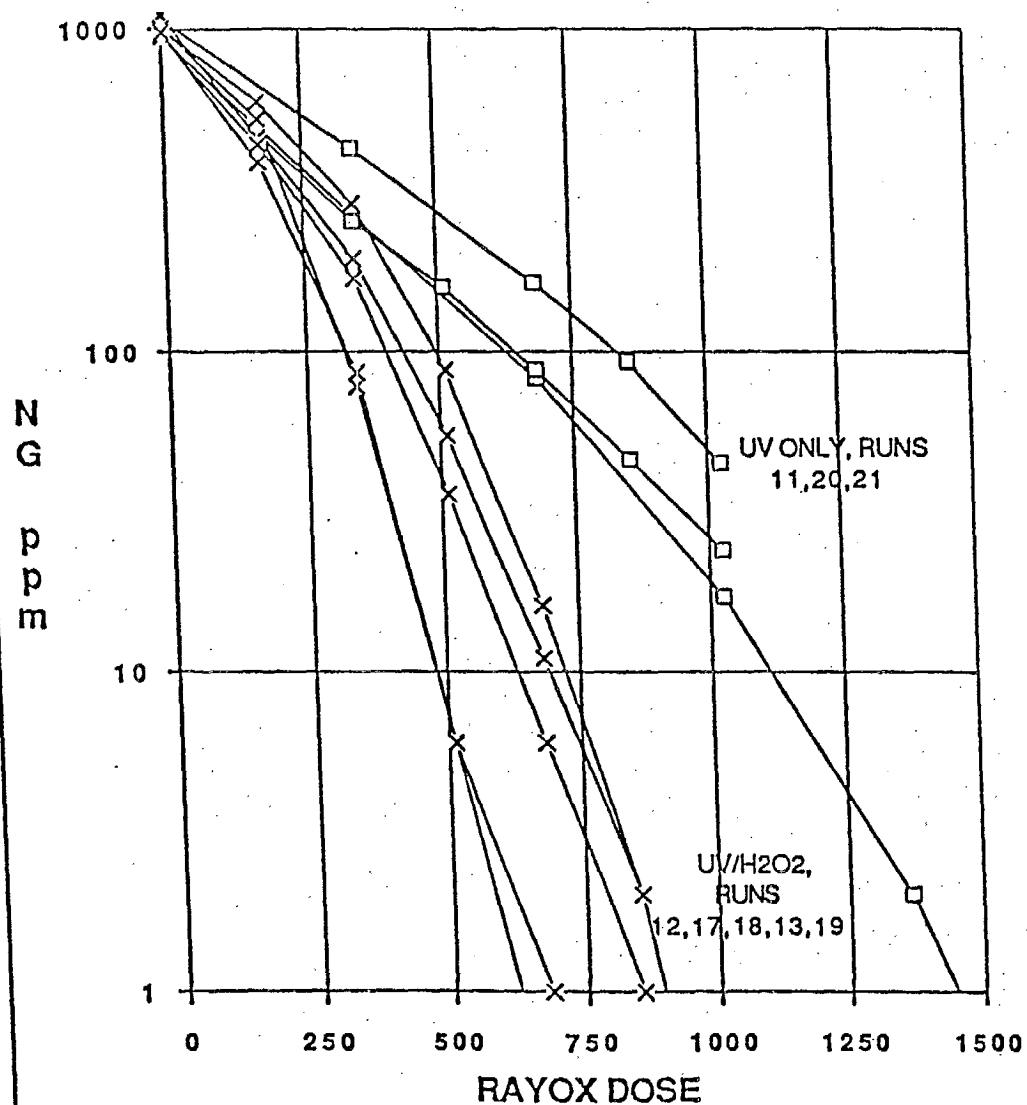


Figure 8 DESTRUCTION OF TMETN IN
COMPOSITE WATER WITH UV
BASED RAYOX

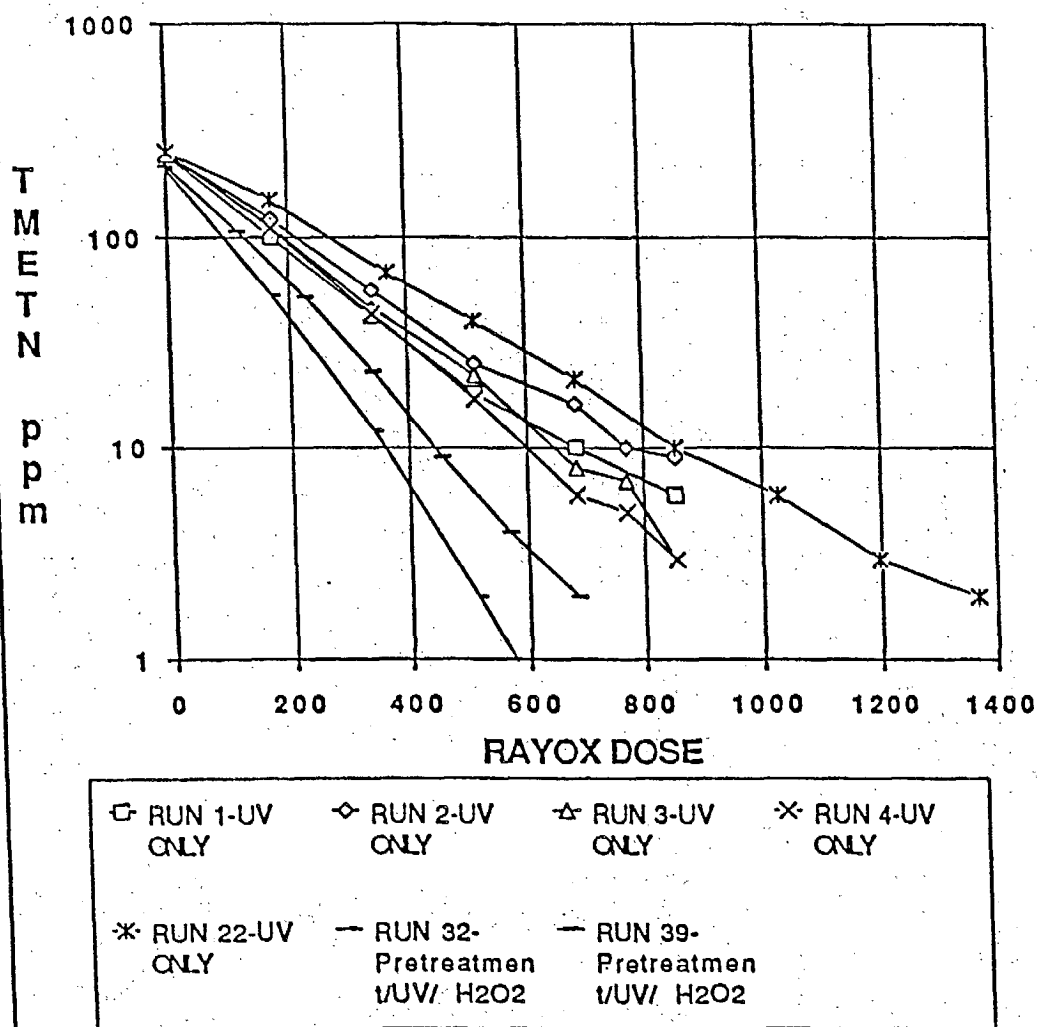


Figure 9

DESTRUCTION OF TEGDN IN COMPOSITE WATER WITH UV BASED RAYOX

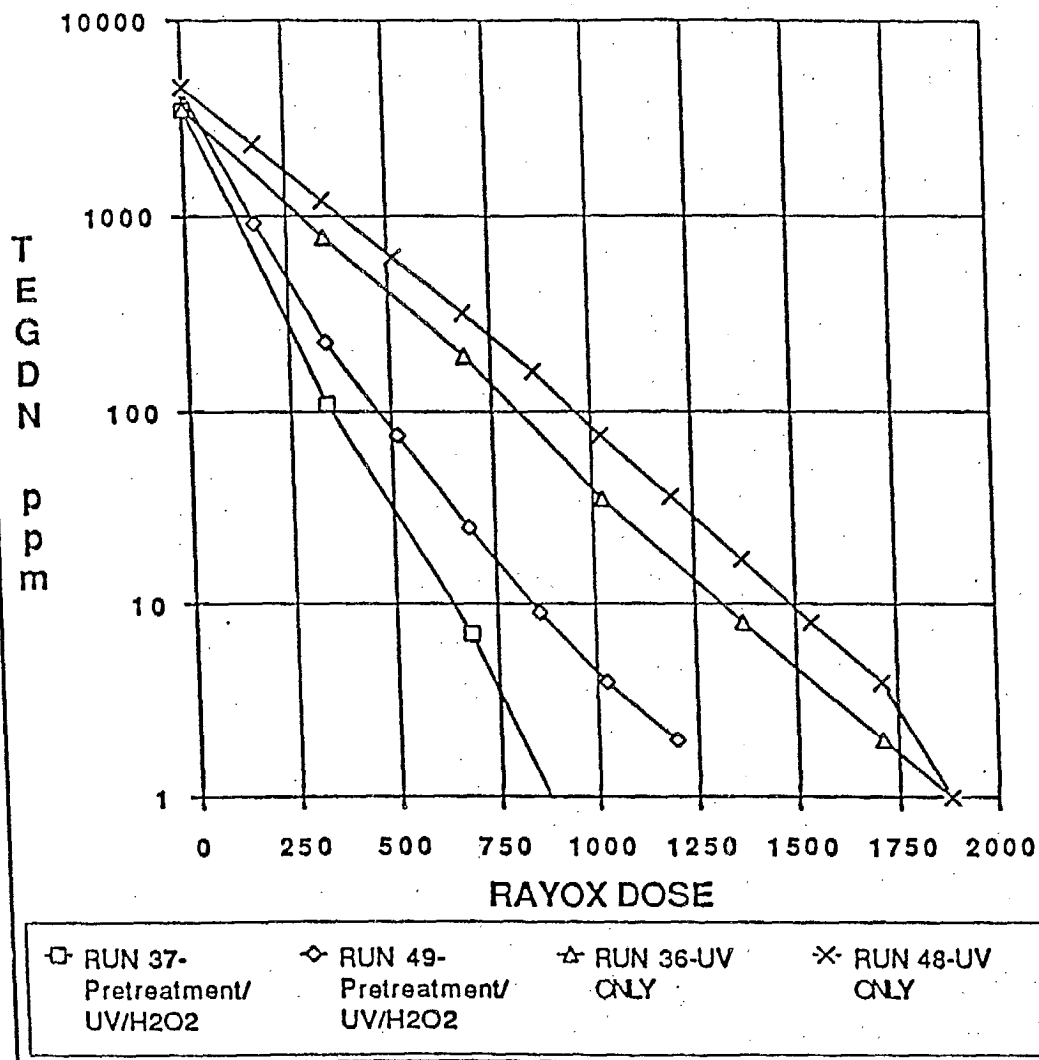


Figure 10 DESTRUCTION OF TMETN IN
RECYCLE WATER WITH UV BASED
RAYOX

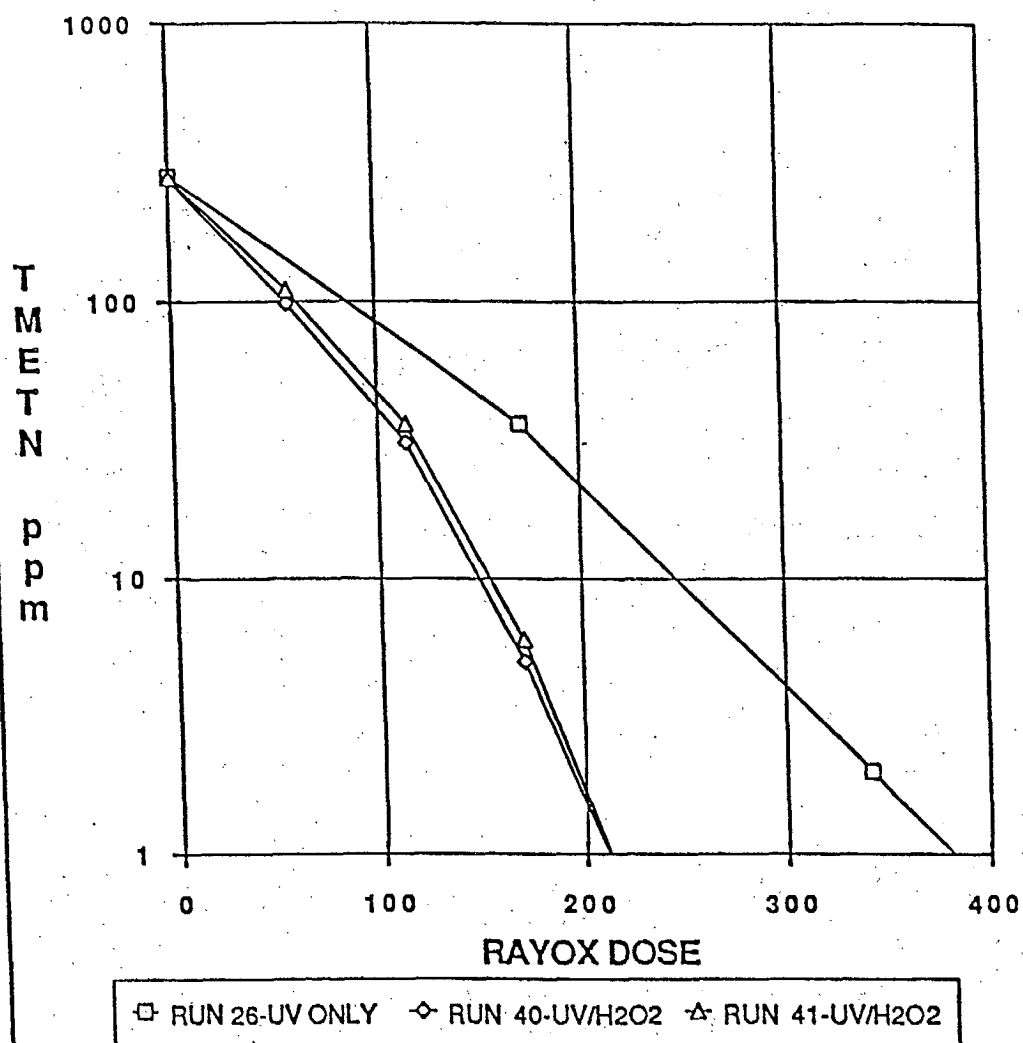


Figure 11 DESTRUCTION OF TEGDN IN
RECYCLE WATER WITH UV BASED
RAYOX

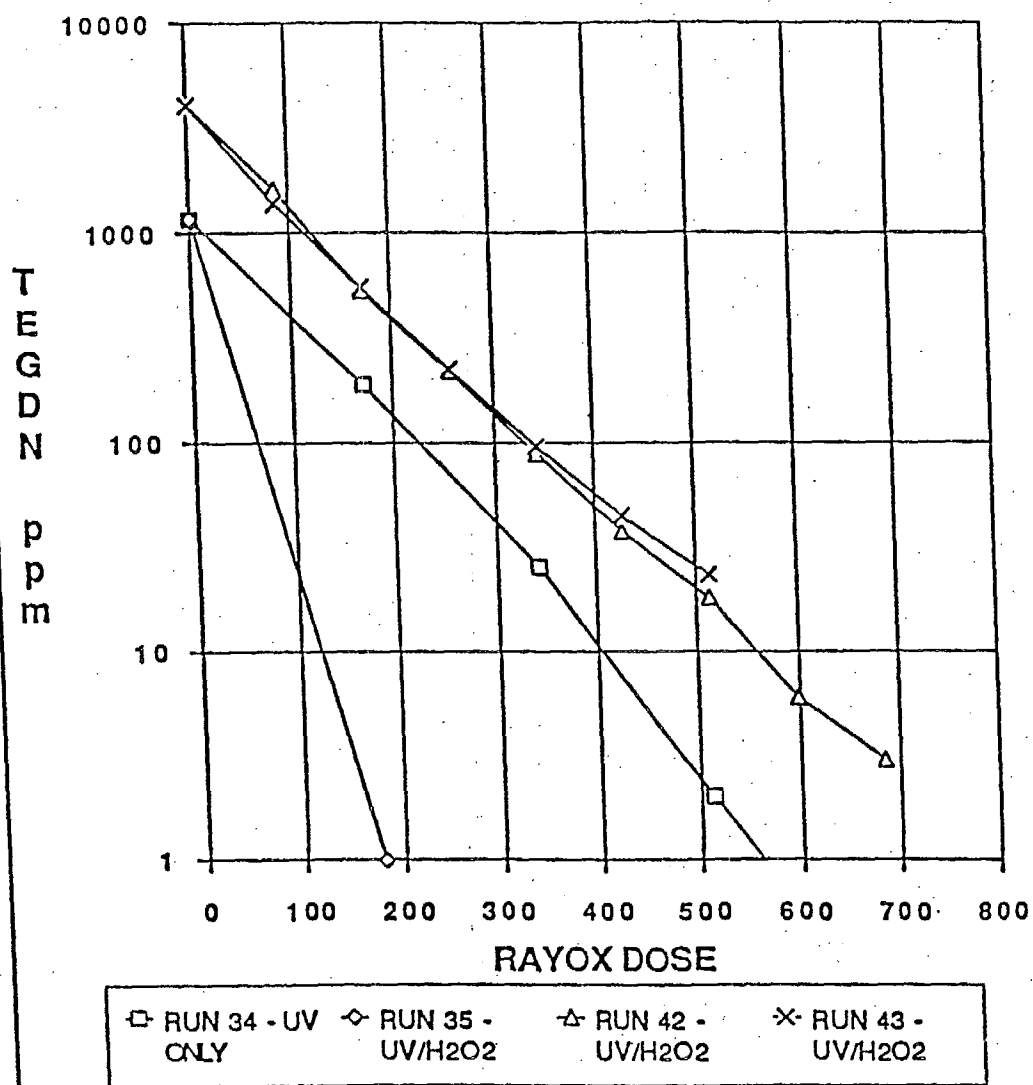


Figure 12

DESTRUCTION OF PGDN IN COMPOSITE WATER WITH UV BASED RAYOX

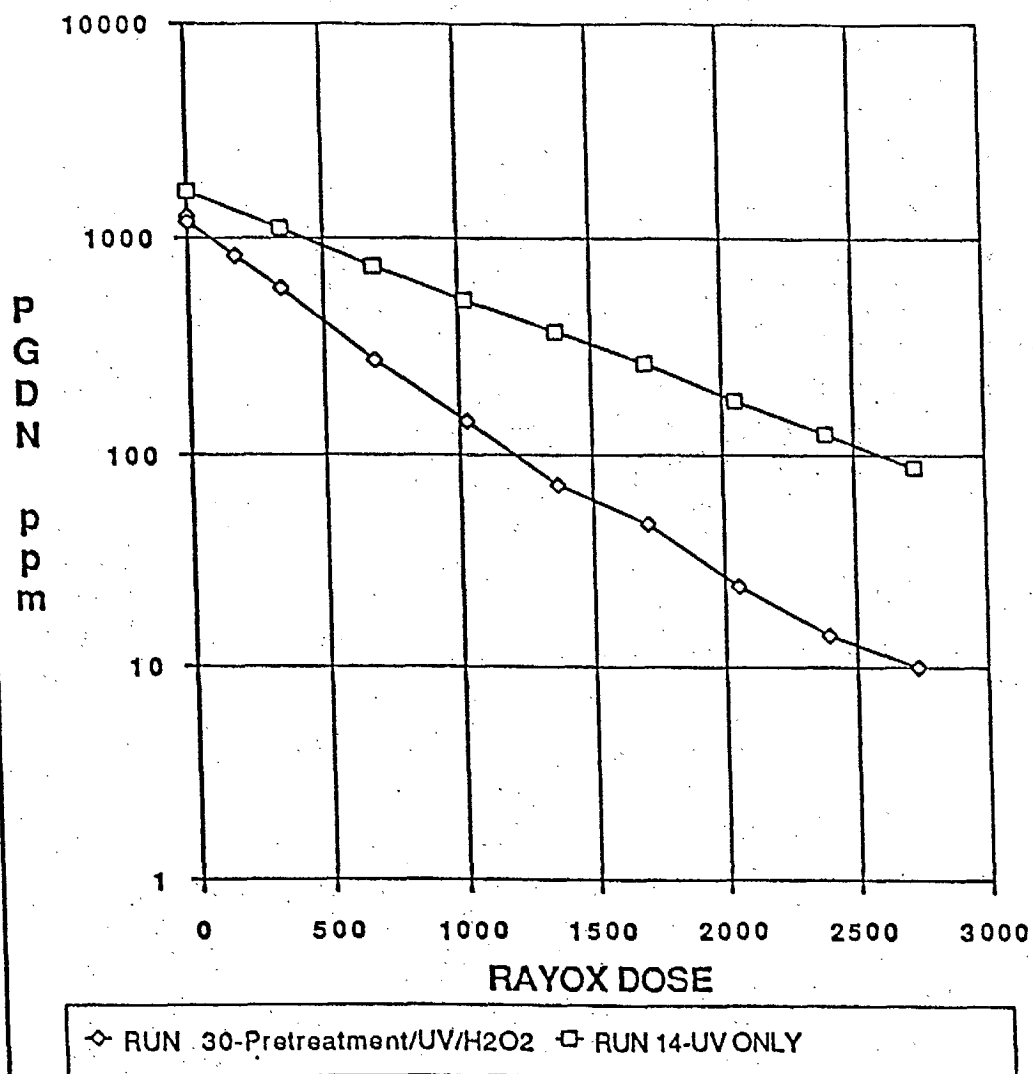
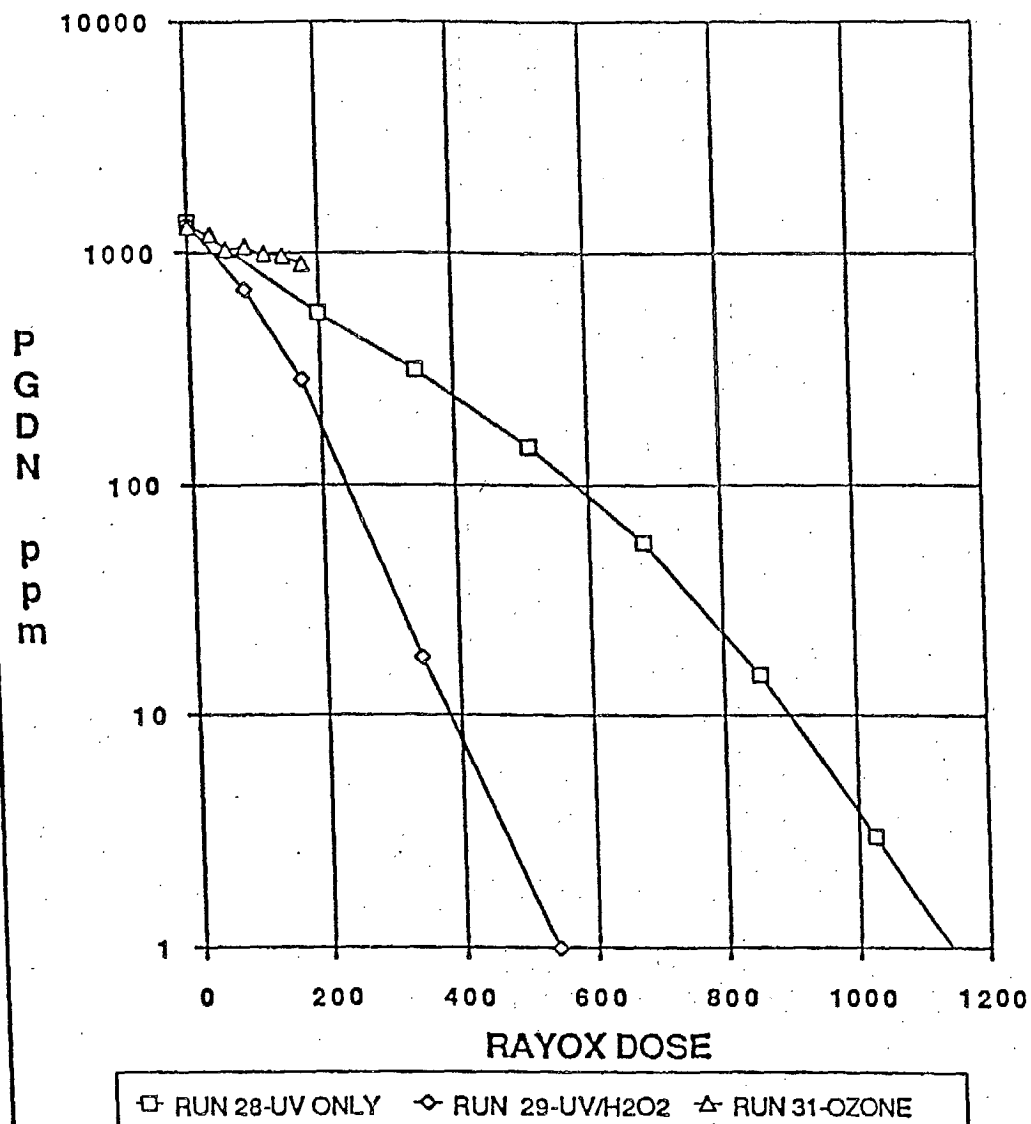


Figure 13 DESTRUCTION OF PGDN IN RECYCLE WATER WITH RAYOX



and reverse osmosis. These techniques are used to remove inorganic foulants and to concentrate organics in dilute waste streams prior to enhanced oxidation.

CONCLUSIONS

The case studies described in this report have provided the reader with an overview of the numerous applications available with the enhanced (advanced) oxidation technology. Based on the results described herein, the total destruction capability of this treatment technique provides an environmentally acceptable method for treating waste streams containing organics at concentrations below 1%. Since many waste streams require more than one technology for effective treatment, EED will continue to incorporate this technology into their process train of technologies for treatment of chemical spills.

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**Efficacy of Steam Stripping in the Removal
of Dichloromethane from Groundwater**

- Part 1 - Laboratory results
 Caroline Ladanowski & Monique Punt of Environment Canada
- Part 2 - Field results
 Caroline Ladanowski & Monique Punt of Environment Canada
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**Efficacy of Steam Stripping in Conjunction with other Technologies
for the Removal of Dichloromethane from Groundwater
(Laboratory results)**

PART 1

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TABLE OF CONTENTS

	Page
ABSTRACT	i
TABLE OF CONTENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
1. INTRODUCTION	1
2. BACKGROUND	1
2.1 Treatment capabilities of various aqueous remediation technologies for dichloromethane	1
2.2 Dichloromethane removal rates from literature using steam stripping	3
2.3 Pre-treatment	4
2.3.1 Acid addition	5
2.3.2 Reagent precipitation	5
2.3.3 Polymer treatment and membrane separation	5
2.4 Steam stripping	6
2.5 Post-treatment	8
2.5.1 Reverse osmosis	8
2.5.2 Enhanced oxidation	8
3. EXPERIMENTAL METHODS	10
3.1 Acid addition	10
3.2 Reagent precipitation	10
3.3 Polymer treatment and membrane separation	10
3.4 Steam stripping	11
3.5 Reverse osmosis	11
3.6 Analytical methods	11
4. RESULTS AND DISCUSSION	12
4.1 Acid addition	12
4.2 Reagent precipitation	13
4.3 Polymer treatment and membrane separation	16
4.4 Steam stripping	17
4.5 Reverse osmosis	22

5. CONCLUSIONS AND RECOMMENDATIONS	24
REFERENCES	25
APPENDIX A - Precipitation of calcium with sodium carbonate at 6°C	26
APPENDIX B - Precipitation of calcium with sodium carbonate at 22°C	28

ABSTRACT

Results of the laboratory scale plan for the applicability of steam stripping, in conjunction with other treatment methods, as a process to remove organic compounds, particularly dichloromethane (DCM), from contaminated groundwater at the Kert Chemicals Industries site are presented. Pre-treatment was necessary to prevent calcium from precipitating during steam stripping. For this purpose, such methods as acidification, reagent precipitation, and polymer treatment with membrane separation were investigated. Both acidification and chemical precipitation were deemed suitable for groundwater pretreatment; although acidification is preferable as it decreases the pH of the groundwater to a suitable level for discharge. Steam stripping was effective in removing more than 99% of the DCM present initially in the groundwater under certain operating conditions on a single pass. In some instances, the treated water was collected and used for a second pass through the steam stripper for further DCM reduction. The suitability of reverse osmosis and enhanced oxidation as final polishing steps to reduce dichloromethane concentration in the stripper effluent was also addressed. Reverse osmosis treatment was effective in removing only up to 49.2% of the DCM initially present in the groundwater and therefore is not recommended for post-treatment. Experiments were not pursued with the laboratory scale enhanced oxidation unit as this unit was not able to operate at the optimum temperature for DCM removal.

LIST OF TABLES

	Page
TABLE I - Treatment capabilities of various aqueous remediation technologies for DCM	2
TABLE II - Volatile organics removal rates using a field scale steam stripper	4
TABLE III - Treatment of groundwater with sulphuric acid at 6°C	12
TABLE IV - Heating of the solutions after acid treatment	13
TABLE V - Heating of the supernatant solution	16
TABLE VI - Removal of calcium using polymer treatment and microfiltration	17
TABLE VII - DCM removal from spiked tap water using steam stripping	18
TABLE VIII - DCM removal from pre-treated groundwater (BH#39) using steam stripping	19
TABLE IX - DCM removal from groundwater (BH#39) using steam stripping	20
TABLE X - DCM removal from groundwater (BH#6) using steam stripping	21
TABLE XI - DCM removal from treated and untreated groundwater (BH#6) using steam stripping	22
TABLE XII - Residual concentrations of DCM after treatment through reverse osmosis unit (mixture of BH#6 and BH#39)	23
TABLE XIII - Residual concentrations of DCM after treatment through reverse osmosis unit (BH#6)	23

LIST OF FIGURES

	Page
FIGURE 1 - Laboratory scale steam stripper	7
FIGURE 2 - Effect of H_2O_2 alone, UV alone, and H_2O_2 plus UV on decomposition of DCM at 20°C, pH6.8. Initial DCM = 53 ppm; Initial H_2O_2 /DCM = 3 (on a molar basis)	9
FIGURE 3 - Effect of temperature on decomposition of dichloromethane (DCM) at pH6.8. Initial DCM = 53 ppm; Initial H_2O_2 /DCM = 3 (on a molar basis)	9
FIGURE 4 - Precipitation of calcium with sodium carbonate monohydrate at 6°C ..	14
FIGURE 5 - Precipitation of calcium with sodium carbonate monohydrate at 22°C ..	15

1. INTRODUCTION

The Emergencies Engineering Division (EED) of Environment Canada and a chemical company in Toronto, Ontario agreed to carry out a joint project to investigate the applicability of steam stripping, in conjunction with other treatment methods, as a process to remove organic compounds, particularly dichloromethane, from contaminated groundwater at an industrial site in Toronto.

Several pre- and post-treatment methods, which may be used in conjunction with steam stripping, to remove inorganics and polish treated water were evaluated. Laboratory scale steam stripping, microfiltration, enhanced oxidation and reverse osmosis were evaluated using samples of groundwater from bore hole numbers 6 and 39. The former well had an extremely high concentration of dichloromethane (3000 ppm) with a moderate amount of calcium while the latter had a relatively lower concentration of dichloromethane (37 ppm) but a significantly higher level of calcium (485.5 ppm). Parameters were varied on the lab scale apparatus to determine the feasibility and optimum conditions of the processes investigated. In accordance with the joint project agreement, the field scale experimental plan will be determined based on the results of the lab-scale runs and discussion with the company.

2. BACKGROUND

Dichloromethane (methylene chloride), DCM, is a highly volatile, colourless liquid that is completely miscible with a variety of lipophilic solvents and is appreciably soluble in water (0.02 g/mL at 20 °C). It is used extensively as an industrial solvent, for paint stripping, as a degreasing agent and as an aerosol propellant.

Health effects induced by DCM have been studied in humans exposed to concentrations up to about 800 ppm in air. Exposure to 868 ppm induced signs of neurotoxicity, including feelings of "light-headedness," difficulties with speech articulation and hand-eye coordination impediments. Chronic exposures to DCM do not produce any demonstrable irreversible effects at concentrations up to about 500 ppm. The evidence for the carcinogenicity of DCM is inadequate in humans, but evidence from animal studies is sufficient to classify it as probably carcinogenic to man.

2.1 Treatment capabilities of various aqueous remediation technologies for dichloromethane

The United States Environmental Protection Agencies Risk Reduction Engineering Laboratory's (RREL), treatability database was consulted to determine the treatment capabilities of various aqueous remediation technologies for DCM. The maximum removal capability for various technologies at different influent concentrations is summarized in Table I.

TABLE I - Treatment capabilities of various aqueous remediation technologies for DCM

[INFLUENT]	TECHNOLOGY	SCALE	DCM REMOVAL (%)
0 - 100 $\mu\text{g/L}$	AS	full	>93.3
0 - 100 $\mu\text{g/L}$	CAC + AirS	full	92.3
0 - 100 $\mu\text{g/L}$	TF	full	77
0 - 100 $\mu\text{g/L}$	AS + Fil	full	26
0 - 100 $\mu\text{g/L}$	PACT	full	>76
> 100 - 1000 $\mu\text{g/L}$	AS	full	99.54
> 100 - 1000 $\mu\text{g/L}$	TF	full	89
> 100 - 1000 $\mu\text{g/L}$	AirS + GAC	full	>99.8
> 100 - 1000 $\mu\text{g/L}$	RO	full	66
> 100 - 1000 $\mu\text{g/L}$	GAC	full	99.00
> 100 - 1000 $\mu\text{g/L}$	AirS	pilot	99.62
> 100 - 1000 $\mu\text{g/L}$	SS	full	99.00
> 1 - 10 mg/L	AS	full	99.74
> 1 - 10 mg/L	SS	full	>99.52
> 10 - 100 mg/L	AS	full	98.4
> 10 - 100 mg/L	WO _x	pilot	99.983
> 10 - 100 mg/L	RO	full	44
> 100 - 1000 mg/L	WO _x	full	99.989
> 100 - 1000 mg/L	AS	bench	99.72
> 1 g/L	SS	full	>99.999

where

AS = activated sludge

CAC + AirS = chemically assisted clarification followed by air stripping

TF = trickling filter

AS + Fil = air stripping followed by filtration

PACT = powdered activated carbon addition to activated sludge

AirS + GAC = air stripping followed by activated carbon (granular)
RO = reverse osmosis
GAC = activated carbon (granular)
AirS = air stripping
SS = steam stripping
WO_x = wet air oxidation

and

$$\text{DCM REMOVAL (\%)} = 100 * (1 - C_e/C_i)$$

where

C_e = concentration of DCM in the effluent stream

C_i = concentration of DCM in the influent stream

2.2 Dichloromethane removal rates from literature using steam stripping

Results from Table I suggest that steam stripping can achieve DCM removal rates greater than 99% from solutions containing more than 1 ppm DCM. In fact, Branscome et al. (1987) investigated the removal of volatile organic compounds (VOCs) from aqueous waste streams by steam stripping and summarized the effectiveness of VOC removal from the waste, the air emissions from the process, and the cost of the treatment process. Short term trials were conducted at two chemical plants (Plants H and I) to determine the effectiveness of steam stripping for the treatment of aqueous waste. The operation at Plant H, which produces primarily ethylene dichloride and vinyl chloride monomer (plus 12 other compounds including DCM) treated approximately 852 L/min of aqueous waste while Plant I which produces one carbon-chlorinated compounds (including DCM and 4 other chlorinated compounds) treated approximately 42 L/min of aqueous waste. Both process streams contained about 6 g/L of VOC. The steam stripper at plant H used a tray column and did not remove solids prior to steam stripping resulting in fouling of the heat exchanger and column. Plant I used a packed column and removed the solids in a decanter prior to steam stripping. In this case, the bottoms did not need to be treated prior to discharge to the river. The sludge generated in pre-treatment may be designated as hazardous waste. The relevant results are summarized in Table II.

TABLE II - Volatile organics removal rates using a field scale steam stripper

	COMPOUND	FEED (ppm)	BOTTOMS (ppm)	DCM REMOVAL (%)
PLANT H	ethylene dichloride	5630	0.097	99.999
	chloroform	271	9.6	99.6
	DCM	1.2	<0.01	>91.16
	total VOCs	6000	9.8	99.8
PLANT I	DCM	4490	0.011	99.999
	chloroform	1270	0.006	>99.999
	carbon tetrachloride	55	<0.005	>99.991
	total VOCs	6000	<0.037	99.999

2.3 Pre-treatment

A pre-treatment method was necessary prior to steam stripping as the presence of high concentrations of calcium and dirt particulate would have caused fouling in the steam stripper and reduce its effectiveness. Scale formation occurs as a result of precipitation of minerals from the cooling water or hot heat exchange surfaces. Scale is a dense, adherent material acting as an insulator causing a dramatic decrease in heat transfer. In severe cases, water flow through heat exchangers can be reduced or cut off completely by heavy scale formation.

Calcium carbonate is the primary scale encountered in groundwater due to its relatively low solubility. The Langelier Saturation Index (L.S.I.) was developed as a simple means to determine the relative calcium carbonate scaling tendency. L.S.I. is the difference between pH of the solution (pH_{soln}) and its saturation pH (pH_{sat}).

$$L.S.I. = pH_{soln} - pH_{sat}$$

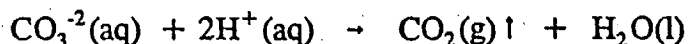
where pH_{sat} is a function of calcium concentration, alkalinity and total dissolved solids concentrations. A positive L.S.I. indicates a tendency towards calcium carbonate scale formation. The larger the L.S.I., the greater the tendency to precipitate calcium carbonate. This tendency can be reduced by either reducing pH_{soln} or increasing pH_{sat} . Calcium

concentration must be reduced in order to increase pH_{nat} .

Three methods of pretreatment were considered for the removal of calcium in the groundwater at the industrial facility: acidification, reagent addition, and polymer binding and membrane separation.

2.3.1 Acid addition

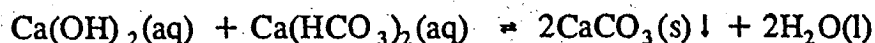
The addition of an acid, such as hydrochloric or sulphuric acid, causes the transformation of carbonate ions into gaseous carbon dioxide which are released from the solution.



In the absence of carbonate ions, no calcium carbonate can be formed; therefore, no precipitation of calcium can take place.

2.3.2 Reagent precipitation

Calcium concentration may be effectively reduced by binding calcium to insoluble compounds such as carbonate, phosphate and oxalate. The simplest method is lime treatment, where water soluble calcium carbonate reacts with calcium hydroxide forming insoluble calcium carbonate.



This method is inexpensive, but would not be effective for the treatment of groundwater from bore hole number 39. Preliminary analysis of this water indicates a high level of $Ca(OH)_2$; thus further addition of $Ca(OH)_2$ would be pointless. Treatment with sodium triphosphate, sodium oxalate or with sodium carbonate hydrate is more costly, however it is much more effective.

2.3.3 Polymer treatment and membrane separation

In some instances, calcium precipitation by acidification or reagent addition does not work; consequently new methods and/or improvements to these existing techniques must be investigated.

The hybrid process of polymer binding combined with membrane separation is a promising technology. A solution containing metals is mixed with a water soluble polymer reagent to form aggregates with the metals. The solution is then passed through a membrane apparatus, where the semipermeable membrane rejects the polymeric compounds, and freely transfers the water and salts of the remaining

unfixed metals into the permeate. The resulting concentrate is enriched by rejected metal ions, whereas the permeate contains only water and salts. This hybrid method combines the high selectivity of a chemical bond with the low energy consumption of membrane separation.

Each case must be evaluated independently as there is no universal method for scale prevention. Important parameters to be considered when choosing a method include the pH and hardness of the solution. A number of different methods must be investigated and the optimum chosen for the particular groundwater.

2.4 Steam stripping

The contaminated water is introduced either at the top or from the middle of the column of the laboratory scale steam stripper. Steam generated from the boiler enters the base of the column. As the steam rises in the column, it contacts the downwardly flowing water phase such that the volatile components are transferred from the liquid to the gas phase. The driving force for such an operation is the concentration differential between the liquid and vapour phases. The technical success of steam stripping hinges on the differences in thermodynamic properties of the two components. The steam leaving the top of the tower contains the volatile contaminants. This stream is condensed and a portion of the condensate can be returned to the column as reflux. The overhead accumulator operates as a decanter for insoluble liquids. The system is fully enclosed, apart from a vent located on top of the decanter, which allows for any vaporized volatiles in the decanter to travel into a fume hood. The section of the tower below the feed point is called the stripping section and is used to increase the purity of the bottoms product. The section above the feed point is called the rectification section and is used to further concentrate the overhead product. When the solution is fed to the top of the column, no rectifying takes place and solely stripping occurs. This situation is normally most effective with less soluble compounds. A simplified process schematic is shown in Figure 1.

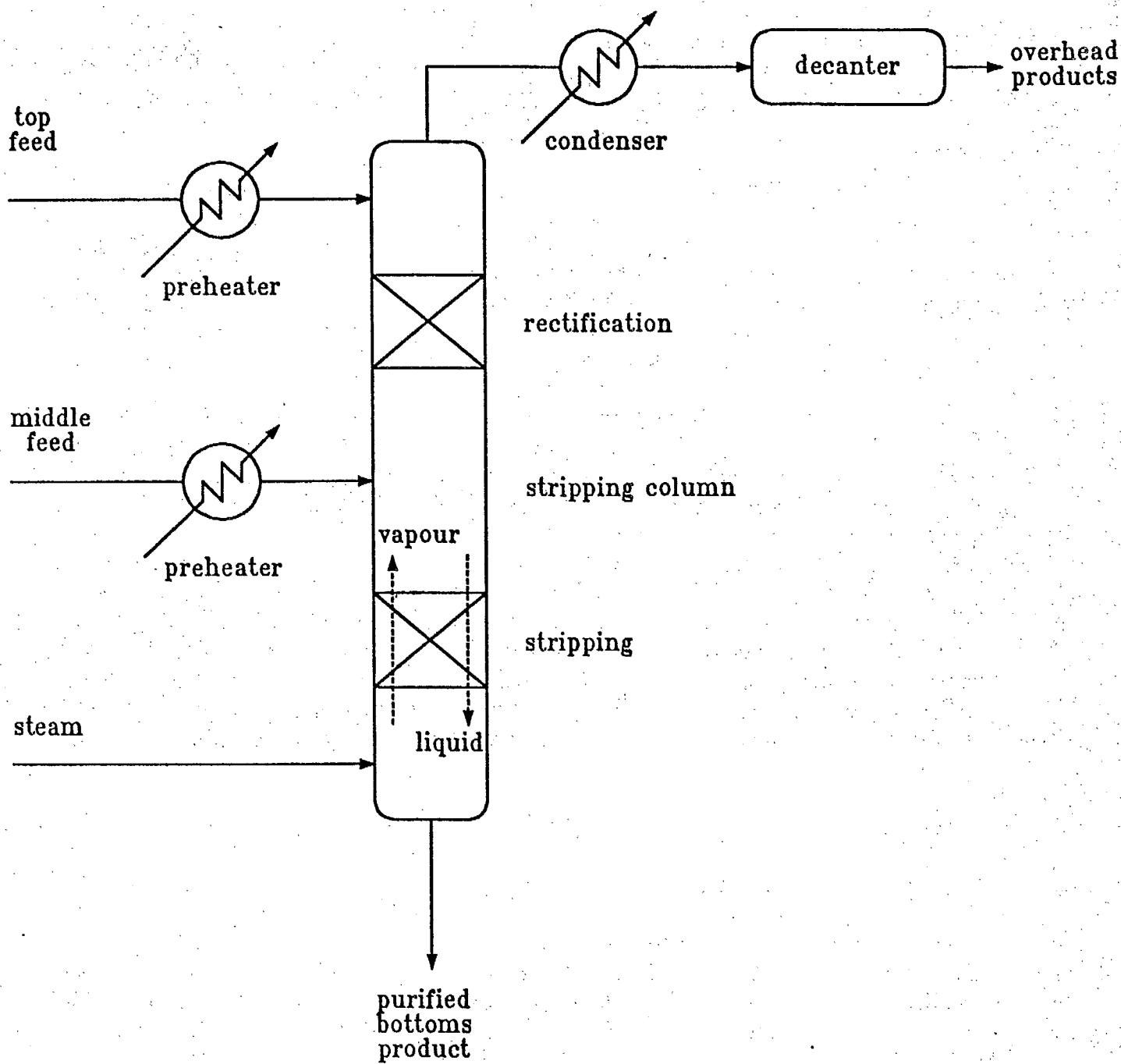


FIGURE 1 - Laboratory scale steam stripper

2.5 Post-treatment

The suitability of reverse osmosis and enhanced oxidation as final polishing steps to further reduce the concentration of DCM prior to discharge was also addressed. As EED does not have the facilities to assess the effectiveness of activated carbon, two bottoms samples from the steam stripping train will be returned to the client for further treatment using activated carbon.

2.5.1 Reverse osmosis

Reverse osmosis is a separation process that can remove very small molecules and ions in solution. The application of high pressures on a semipermeable membrane forces the flow of solutes producing a concentrate stream and a permeate stream. The performance of a membrane on a particular solution can be evaluated based on the percent rejection of the solute molecules from the feed stream.

$$\text{DCM REJECTION (\%)} = 100 * (1 - C_p/C_f)$$

where C_p = concentration of solute in the permeate stream
 C_f = concentration of solute in the feed stream

2.5.2 Enhanced oxidation

According to studies by Sundstrom, W. and Klei, E.H. (1986), DCM destruction in the presence of ultraviolet light and hydrogen peroxide is not economically feasible. A strong synergistic effect is shown in Figure 2 when hydrogen peroxide and ultraviolet light are used in combination, though after three hours, 15% of the DCM remains in solution. The simplified reaction takes place as shown below:

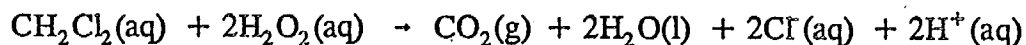


Figure 3 demonstrates the influence of temperature on DCM removal. DCM may be reduced to 1% in less than two hours once the temperature is increased to 40°C. However, this sample was run at its boiling point, therefore reduction of DCM may have been simply due to evaporation. In any case, the lab scale unit available at EED is not able to operate at this temperature, and therefore this situation was not further investigated.

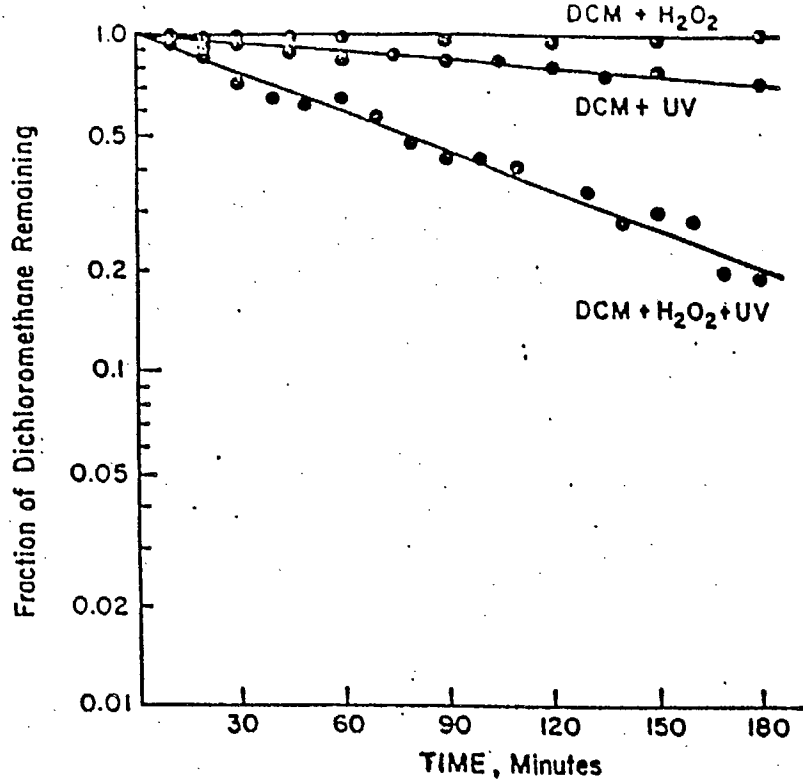


FIGURE 2 - Effect of H₂O₂ alone, UV alone, and H₂O₂ plus UV on decomposition of DCM at 20°C, pH6.8. Initial DCM = 53 ppm; Initial H₂O₂/DCM = 3 (on a molar basis)

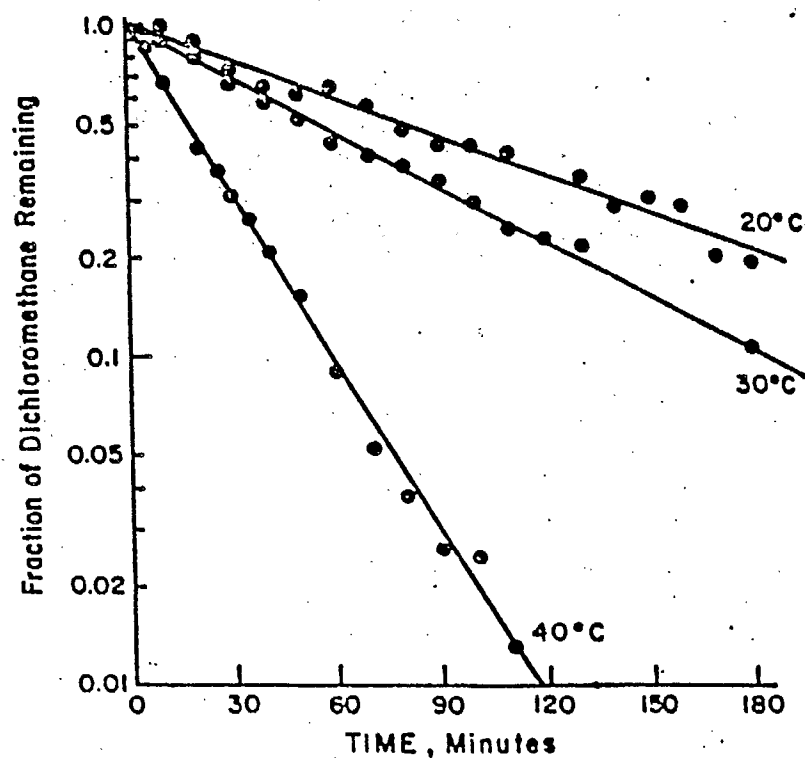


FIGURE 3 - Effect of temperature on decomposition of dichloromethane (DCM) at pH6.8. Initial DCM = 53 ppm; Initial H₂O₂/DCM = 3 (on a molar basis)

3. EXPERIMENTAL METHODS

Pre-treatment experiments were carried out on groundwater from bore hole number 39. Steam stripping and reverse osmosis experiments employed groundwater from bore hole numbers 6 and 39. The samples of groundwater were stored at a temperature of 6°C to prevent volatilization.

3.1 Acid addition

One hundred and fifty millilitre aliquots of groundwater were used in this experiment. Although hydrochloric acid is the most common acidifying agent, sulphuric acid (H_2SO_4) was employed because of its lower cost and reduced health risk with respect to hazardous vapours. According to analysis done by Barringer Laboratories, the concentration of sulphate (5.5 mg/L) found in a sample of groundwater from bore hole number 39 was significantly lower than that of chloride (146.0 mg/L) which further justifies the use of sulphuric acid. Different amounts of H_2SO_4 were added to the groundwater samples. The solutions obtained varied in pH units from 6 to 12.4 and were mixed vigorously for one minute. Samples for analysis were taken at specific time intervals, and then placed in the refrigerator at 6°C. Concentrated nitric acid was then added to the samples to stabilize them and prevent further precipitation.

3.2 Reagent precipitation

One hundred and fifty millilitre aliquots of groundwater were also used in this experiment. Sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) was used as a precipitating agent. Different amounts of sodium carbonate monohydrate were added to the samples of groundwater and the solutions obtained were mixed vigorously for one minute. The effect of temperature on reagent precipitation was investigated at operating temperatures of 6°C and 22°C which are typical for groundwater. Samples of the supernatant were taken at specific time intervals. Concentrated nitric acid was added to the samples as mentioned above.

Fifty millilitre samples of groundwater (after reagent precipitation or acidification) were heated in a water bath for 3 hours at a temperature of 82°C to simulate operating conditions on the steam stripper.

3.3 Polymer treatment and membrane separation

Polyacrylic acid with an average molecular weight of 50,000 was used as a polymeric binding agent. An aliquot of groundwater was vigorously mixed with the polymer. The polymer concentration in the solution obtained was 1 g/L while the volume of the solution was 3.5 litres. The formation of insoluble substances and their precipitation took place in this experiment. The precipitate formed was removed from the clear solution by gravity filtration (filter paper size #6). The filtrate was then put into a membrane bench-scale

installation. Microfiltration units ENKA type MD 020 TP2N and MEMBRALOX type ITI.706 W2.5-LI. were used, with pore sizes of 0.2 and 0.8 micron, respectively. Feed flow was 3 L/min and transmembrane pressure was 101 kPa (14.7 psig).

3.4 Steam stripping

The contaminated water was preheated to approximately 75°C prior to entry from either the top or middle of the column. Feed rate was varied between 70 and 194 mL/min. Feed volume was usually between 1 and 2 litres and run time was approximately 5 to 30 minutes. Steam generated from the boiler entered the base of the column at a constant rate of 9.2-9.3 g/min. The feed/steam ratio was varied between 7.5 and 21. There was insufficient volume of tops to warrant refluxing. The tower was fitted with raschig rings to enhance contact between the two phases. A diffusion plate was placed at the top of the column to avoid channelling of the liquid. In addition, the column and boiler were insulated with fibreglass to prevent excessive heat losses. As it was quite possible that one pass through the steam stripper would not bring the DCM concentration to an acceptable level, the bottoms of most runs were passed through the steam stripper a second time.

3.5 Reverse osmosis

Ideally, the treated bottoms obtained from the steam stripper would be passed through the reverse osmosis (RO) unit in order to determine how effectively clean water could be produced. This water could then serve in the steam stripper boiler during field scale trials. However, the volume of sample required for the lab scale reverse osmosis unit was greater than the volume of sample provided by the steam stripper. Hence, one litre of each bore hole sample was diluted to the approximate treated water concentrations obtained during the steam stripping runs, producing approximately 100 litres of contaminated water. The sample was then passed through a 5 micron pre-filter onto a thin film composite salt water high rejection Filmtec (SW30-HR 2540) membrane. The maximum operating pressure and temperature were 5516 kPa (800 psig) and 40°C while the maximum feed rate and recirculation rate were 18.9 L/min and 15.1 L/min.

3.6 Analytical methods

DCM was detected by a purge and trap gas chromatographic procedure. Calcium was measured by atomic absorption.

4. RESULTS AND DISCUSSION

4.1 Acid addition

Results of this series of experiments are presented in Table III. The calcium remained in solution over a broad range of pH, which was adjusted by the addition of sulphuric acid. In fact, the addition of sulphuric acid increased the solubility of calcium to some extent. The high ionic strength in these solutions may be responsible for the phenomenon.

TABLE III - Treatment of groundwater with sulphuric acid at 6°C

TIME (min)	pH OF SOLUTION							
	12.4*	11.9	11.4	10.7	9.8	9.0	7.4	6.5
	CALCIUM CONCENTRATION IN SOLUTION (ppm)							
5	459.35	435.66	466.27	434.66	407.98	372.42	457.38	456.39
15	443.55	414.90	392.18	381.31	403.04	425.76	397.12	395.14
30	429.72	414.90	447.50	411.93	409.96	311.17	419.84	433.67
60	442.56	391.19	417.86	427.74	422.80	363.53	402.05	400.08
120	509.76	549.25	408.97	415.89	459.35	419.84	416.87	451.45
240	416.87	409.96	416.87	402.05	425.76	410.95	407.98	423.79
20 hrs.	383.28	389.21	403.04	391.19	400.08	401.07	400.08	400.08

* No acid was added

Approximately 24 hours after acidification, solutions were placed in a water bath and heated for three hours. As shown in Table IV, at pH 10.7 and lower, no calcium precipitation took place, whereas at higher pH, precipitation was significant. Sulphuric acid appeared to be an effective method for stabilizing calcium in groundwater providing pH is kept below 10.7.

TABLE IV - Heating of the solutions after acid treatment

Temperature for heating = 82°C

Period of heating = 3 hours

SAMPLES	pH OF SOLUTION							
	12.4*	11.9	11.4	10.7	9.8	9.0	7.4	6.5
	CALCIUM CONCENTRATION IN SOLUTION (ppm)							
Groundwater	485.5	485.5	485.5	485.5	485.5	485.5	485.5	485.5
Solution after acidification and exposure **	383.3	389.2	403.0	391.2	400.1	401.1	400.1	400.0
Solution after acidification, exposure and heating	195.5	336.7	394.2	430.9	429.8	430.9	452.9	440.3
Weight of precipitated Ca from 1 m ³ of groundwater (g)	185.8	52.5	8.8	0	0	0	0	0

* No acid was added

** Exposure was extended over 20 hours at a temperature of 6°C

4.2 Reagent precipitation

Sodium carbonate monohydrate was chosen as a precipitating agent because lime would not be effective at extremely high pH of groundwater (12.4). The results obtained from the sedimentation experiments at temperatures of 6°C and 22°C are presented in Figures 4 and 5 respectively. Tabular results are presented in Appendices A and B.

In Figure 4, results indicate an increase in precipitation rate and a decrease in the residual amount of calcium in the solution for increasing sodium carbonate monohydrate concentration. Three grams per litre of sodium carbonate monohydrate is enough to remove calcium almost completely (residual calcium concentration is 0.28 ppm). The precipitation rate does not appear to be significantly affected by temperature over the sodium carbonate monohydrate range investigated.

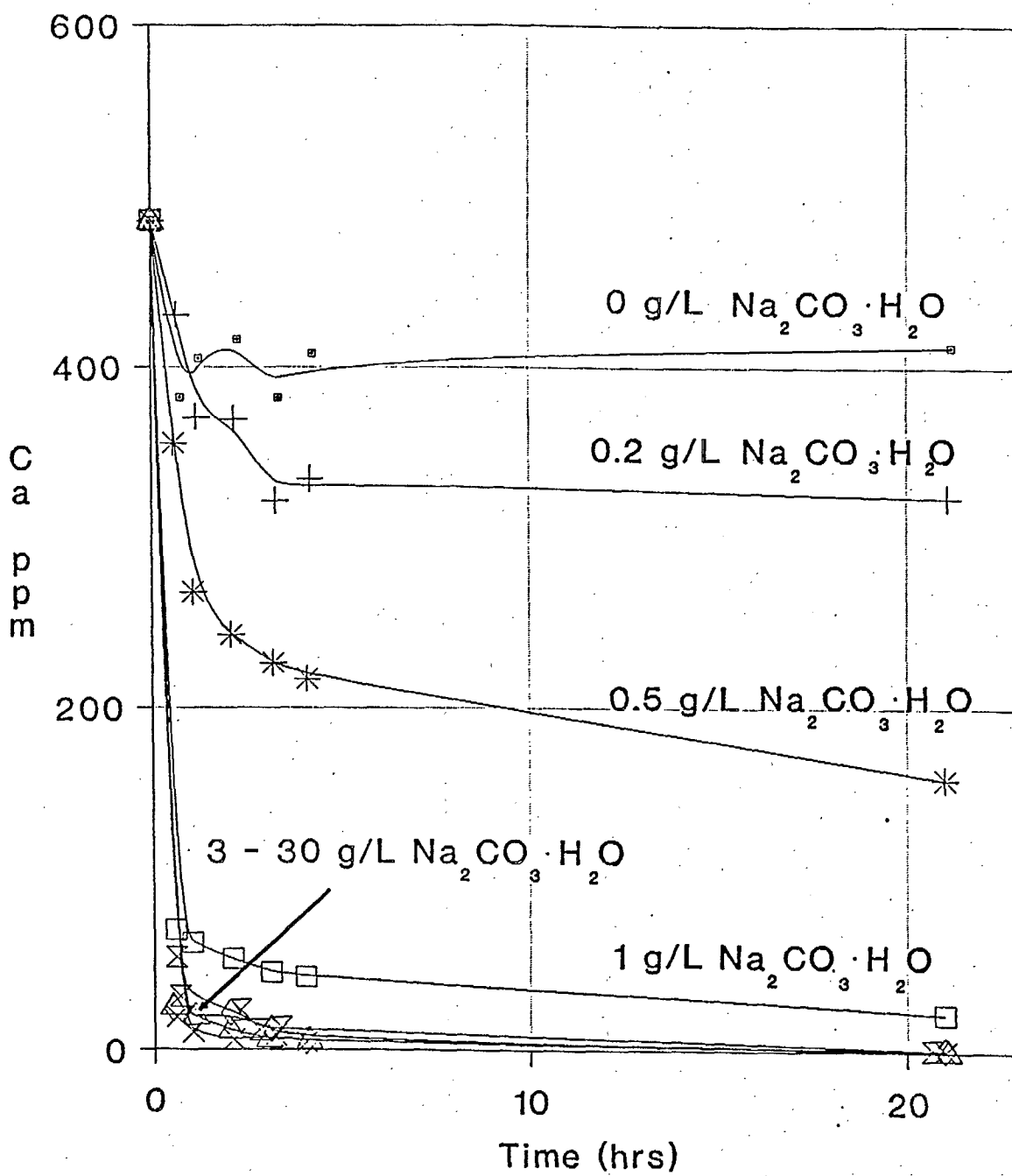


FIGURE 4 - Precipitation of calcium with sodium carbonate monohydrate at 6°C

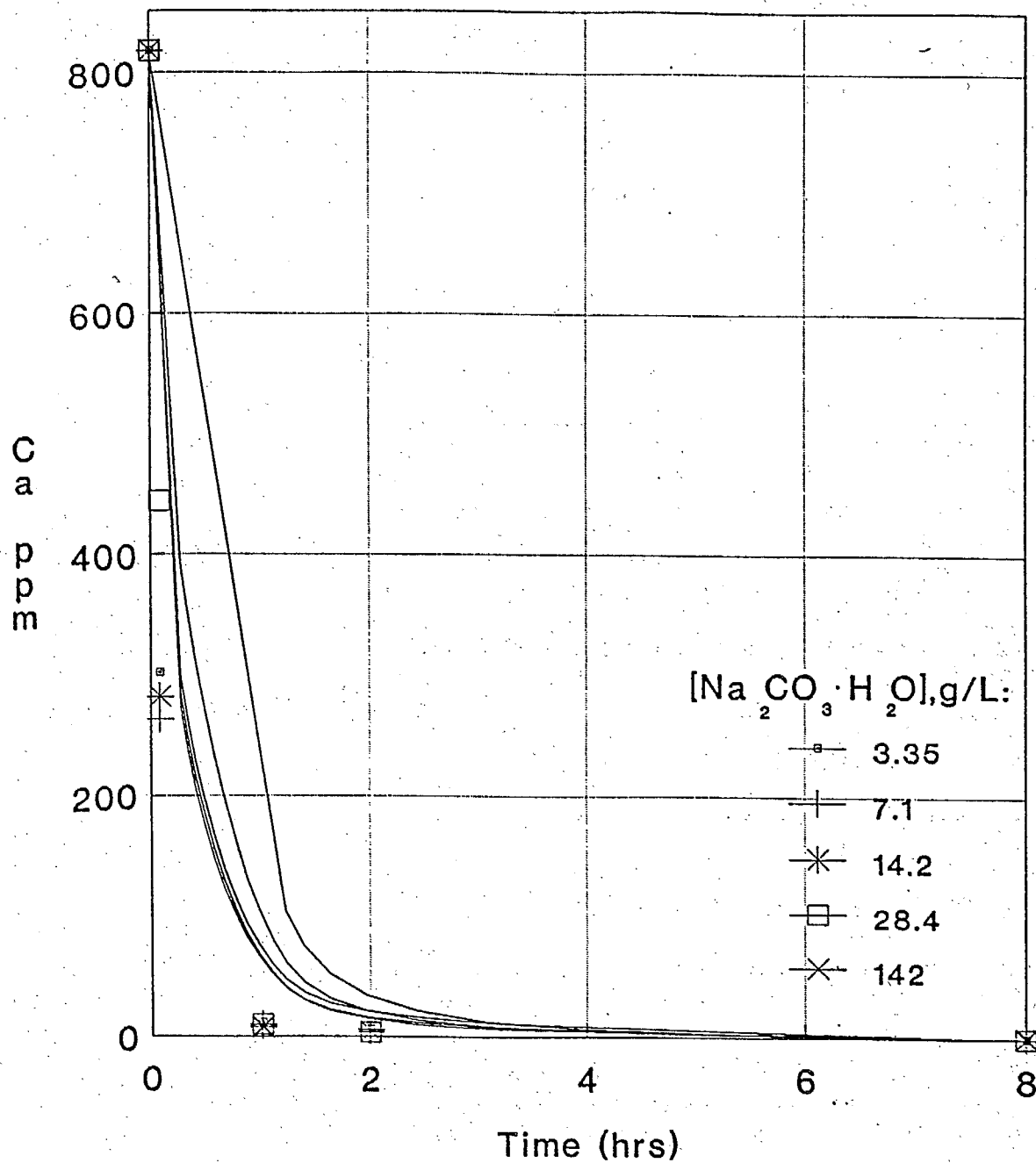


FIGURE 5 - Precipitation of calcium with sodium carbonate monohydrate at 22°C

To simulate steam stripping operating conditions, the supernatant solutions, after 25 hours of precipitation at 6°C, were heated in a water bath for three hours and those results are presented in Table V. Results from Table V indicate that reagent precipitation as a pre-treatment is valid, providing the concentration of sodium carbonate monohydrate is greater than 3 grams per litre.

TABLE V - Heating of the supernatant solution

During sedimentation, temperature = 6°C

During heating, temperature = 82°C

Heating time = 3 hours

SAMPLES	CONCENTRATION OF $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (g/L)				
	0	0.2	0.5	1.0	3.0
	CALCIUM CONCENTRATION IN SOLUTION (ppm)				
Raw Groundwater	485.5	485.5	485.5	485.5	485.5
Solution after sedimentation	411.9	323.9	159.1	21.8	0
Solution after sedimentation and heating	133.2	62.7	0	0	0
Weight of precipitated Ca from 1m ³ of groundwater during heating (g)	278.7	261.2	159.1	21.8	0

4.3 Polymer treatment and membrane separation

A yellowish precipitate formed immediately after mixing groundwater and polyacrylic acid. The precipitate was separated from the solution by gravity filtration, and further treatment using microfiltration of the filtrate was then carried out. The results of this experiment are presented in Table VI. As shown in Table VI, approximately 80% of total calcium content was removed by gravity filtration. Microfiltration proved ineffective in producing a significant change of calcium concentration.

TABLE VI - Removal of calcium using polymer treatment and microfiltration

SAMPLE	CALCIUM CONCENTRATION IN SOLUTION (ppm)
Raw groundwater	850
Supernatant	234
Permeate of treated supernatant	217

The pH of the solution offers a possible explanation of these results. At very high pH of groundwater (12.4), the solubility of calcium salt of polyacrylic acid is so low that it precipitates. All polyacrylic acid is bound to the precipitate, therefore the remaining calcium ions in solution pass freely through the membrane.

Increasing the concentration of polyacrylic acid reduces the residual concentration of calcium ions in solution after sedimentation. However, an increase in polymer reagent results in increased cost for pre-treatment. The negative results obtained in this experiment do not necessarily signify that polymer treatment combined with membrane separation cannot be used for calcium removal. However, in this particular case, extremely high pH and calcium concentrations made this process less effective.

4.4 Steam stripping

Groundwater analyzed by Barringer Laboratories revealed extremely high levels of DCM (25,500 ppm) in bore hole number 6. Preliminary experiments investigated the capability of the laboratory scale steam stripper to remove high concentrations of DCM from water. Initially, tap water was spiked with DCM, up to approximately 2% by weight as this was the expected concentration in bore hole number 6. From Table VII, DCM removal from spiked tap water using steam stripping was over 80% in a single pass. The treated water from RUN#2 was collected and used for a second pass through the steam stripper as RUN#3. This resulted in an overall DCM removal of 95.7% on two passes through the steam stripper.

TABLE VII - DCM removal from spiked tap water using steam stripping

RUN #	FEED* RATE mL/min	FEED: STEAM** RATIO	CONCENTRATION OF DCM (ppm)			DCM REMOVAL (%)
			FEED	TOPS	BOTTOMS	
1	140	15.1	15 179	3475	2941	80.6
2	194	20.9	20 985	na***	2594	87.6
3	194	20.9	2594	5474	909	65.0 (95.7)****

* feed was to middle of column

** steam rate was 9.3 g/min

*** na = not analyzed

**** () = overall DCM removal rate for double pass run

Table VIII presents the results of DCM removal from groundwater (bore hole number 39) using steam stripping after pre-treatment. Feed was introduced to the top of the column for all runs listed in Table VIII. Feed for RUN#1 was the clear solution obtained after sedimentation using sodium carbonate monohydrate on groundwater. The treated water from RUN#1 was collected and used for a second pass through the steam stripper as RUN#2. The overall DCM removal was 86.7% on two passes through the steam stripper unit. Feed for RUN#3 was the filtrate obtained after passing groundwater through the microfiltration unit. The treated water from RUN#3 was collected and used for a second pass through the steam stripper as RUN#4. The overall DCM removal rate was 48.5% on two passes through the steam stripping unit.

TABLE VIII - DCM removal from pre-treated groundwater (BH#39) using steam stripping

RUN #	FEED* RATE mL/min	FEED: STEAM** RATIO	CONCENTRATION OF DCM (ppm)			DCM REMOVAL (%)
			FEED	TOPS	BOTTOMS	
1	140	15.1	26.19	20.95	6.39	75.6
2	140	15.1	6.39	10.67	3.59	43.8 (86.7)***
3	140	15.1	2.27	19.07	1.76	22.5
4	140	15.1	1.76	31.78	1.17	33.5 (48.5)

* feed was to top of column

** steam rate was 9.3 g/min

*** () = overall DCM removal rate for double pass run

The pH of groundwater from bore hole number 39 was adjusted from 12 to 8.3 units by the addition of sulphuric acid in order to stabilize the calcium and meet water disposal requirements. This solution was then filtered (filter paper size #1) and fed to the top of the column. DCM removal rates for different feed rates from the top of the column for single and double pass steam stripping are presented in Table IX. The initial DCM concentration in the feed was about 30 ppm. The removal rate at the various feed rates investigated, was over 90% on a single pass. The overall DCM removal rate increased to over 99% when the treated water was passed a second time through the steam stripping unit.

TABLE IX - DCM removal from groundwater (BH#39) using steam stripping

RUN #	FEED* RATE mL/min	FEED: STEAM** RATIO	CONCENTRATION OF DCM (ppm)			DCM REMOVAL (%)
			FEED	TOPS	BOTTOMS	
1	70	7.5	37.3	>249.6	0.67	98.2
2	70	7.5	0.67	>99.1	0.16	76.1 (99.6)***
3	110	11.8	31.0	>4.1	3.1	90.0
4	110	11.8	3.1	>126.0	0.17	94.5 (99.5)
5	140	15.0	31.0	>138.3	0.65	97.9
6	140	15.0	0.65	>105.9	0.10	84.6 (99.7)

* pH of feed was to top of column

** steam rate was 9.3 g/min

*** () = overall DCM removal rate for double pass run

The natural pH of groundwater from bore hole number 6 was 7.0 units which satisfies effluent discharge requirements, thus pre-treatment only involved filtering (filtrate paper size #1) prior to steam stripping. The solution was then fed to the middle of the column. DCM removal rates for various feed rates to the top of the column for single and double pass steam stripping are presented in Table X. The initial DCM concentration in the feed was above 3000 ppm. The removal rate at the various feed rates investigated was over 97% on a single pass. The overall DCM removal rate increased to over 99% when the treated water was passed a second time through the steam stripping unit.

TABLE X - DCM removal from groundwater (BH#6) using steam stripping

RUN #	FEED* RATE mL/min	FEED: STEAM** RATIO	CONCENTRATION OF DCM (ppm)			DCM REMOVAL (%)
			FEED	TOPS	BOTTOMS	
7	70	7.5	3000	> 8097	23.75	99.2
8	70	7.5	23.75	> 5746	11.4	52.0 (99.6)***
9	110	11.8	3000	> 17816	3.1	99.9
10	110	11.8	3.1	> 6720	0.5	83.9 (99.9)
11	140	15.0	4222	> 7971	106.2	97.5
12	140	15.0	106.2	> 11276	36.0	66.1 (99.1)

* feed was to the middle of column

** steam rate was 9.3 g/min

*** () = overall DCM removal rate for double pass run

In order to determine whether the inorganics in the water actually affect the steam stripping column and the steam stripping efficiency, approximately 2 litres of unfiltered sample from bore hole number 6 were run through the unit using the variables found to be most effective during the single pass runs. Results are shown in Table XI and are somewhat surprising as the unfiltered feed yielded a higher DCM removal rate than the filtered sample. A plausible explanation is the settling of soil particles which entrap part of the DCM removing it from the analyzed solution.

TABLE XI - DCM removal from treated and untreated groundwater (BH#6) using steam stripping

RUN#	FEED* RATE mL/min	FEED: STEAM** RATIO	CONCENTRATION OF DCM (ppm)			DCM REMO VAL (%)
			FEED	TOPS	BOTTOM S	
13 unfiltered	70	7.5	5209.8	19221	52.0	99.0
14 filtered	70	7.5	3340.7	na***	434.7	87.0

* feed was to top of column

** steam rate was 9.3 g/min

*** na = not analyzed

In theory, in order to obtain a concentrated overhead product with a soluble contaminant such as DCM, it is necessary to use a feed point near the middle of the stripper column to allow rectification to take place. However, laboratory scale steam stripping results indicate an indifference to feed location. In addition, theory recommends a low feed/steam ratio to enhance DCM removal from contaminated water. However, at the feed flowrates investigated, there was no significant change in the effectiveness of steam stripping at different feed/steam ratios.

4.5 Reverse osmosis

It would be expected that DCM, with a molecular weight of 86, would be easily rejected in the reverse osmosis unit. However, the results shown in Tables XII and XIII state otherwise. The low percent rejections obtained can be explained by the hindrance DCM has to hydration, making its effective molecular radius much smaller than an ion such as sodium. Sodium has a much lower molecular weight (23) yet binds readily to water. A sample of permeate taken after 12 minutes was unreliable and therefore not included in Table XII.

The decrease in percent DCM rejection in Table XIII can be explained by the higher operating temperature. This increase in temperature will cause the bound water on the membranes surface to become thinner, making the effective membrane pore size larger, therefore more permeable to solute molecules. The unexpected decrease in concentrate concentration of DCM may also be explained by the operating temperatures of 35°C and 40°C where some losses of DCM are attributable to evaporation.

TABLE XII - Residual concentrations of DCM after treatment through reverse osmosis unit (mixture of BH#6 and BH#39)

TIME (min)	T (°C)	FLOWRATES (L/min)		CONCENTRATION OF DCM (ppm)		DCM REJECT- ION (%)
		CONCEN- TRATE	PERMEATE	CONCEN- TRATE	PERMEATE	
0	24	0.4	0.7	13.2	-	-
30	40	0.4	0.7	11.1	6.7	49.2

TABLE XIII - Residual concentrations of DCM after treatment through reverse osmosis unit (BH#6)

TIME (min)	T (°C)	FLOWRATES (L/min)		CONCENTRATION OF DCM (ppm)		DCM REJECT- ION (%)
		CONCEN- TRATE	PERMEATE	CONCEN- TRATE	PERMEATE	
0	22.4	0.4	0.7	28.6	-	-
12	35	0.4	0.7	27.6	16.2	43.4
30	40	0.4	0.7	27.7	17.5	38.8

5. CONCLUSIONS AND RECOMMENDATIONS

It can be concluded from the experimental results that both acidification and chemical precipitation may be used for groundwater pre-treatment. Acidification seems to be preferable because acidification itself is necessary to decrease pH of groundwater before its discharge. To meet sanitary requirements, pH of discharged water must be in the range of 6.5 - 8.5 units. In this pH range, calcium precipitation does not occur. Therefore, acidification with sulphuric acid to pH 8.5 is recommended as an optimum pretreatment method. Polymer treatment combined with membrane separation was not effective in removing calcium from this particular groundwater.

According to the laboratory scale results, dichloromethane can be sufficiently removed from groundwater using steam stripping, operating under near optimum conditions (feed to middle of the column and low feed/steam ratio) so that secondary treatment may not be necessary and the treated water may be discharged. It should be noted that EED's field scale unit is expected to provide greater removal efficiencies than the laboratory scale unit. The packing to column diameter ratio in the laboratory scale unit is larger than that of the field scale unit, reducing the contact area between the steam and the contaminated liquid.

Steam stripping is a feasible alternative to conventional technologies such as air stripping and carbon adsorption due to the cost required to meet current regulatory emissions and disposal requirements. The primary advantage of steam stripping over air stripping is that steam is condensable, allowing for removal of VOCs for recovery and disposal in a concentrated form, thus eliminating atmospheric emissions. Steam stripping has a higher capital cost than air stripping. Steam stripping can be costly to operate due to the expense of producing steam, but less expensive than combination of air stripping and off gas treatment (carbon adsorption).

Reverse osmosis treatment was effective in removing only up to 49.2% of the dichloromethane initially present in the groundwater and therefore is not recommended for post-treatment. Experiments were not pursued with the EED laboratory scale enhanced oxidation unit as this unit was not able to operate at the optimum temperature (40°C) for dichloromethane removal.

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APPENDIX A - Precipitation of calcium with sodium carbonate at 6°C

TIME (hrs)	CONCENTRATION OF Na ₂ CO ₃ ·H ₂ O (g/L)								
	0	0.2	0.5	1.0	3.0	5.0	10.0	20.0	30.0
	CALCIUM CONCENTRATION IN SOLUTION (ppm)								
0	485.48	485.48	485.48	485.48	485.48	485.48	485.48	485.48	485.48
0.33									31.84
0.5						23.24	24.67		
0.58			354.94	69.87	18.21			53.37	
0.67		430.57						30.41	
0.75	381.88								23.24
1				61.98	9.6	17.5			
1.08			267.91				18.93		
1.17		370.48							
1.25	404.67								
1.83									16.78
2						21.08	11.04		
2.08			243.05	52.65	5.3				
2.17		369.45							
2.25	416.07							22.52	
2.75								11.04	9.6
3							6.02		
3.08				44.76		11.76			
3.17			226.47		8.17				
3.25		321.79							
3.33	381.88							12.47	
3.75									10.32

TIME (hrs)	CONCENTRATION OF $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (g/L)								
	0	0.2	0.5	1.0	3.0	5.0	10.0	20.0	30.0
4				41.89	3.87	4.58			
4.08			217.15				5.3		
4.17		334.22							
4.25	407.78								
20.66								1	0.28
21			159.13	21.8	0.28	1			
21.08		323.86					0		
21.17	411.92								

APPENDIX B - Precipitation of calcium with sodium carbonate at 22°C

TIME (hrs)	CONCENTRATION OF $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (g/L)				
	3.35	7.1	14.2	28.4	142
	CALCIUM CONCENTRATION IN SOLUTION (ppm)				
0	817.3	817.3	817.3	817.3	817.3
0.08	302.14	263.97	282.5	443.5	
1	11.3	10.22	8.06	9.86	6.97
2	11.3	5.89	3.72	3.36	3.72
8	0.01	0.001	0.001	0.001	0.44

**Efficacy of Steam Stripping in Removal of
Dichloromethane from Groundwater**

(Field Results)

PART 2

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INTRODUCTION

Numerous pump and treat technologies are available to assist in the remediation of groundwater contaminated with organic chemicals. Some of the commercially available systems, such as air stripping and activated carbon adsorption, merely transfer pollution from one medium to another or are too expensive to be economically viable. The use of steam stripping to remove volatile organic contaminants (VOC's) from groundwater is an alternative approach which is both environmentally safe, since the contaminant being recovered is not discharged to the environment, and cost effective in terms of unit operation and contaminant disposal¹.

The following paper describes the results of laboratory and pilot scale field studies to evaluate the suitability of steam stripping as a remedial technology to remove dichloromethane (DCM) from groundwater.

SITE HISTORY AND DESCRIPTION

Marshall Macklin Monaghan Limited were retained by an industrial client to evaluate and implement the most cost effective remedial strategy to decontaminate soil and groundwater at an industrial facility in Toronto, Canada. Groundwater at the facility had been contaminated with DCM when an underground tank ruptured during filling in the early 1970's. Following the incident the tank was repaired in-situ and continued to be used for solvent storage until its removal in 1989. During decommissioning of the site it was discovered that the original tank rupture had produced an Aqueous Phase Liquid contaminant plume (APL) and possibly a Dense Non Aqueous Phase Liquid (DNAPL) which extended beneath the manufacturing facility and covered an area of approximately 40 m by 60 m (Figure 1).

GEOLOGIC AND HYDROGEOLOGIC SETTING

Ground surface slopes gently towards the southeast corner of the property and has approximately three meters relief.

The site is located near the contact of three Quaternary units: shallow and deep water lacustrine sediments and the Wildfield Till. The lacustrine sediments are part of the Lacustrine-Wildfield Till Complex. These deposits consist of both fine-grained silts and clays as well as coarser grained sand and gravel deposits. Interstratified with the coarser sediments can be till-like sediment similar to the Wildfield Till. Underlying the lacustrine Wildfield Till Complex is the dark grey, fine grained Wildfield Till. The Halton Till and older interglacial fluvial and alluvial sediments may underlie the Wildfield Till and at depth the Wentworth and Sunnybrook Till may also be present.

The drilling program conducted on the site revealed a complex stratigraphy of interstratified silts and clays as well as coarser sands, gravel and till. The stratigraphy on the site consists of approximately 2 meters of reworked sandy silt of unknown origin, perhaps fill, or coarse grained deltaic sediment. Underlying the reworked sediment is approximately 9 meters of the Lacustrine-Wildfield Till complex. This forms a fining upward sequence from interstratified Wildfield Till and gravel at approximately 9.5 meters depth to a silty clay at 2 meters depth. Underlying the Wildfield Till is approximately 4 meters of stratified silts, sands and gravels associated with older alluvial and fluvial deposition. At approximately 14 meters depth an older till unit is found, possibly the Halton Till.

The hydraulic conductivity of the Lacustrine-Wildfield Till Complex, where most of the groundwater contamination was detected was 3.7×10^{-4} cm/s as measured by rising head piezometer tests. The hydraulic conductivity of the deeper, less contaminated aquifer beneath the Lacustrine-Wildfield Till unit was 9.0×10^{-4} cm/s. The direction of groundwater flow in the Lacustrine-Wildfield Till Complex beneath the plant is towards the south east. Groundwater flow direction in the lower aquifer was not determined.

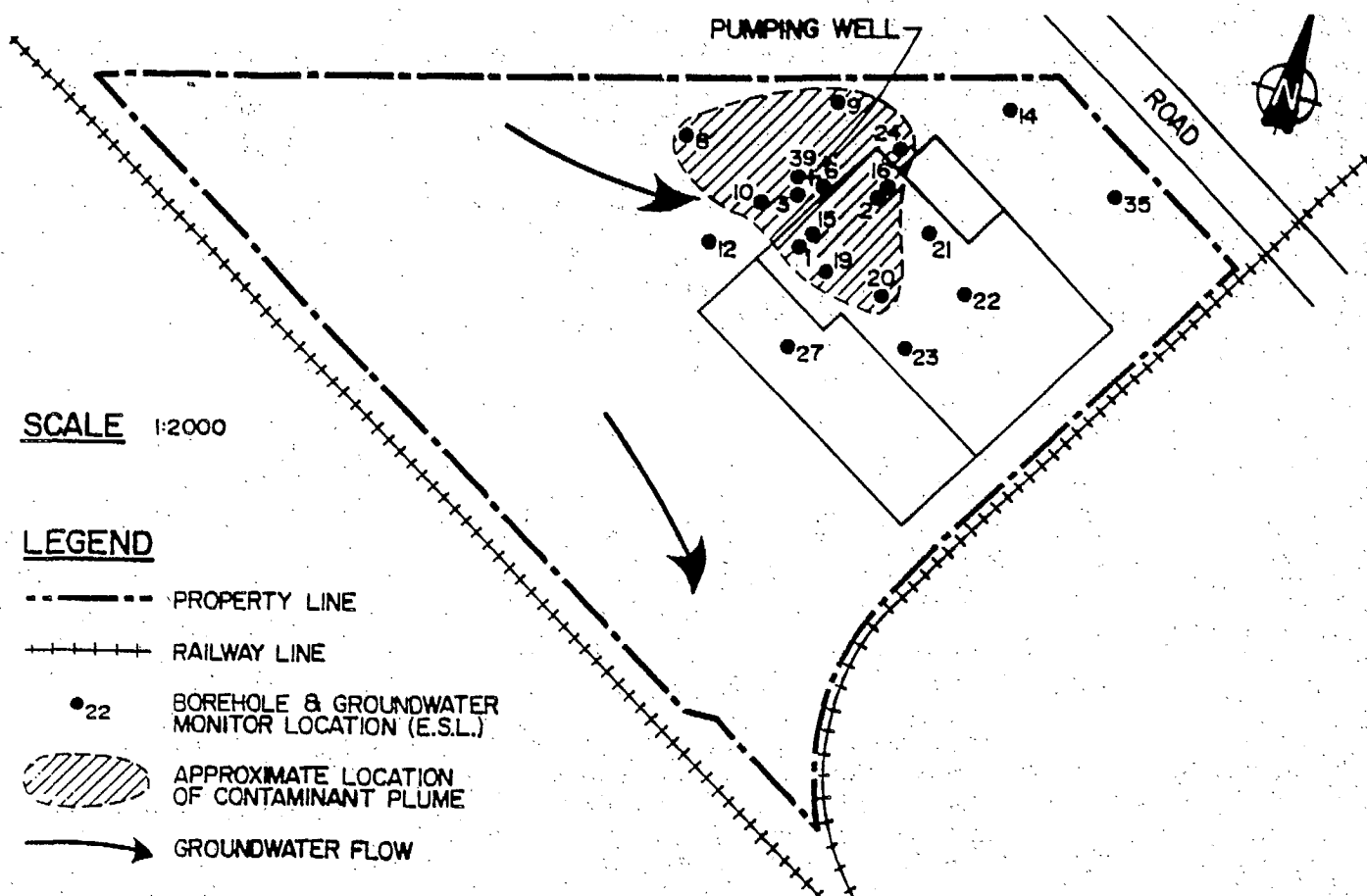


Figure 1. Site layout and approximate distribution of APL plume.

GROUNDWATER CHEMISTRY

Initial groundwater chemistry data indicated that contamination was largely confined to the upper aquifer located in the Lacustrine-Wildfield Till Complex. The main contaminant found in this zone was DCM which was detected in concentrations approaching the upper solubility limit of DCM in water (20,000 ppm @ 20°C). Smaller concentrations of other chlorinated aliphatic and unchlorinated aromatic compounds (Table 1) were also detected. The high concentration of DCM detected in groundwater suggested that a plume of DNAPL might be present in the immediate area of the original spill and possibly beneath the manufacturing facility.

Dichloromethane was the preponderant contaminant detected in the lower aquifer located beneath the Wildfield Till Unit. The maximum DCM concentration detected in this zone was 160 ppm, several orders of magnitude less than detected in the upper aquifer². Based on the hydrogeological information available to date, it is not possible to assess if the upper and lower aquifers are hydraulically connected. The difference in DCM concentration, however, suggests that the two aquifers are not intimately connected.

Table 1. Maximum contaminant concentration in groundwater

Contaminant	Concentration (ppm)
Dichloromethane	25,000
1,1-Dichloroethene	4.50
1,1-Dichloroethane	36.80
Chloroform	0.35
1,1,1-Trichloroethane	4.80
Trichloroethene	1.04
Dibromochloromethane	0.01
Tetrachloroethane	3.50
Toluene	26.00
o,m,p-Xylene	1.02

Given the time that has elapsed since the occurrence of the DCM spill, it is surprising that the areal extent of groundwater contamination was not significantly larger. The probable reason for this is that the Wildfield Till unit which appears to have retarded the downward migration of DCM to the lower aquifer, rises by several meters in a south easterly direction beneath the plant building. This elevation of the till unit therefore presents a physical barrier which has contained the DCM spill to the relatively localized area indicated in Figure 1.

REMEDIAL STRATEGY DEVELOPMENT

The remedial options considered to decontaminate the soil and groundwater on the site included biodegradation, excavation and removal, in-situ stabilization, in-situ containment and vacuum extraction coupled with pump and treat technology. The lateral and vertical containment of the contaminant plume by the geology of the site together with the fact that a significant portion of the contaminant plume lay beneath the manufacturing facility were major factors in selecting the most suitable remedial option. Vacuum extraction coupled with pump and treat technology was determined to be the most cost effective remedial strategy to decontaminate the soil and groundwater on the site. In view of the high cost generally associated with groundwater remediation, a pilot scale study was considered necessary in order to evaluate the feasibility of the pump and treat component of the overall remedial strategy prior to moving to a full scale treatment system.

The Emergencies Engineering Division of Environment Canada was known to be actively pursuing the potential of steam stripping as a groundwater remediation technology and had built both a bench scale and a pilot scale unit. Marshall Macklin Monaghan Limited therefore approached the Emergencies Engineering Division for assistance in evaluating the efficiency of steam stripping in removing DCM from groundwater.

The United States Environmental Protection Agencies Risk Reduction Engineering Laboratory's treatability database was accessed to evaluate the known efficiencies of various pump and treat technologies in the removal of DCM from water.

The data indicated that of the technologies available, steam stripping gives the greatest removal efficiencies for DCM concentrations greater than 1 ppm. Steam stripping was considered to be more cost effective than more established VOC treatment technologies, such as air stripping and activated carbon adsorption. With air stripping, significant costs would be incurred in meeting current air emission standards. Similarly, the lower removal efficiency of activated carbon coupled with regeneration and/or disposal of DCM contaminated carbon waste tended to make it more expensive.

STEAM STRIPPING PROCESS

Steam stripping is a separation process which utilizes differences in the thermodynamic properties of liquids. It is a process by which one or more components of a liquid mixture (usually water and an organic species) is transferred to the vapour phase. The driving force for the separation is the concentration differential of the organic component(s) between the liquid and vapour phases. Removal efficiency is highly dependent on a number of factors including Henry's Law Constant, temperature, vapour pressure and steam-to-water ratio. An increase in any of these parameters produces a corresponding increase in removal efficiency, assuming all other factors remain constant³. Other factors which influence removal efficiencies include the size and type of column packing and the ratio of column diameter to packing diameter.

ANALYTICAL METHODS

Dichloromethane concentrations in water were measured by purge and trap gas chromatography during the laboratory and optimization portion of the trials. A photo ionization detector gas chromatograph capable of measuring DCM levels down to 0.1 ppm was used for analysis during the field scale evaluation.

LABORATORY SCALE EVALUATION

Laboratory scale evaluation showed that DCM could be removed from groundwater using steam stripping⁴. Greater than 99 % removal efficiencies were achieved when operating at near optimum conditions. In the laboratory experiments, the feed rate was varied between 70 and 194 mL/min with a run time which varied from 5 to 30 minutes. Steam was fed at a constant rate of 9.2 g/min resulting in a feed-to-steam ratio which varied between 7.5 and 21.

As part of the optimization procedure, contaminated groundwater was fed to both the middle and top of the column. Theoretically, a feed point near the middle of the column together with a low feed-to-steam ratio would enhance DCM removal. Laboratory scale results however, showed only a small increase in removal efficiency when groundwater was fed to the middle of the column. The laboratory scale evaluation indicated that DCM removal efficiencies of greater than 99.9 % could be achieved in the pilot scale steam stripping unit using a two pass system. The DCM concentration in groundwater could therefore be reduced from an average value of 3,500 ppm to less than 1 ppm.

High levels of calcium were detected in the groundwater during the laboratory evaluation. In turn, these levels were associated with high pH levels in the groundwater samples. In order to minimize scaling in the steam stripping unit, various pre-treatment methodologies to reduce the calcium levels were investigated. Scale build up would tend to reduce the throughput of the unit and could affect DCM removal efficiencies. It was shown that calcium scaling would not occur if the pH of groundwater was between 6.5 and 8.5 units. If high pH groundwater was encountered during the field trial, sulphuric acid would be added to bring the pH below 8.5.

FIELD SCALE RESULTS

The process flow diagram for the field scale trial is shown in Figure 2. The pH of the groundwater was monitored during the optimization portion of the trial to determine whether pre-treatment would be required prior to feeding to the steam stripper. The average pH of pumped groundwater was 7 units, therefore pre-treatment was not necessary.

Seven optimization runs were made. During these runs, the contaminated groundwater was introduced either at the top or to the middle of the column. Steam was provided by a 1,150,000 kJ/hr oil fired burner. Although the design flow rate for the feed was 2,000 L/h, the flow rate obtained during the optimization run varied from 900 L/h to 450 L/h resulting in a corresponding variation in the feed-to-steam ratio of 2 to 4.5. The length of the runs varied from 45 minutes to almost five hours. Run length was normally determined by the tank space available to store treated groundwater. Based on the results of the laboratory evaluation, an agreement was reached with the local pollution authority to permit the discharge of treated groundwater with a DCM concentration of less than 1 ppm to sanitary sewer.

Preliminary results from the optimization runs (Table 2, Runs 1 to 7) showed that when groundwater was fed to the top of the column, removal efficiencies of up to 99.7 % were achieved in a single pass and up to 98.7 % removal was achieved in a second pass⁵. The overall removal efficiency, therefore, for two passes through the unit was up to 99.99 %, giving DCM levels of less than 1 ppm in the treated groundwater.

DCM removal rates increased slightly when the groundwater was fed to the middle as opposed to the top of the column. After one pass, removal efficiencies varied from 99.7 % to 99.99 % giving DCM levels as low as 0.9 ppm in first pass treated water. A second pass through the unit reduced DCM levels to 0.7 ppm.

Optimal operating conditions for the field trial were therefore realized by feeding to the middle of the column at maximum steam flow.

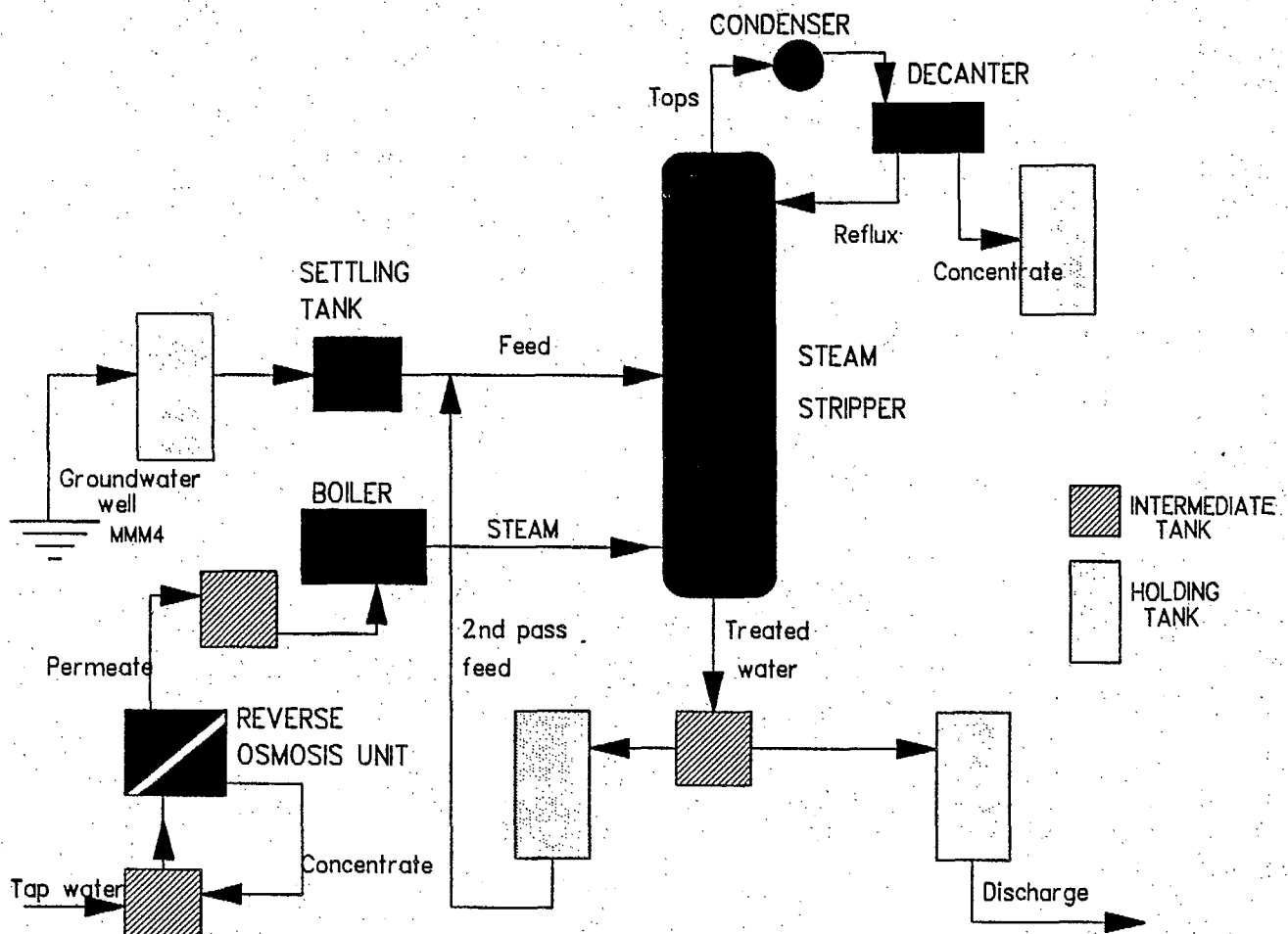


Figure 2. Field process flow diagram.

Table 2. Concentration and percent removals of dichloromethane

Run no.	Feed description	Feed location	Time (min)	Concentration of DCM (ppm)		Percent DCM removal
				Feed	Bottom	
1	groundwater	top	45	9591	63	99.34
			120		130	98.64
2	groundwater	top	45	7993	25	99.69
3	2nd pass	top	30	73	112	0.00
			70		13	82.19
			130		14	80.82
4	2nd pass	top	85	73	0.98	98.66
			130		10	86.30
5	groundwater	midway	60	12,605	34	99.73
			175	2328	1.1	99.95
			295	10,470	0.9	99.99
6	2nd pass	midway	80	12	3.4	71.67
			220		0.7	94.17
7	groundwater	midway	80	9736	5.7	99.94
			155		2.1	99.98
			230		11.9	99.88
			285		0.9	99.85
12	groundwater	midway	195	1091	0.5	99.95
			435	658	3.9	99.41
19	groundwater	midway	30	2152	0.6	99.97
			160	2341	6.5	99.72
29	groundwater	midway	95	1262	3.8	99.70
			470	807	trace	100.00
33	groundwater	midway	90	1096	2.2	99.80
			305	1127	ND*	100.00
			470	672	ND	100.00
34	groundwater	midway	80	1436	0.8	99.94
			265	1658	ND	100.00
36	2nd pass	midway	60	13	0.3	97.69
			180		ND	100.00
			290		ND	100.00
			470		ND	100.00
40	groundwater	top	210	2987	ND	100.00
			270	2829	ND	100.00
41	2nd pass	top	55	49	ND	100.00
			170	14	ND	100.00
			330	18	ND	100.00
43	groundwater	top	140	1666	ND	100.00
			260	1409	ND	100.00
			345	2924	ND	100.00
44	2nd pass	top	45	21	ND	100.00
			190	1	ND	100.00
			230	trace		

* ND = non detectable

FIELD SCALE DISCUSSION

Contaminated groundwater was treated using the steam stripper over a three month period to evaluate the potential of pump and treat technology to remove DCM from groundwater at the site. During this time, approximately 50,000 L of contaminated groundwater was processed. Approximately 6,500 L of a two phase dichloromethane/water mixture was obtained of which an estimated 120 L was pure DCM. The remaining 43,500 L of treated groundwater, having a concentration of less than 1 ppm, was discharged to sanitary sewer. Data for selected runs showing DCM concentration in the feed and treated water and percent DCM removed are presented Table 2.

For the first month of operation, the flow meter for the feed stream was faulty. An accurate measure of the flow rate was not available until the second month, by which time the flow rate had decreased from the 900 L/hr flow rate achieved in the optimization runs to 200 L/hr. The feed-to-steam ratio therefore was reduced from more than 2:1 to 1:1. Operation of the unit under these conditions was inefficient since large volumes of condensate were produced giving lower DCM concentrations in the condensate. The decrease in the flow rate may be attributed to fouling of the column by suspended solids in the groundwater. The flow rate improved to approximately 900 L/h after rinsing the column with hydrochloric acid (pH 4) and redirecting the feed to the top of the column. Although the optimization study indicated that feed to the middle of the column was preferable, percentage removals were found to be marginally better when groundwater was fed to the top of the column.

At the lower feed rates, removal efficiencies of greater than 99.9% were routinely achieved, and in some instances (Runs 29, 33, 34, 40 and 43) the concentration of DCM in treated groundwater after one pass through the steam stripper was below the analytical detection limit. However, because the performance of the unit was not sufficiently consistent, a second pass was generally required to reduce the concentration of DCM in the treated groundwater to less than 1 ppm.

The field trial demonstrated that steam stripping offers considerable potential as a treatment technology to remove VOC's from groundwater. The long term use of the pilot scale unit has shown that regular rinsing of the column with acidic solution is necessary in order to maintain an optimum feed rate and removal efficiency.

EFFECTIVENESS OF PUMP AND TREAT SYSTEM ON DCM REMOVAL

Prior to commencing the field trial, a 10 cm diameter pumping well with a 1.5 m screen was installed in the upper aquifer in the area of the original DCM spill. A 5 cm diameter electric pump was installed in the well just above the top of the screen. Groundwater was pumped to the steam stripper feed tank at an average rate of 330 L/h.

The impact of the pilot scale field trial on DCM concentrations in groundwater was evaluated by monitoring groundwater from selected boreholes both within the sphere of influence of the APL plume and on the periphery of the plume. Groundwater in the lower aquifer was also monitored to assess the effect of pumping on the vertical movement of DCM between the two aquifers. The change in concentration of DCM in the monitoring wells over time are shown in Table 3.

The effect of pumping on DCM concentrations in three of the most contaminated wells is illustrated in Figure 3.

As expected, quite dramatic reductions in DCM concentrations were achieved initially as highly contaminated groundwater was removed and replaced by previously uncontaminated groundwater. Following this first rush the concentration of DCM in groundwater stabilized at around 400-600 ppm in wells 1 and 24 and around 4000 ppm in well 2C. The DCM concentration in well 2A which was installed in the lower aquifer showed little change over the duration of the trial. It is probable therefore that downward migration of contaminants would not be a potential problem in remediation of this site.

In order to assess the overall effectiveness of the pump and treat strategy, groundwater pumping was curtailed for a period of one month towards the end of the trial and the change in DCM concentration in each of the wells was monitored. As Figure 3 shows, DCM concentrations remained relatively static in wells 1 and 24 and increased only slightly in well 2C before levelling off at around 3400 ppm.

Table 3. Concentration of dichloromethane in monitoring wells.

Date	Well																
	1	2A	2C	6	8	9	10	12	14	15	21	22	23	24	27	35	39
Concentration of DCM (ppm)																	
91 06 03				1400													20.3
91 07 03			9710														
91 08 12	3500	160	5975		0.011	0.007	1.3	0.013	0.009	16800	0.004	0.01	0.008	150	0.003	0.004	
91 12 09	1392		2831		--		--	ND*	--		ND	ND	ND	1008	ND	ND	
91 12 31	1571		2384		--		--	ND	--		ND	ND	ND	851	ND	ND	
92 01 05	529		2529		ND		--	ND	ND		ND	ND	ND	591	ND	ND	
92 01 08	568		3102								ND						
92 01 13	732		3277		ND		--	ND	ND		ND	ND	ND	752	ND	ND	
92 01 15	731		3899								ND						
92 01 17	584		3005		ND		--	--	--		ND	ND	ND	695	ND	ND	
92 01 20	538		4089		ND		40							758			
92 01 21		85															
92 01 22	600		3693		ND		--	ND	ND		ND	ND	ND	740	ND	ND	
92 01 24	493		3499		ND									595			
92 01 27	472		3699		ND		18	ND	ND		ND	ND	ND	728	ND	ND	
92 01 31	427		3832		ND		8							678			
92 02 03	411		3389		ND		--	ND	ND		ND	ND	ND	671	ND	ND	
92 02 05	392	161	3372		ND		trace							494			

* ND = non detectable

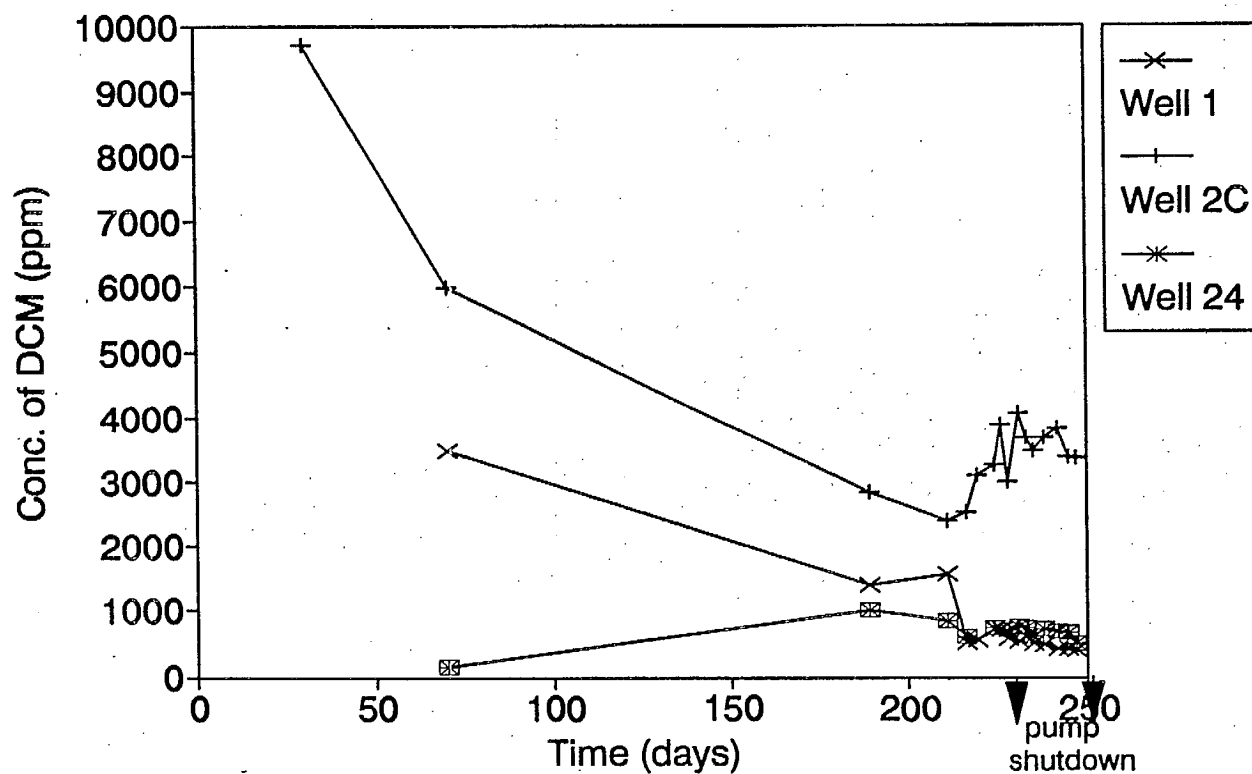


Figure 3. DCM concentration in three monitoring wells

CONCLUSIONS

Based on these preliminary findings, it would appear that a pump and treat system would be a suitable remedial strategy to decontaminate groundwater on this site.

Steam stripping has been shown to be a technically feasible and effective method for removing DCM from groundwater.

The evaluation of the steam stripper indicated that there is not a significant difference in the removal efficiency between feeding to the middle or to the top of the column. Greater than 99.9% of the dichloromethane was removed after two passes through the steam stripper, giving a final discharge concentration less than 1 ppm.

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SELECTIVE REMOVAL OF METAL IONS FROM GROUNDWATER

BY POLYMERIC BINDING AND MICROFILTRATION

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SUMMARY

A hybrid membrane separation technique was investigated for the selective removal of metals from groundwaters. This two-step process included the addition of a water soluble polymer to bind the metals and was followed by microfiltration. This method was used for the extraction of hazardous components of groundwater and for reduction of hardness. The influence of several process parameters the efficiency of the membrane separation was studied. This paper describes results of the experiments carried out on a bench-scale level.

INTRODUCTION

The method of separating and concentrating metal ions, which included selective binding of targeted ions by water soluble polymers and subsequent membrane separation of formed macromolecular compounds from unbound components, has been investigated since late 60's [1]. During this period, different applications of this method, varying from the removal of toxic components of industrial wastes [2] to the chemical analysis [3], were developed. It was revealed that almost any metal from the Periodic Table could be separated from other components of a solution using this process [4]. Moreover, it could be used for non-metals, like iodine [5] or phenol [6], as well.

The main parameter characterizing the effectiveness of the membrane separation process is the rejection of metals (or a certain metal) by the membrane:

$$R = 1 - C_p/C_f \quad (1)$$

where C_p and C_f are concentrations of the metal(s) in the permeate and in the feed (initial solution), respectively.

It was demonstrated [7] that in the case of polymer binding, rejection of a metal is expressed as a product of a polymer rejection R_p and the binding degree of a metal to a polymer Φ :

$$R = R_p * \Phi \quad (2)$$

As it follows from the expression (2), the higher the binding degree and the polymer rejection, the higher the metal rejection.

Since it was assumed that the pore size of a membrane had to be small enough for the complete removal of the formed metal-polymeric compounds, reverse osmosis or ultrafiltration as the separation techniques were used for all of these purposes.

On the other hand, it is a well known fact that when polymer solutions are filtered through membranes, sorption of polymers occurs on the surface and inside the pores [8] as well as formation of dynamic membranes [9] take place. These phenomena affect the semi-permeable properties of membranes and normally result in an increase in solute rejection. With this method, solute molecules, whose size is much smaller than the pore size of a membrane, may be partially or completely rejected by the membrane [10].

For cylindrical pores and laminar liquid flow, a water flux j_b through a pore with the diameter d_0 can be calculated according to Poiseuille's equation:

$$j_b = (128 * P * d_0^4) / (l * \eta) \quad (3)$$

where P is a transmembrane pressure, l is the pore length and η is viscosity of water.

In the case of an adsorbing polymer, the effective diameter of the pore "shrinks" and becomes equal to d_s which results in a decreased water flux j_s :

$$j_s = (128 * P * d_s^4) / (l * \eta) \quad (3a)$$

Assuming equations (3) and (3a), the diameter of the pore after sorption can be expressed through its initial diameter and the water fluxes prior and after polymer adsorption:

$$d_s = d_0 * (j_s / j_b)^{0.25} \quad (4)$$

or, using the values of total water fluxes through the membrane prior (J_0) and after (J_s) adsorption:

$$d^s = d_0 * (J_s / J_0)^{0.25} \quad (4a)$$

Thus, the thickness of the sorbed polymer layer δ can also be found through the reduction of a water flux through the membrane:

$$\delta = 0.5[1-(J_s/J_0)^{0.25}] \quad (5)$$

It has been shown [8] that Poiseuille's equation can be used for the calculation of the thickness of the sorbed polymer layer inside the pores of ultrafiltration membranes.

Polyelectrolytes, which are the most commonly used group of polymeric binding agents, have a great sorption ability due to the presence of charged groups in their macromolecules which interact with the membrane. One would expect that they may modify a microfiltration membrane as well so that the treated membrane will also to reject them.

This hypothesis has recently been investigated. The remainder of this paper describes the experimental results carried out. Several metals were chosen for the experiments. The first group of metals is represented by calcium, iron and manganese. The presence of these elements in groundwater is the serious problem in water treatment processes such as: heating, boiling, reverse osmosis, etc., under varying operational conditions. The low soluble compounds of these metals may deposit throughout the treatment units and cause a reduction in system efficiency. Other metals, such as lead, copper and nickel, are human health hazardous and must be removed from drinking water.

EXPERIMENTAL

A. Materials

Both real and spiked groundwater samples were used for the tests. Calcium, iron, manganese, lead, copper and nickel were the target components. The concentrations were varying in the range of 1 - 50 mg/l per metal.

Synthetic polyelectrolytes containing carboxylic, imino-, and sulfonic groups were used as the macromolecular binding agents. Data on the polymers are summarized in Table 1. Polymers were used as obtained from manufacturers without further purification. The polymers concentrations were in the range of 10-300 mg/l.

B. Methods

Microfiltration and ultrafiltration experiments were carried out on a bench-scale cross-flow membrane installation. The installation contained a membrane module, a recirculating pump, a flow-meter, pressure gauges, and both feed and permeate tanks. Flat-sheet and tubular membranes, both polymeric and ceramic were used for the tests. Table 2 details the main characteristics of the membranes.

Experiments were performed at room temperature and at transmembrane pressures ranging from 0.3 to 1.5 bar (4.4 - 22.4 psi). Transmembrane fluxes were corrected to 25°C. Feed flow was 0.05 l/s (0.8 gal/min). Solutions of hydrochloric acid and sodium hydroxide were used for pH adjustment.

The concentrations of metals in the feed solution, retentate and permeate were measured by atomic absorption (Perkin Elmer, Model 3100). The concentrations of polymers were determined by UV spectroscopy (Perkin Elmer, Model Lambda 2).

The observed retention coefficients R were determined from expression (1). The R values were reproducible to within + 5%.

RESULTS

A. Ultrafiltration of Polyelectrolytes Solutions

Figure 1 shows results of the filtration of polyacrylic acid through the ZETAPOR microfiltration membrane with an average pore size of 1.2 micron. The shape of the retention curves seems to be quite pronounced: the higher the molecular weight of the polymer, the higher its rejection by the membrane. It should be noted that the rejection is significantly affected by pH. It can also be noted that polyacrylic acid with the molecular weight 750,000 and higher is rejected almost completely at pH 7.5.

In order to evaluate the effect of polymer adsorption in the retention of the polymer by the membrane, the thicknesses of the sorbed polymer layers were calculated. To obtain these values, fluxes of the distilled water through the membrane were measured. An increase in the molecular weight resulted in a decrease in the water flux (Fig.2). As shown in Fig.2, the higher the pH, the lower the flux through the membrane. Data on effective pore diameters and thicknesses of sorbed polymer layers, which were calculated using equations (4a) and (5), are summarized in Table 3.

If one considers, for example, the polymer with the molecular weight 750,000. The mean diameter of its macromolecules should be in the range 120-150 nm [11]. However, Table 3 demonstrates that at pH 7.5 the polymer with this molecular weight causes the formation of the sorbed layer with the thickness of 495 nm, which is more than the diameter of the macromolecules. This reveals the fact that the adsorption has a polymolecular character, i.e. the sorbed layer consists of several monomolecular layers of polymeric molecules. According to the experimental results, the thickness of sorbed layers is less at lower pH. One explanation can be that the neutral, or protonated form of PAA, which exist at lower pH, has less sorption ability than ionized form of this polyacid, which exist at higher pH [12].

It is to be expected that microfiltration of adsorbing polyelectrolytes is affected by a large number of process parameters, such as temperature, feed concentration, membrane material, time of filtration, transmembrane pressure, etc. Systematic investigation of these parameters has not been attempted in this study. However, similar results (high rejection on microfiltration membranes) were obtained for polyethylenimine (PEI) and poly(styrenesulfonic acid) (PSSA). For example, rejection of PEI at pH 8.1 was 0.998 on ENKA (0.2 micron) and 0.986 on MEMBRALOX (0.8 micron) membranes. It can be assumed, that due to the great adsorption ability of polyelectrolytes, which decrease the pore size, their high rejection on microfiltration membranes can be obtained. Of course, the separation must be performed under pre-selected circumstances.

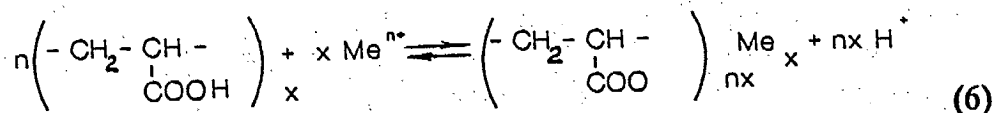
B. Removal of Ca, Fe and Mn with Polyacrylic and Polystyrenesulfonic Acids

Figure 3 presents the results of the microfiltration of a solution containing calcium, iron, and manganese. Polyacrylic acid was used as the binding agent. Similar results were obtained when the sodium salt of polyacrylic acid (Fig.4) or polystyrenesulfonic acid (Fig.5) were used as the binding agents. The following regularities should be noted:

- decreasing pH results in decreasing retentions of both polymer and metals;
- at the same pH level, retention of metals increases in the order: Ca < Mn < Fe;

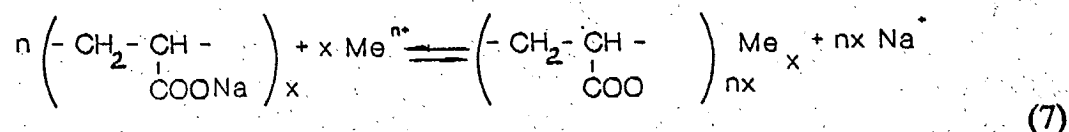
These phenomena may be explained in the following way:

Polyacrylic acid has the properties of a typical weak cation exchange resin where protons of carboxylic groups may be replaced by metal ions Me^{n+} :



An increase in proton concentration, i.e. a decrease in pH, causes the chemical equilibrium (6) to shift to the left. This decreases the binding degree Φ , and, according to the expression (2), reduces rejection R. This explains the results presented in Fig. 3.

In case of sodium salt of polyacrylic acid, sodium ions were replaced:



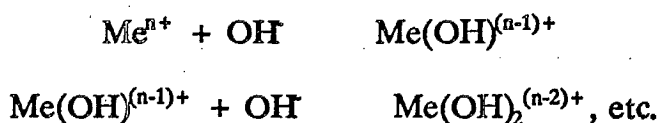
Decreasing pH in this system promotes the generation of an inactive protonated form of polyacrylic acid $(CH_2CHCOOH)_x$ and decreases R. This explains the results presented in Fig.4.

In all cases, the binding degree of metals increases in the order: $\text{Na} < \text{Ca} < \text{Mn} < \text{Fe}$ (rejection of sodium was equal to zero in all experiments which means that it was replaced by all metals: iron, calcium, and manganese). It should be noted that the same regularity occurs for solid weak acidic cation exchange resins containing carboxylic groups [13]. One can see that at a certain range of pH, rejection of iron differs significantly from rejection of calcium or manganese. This method, therefore, may be used not only to remove all these metals, but to separate them as well.

Similar phenomena take place when PSSA is used as a binding agent. Here, decrease in pH generates the formation of an inactive protonated form of PSSA, which prevents the formation of metal-polymeric compounds. This explains the results presented in Fig.5.

Increasing the polymer concentration will cause an increase in the binding degree Φ and, according to the equation (2), increase of rejection (R). This is confirmed by the experimental results presented in Fig.6. The rejection increases with an increasing polymer concentration and reaches approximately 0.995 at a polymer concentration of 300 mg/l. At these conditions, the majority of the metal ions are bound to the polymer so that further polymer addition does not increase R.

It must be noted that at lower polymer concentrations, the phenomena of metal hydroxide formation occurs. In fact, at a polyacrylic acid concentration of 100 mg/l, the rejection of metals first increases, reaches the maximum at neutral pH, then drops (Fig. 7). Increasing pH reinforces not only the binding of metals to polymer, but also causes the formation of metal hydroxides which are unable to interact with the polyacid:



In this case, polymer and hydroxyl ions are competitors in the reaction with metal ions. Therefore, increasing pH at a polymer deficit promotes hydroxide formation and results in a reduced metal rejection.

C. Removal of Heavy Metals with Polyethylenimine

Polyethylene was chosen for this series of experiments since it is known that it forms stable complexes with transitive metal ions [5,15]. The results of copper, lead and nickel removal with PEI are presented in Fig.8. In this figure, one can see the same regularity as in the case of Fe, Ca and Mn removal using polyacids: the higher the pH, the higher the metals rejection. The explanation of this phenomenon appears to be as follows. In aqueous

solutions PEI can exist in two forms: neutral, in which it is able to form complexes with metal ions, and protonated, in which it can not interact with them. Decreasing the pH causes an increase in the degree of protonization of the polymer and results in a decreased metals rejection. The results obtained in this series of experiments correspond quite well to the results of ultrafiltration removal of heavy metals with PEI [5].

D. Regeneration of the Polymeric Binding Agent

The cost effectiveness of this recovery and separation technique can be significantly improved by regenerating the polymeric binding agent. At a lower pH, the metal ions rejection is significantly lower than at a higher pH. Hence, by acidifying the concentrate and then filtering it, separation of the metal ions from the polymer is possible. The polymer rejected by the membrane may be re-used for binding of metal ions in a new portion of the groundwater. The results obtained with the regenerated polymer are listed in Table 4.

From Table 4, one can see that the rejection of calcium was stable through-out the five cycles when the pH was held at 2.0. The rejection; however, deteriorated significantly when the pH was maintained at 4.0. This phenomena can be explained as follows: at pH 4, most of iron remains bound to the polymer while the calcium and manganese are substituted by protons on the polymer. As shown in Figure 3, iron is highly rejected at pH 4 (therefore, bound to the polymer) while the other two metals pass through the membranes. As each regeneration cycle proceeds, more and more iron is built up within the system, occupying the otherwise available binding spaces on the polymer. This leads to a reduced rejection of the other two metals, calcium and manganese. At pH 2; however, all metals are dissociated from the polymer during the regeneration and all the polymer spaces are free to bind with the metals.

It should be also kept in mind that the lower the pH of a solution, the thinner the layer of adsorbed polymer inside the pores of the membrane. This may result in a decreased rejection of the polymer by the membrane; therefore, the polymer losses will be inevitable. To avoid this, ultrafiltration instead of microfiltration could be recommended for regeneration. Even if the polymer sorption is negligible, the pore size of an ultrafiltration membrane will be small enough for the complete rejection of the polymer, whereas metals will still pass through the membrane freely.

CONCLUSIONS

1. The hybrid method involving polymer binding and microfiltration may be used for the removal of metal ions from groundwater. Membrane separation is possible due to the formation of a polymer layer inside the pores and on the surface of a microfiltration membrane.
2. Metals rejection depends upon experimental conditions including pH and polymer concentration. For all the polymers studied in the present work, an increased pH results in an increased metals rejection.
3. Polymeric reagents may be regenerated from the concentrate stream by concentrate acidification and its subsequent membrane separation. To avoid the losses of a polymer in its regeneration, ultrafiltration instead of microfiltration is recommended.

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LIST OF CAPTIONS

- Fig.1. Rejection of polyacrylic acid (R) on the ZETAPOR membrane vs. the molecular weight. Polymer concentration - 100 mg/l; transmembrane pressure - 0.3 bar.
- Fig.2. Flux of distilled water ($J [m^3 \cdot m^{-2} \cdot hr^{-1}]$) through the ZETAPOR membrane previously treated with polyacrylic acid vs. the molecular weight of PAA. Transmembrane pressure: 0.3 bar.
- Fig.3. Rejections of metals (R) as a function of pH. Polymer: PAA(90,000); membrane: ENKA; metals concentration; 10 mg/l; PAA concentration: 300 mg/l; transmembrane pressure: 0.3 bar.
- Fig.4. Rejections of metals (R) as a function of pH. Polymer: Alcosperse AS-104; membrane: MEMBRALOX; other experimental conditions: see Fig.3.
- Fig.5. Rejection of metals (R) as a function of pH. Polymer: PSSA; other experimental conditions: see Fig.3.
- Fig.6. Rejection of calcium (R) vs. Aquatreat AR-4 concentration. Membrane: MEMBRALOX; Ca concentration: 30 mg/l; transmembrane pressure: 1 bar.
- Fig.7. Rejection of calcium (R) at the polymer deficit vs. pH. Polymer: PAA (90,000); membrane: ENKA; Ca concentration: 30 mg/l; polymer concentration: 100 mg/l; transmembrane pressure: 1 bar.
- Fig.8. Metals rejection (R) as a function of pH. Polymer: PEI; metals concentration: 10 mg/l; PEI concentration; 100 mg/l; transmembrane pressure: 1 bar.

FIGURE 1. REJECTION OF POLYACRYLIC ACID (R) ON THE ZETAPOR
MEMBRANE VS. THE MOLECULAR WEIGHT.

POLYMER CONCENTRATION - 100 MG/L; PRESSURE - 0.3 BAR

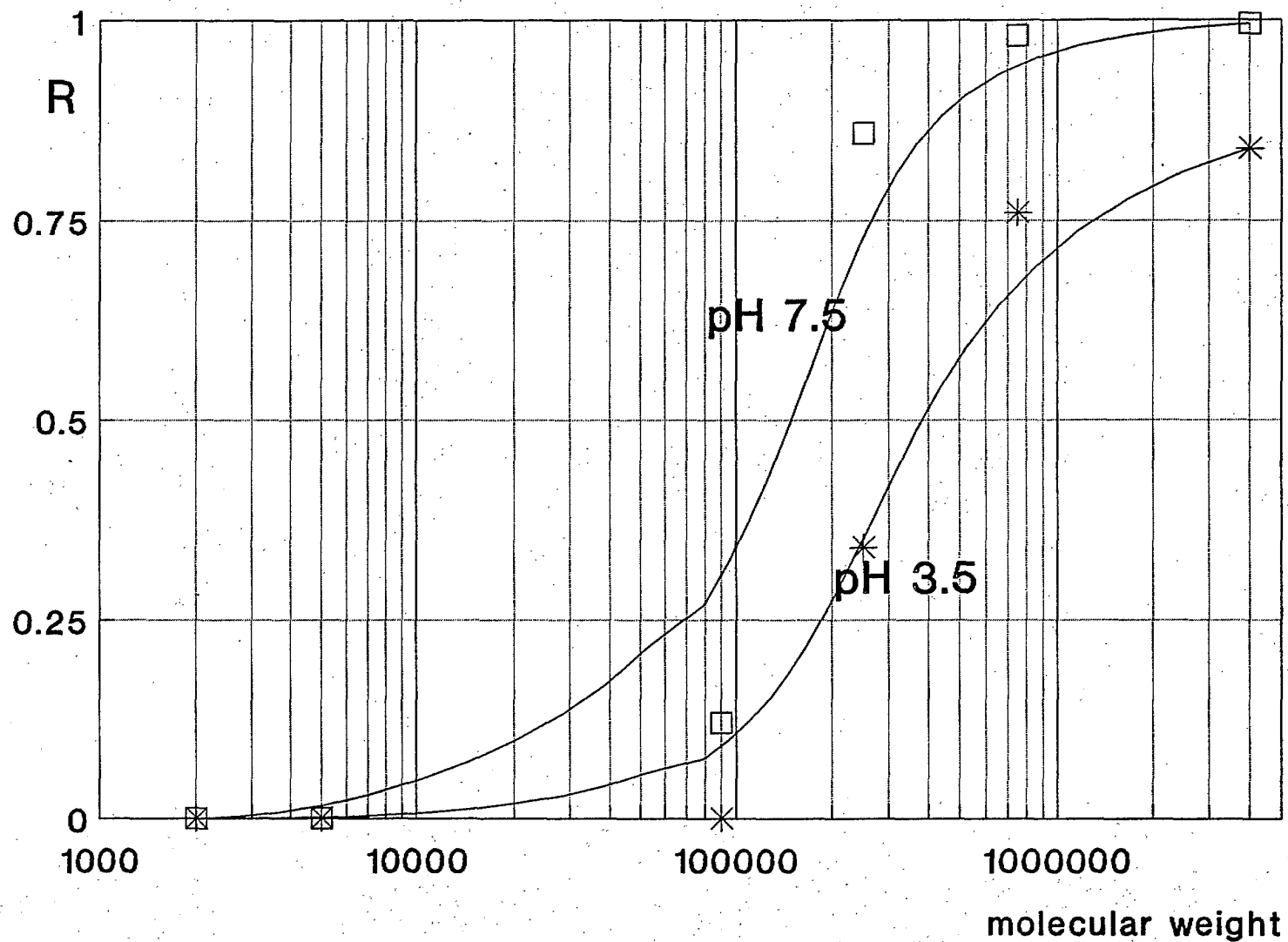


FIGURE 2. FLUX OF DISTILLED WATER (J[M/HR]) THROUGH
THE ZETAPOR MEMBRANE PREVIOUSLY TREATED WITH POLYACRYLIC
ACID VS. THE MOLECULAR WEIGHT OF PAA. PRESSURE - 0.3 BAR

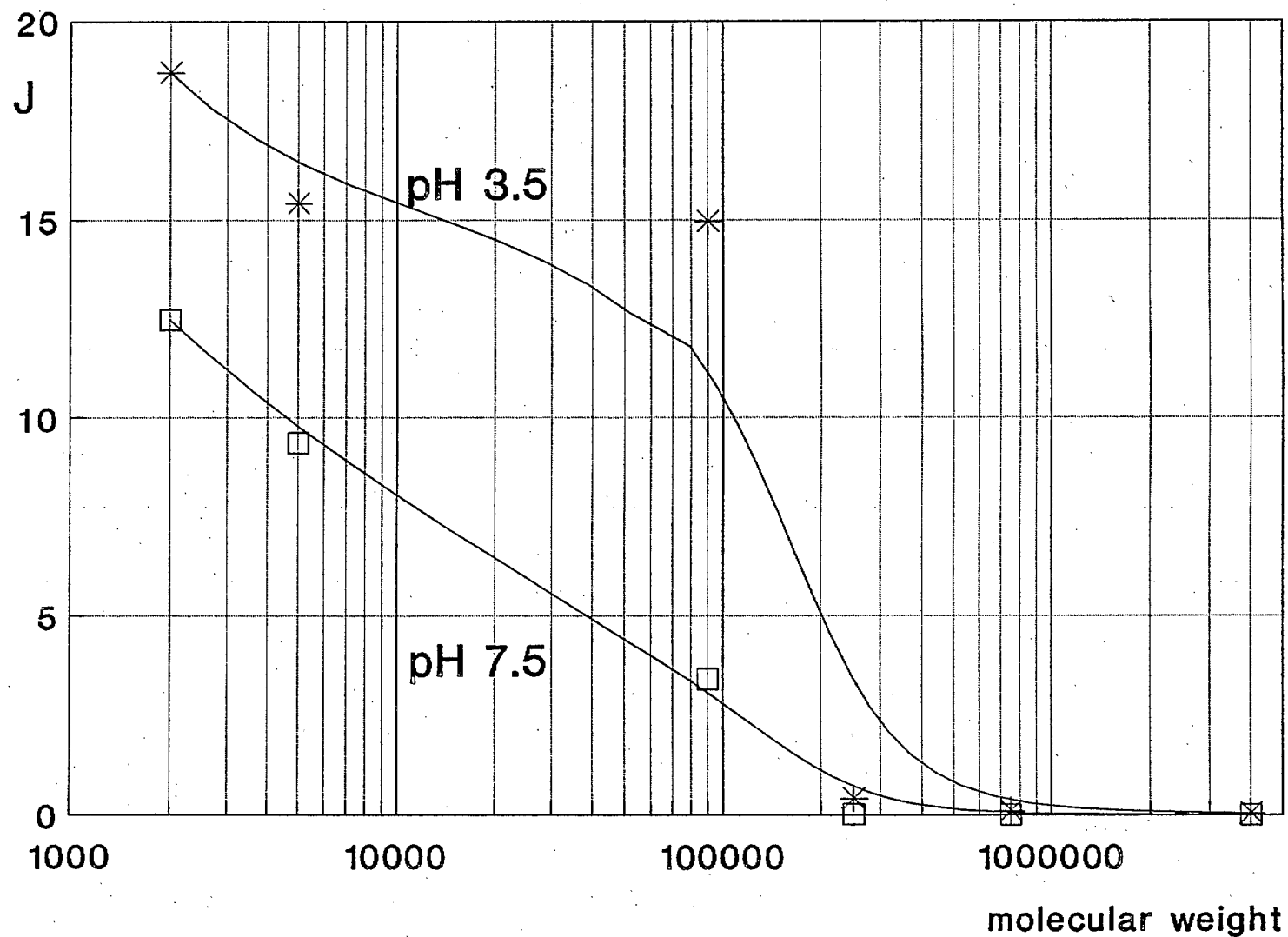


FIGURE 3. REJECTIONS OF METALS AS A FUNCTION OF pH.
POLYMER: PAA(90,000); MEMBRANE: ENKA; METALS CONCENTRATION:
10 MG/L; PAA CONCENTRATION: 300 MG/L; PRESSURE: 0.3 BAR

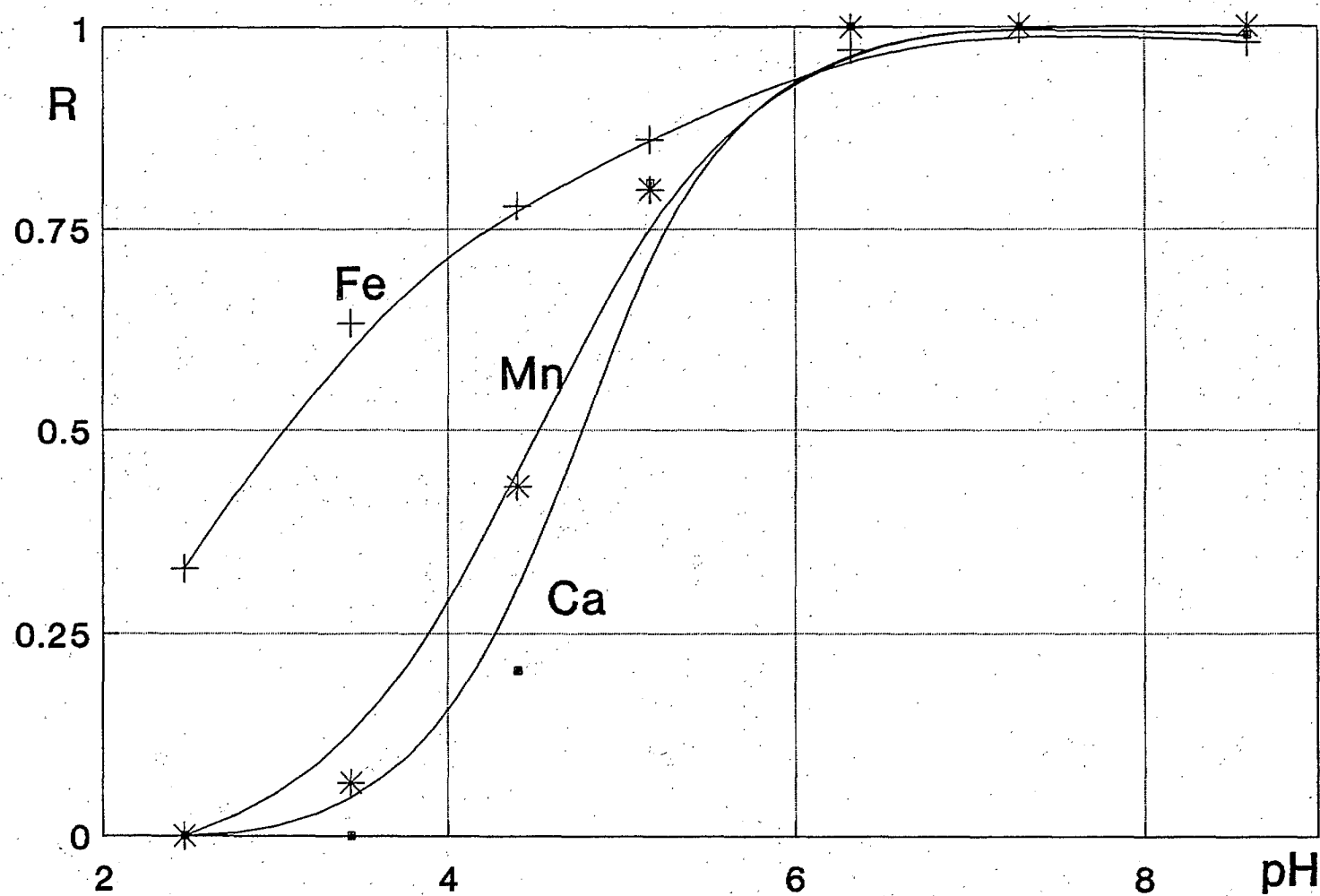


FIGURE 4. REJECTIONS OF METALS (R) AS A FUNCTION OF pH.
POLYMER: ALCOSPERSE 104; MEMBRANE: MEMBRALOX;
OTHER EXPERIMENTAL CONDITIONS: SEE FIGURE 3.

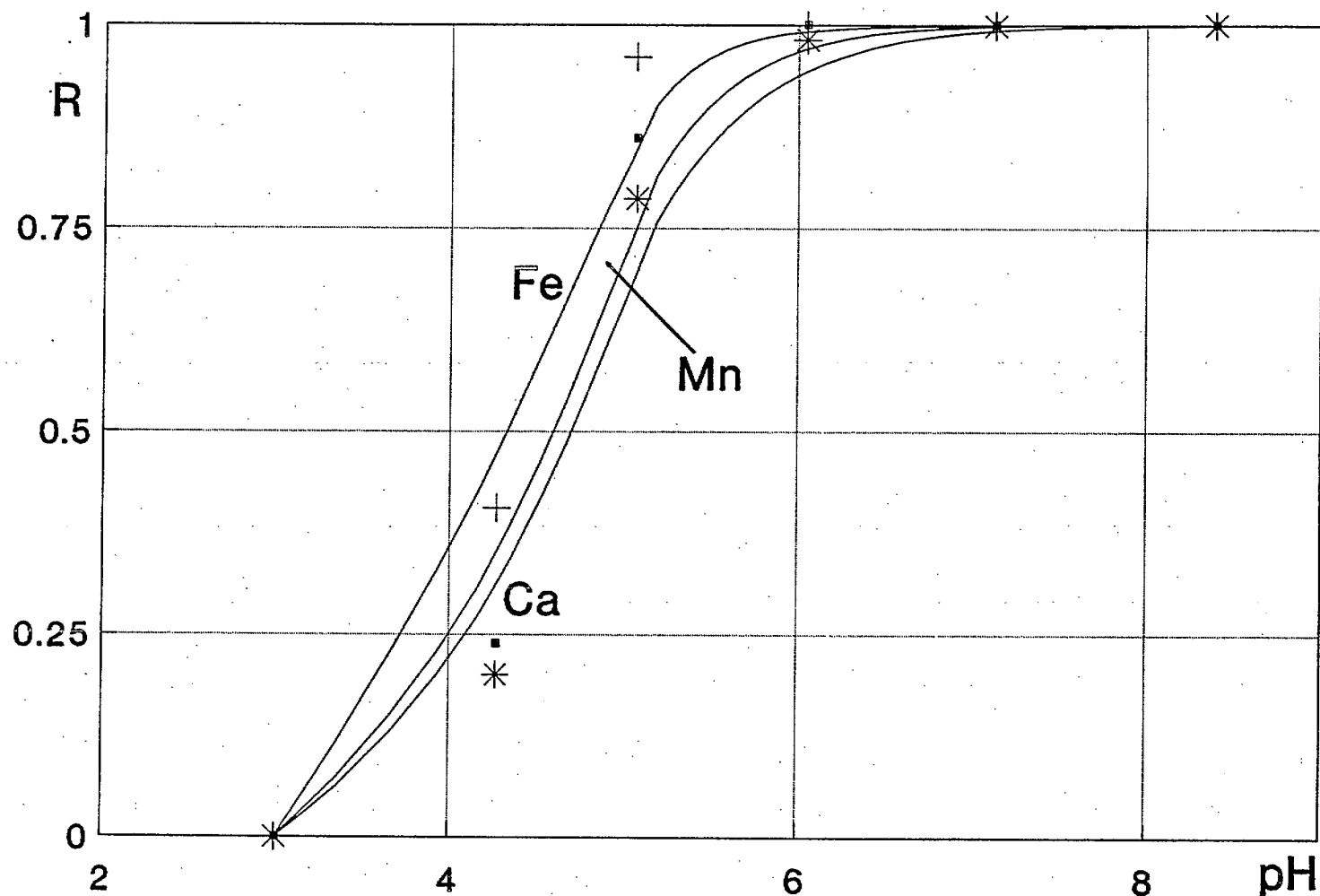


Fig. 4. K. Volehek et al.

FIGURE 5. REJECTION OF METALS (R) AS A FUNCTION OF pH.
POLYMER: PSSA; OTHER EXPERIMENTAL CONDITIONS: SEE FIGURE 3.

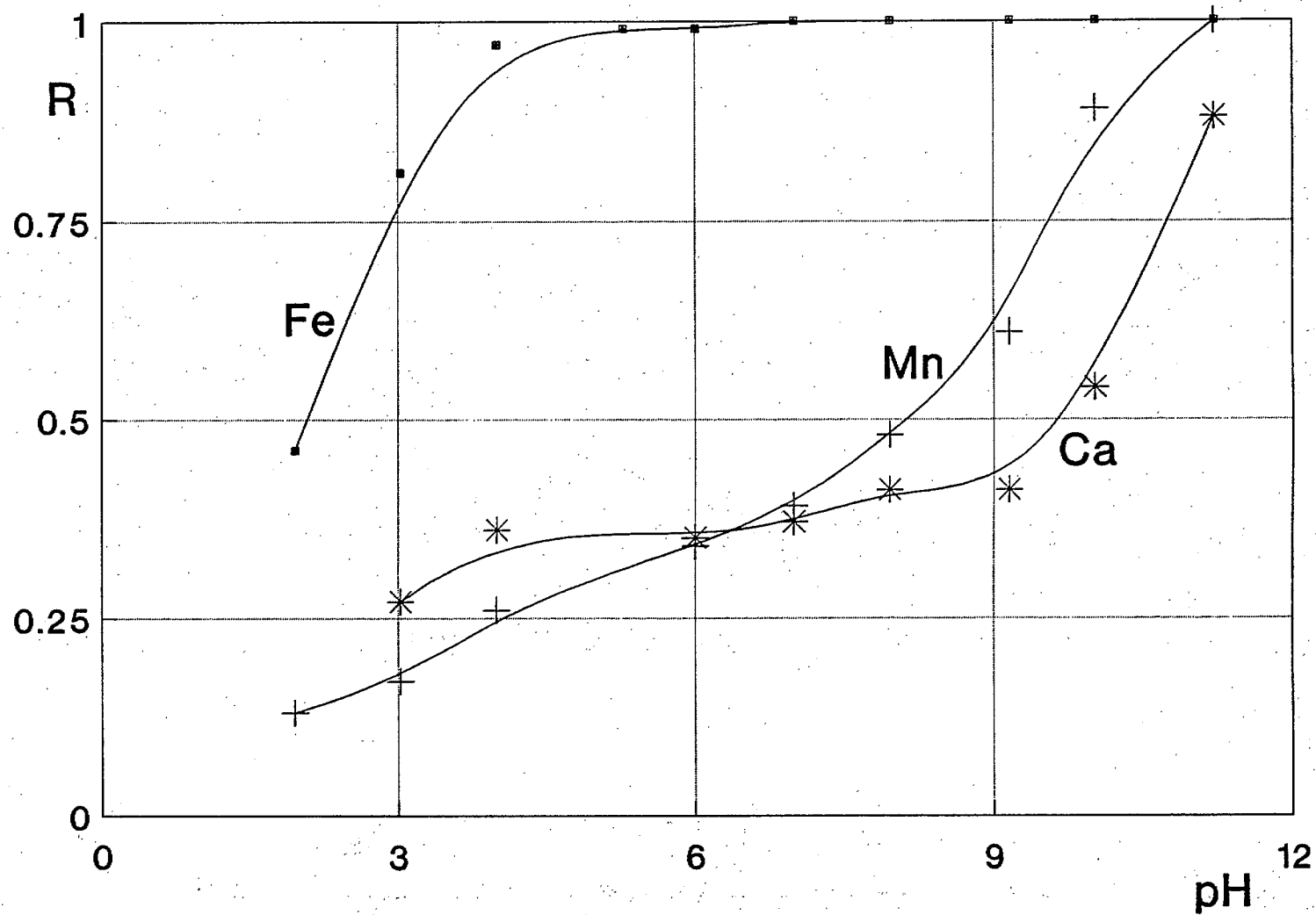


FIGURE 6. REJECTION OF CALCIUM (R) VS. AQUATREAT AR-4
CONCENTRATION. MEMBRANE: MEMBRALOX; CA CONCENTRATION:
30 MG/L; PRESSURE: 1 BAR

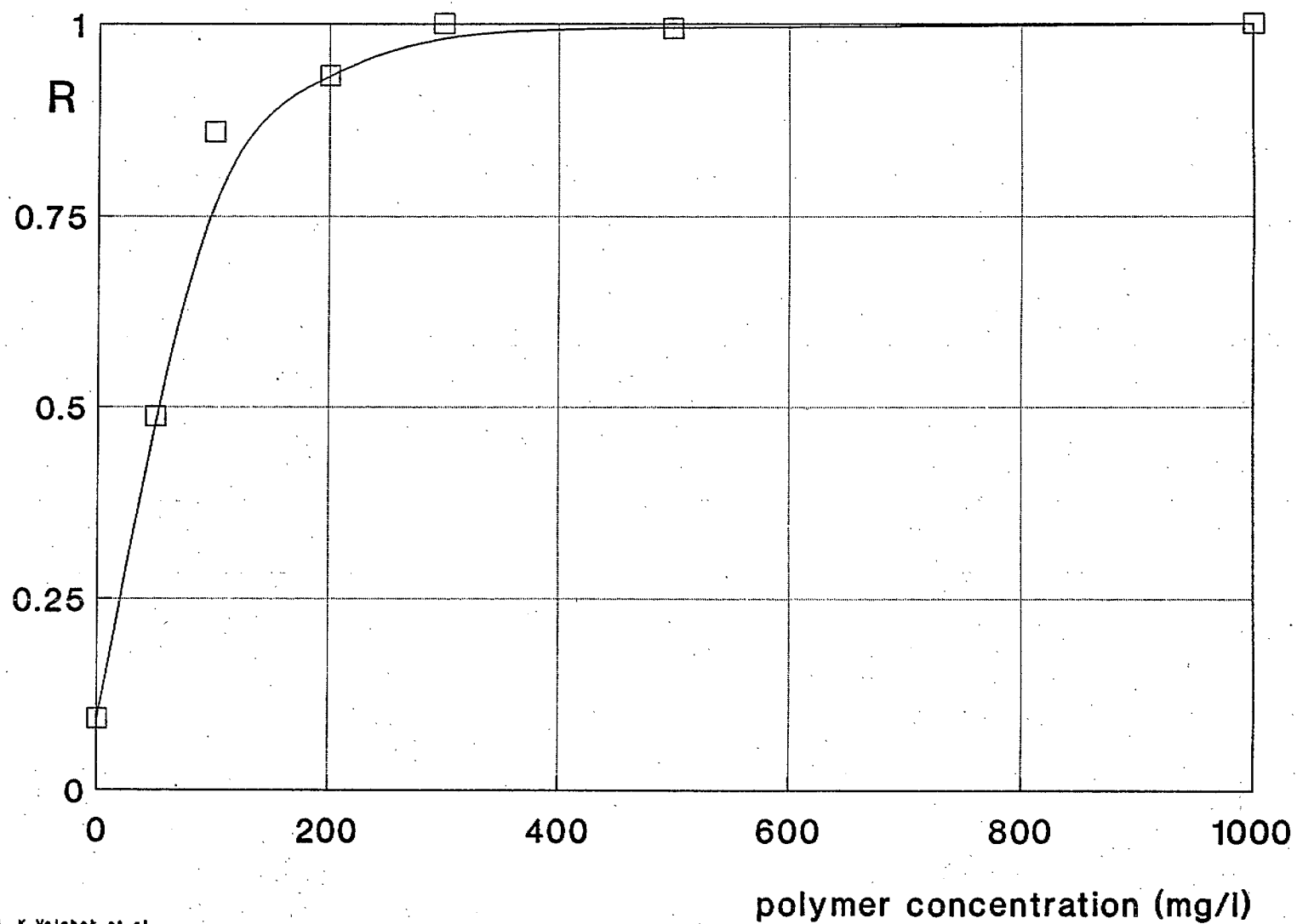


Fig. 6. K.Volchek et al.

FIGURE 7. REJECTION OF CALCIUM (R) AT THE POLYMER DEFICIT
VS. pH. POLYMER: PAA(90,000); MEMBRANE: ENKA;
CA CONCENTRATION: 30 MG/L; PRESSURE: 1 BAR

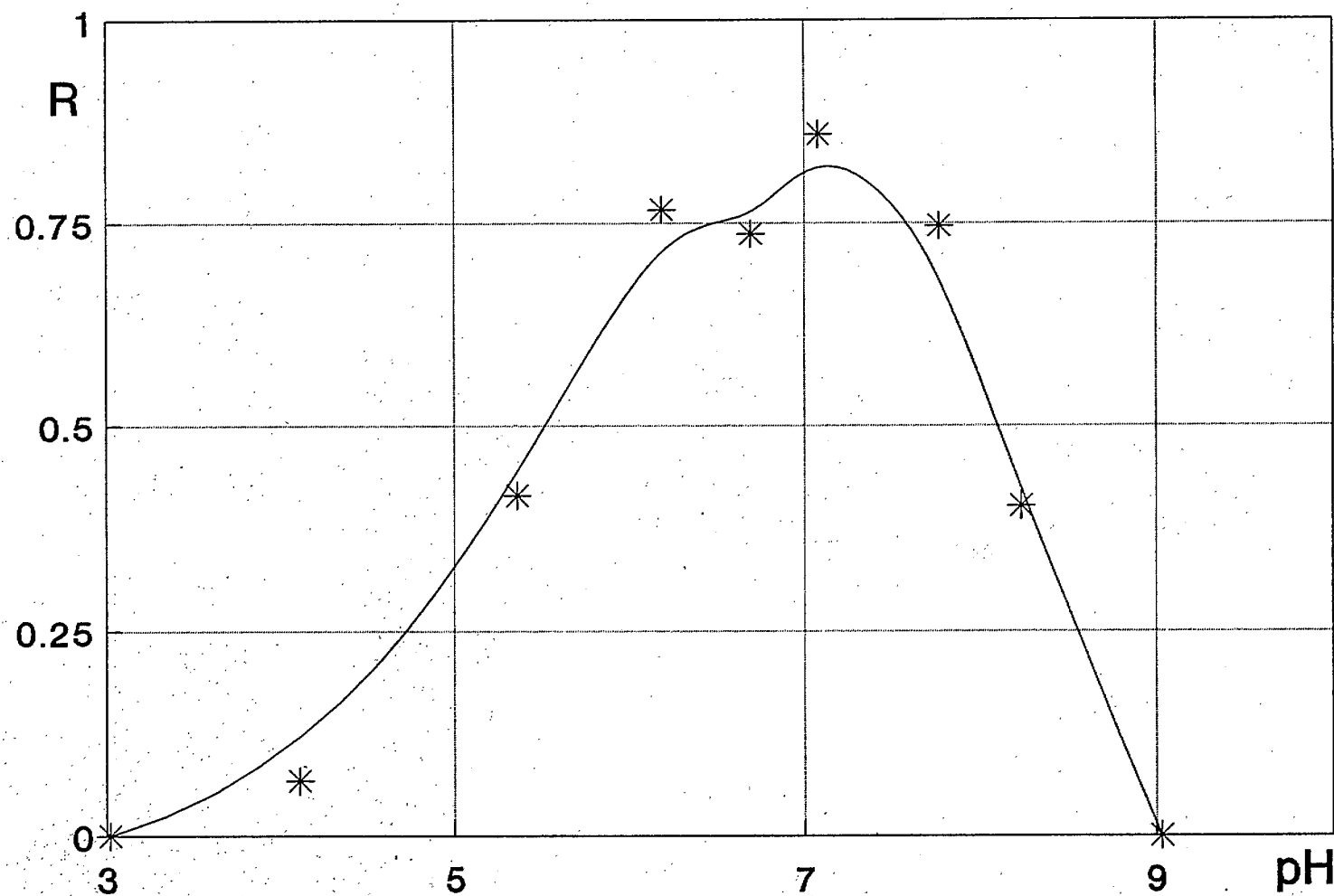


FIGURE 8. METALS REJECTION (R) AS A FUNCTION OF pH.
POLYMER: PEI; METALS CONCENTRATION: 10 MG/L;
PEI CONCENTRATION: 100 MG/L; PRESSURE: 1 BAR

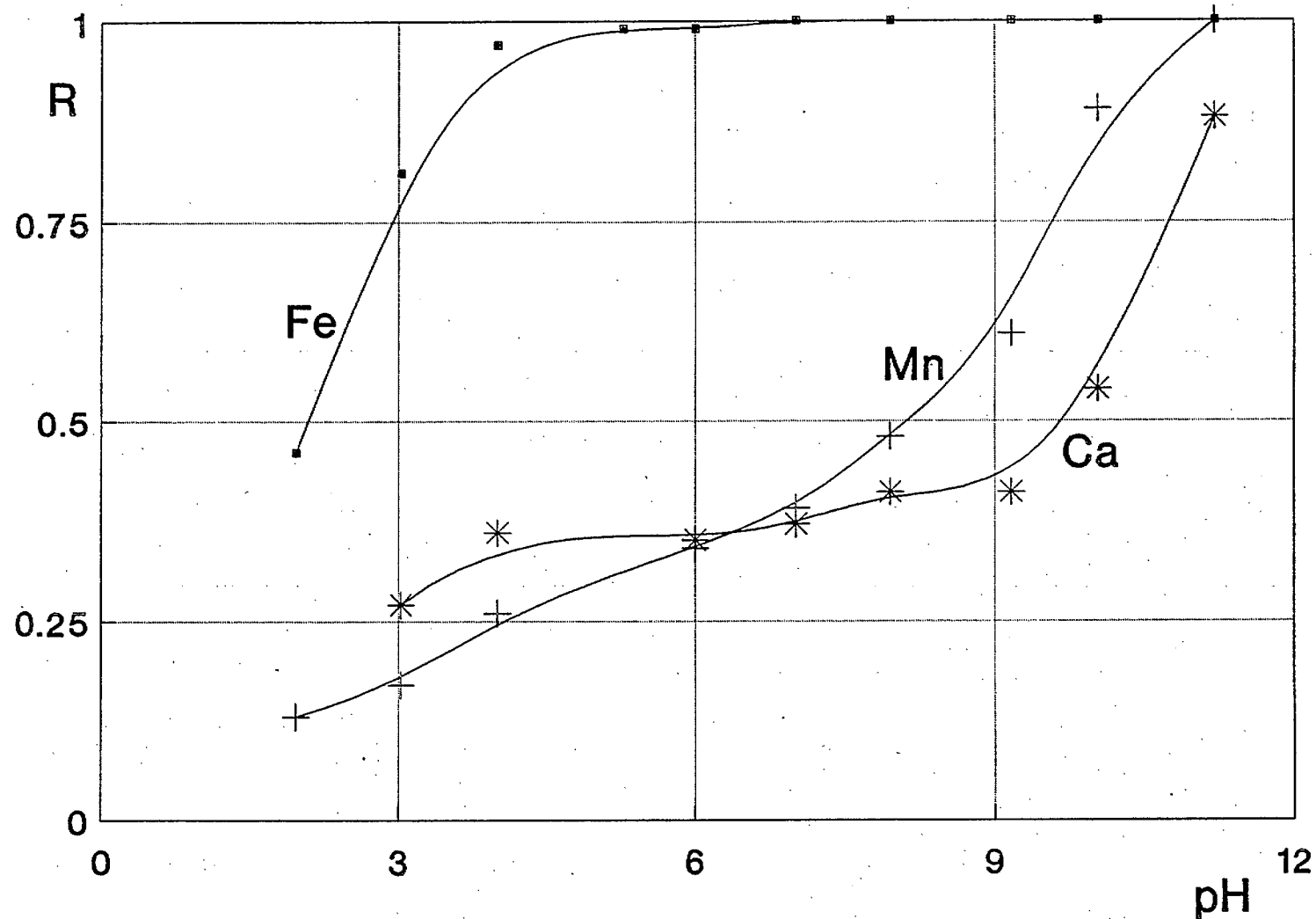


Table 1.
Polymeric binding agents

Polymer	General formula	Average molecular weight	Supplier
Polyacrylic acid (PAA)	$\left(\begin{array}{c} \text{CH}_2 - \text{CH} - \\ \\ \text{COOH} \end{array} \right)_x$	2,000 5,000 90,000 250,000 750,000 4,000,000	Aldrich Chemical Co.
Polyethylenimine (PEI)	$(-\text{CH}_2-\text{CH}_2-\text{NH}-)_x$	50,000-60,000	Aldrich Chemical Co.
Polystyrenesulfonic acid (PSSA)	$\left(\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{SO}_3\text{H} \end{array} \right)_x$	70,000	Polysciences, Inc.
Aquatreat AR-4*	polyacrylic acid	59,000	Alco Chemical Co.
Alcosperse AS-104*	sodium polyacrylate	60,000	Alco Chemical Co.

* technical data from [14]

TABLE 2.
TEST MEMBRANES CHARACTERISTICS

Membrane	Average pore size, microns	Membrane material	Shape	Manufacturer
ZETAPOR	1.2	nylon	flat-sheet	Cuno, Inc.
ENKA	0.2	poly-propylene*	tubular	Enka AG
MEMBRALO X	0.8	ceramic	tubular	Alcoa Separ. Technol., Inc.
BIOKEN	10,000**	poly-ethersulfone	flat-sheet	Bioken Separ., Inc.

* the membrane was hydrophylized with aqueous solution of isopropyl alcohol

** molecular weight cut-off for the ultrafiltration membrane

TABLE 3.
Dependence of the effective pore diameter (d) and the thickness
of an adsorbed polymer layer (δ) on the molecular weight
of polyacrylic acid

Molecular weight	pH 3.5		pH 7.5	
	d, nm	δ , nm	d, nm	δ , nm
2,000	1176	12	1062	69
5,000	1120	40	988	106
90,000	1112	44	768	216
250,000	454	373	210	495
750,000	314	443	168	516
4,000,000	261	469	160	520
4,000,000	684*	258*		

* at pH 1.84

Membrane: Zetapor; Polymer concentration: 100 mg/l;
Transmembrane pressure: 0.3 bar.

TABLE 4.
DATA OF THE RECYCLED REGENERATED* PAA

Regeneration at pH 2.0		Regeneration at pH 4.0	
Cycle No.	Rejection of Ca	Cycle No.	Rejection of Ca
0	0.998	0	0.995
1	0.979	1	0.992
2	0.984	2	0.972
3	0.989	3	0.949
4	0.993	4	0.841

* regeneration was carried out using the BIOKEN ultrafiltration membrane in order to decrease losses of the polymer at lower pH.

Oil Spill Sorbents: Testing Protocol and Certification Listing Program

by

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INTRODUCTION

A universally accepted standard method for testing oil spill sorbents is not currently employed by the majority of sorbent manufacturers. End-users are limited to manufacturers' and distributors' claims which may be perceived as being biased. Environment Canada has spearheaded a drive to develop an official Canadian standard for the testing and certification of sorbents using the Canadian General Standards Board (CGSB) as the certification body. It is anticipated that Environment Canada will provide a system to maintain an unprejudiced method for testing oil spill sorbents.

BACKGROUND

Environment Canada's Emergencies Engineering Division (EED) is mandated to evaluate existing technologies and act as a proving ground for technologies deemed new and innovative in areas of Oil and Chemical Spill Cleanup. The sorbent testing program had its beginnings in 1974 when Environment Canada released its first publication entitled "Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents". Updates to this publication were release every four or five years. The time lag between publications and the limited number of sorbents tested were acceptable limitations to this program as interest in sorbents was relatively limited. Since that time; however, interest in sorbent performance evaluation has grown steadily. Recent events including the Exxon Valdez spill in Prince William Sound and the spills during the Gulf War spurred renewed interest in sorbents.

Manufacturers and Distributors were aggressively marketing their products to Government, Oil Spill Co-ops, and other Non-Government Organizations (NGOs). These end-users had limited third party data from which they could base a purchasing decision. First Responders, sceptical of the performance and safety aspects associated with some sorbents, requested that sorbents pass some sort of approval mechanism before being considered. It was this demand for an approval mechanism that catalyzed the development of the sorbent evaluation and certification program.

PROGRAM DEVELOPMENT

As requests for sorbent performance information grew, it became obvious that an ongoing evaluation system was warranted. Requests for "approving" or "certifying" sorbents could not be met simply because such a mechanism did not exist. At this point EED began talks with the Canadian General Standards Board (CGSB). This Federal Government Agency is one of only five National Standardizing bodies in Canada. A committee was formed through the CGSB consisting of equal representation from interested parties, producers, and end-users throughout North America. This led to the development of a new test procedure based upon work Environment Canada had performed in the past¹, but also incorporating methods from the American Society for Testing and Materials (ASTM)². These protocols currently enjoy top status as sorbent test protocols in North America.

CGSB SORBENT CERTIFICATION AND LISTING PROGRAM

The CGSB Sorbent Certification and Listing Program currently consists of two documents. One is a standard for sorbent materials, while the other specifically defines testing procedures for sorbents used on crude oil and similar spills. The program is structured in this fashion to allow the introduction of additional testing protocols. One anticipated protocol will deal specifically with testing sorbents for use with aggressive chemicals.

Standard C**/CGSB-183.1 encompasses "Sorbent Materials" and relates to operational and performance criteria for the clean-up and control of oil and hazardous substances spills. It is within the "Sorbent Materials" document that testing protocol terms and calculations are explicitly defined. Sorbents are classified by physical type based on ASTM F726-81 (1986) as follows:

- Type I: sheet, pad, blanket, mat
- Type II: loose - unconsolidated, particulate material
- Type IIIa: pillows and socks - sorbent material contained by an outer fabric or netting.
- Type IIIb: booms - sorbent material contained by outer fabric or netting which has a lengthwise dimension exceeding other dimensions by a factor of at least five and whose sorption capacity would be significantly altered if cut to meet Type I size requirements.

Type IIIc: sweeps

Type IV: agglomerated unit - pom pom, yarn, or netting which offer low impedance to highly viscous fluids.

An Interim Standard is now in place, but is limited to testing Type I and Type II sorbents. It is anticipated that testing protocols for remaining Types will be incorporated into the official Standard during the fourth quarter of 1992.

Sorbents are also classified by category which determines the recommended type of application as follows:

L-W category: sorbents which are recommended for sorbing spills on water or land.

L category: sorbents which are recommended for sorbing spills exclusively on land.

W category: sorbents which are recommended for sorbing spills exclusively on water.

I-S category: sorbents which are recommended for sorbing spills in an industrial setting (aggressive chemicals).

ALTERNATE: encompass all sorbents which technically fail tests, but possess at least one redeeming characteristic which warrants further consideration.

The Sorbent Materials Standard goes on to identify nine sorbent characteristics which should be considered. Specific labelling and Material Safety Data Sheets are a requirement, as are sturdy storage properties.

Testing Procedure

Standard C**/CGSB-183.2 covers laboratory conducted performance tests for all forms of sorbent materials, regardless of their mode of action, for the sorption of crude oil, its contained natural components, and mixtures thereof.

Performance Characteristics

Specific characteristics were initially identified as being highly desirable. They are as follows:

- Buoyancy: Data obtained would allow confirmation that a particular sorbent may be suited for use in a spill on water. Sorbents that sink may pose a threat to aquatic life by transporting hazardous liquids to the sediment causing infiltration into the entire food chain.
- Low Water Pick-up: Non-selective sorbents may pick up water in addition to oil if placed in an aquatic environment. This may not prove to be a major

hindrance if the sorbent remains floating; however, any water sorbed would displace the spilled oil, thus hindering performance.

- **High Oil Pick-up:** The rate of pick-up in addition to the sorbent's capacity would be tested. A sorbent's ability to be "self acting" could limit the application to specific spill scenarios.
- **Reuse:** Some sorbents allow the sorbed liquid to be extracted via mechanical or chemical means enabling reuse. This could limit the amount of solid waste generated during a spill cleanup operation. Safety aspects of attempting reuse should be carefully considered.
- **Low Rate of Release:** Liquids sorbed by most sorbents are released back into the environment to some degree. The extent of release will vary dramatically depending upon the sorbent used. The importance of this release depends upon the specific spill scenario, and storage equipment available at the spill site.

Test Method

The following tests have been established to evaluate the performance of sorbents on oil and water. The procedures followed are condensed versions of the test methods outlined by the Canadian General Standards Board.

Degradation Pre-Test (Static): This test measures the sorbent's hydrophobic characteristics in addition to determining buoyancy of a sorbent. A test cell (crystallizing dish having a diameter of 190 mm) is filled with a layer of water approximately 80 mm deep. If Type II sorbent is being tested, a mesh basket having openings of approximately 1 mm is lowered into the crystallizing dish. The sorbent sample (Type I: 13 cm x 13 cm, Type II: 10 grams) is placed into the cell. The test cell is then covered and left for 15 minutes. After 15 minutes the sorbent is removed from the water and observations are noted. The sorbent is weighed to determine water pick-up. Samples that pass are then prepared for the Degradation Test (Static).

Degradation Pre-Test (Dynamic): This test is used to determine the buoyancy of sorbents in simulated wave conditions. If the sorbent passes this test for buoyancy, it is then very unlikely that the sorbent will sink in most applications. Sample pieces of the sorbent (Type I: 16 pieces of 3 cm x 3 cm, Type II: 3-5 grams) are placed in a 2 litre jar which is half filled with water. The container is then placed on its side and mounted on a shaker table set at a frequency of 10 cycles per minute for a duration of 15 minutes. The sorbent is then removed from the water and observations are noted. The sorbent is weighed to determine water pick-up.

Degradation Test (Static): This is a test for buoyancy, sorbent capacity, and oil retention. A sorbent sample from the static pre-test is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left undisturbed for a period of at least 48 hours. The sorbent is then removed and hung from a balance (Type I: hung vertically using a clip, Type II: hung horizontally using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 15 seconds, 30 seconds, 1 minute,

2 minutes, 5 minutes, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent in order to determine water pick-up.

Degradation Test (Dynamic): This test follows the methodology of the Degradation Pre-Test (Dynamic) with the exception that 150 ml of crude oil is introduced into the 2 L jar. Observations of the sorbent's behaviour during agitation are recorded. After 15 minutes the sorbent is removed and weighed to determine oil pick-up. Mechanical compression is used to extract liquid from the sorbent to determine water pick-up for comparison with the static test.

L-W Category Test: This is a test for sorbent capacity and reuse. A fresh sorbent sample is placed on a 5 mm layer of crude oil floating on an 80 mm layer of water. The sample is left for a period of 15 minutes. The sorbent is then removed and left to drip for 30 seconds before being weighed (Type I: hung by clip, Type II: hung by basket). Observations pertaining to the physical conditions of the sorbent are recorded. Mechanical compression is used to extract remaining liquid from the sorbent for reuse testing and water content determination. The data is also compared with Degradation Test (Static) results.

L Category Test: This is a test for sorbent capacity, reuse and retention. A fresh sorbent sample is placed on a 7.5 mm layer of crude oil. The sample is left for a period of 15 minutes. The sorbent is then removed and hung from a balance (Type I: hung vertically using a clip, Type II: hung horizontally using a basket). Observations pertaining to the physical condition of the sorbent are recorded. The weight of the sorbent is measured as oil drips after 15 seconds, 30 seconds, 1 minute, 2 minutes, 5 minutes, and 30 minutes. A retention profile is obtained from this data, as is the sorbent's capacity. Mechanical compression is used to extract remaining liquid from the sorbent for reuse testing.

W Category: Data obtained from the L-W test and the Degradation Test (Dynamic) will determine if a sorbent should be designated for the W Category. A sorbent requiring agitation would not be recommended for use on land thus may fall into the W Category.

I-S Category Test: This testing procedure is currently under review.

Non Performance - Handling

This information is provided by the manufacturer for the benefit of the end-user, but is not a requirement for certification.

- **Tensile Strength:** This characteristic becomes extremely important when dealing with sorbent booms. This characteristic determines the ability of a boom to retain its' integrity under the strain of currents and wave action.
- **Storage:** Ideally, a sorbent would occupy a minimum of storage space, while

exhibiting a high sorption capacity. Storage space within facilities is often very limited.

- Disposal: Proper and safe disposal methods should be addressed before application of any sorbent to a spill. Regulations may limit options.
- Static Resistance: In very dry conditions (desert or arctic) static resistance becomes an important safety concern. Specific conditions would have to be met before a static spark could ignite a flammable liquid. Steps should be taken to ensure safe working practices are enforced and working environments should be carefully scrutinized for ALL possible sources of static charge.

FUTURE AREAS OF DEVELOPMENT

Test liquids used in the Interim Standard represent a cross-section of viscosities for oil were chosen based upon suitability and availability. It is the intention of the CGSB General Sorbent Committee to expand upon this list to encompass hazardous liquids which are frequently spilled during transportation and in industrial settings. It is also the intention of the committee to expand into the area of sorbent boom testing.

CONCLUSIONS

This program should benefit both manufacturers and users. Manufacturers will be given the opportunity to have their products tested by impartial third party laboratories and certified to that effect. Users will be able to select products from manufacturers and compare data objectively. The reader should note that this program is prototype in nature. EED hopes to expand this type of program to encompass booms, skimmers, and related spill response equipment. A centralized database of performance and non-performance data pertaining to oil and hazardous liquid spills is the long-term goal.

ACKNOWLEDGEMENTS

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APPENDIX A

C**/CGSB-183.2

CANADIAN GENERAL STANDARDS BOARD Draft Method for Testing Sorbents

1. SCOPE

- 1.1 This method covers laboratory-conducted performance tests for all forms of sorbent materials, regardless of their mode of action, for the sorption of crude oil, its contained natural components and mixtures thereof.
- 1.2 The testing and evaluation of a product against this standard may require the use of materials and/or equipment that could be hazardous. This document does not purport to address all the safety aspects associated with its use. Anyone using this standard has the responsibility to consult the appropriate health and safety practices in conjunction with any existing applicable regulatory requirements prior to its use.

2. APPLICABLE PUBLICATIONS

- 2.1 The following publications are applicable to this method
 - 2.1.1 Canadian General Standards Board
25-GP-1M Method 44.1,
 - 2.1.2 Environment Canada
A Catalogue of Crude Oil and Oil Product Properties, 1990 EETD.
- 2.2 Reference to the above publications and to other standards is to the latest issues unless otherwise specified by the authority applying this standard. The sources for the publications are shown in the Notes Section 13.

3. PRINCIPLE

- 3.1 The sorbent materials are tested using established tests for factors relating to performance and handling.

4. SIGNIFICANCE AND USE

- This method is to be used as a basis for comparison of sorbents in a consistent manner and to present their characteristics and properties of value during their lifecycle. The sorbents shall be classified in the following types and categories.
- 4.1 Types
 - 4.1.1 Type I: sheet, pad, blanket.
 - 4.1.2 Type II: loose - unconsolidated, particulate material.
 - 4.1.3 Type III: enclosed
 - Type III Series A: pillows and socks - sorbent material contained by an outer fabric or netting.
 - Type III Series B: booms - sorbent material contained by outer fabric or

netting which has a lengthwise dimension exceeding other dimensions by a factor of at least five and whose sorption capacity would be significantly altered if cut to meet Type I size requirements.

Type III Series C: sweeps

- 4.1.4 Type IV: agglomerated unit - pom pom, yarn, or netting which offer low impedance to highly viscous fluids.

4.2 Categories

- 4.2.1 The L-W category refers to sorbents which are recommended for sorbing spills on land or water.
- 4.2.2 The L category refers to sorbents which are recommended for sorbing spills exclusively on land.
- 4.2.3 The I-S category refers to sorbents which are recommended for sorbing spills in an industrial setting.
- 4.2.4 The W category refers to sorbents which are recommended for sorbing spills on water only.
- 4.2.5 The ALTERNATE category will encompass sorbents which do not meet the requirements of the above categories but possess at least one redeeming characteristic which warrants further consideration.

5. APPARATUS AND MATERIALS

- 5.1 Test Cells (open): The dimensions of the test cells shall be of a large enough size to enable sorbent sample to float freely within the test basket. The following is a recommended vessel for Type I and Type II sorbents: Pyrex 190 mm (diameter) X 100 mm (depth) crystallizing dish with a watch glass or glass plate cover to accommodate a sample size not less than 130 mm (L) by 130 (W) or 6 grams. Type IIIa, Type IIIb, and Type IV may require larger cells to accommodate the sorbent sample dimensions.
- 5.2 Test Cells (enclosed): Test cells for use with shaker table should be large enough to enable wave action to thoroughly mix water and test liquid with sorbent. A 4L glass jar with a screw type lid is recommended.
- 5.3 Basket for Type II test: The basket shall be of a sufficient size and strength to accommodate the sample size and weight when saturated. A stainless steel basket having 1.5 mm¹ openings is recommended. The basket must not be so tall as to interfere with the lid.
- 5.4 Basket type IIIa, IIIb, IV test: The basket shall be of sufficient size and strength to accommodate the sample size and weight when saturated. A stainless steel mesh having 5 mm openings is recommended.

¹ The mesh should retain the sorbent, yet allow free oil to drain away from the sorbent.

- 5.5 Cold room or ice-cooled bath or equivalent to maintain a temperature of 15°C.
- 5.6 Top Loading Balance: 0.01 g resolution. A range of up to 400 g is recommended for sorbents of Type I, Type II. A higher upper limit may be necessary for Type IIIa, Type IIIb and Type IV configurations.
- 5.7 20 cm diameter weighing pans (non-stick coated pan or lined pan recommended for ease in cleaning).
- 5.8 Wringer-type Press: Hand operated with a double roller design not dissimilar to wringer-type washing machines. Tension to rollers should approximate 200 Newtons (45 lb_f) (eg. 20 kg weight).
- 5.9 Plate Press: Hydraulic press or similar device able to apply 1000 Newtons (224 lb_f) of force (eg. 100 kg weight) on top plate measuring 15 cm x 15 cm.
- 5.10 Graduated Conical Centrifuge Tubes (100 ml capacity).
- 5.11 Shaker table capable of producing a frequency of 150 cycles/min and an amplitude of 3 cm (Eberbach Shaker Table or equivalent).

6. TEST LIQUIDS

- 6.1 The types of fluids to be tested should be representative of the wide variety of fluids that sorbents could be used to clean up. The testing will be restricted to the following liquids.

- 6.1.1 Diesel Fuel Oil Grade 2-D, Automotive diesel fuel oil
 API GRAVITY: 39.4 (EETD 84) (15/15°C)
 DENSITY: 0.827 g/ml @ 15°C (EETD 85) DYN. VISCOSITY: 2.7 cP @ 15°C (EETD 85)
- 6.1.2 Crude Oil Alberta Sweet Mixed Blend
 API GRAVITY: 37.0 (EETD 84) (15/15°C)
 DENSITY: 0.839 g/ml @ 15°C (EETC 84) DYN. VISCOSITY: 9.2 cP @ 15°C (EETD 85)
- 6.1.3 Weathered Crude Alberta Sweet Mixed Blend (7 day weathered-25% volumetric loss)
 DENSITY: 0.883 g/ml @ 15°C (EETD 84) DYN. VISCOSITY: 48 cP @ 15°C (EETD 85)
- 6.1.4 Fuel Oil #6 Bunker C Fuel Oil (Fuel Oil Number 6)
 API GRAVITY 12.3 (EETD 88) (15/15°C)
 DENSITY: 0.974 g/ml @ 15°C (EETD 84) DYN. VISCOSITY: 48,000 cP @ 15°C (EETD 88)

Care must be taken when dealing with volatile liquids to ensure excessive evaporation does not occur.

7. CONDITIONING

- 7.1 Sorbents shall be inspected upon receipt by the testing agency and damaged specimens shall be removed and placed as needed.**
- 7.2 Condition all sorbent test specimens at $20 \pm 3^{\circ}\text{C}$ and $60 \pm 5\%$ relative humidity for not less than 24 h prior to testing. Condition specimens in a fully exposed state with no coverings or wrapping that would hinder the ambient equilibration process.**

8. NON-PERFORMANCE HANDLING

- 8.1 Storage**
- 8.2 Disposal**

9. PROCEDURE

9.1 Static Water Test: This procedure is designed to test for water pick-up under stagnant conditions. This test is performed at room temperature.

9.1.1 Type I Sorbent: The test cell is filled with a layer of water (80 mm). Approximately 130 mm x 130 mm square of a weighed sorbent sample is lowered into the test cell. The sorbent should float freely on the water. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes (± 20 sec) check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent vertically with a clip and let drain hanging over the cell for 30 seconds (± 3 sec). Place a tared weighing pan under the sorbent to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Retain the sorbent sample for use in the Static Long Term Sorption test. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.1.2 Type II Sorbent: The test cell is filled with a layer of water (80mm). A sorbent sample of approximately 200 ml is weighed then placed in a basket which is lowered into the test cell. The sorbent should float freely on the water. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes (± 20 sec) check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent with the basket and let drain over the cell for 30 seconds (± 3 sec). Place the basket over a tared weighing pan to catch any additional drips and immediately transfer the sorbent to the pan. Record the weight. Retain the sorbent sample for use in the Static Long Term Sorption test. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.1.3 Type IIIa Sorbent: *Not available at this time*

9.1.4 Type IIIb Sorbent: *Not available at this time*

9.1.5 Type IV Sorbent: *Not available at this time*

9.2 Long Term Static Sorption test: This procedure is designed to test for oil pick-up and determine hydrophobic properties of a sorbent sample. This test is performed at 15°C.

9.2.1 Type I Sorbent: Lower the wetted sample from the Static Water Test with a clip on a 5 mm layer of crude oil on excess water bath (80 mm or more) at 15°C. After a minimum of 24 hours check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent vertically with the clip and immediately hang from the balance. Place a tared

weighing pan under the hanging basket to catch any drips. Record the weight of the saturated sorbent at 30 seconds, 45 seconds, 1 minute, 2 minutes, 5 minutes, 15 minutes and 30 minutes. At the 30 minute mark transfer the sorbent to the pan. Transfer the sample and any residual liquid that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is distinctly visible in the conical tube then water content may be read directly. Reweigh the pressed sorbent and record the value. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Observations should include but not be limited to: buoyancy, disintegration, and appearance. The sorbent must remain structurally sound at saturation while being held along a side (avoid hanging by corner) of the sample and must not sink. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

- 9.2.2 Type II Sorbent: Lower the basket containing the wetted sample from the Static Water Test on a 5 mm layer of crude oil on excess water bath (80 mm or more) at 15°C. After a minimum of 24 hours check the condition of the sorbent. If the sample sinks go directly to step 9.5, otherwise remove the sorbent with the basket and immediately hang the basket from the balance. Place a tared weighing pan under the hanging basket to catch any drips. Record the weight of the basket with the saturated sorbent at 30 seconds, 45 seconds, 1 minute, 2 minutes, 5 minutes, 15 minutes and 30 minutes. At the 30 minute mark transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force (224 lb_f). This action may be cycled up to five times to extract remaining oil. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is distinctly visible in the conical tube then water content may be read directly. Reweigh the pressed sorbent and record the value. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Observations should include but not be limited to: buoyancy, disintegration, and appearance. The sorbent must not sink. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run (g/g) deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

- 9.2.3 Type IIIa Sorbent: *Not available at this time*
9.2.4 Type IIIb Sorbent: *Not available at this time*
9.2.5 Type IV Sorbent: *Not available at this time*

9.3 Dynamic Test: This procedure is designed to test for water pick-up and to determine oleophilic properties of a sorbent sample under dynamic conditions. This test is performed at room temperature.

9.3.1 Sample pieces of the sorbent (Type I: 4 pieces of 6 cm x 6 cm, Type II: 200 ml) are placed in a 4 litre jar which is half filled with water and sealed. The container is then placed on it's side and mounted on a shaker table set at a frequency of 150 cycles per minute and an amplitude of 3 cm for a duration of 15 minutes. If the sample sinks go directly to step 9.5, otherwise remove the sorbent by straining the contents of the jar through a mesh basket to catch the sorbent. The jar is half filled with fresh water and 10 ml of crude oil is added. The sorbent sample is returned to the jar which is then sealed. The container is placed on it's side and mounted on a shaker table set at a frequency of 150 cycles per minute and an amplitude of 3 cm for a duration of 15 minutes. The jar is allowed to settle for a period of 2 minutes, at which time observations are recorded. Observations include but are not limited to: quantity of sorbent submerged, physical appearance of sorbent, and persistence of oil sheen.

9.4 L-W test: This procedure will determine the amount of test liquid that a sorbent will pick up in 15 minutes. Fresh samples are used for this test which is performed at 15°C.

9.4.1 Type I Sorbent: The sorbent to be tested should be cut with a sharp edge to minimum dimensions of 130 mm x 130 mm square. The sorbent is then weighed and the value is recorded. The test cell is filled with an initial layer of water (80 mm or more) and a quantity of test liquid to produce the required thickness for the test. The required thickness for diesel fuel is 2.5 mm, while 5 mm is required for crude oil, bunker C, and weathered crude oil. The sorbent is lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes \pm 20 seconds (sorbent should be flipped at 8 minute mark) remove the sorbent with a clip and let drain hanging over the cell for 30 seconds (\pm 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Transfer sample and any residual liquid that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Reweigh the pressed sorbent and record the sample weight. Collect liquid in a graduated conical centrifuge tube for water content determination. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). Each sorbent sample shall be tested through five complete sorption cycles or until it's sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), Low Reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more

than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.4.2 Type II Sorbent: The sample size of the sorbent to be tested should be approximately 200 ml. The sorbent is weighed and the value is recorded. The test cell is filled with an initial layer of water (80 mm or more) and a quantity of test liquid to produce the required thickness for the test. The required thickness for diesel fuel is 2.5 mm, while 5 mm is required for crude oil, bunker C, and weathered crude oil. The sorbent is placed in a basket which is then lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes \pm 20 seconds remove the sorbent with the basket and let drain over the cell for 30 seconds (\pm 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force. This action may be cycled up to five times to extract remaining oil. Collect liquid in a graduated conical centrifuge tube for water content determination. Reweigh the pressed sorbent and record the sample weight. If the meniscus is not distinctly visible, the emulsion may be broken by adding a small quantity of toluene to the centrifuge tube (approximately 10-20 ml). All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.4.3 Type IIIa Sorbents: *Not available at this time*

9.4.4 Type IIIb Sorbents: *Not available at this time*

9.4.5 Type IV Sorbents: *Not available at this time*

9.5 L Test: This procedure will test the amount of pure test liquid that a sorbent can pick up in 15 minutes. Fresh samples are used for this test which is performed at 15°C.

9.5.1 Type I Sorbent: The sorbent to be tested should be cut with a sharp edge to minimum dimensions of 130 mm x 130 mm square. The sorbent is then weighed and the value is recorded. The test cell is filled with an initial layer of test liquid. The required thickness for all test liquids is 7.5 mm. The sorbent is lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes \pm 20 seconds (sorbent should be flipped at 8 minute mark) remove the sorbent vertically with a clip and let drain hanging over the cell for 30 seconds \pm 3 seconds. Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Transfer sample and any

residual oil that remains in the pan to the wringer press and squeeze the sorbent through the press five times. Reweigh the pressed sorbent to determine and record the sample weight. Each sorbent sample should be tested through five cycles or until its sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), low reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.5.2 Type II Sorbent: The sample size of the sorbent to be tested should be approximately 200 ml. The sorbent is weighed and the value is recorded. The test cell is filled with an initial layer of test liquid. The required thickness for all test liquids is 7.5 mm. The sorbent is placed in a basket which is then lowered into the cell. The sorbent should float freely on the test liquid. Place a lid on the cell to prevent evaporation and to protect the cell. After 15 minutes \pm 20 seconds remove the sorbent with the basket and let drain over the cell for 30 seconds (\pm 3 sec). Place a tared weighing pan under the sorbent sample to catch any additional drips and immediately transfer the sorbent to the pan. Determine and record the sample weight. Weigh the empty basket for future calculations. Transfer the sample and any residual liquid that remains in the pan to the plate press and squeeze the sorbent with 1000 Newtons of force. This action may be cycled up to five times to extract remaining oil. Reweigh the pressed sorbent to determine and record the sample weight. Each sorbent sample should be tested through five cycles or until its sorbency is reduced to 50% of its initial value or until disintegration. Sorbents will be classified as High Reuse (5 cycles), Medium Reuse (3 or 4 cycles), low reuse (1 or 2 cycles), or No Reuse. All tests are triplicated with the median of the three runs being used for calculations. If the value of any run deviates by more than 15 % from the mean of the three runs, then the samples shall be rejected and the test repeated with three new specimens.

9.5.3 Type IIIa Sorbents: *Not available at this time*

9.5.4 Type IIIb Sorbents: *Not available at this time*

9.5.5 Type IV Sorbents: *Not available at this time*

9.6 I-S Test: *not available at this time*

10. **CALCULATIONS** - Using data from section 9 calculate the following:

10.1 Static Water Test: Use values obtained in 9.1 and state value of water uptake as grams water per gram of sorbent.

10.2 Long Term Static Sorption Test: Use values obtained in 9.2 and state value of test fluid sorbed as grams of test liquid per gram of sorbent and state value of water uptake as grams water per gram of sorbent. Calculate and display

water percentage of total uptake. Calculate and draw profile of retention (curve) from values obtained at 30 sec, 45 sec, 1 min, 2 min, 5 min, 15 min, 30 min.

10.3 Dynamic Test: No calculations required - observations are recorded.

10.4 L-W Test: Use values obtained in 9.4 and state value of test fluid sorbed as grams of test liquid per gram of sorbent. (Volume of test liquid per gram of sorbent should also be calculated and recorded). Use values obtained in 9.3 and state value of water sorbed as grams of water per gram of sorbent. Calculate and display water percentage of total uptake. Determine reuse potential for each test liquid.

10.5 L Test: Use values obtained in 9.5 and state value of test fluid sorbed as grams of test liquid per gram of sorbent. (Volume of test liquid per gram of sorbent should also be calculated and recorded). Determine reuse potential for each test liquid.

10.6 I-S Test: *Not available at this time*

10.6 Reaction Time: A quantitative comparison will be made between long term sorption in 9.2 and the crude oil uptake in section 9.4. Any sorbent that has not reached 92% saturation by the 15 minute mark will be designated as a slow sorbent. (Assuming sorbents reach saturation within 24 hours).

10.7 Storage Density: The storage density is calculated (kg sorbent/m^3) based on manufacturer's packaging.

11. ADDITIONAL TESTS

11.1 An additional specialized test method may be employed by the authority having jurisdiction if these test methods are shown to severely hamper a sorbents performance.

12. REPORT

Data acquisition format - currently under review

13. NOTES

13.1 Related Publications

ASTM

Environment Canada

F726-81 Sorbent Performance of Adsorbents

F716-82 Sorbent Performance of Absorbents

Selection Criteria and Laboratory Evaluation of Oil Spill Sorbents, an Update, Update II, Update III, Update IV.

- 13.2 The publications referred to in par. 2.1.1 may be obtained from the Canadian General Standards Board, Sales Unit, Ottawa, Canada, K1A 1G6. Telephone (819) 956-0425 or 956-0426.
- 13.3 The ASTM publications referred to in par 13.1 may be obtained from ASTM, 1916 Race Street, Philadelphia, PA 19103, U.S.A. or from the Standards Council of Canada, Standards Sales Branch, 350 Sparks Street, Suite 1200, Ottawa, Ontario K1P 6N7.

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THE SEPARATION OF STABLE WATER-IN-OIL EMULSIONS

by

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ABSTRACT

A method for the separation of stable water-in-oil emulsions into clean dischargeable water and reusable oil is being investigated. The technique involves the use of a recyclable solvent and subsequent distillation and/or membrane treatment. This method would be used as a post treatment for recovered emulsions and should significantly reduce the volume of recovered oils. This paper describes results of experiments carried out on a bench scale level.

INTRODUCTION

Stable oil-in-water emulsions are a major problem in the recovery of spilled oils. The actual amount of oil in the recovered emulsions can be as low as ten percent. These emulsions have properties that are very different from their original oils; the viscosity increases dramatically and they exhibit thixotropic properties.¹ This causes difficulties in the storage and disposal of these emulsions. Due to their chocolate brown colour and mayonnaise like constancy these special type of emulsions are called "chocolate mousse", or "mousse".

Current methods for treating "chocolate mousse" are burning or chemical demulsification. Incineration is a commonly used method for oil spill clean-up. This technology is governed by the combustibility of oil-on-water, the spreading velocity of the slick, the nature of the crude, the degree of weathering of the oil, and the oil's water content. The latter is of most interest to us, since emulsions can contain from 10% to 80% water. Emulsified oil cannot readily be ignited, and can therefore impair the burning process. A series of tests showed that a heavy crude emulsion cannot be burned with as little as a 10% water volume,

while others burned at 70% water content.² Finally this method does not permit one to collect and reuse the oil.

Chemical dispersants are employed to disperse the oil in the water column by reducing the surface tension at the oil water interface. This reduction in surface tension also inhibits the formation of emulsions. Dispersants are most effective when used to prevent the formation of emulsions. Once an emulsion has been formed the amount of surfactant needed increases by the order of a couple of magnitudes. Environment Canada specifies situations best suited for the use of surfactants.³ A few disadvantages mentioned are that: dispersants eliminate the possibility of recovering the oil; the dispersants themselves cannot be reused; the time required for the aerial-application of the chemical is much greater than that of the oil to weather and become resistant to the dispersant's effect and; there is a lack of knowledge on the fate of the volumes of dispersed oils.

Difficulties in the treatment of these "mousses" have lead Environment Canada's Emergency Engineering Division to investigate methods for the separation of "mousse" into reusable oil and clean dischargeable water. This project will investigate the separation of water-in-oil emulsions by solvent extraction, using a recyclable solvent, and membrane treatment as a wasteless process. Originally a membrane method was investigated. During the preliminary tests it became evident that the use of membranes alone would not be adequate to acquire the desired separation (due to the rheological properties of the mousse.) It was then proposed to dilute the mousse with solvent to "thin" it out. During the search for a solvent it was discovered that certain solvents alone would separate the mousse. This finding lead to the proposal of the following method.

A solvent would be used to separate the emulsion into its two phases, the oil phase and the aqueous phase. The solvent could be recovered by distillation, which could then be reused in the process.

The scope of these preliminary experiments will be limited to two artificially fabricated chocolate mousses with variable water contents. Membranes of various manufacture and pore size were tested for their efficiency in separating the mousse into oil and free water. A range of solvents were also tested for their effectiveness as emulsion separators. The recovery methods tested included distillation, gravity separation, membrane separation, both conventional and pervaporation, and the development solvent stripping apparatus. The experiments were carried out on a laboratory scale, using various test apparatus.

EXPERIMENTAL

Emulsions were prepared using an electric kitchen blender. This was done by adding simulated sea water (3.5 % NaCl in deionized water) to the oil until the desired emulsion was formed. The oils used were a mixture of weathered Alberta Sweet Mix Blend (ASMB) and bunker C (50% W/W) and California Heavy crude and ASMB (30/70 W/W). The former resulted in an emulsion of approximately 50% water while the latter was around 70%. Emulsions of up to 82% water can

be created, but this would require a more robust blender than the one provided.

The membrane separation tests were performed on two types of apparatus. The first type was a batch stirred cell. This unit required 50 mL of test material. Pressure was generated by compressed nitrogen gas, up to 100 Psi, depending on the requirements of the membrane being tested. This unit required a considerable amount of time to clean between runs, and was abandoned in favour of a syringe type of test cell (FIG 1). This test cell could contain up to 10 mL of emulsion. Various types of membranes and pore sizes were tested.

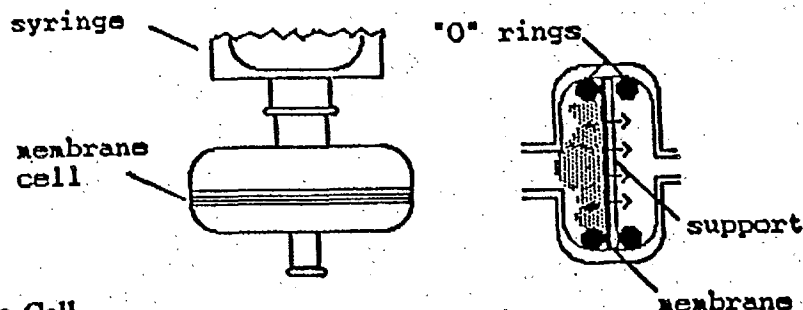


Figure 1 Membrane Cell

The apparatus used for solvent contacting is the same as that for solvent recovery. This is a simple distillation unit. It consisted of a 500mL round bottom flask, a liebig condenser, and a collection flask. In order to minimize evaporation of the solvent, a condenser was also connected to the vent. Contacting of the solvent was carried out in the round bottom flask. In order to separate the two phases the bottoms of the distillation was transferred to a separatory funnel and allowed to settle.

The solvent stripping unit was a modified distillation apparatus where by solvent vapours enter from the bottom of a condenser heated to reduce condensation of the solvent. This condenser acts as the contacting column. The emulsion enters through the top of the contacting column via a syringe. The treated emulsion is collected at the bottom of the contacting column in its two phases. The solvent vapours exit the contacting column at the top through an other condenser whereby the solvent is collected for reuse in the process.

The pervaporation trials were carried out using a pervaporation unit at the National Research Council of Canada. The unit consists of a batch stirred membrane cell, condensation vessel, and a vacuum pump. Liquid nitrogen was used to condense vapours.(FIG 2) The membrane tested was a hydrophobic silicon rubber 1 mil. membrane from General Electric #1048.

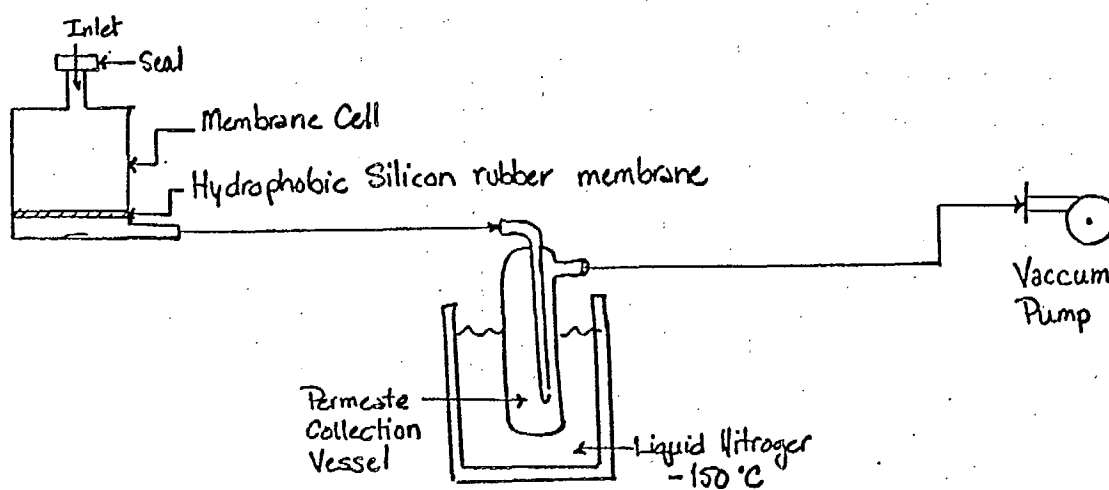


Figure 2. Pervaporation Set up

Various analytical techniques were employed for the determination of the various parameters in this study. Acetone content was determined by gas chromatography. Water content by Karl Fisher titration, and oil content by ultraviolet spectrophotometry. The first two methods were more reliable than the spectroscopy since they suffer less from matrix interferences.

RESULTS AND DISCUSSION

Direct Membrane Treatment

Direct membrane separation is a proven method that works very well for the separation of various kinds of emulsions. An attempt was made to evaluate the performance of membranes for the separation of this special type of emulsion "chocolate mousse". The membranes tested are listed in Table 1 along with the results.

Table 1 - Membrane separation of emulsion using CUNO Life Sciences Division (SN-charged and NU-uncharged) flat sheet nylon membranes at 200 psi, 22°C through membrane cell, emulsion was 50% water content.

Membrane Pore Size & Charge	Observations
0.1 μ C	no permeation
0.1 μ N	no permeation
0.2 μ N	no permeation
0.2 μ C	no permeation
.45 μ N	permeation no separation
.45 μ C	permeation no separation
0.8 μ N	permeation no separation
0.8 μ C	permeation no separation
1.2 μ C	permeation no separation
1.2 μ N	permeation no separation

Note: C ... charged membrane surface
N ... uncharged membrane surface

As can be seen by the results, no significant separation occurred in any of the trials. This could be due to the nature of the emulsion. Where permeation occurs the emulsion passes through the membrane as a microemulsion and does not undergo separation. When the pore size of the membrane is smaller than the size of the microemulsion the flow through the membrane is inhibited by the high viscosity of the fluid. To alleviate this, it was proposed to try to change the nature of the emulsion by the addition of solvents.

Solvent Treatment

Various solvents were tested for their effectiveness in reducing the viscosity of the emulsions. These included acetone, methyl-ethyl ketone, methyl-isobutyl ketone, dichloromethane, hexane, cresol, methanol, and isopropanol. While testing these solvents, it became apparent that the solvents alone could be used to break the emulsions.

Table 2 - Efficiencies of solvent extraction of chocolate mousse with mixing and settling methods of a 1:1 ratio of solvent to emulsion. 50% water emulsion was used.

Solvent	% of Total Oil Recovered
Acetone	> 99%
Acetone/Methanol 1:1	Separation, but not complete
Acetone/Water 2:1	98.8%
Chloroform	no separation
Dichloromethane (DCM)	85%
Freon 113	no separation
Hexane	50%
Isopar"M"™	no separation
Methanol	new emulsion

The best results were for dichloromethane(DCM), and acetone. Acetone was chosen in that it is nonchlorinated, and performed significantly better than DCM.

Optimization tests were carried out to determine the best solvent to emulsion ratio. It was found that a one to one (1:1) ratio worked best.

Table 3 - Tests with different percentages of acetone. Mixing and settling method using 50% water emulsion.

% ACETONE TO EMULSION	% OF TOTAL OIL RECOVERED
10	N.A.
20	40
30	71
40	98
50	99.4
70	95

The products obtained by mixing acetone and emulsion had different characteristics depending on the amount of solvent used. At 10% acetone by weight, there was a partial destruction of the emulsion, leaving behind a thin oily phase, as well as some residual emulsion. As the amount of solvent was increased so was the total amount of emulsion destroyed and separation achieved.

This ratio was then tested on emulsions with different water contents ranging from 39% to 83%. The amount of oil recovered in all the cases did not change significantly to the amount of water present. A 50% acetone to emulsion ratio may be excessive, and further optimization experiments are required to reduce the amount of solvent utilized for such a separation.

Solvent Recovery

In order to recover the acetone for reuse it was decided to use a distillation apparatus. Two configurations were tested. The first was to mix the solvent with the emulsion, separate the two phases, and distil each phase. The second method is to mix the solvent with the emulsion, distil the mixture, and then separate the phases. The latter method was decided upon since the heating energy facilitates the solvent in separating the emulsion, and that only one distillation step is required to recover the solvent. The tops consist of mostly acetone, along with some light hydrocarbons from the oil. It is important not to use excessive heat so as to retain the lighter hydrocarbons present in the crudes. Upon separation of the bottoms, the oil phase consisted of mostly oil. The aqueous contains mostly water with some acetone and trace amounts of oil. The acetone content of the water phase ranged from 2 to 16 percent. Since acetone alone does not form an azeotrope with water⁴ the distillation should be able to remove almost all of the acetone. In reality this is not the case. The lowest concentration achieved with our system was 2% acetone in the aqueous phase. This could be due to the formation of a multiple azeotropic mixture with salt and/or trace hydrocarbons. A secondary distillation, or membrane treatment (pervaporation) may resolve this problem. It also seems beneficial to allow the aqueous phase to contain a small

percentage of acetone so that the emulsion does not reform in the distillation apparatus. The emulsion reformed only once during the distillation process, and that was the only time the solvent attained 2 percent in the aqueous phase.

The recycled solvent can be used many times. Its properties as a demulsifier deteriorate only slightly after the first cycle and then remain stable. In this study the same regenerated solvent was successfully used in all the experimental runs.

Table 4 - Results for the separation of different emulsions by distillation with acetone at a 1:1 ratio.

Water Content of Emulsion (%)	Aqueous Phase		Oily Phase		Distillate	
	% Ac	% Water	% Ac	% Water	% Ac	% Water
45.7	16.6	-	2.9	0.03	85.8	-
64.0	3.7	93.8	4.5	-	-	4.8
74.3	2.3	77.6	1.3	0.13	75.6	1.73
82.0	-	-	4.5	1.26	-	-

Solvent Vapour Stripping

Another method that was looked into was the use of a counter current solvent stripping apparatus. This set up would allow the use of a continuous mode of operation, whereby the solvent could be used recycled in a closed loop, and the emulsion would flow through the system (FIG 3). When the emulsion contacted the solvent vapour, an immediate change occurred. The emulsion became dark on the perimeter and water droplets emerged. The set up used was very crude and did not have adequate insulation or contacting surface. Even though, the results obtained warrant further study. The mass of the recovered oil was equal to the oil portion of the emulsion treated. The same was found for the water portion. This method showed promise and will be studied further.

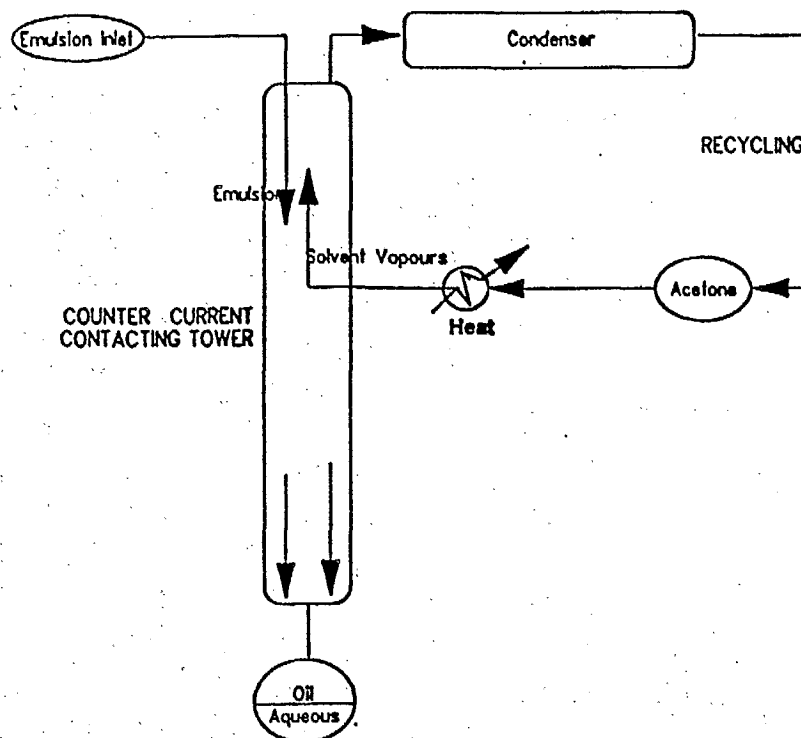


Figure 3. Solvent Vapour Stripping

Post Treatment of the Produced Water

Membrane Liquid Separation

Post treatment of the produced water included direct membrane separation and pervaporation. Membrane separation was only capable of removing on average 50% of the dispersed oil in the collected aqueous phase. It is shown in Table 5 that all the membranes tested, from UF to NF, were equally effective in the retention of the larger oil droplets. Since 40 to 60 percent of the oil remaining in the aqueous phase is present in a dissolved form it can not be retained by MF, UF, or even NF membranes. The rest of the oil is present in the form of suspended droplets (oil-in-water emulsion). This emulsion can readily be rejected by all of these membranes.

Pervaporation

To improve the process water quality, and to recover acetone from this mixture, pervaporation trials were carried out. A hydrophobic silicone rubber membrane was used in this series of experiments. The pressure on the permeate side was varied between 5 and 11 mm Hg. The temperature ranged between 20 and 50 C. Results showed that the acetone preferably passed through the membrane so that the acetone concentration in the permeate was 3 to 4 times higher than in the starting aqueous phase. It was found that by increasing the temperature, the permeate flux might be increased sufficiently without compromising the quality of the separation.

Table 5 - Post-Treatment to Remove Oil from the Aqueous Phase with Different Membrane Systems. Only the Desal5 run was done in the Stainless Steel Stirrer Cell.

Membrane Type	t (°C)	P (psi)	Perm Flow-rate (L/m ² *hr)	Perm Conc. of oil (ppm)	% R of Oil
Amicon YM 30K	24	40	300	36.92	50.2
Amicon YM 100K	24	40	900	37.44	49.5
Bioken 10K	25	40	340	19.06	57.1
Bioken 30K	25	40	320	25.75	42.0
Bioken 100K	25	40	630	27.54	62.8
Cuno 0.8 μ NU	25	20	720	21.26	52.2
Cuno 0.8 μ SN	25	20	830	25.33	43.0
Cuno 1.2 μ NU	24	40	4800	29.93	67.3
Cuno 1.2 μ SN	24	40	5480	81.39	11.2
Filtron Modified	25	40	3190	45.56	69.5
Filtron Omega 30K	25	40	510	34.74	76.7
Desal 5 NF Hydrophilized	27	100	7	78.43	53.5

CONCLUSIONS

The results of these preliminary tests show that stable water-in-oil emulsions can be separated quite readily with a regenerated solvent system. The only products of these systems are oil, which can be sent to a refinery, and dischargeable water. The recycled solvent can be used many times with out any significant decrease in separation efficiency. In order to enhance the throughput of the system a solvent vapour stripping method was invented. This solvent vapour stripping also improves the quality of the products and the recycled solvent. Membrane methods can be used as a post treatment for the produced water in order to better comply with discharge limits.

ACKNOWLEDGEMENTS

The authors express their thanks to Dr. T. Matsura and Mr. R. Tyagi of the National Research Council of Canada for their assistance in performing the pervaporation tests.

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A COMPARISON OF STEAM STRIPPING AND AIR STRIPPING FOR THE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM WATER

by

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INTRODUCTION

For many years air stripping has been used to remove volatile organic compounds (VOCs) from water. Recently controversy has surrounded the use of air stripping because of the potential air pollution problem. Usually, the solution to this problem is to treat the off-gas from the air stripper with a carbon adsorption, but this method also causes concern, because the expense of incinerating or regenerating the carbon is relatively large. Landfilling of the carbon may not be as expensive, but in many areas contaminated carbon is considered a hazardous waste and, therefore, secure landfill space for this type of material is difficult to find.

In 1986, the Emergencies Engineering Division (EED) (formally the Environmental Emergencies Technology Division) began looking at alternative methods for VOC removal from water for use in emergency and contaminated site situations. Steam stripping was one of the technologies investigated. An initial study performed by CH2MHill Engineering Consultants of Calgary showed that steam stripping is a cost effective method for removing of VOCs from water (1). It also showed that some semi-volatile compounds (semi-VOCs) could be removed by steam stripping which could not be removed by air stripping.

Following this study, EED contracted CH2MHill to construct a mobile steam stripping unit. The unit was used for the first time during a demonstration at a contaminated site in Gloucester, Ontario, during the summer of 1990. Two air stripping designs have also been tested at this site. A general comparison can be performed based on the data obtained during the Gloucester trials.

AIR STRIPPING - THEORY AND DESIGN

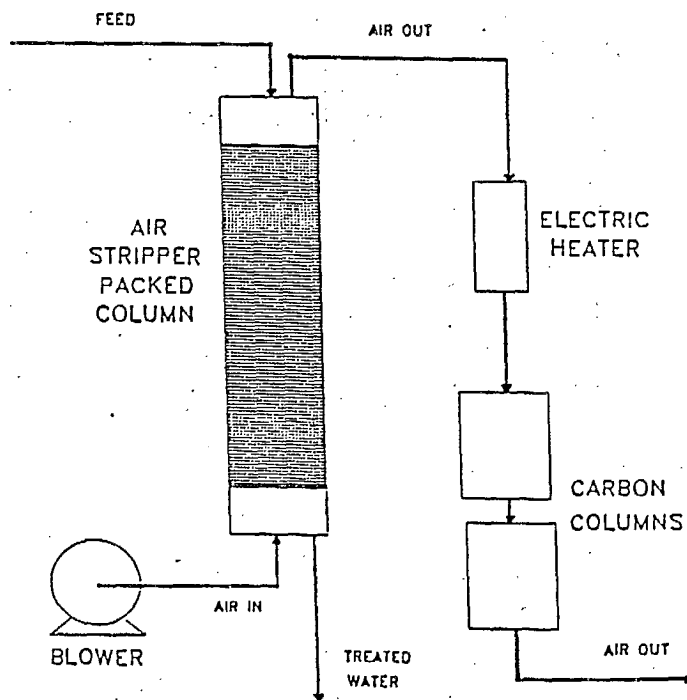
Generally, air stripping units allow air to come into contact with contaminated water causing the VOCs to transfer from the water to the air. The contact between the two phases is achieved by a variety of methods. Most traditional air stripping columns are counter-current packed columns. These systems have high mass transfer of VOCs, which results in high removal efficiencies. Several other air stripping designs exist, including cross-flow towers, multi-stage aerators and spray column air strippers (2).

At the Gloucester landfill two air stripping designs have been evaluated, a packed column air stripper and a multi-stage aerator. Both systems used carbon adsorption for off-gas treatment.

In 1986, the packed column was tested by members of Environment Wastewater Technology Centre (WTC) at this site (3). Figure 1 shows a schematic of this system. The air stripping column was 180cm high and 15cm in diameter. Both Intalox saddles and Rashing rings were evaluated as packing types. Packing diameters of 1.3cm and 1.9cm were tested for each packing type. In all cases the column diameter to packing diameter ratio was greater than eight. The feed stream entered the column at the top through a distribution nozzle while air entered through the bottom from an air blower.

The off-gas was treated through two activated carbon columns placed in series. The carbon used was Calgon's BPL type. Before being passed through the carbon columns the relative humidity of the off-gas was reduced by passing the gas through an electric heater.

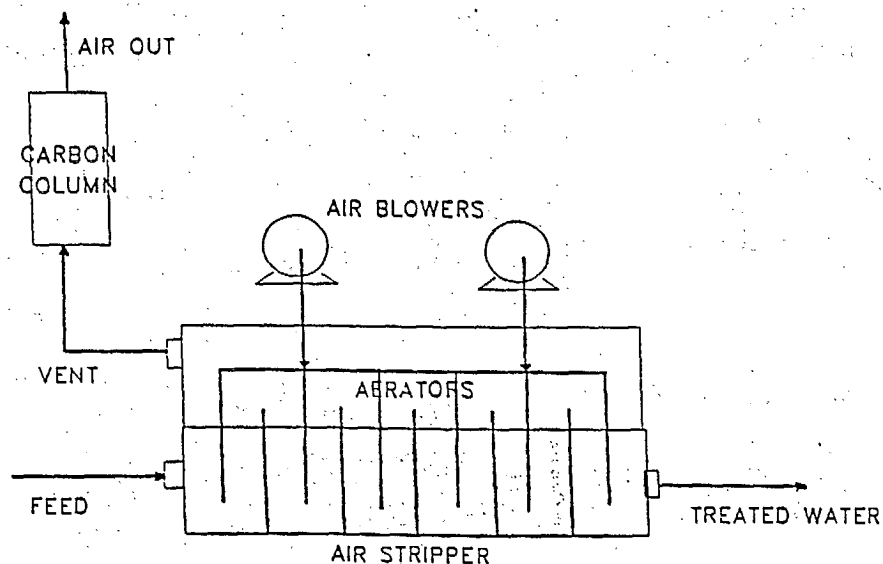
FIGURE 1: WTC AIR STRIPPING PACKED COLUMN SCHEMATIC (3)



In 1990, a multi-stage aerator was evaluated at the Gloucester landfill site. A schematic of the system used is shown in Figure 2. The system was provided by Lowry Engineering Inc. of Unity, Maine. This unit consisted of a 2.1m(L) by 0.7m(W) by 0.8m(H) high density polyethylene vessel with an airtight lid. The vessel was separated into six stages, each containing one aerator (4). As requested by the Ontario Ministry of Environment, a carbon adsorption unit was added to the air vent system, to treat the off-gases.

For low flow applications, the stage aerator has proven to be more cost effective than packed column designs, because a smaller unit is required to achieve a similar removal efficiency to a packed column. The packed tower is dependant on the air to water ratio and the packing height. For some compounds the required packing heights are very high and therefore two towers are frequently required. The stage aerator is dependant only on the air to water ratio so that, for difficult to remove compounds, there is not a requirement to increase the size of the unit.(4)

FIGURE 2: LOWRY MULTI-STAGE AERATOR SCHEMATIC (4)



STEAM STRIPPING - THEORY AND DESIGN

Steam stripping is based on the same concept as air stripping except that steam is used as a stripping medium to remove organic compounds from contaminated water. The steam containing the organic compounds can be condensed, resulting in a concentrated water stream instead of contaminants remaining in the gas phase, as with the air stripping process.

In the steam stripping process, the steam is fed into the bottom of the column while the feed stream enters into either the middle or the top of the column. The liquid feed stream comes into contact with the steam within the packing, causing volatile and some semi-volatile compounds to be transferred from the liquid to the vapour phase. This transfer is driven by the potential created by the concentration gradient between the liquid and vapour phases. The outlet vapour stream (tops) is condensed and sent to a decanter to separate any sufficiently concentrated organics from the aqueous stream. The treated liquid outlet (bottoms) can either be re-injected into the groundwater well or, if the outlet levels are above discharge limits, treated further. If the bottoms stream is very low in organics and de-ionized, it can be used to feed the boiler and therefore close the process cycle.

The system is set-up so that the aqueous phase from the decanter can be recycled back into the top of the column. If there is no phase change in the decanter then a specific percentage of the decanter inlet flow is refluxed. If the stream to be treated contains very volatile or low solubility contaminants then a reflux stream may not be needed.

The EED steam stripping unit was built in 1987 by CH2MHill Engineering Limited in Calgary, after a feasibility study showed that steam stripping is an efficient process for removing volatile and semi-volatile organics from water. Its design is based on a typical industrial steam stripper, but the unit is fully mobile and can be disassembled to fit into an 18 foot cube van. The design specifications of the unit were based on the requirement that the unit be mobile and adaptable to remote areas and the Canadian climate. The ease of transport, set up and take down makes it ideal for emergency situations.

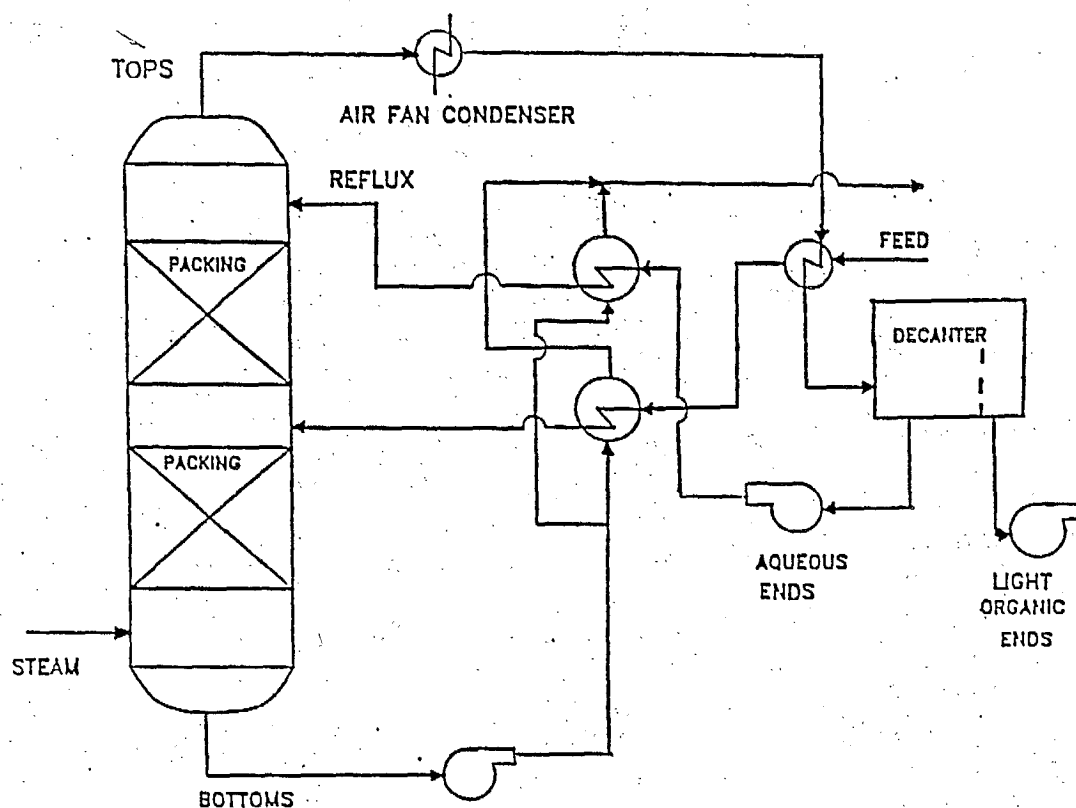
A detailed process flow diagram, of the EED system, is shown in Figure 3. This unit has a design feed rate of 2000L/h and a steam to feed ratio of up to 20%. The stripping section consists of a 0.31 diameter by 8.38m high column packed with 25.4mm diameter pall rings.

From the system diagram it can be seen that the heat transfer potentials have been used efficiently within the system. The feed and reflux streams are preheated by the purified liquid leaving the bottom of the column. The overhead, contaminant rich vapour, is initially condensed using an air cooled

condenser. The stream is further cooled using the cold feed stream.

The system is fully enclosed, apart from a vent located on top of the decanter. This vent allows any vaporized volatiles in the decanter to travel through a small carbon column before entering the atmosphere.

FIGURE 3: EED STEAM STRIPPING SCHEMATIC (1)



COMPARISON BETWEEN AIR STRIPPING AND STEAM STRIPPING

Both steam stripping and air stripping have distinct advantages and disadvantages as VOC treatment technologies. Steam stripping units generally have a higher capital cost than air stripping. As well, steam stripping can be costly to operate, because of the expense of producing the steam, but in many cases steam stripping will prove to be less expensive than the combination of air stripping and off-gas treatment.

Due to recent regulations it is required, in most areas, to have some form of off-gas treatment for air stripping systems. In the U.S., almost all states are initiating air toxicity programs, and because most VOCs are considered toxics, air strippers will be affected by these regulations. As well, the U.S. Superfund Amendment Reauthorization Act of 1986 (SARA) guidelines also require that the remediation of U.S. EPA superfund sites takes place without using technologies which transfer the contaminants from the water into the air. (5)

In most cases, the off-gas treatment used with air strippers is carbon adsorption. The addition of a carbon unit to an air stripping process greatly increases the treatment cost. The carbon either has to be landfilled as a hazardous waste, incinerated or regenerated. The regeneration usually involves thermal treatment or steam stripping. There is also added cost because, the relative humidity of the air must be reduced to less than 50% by a heating system in order for the carbon to effectively adsorb the contaminants in the air (5).

Carbon adsorption units must also be monitored closely because several compounds, such as 1,2-dichloroethane, readily desorb after being adsorbed on the carbon (6). As soon as breakthrough takes place the carbon column must be removed. For this reason, a backup carbon column is always required and a continuous monitoring program must be incorporated into the system.

Table 1 compares the various treatment aspects of air stripping, air stripping with off-gas treatment and steam stripping. The range of contaminant types which can be treated with steam stripping is much greater than with air stripping. Generally, compounds with Henry's law constants greater than 10^6 atm m^3/mol can be removed well with steam stripping, whereas for a compound to be removed by air stripping it must have a Henry's law constant greater than 10^3 atm m^3/mol (7). This indicates that there are several compounds which can be removed by steam stripping which cannot be removed by air stripping, including several alcohols, phenols, aldehydes and amines. Preliminary data show that the EED steam stripper is able to remove several of these compounds. Data from other steam stripping studies provide chlorinated phenol steam stripping removal efficiencies in the 75% - 99% range (1,8,9).

In an ideal mixture, steam stripping would not be able to remove compounds which have a lower volatility than water, but in actual fact many mixtures of dilute organic compounds in water form non-ideal mixtures which result in low boiling azeotropes. These azeotropes increase the relative volatility, making the compounds removable by steam stripping. Again, this phenomenon shows that steam stripping has the potential to remove far more compounds than air stripping.

Steam stripping will concentrate contaminants in the decanter and if the concentration is high enough (ie. above the solubility) the compounds will

separate and can be decanted. In this form, the small volume of recovered contaminants can then be destroyed by other treatment methods at a low cost. If an individual component or a valuable combination of compounds are being removed, the compound(s) can be recovered for reuse.

TABLE 1: BASIC COMPARISON OF STEAM STRIPPING AND AIR STRIPPING

	AIR STRIPPING (PACKED COLUMN)	AIR STRIPPING WITH CARBON TREATMENT OF OFF-GAS	STEAM STRIPPING
RANGE OF TREATABLE CONTAMINANTS	VOCs Henry's law constant $> 1 \times 10^{-3}$ (atmm ³ /mol)	VOCs Henry's law constants $> 1 \times 10^{-3}$ (atmm ³ /mol)	VOCs and semiVOCs Henry's law constant $> 1 \times 10^{-6}$ (atmm ³ /mol)
STATE OF WASTE STREAM	air	spent carbon	contaminants concentrated in water

In general, steam stripping capital costs are greater than air stripping, because the stainless steel column required and the boiler, used to generate steam, are expensive. Air stripping with carbon off-gas treatment systems are relatively inexpensive, because many of the components are normally constructed from PVC.

Table 2 gives several examples of air stripping and steam stripping operating costs. These costs have been taken from various sources and in many cases the numbers have been converted to Canadian dollars and 1991 dollars. These costs could also vary greatly depending upon contaminant type and contaminant concentration. For these reasons the numbers can only be compared on a very general basis.

In comparing the increase in cost when carbon and carbon with regeneration is added to an air stripping unit it can be seen that the operating costs increase significantly. Using the costs presented in Table 2, the operating costs increases from 4 to 23 times when a carbon system is added and from 9 to 72 times when a carbon and a regenerating system are added. The estimated cost for regenerating carbon ranges from \$0.48 to \$1.11/m³ (10). This range covers various regeneration methods, contaminant types and inlet concentrations.

Steam stripping unit operating costs are approximately 11 to 36 times greater than simple air stripping operating costs. However, when comparing steam stripping with air stripping plus carbon and carbon regeneration the costs are comparable for small units and the steam stripper costs are lower for the larger units.

There are also methods of lowering the costs of steam strippers even further by utilizing the latent heat resulting from the compression of the overhead vapour. Dow chemical has developed a system which adds "Mechanical Vapour Recompression" (MVR) to the system in order to transfer this heat to the production of steam for the system. Using actual case studies, Dow has quoted operating costs of \$0.10-0.12/m³ for a 1090-1363m³/d system using MVR (1991/cdn \$).(8)

The higher steam stripping operating costs quoted in Table 2 are generally costs for treating some of the less volatile compounds, which require higher steam to feed ratio. Because this range covers compounds which are removable by steam stripping and not air stripping, care should be taken when comparing these higher costs with the air stripping costs.

TABLE 2: EXAMPLES OF STEAM STRIPPER AND AIR STRIPPER OPERATING COSTS

AIR STRIPPING ALONE (PACKED COLUMN)	AIR STRIPPING WITH CARBON OFF-GAS TREATMENT	AIR STRIPPING WITH CARBON OFF-GAS TREATMENT AND CARBON REGENERATION	STEAM STRIPPING WITH REFLUX AND RECTIFICATION SECTION
\$0.02/m ³ 1050m ³ /d (3)	\$0.33/m ³ 1050m ³ /d (3)	\$0.81-1.44/m ³ 1050m ³ /d (3,10)	\$0.22-0.26/m ³ 1090-1363m ³ /d (8)
\$0.12-0.17/m ³ 378m ³ /d (12) ¹	\$0.47-3.93/m ³ 378m ³ /d (12) ¹	\$0.95-5.04/m ³ 378m ³ /d (10,12) ¹	\$2.26-6.12/m ³ 48m ³ /d (1)

1. includes labour and maintenance costs

It is possible that, even with the addition of a method to destroy the compounds in the steam stripper's concentrated waste stream, the steam stripping operating costs would be comparable to air stripping with carbon regeneration. For example, a 48m³/d steam stripping unit, such as the EED unit, run at a steam to feed ratio of 10% would produce 4.8m³/d of concentrated waste. If the waste stream were to be destroyed using enhanced oxidation, the operating cost would only increase by \$0.10 to \$0.20/m³ (11). This cost is based on the feed flowrate to the steam stripper and the enhanced oxidation costs for destroying VOCs, in the low ppm range, in water. Because the capital cost of an enhanced oxidation system can be very high, a full cost analysis must be performed in order to compare this process train with air stripping and off-gas treatment. As well, technology development has recently begun in the area of destruction of off-gas streams from air strippers using enhanced oxidation. This could also be a very cost effective system.

AIR STRIPPING GLOUCESTER RESULTS

During the 1986 Gloucester trial, the WTC packed column air stripper evaluation involved testing the two packing types, two packing sizes, two water flowrates (8L/min and 4L/min) and air to water ratios ranging from 15 to 110. (3)

The air stripping results from this trial showed that the range of removal efficiencies of the VOCs in the groundwater was 60% to 99.9%. The best removals were obtained using a 4L/min water flowrate, an air to water ratio of 110:1 and 1.3cm Rashing rings. The results using these conditions are presented in Table 3.

TABLE 3: PACKED TOWER AIR STRIPPER - GLOUCESTER 1986 BEST OBSERVED RESULTS (3)

feed rate = 4L/min Air:Water=110

COMPOUND	FEED ($\mu\text{g/L}$)	TREATED WATER ($\mu\text{g/L}$)	% REDUCTION IN CONC.
1,1 DICHLOROETHENE	13	0.2	98.5
TRICHLOROETHENE	17	0.2	98.8
1,1,1 TRICHLOROETHANE	41	0.1	99.8
TOLUENE	5	0.3	94.0
BENZENE	11	0.1	99.1
1,1 DICHLOROETHANE	34	0.3	99.1
CHLOROFORM	30	1.0	96.7
1,2 DICHLOROETHANE	76	4.0	94.7

During the multi-stage aerator evaluation, in 1990, the effect of altering the air to feed ratio was investigated (13). The feed was pre-treated using either a $0.21\mu\text{m}$ cross-flow microfiltration system or $5.0\mu\text{m}$ dead-end cartridge filters. The pH varied from 7.3 to 8.3. The feed was kept constant at 37.9L/min. The air supply was varied by varying the horsepower and number of blowers. The combinations ranged from using one 1HP blower to using three 2HP blowers. Throughout each run the back pressure from the system remained between 4.5 - 7.7 KPa.

The runs utilizing three 2HP blowers resulted in discharge concentrations below the remediation targets on all compounds of interest. Using fewer than 2HP blowers or using the 1HP blowers significantly reduced the concentrations of the VOCs but the required discharge limits were not reached for all compounds. Table 4 shows the results obtained using two 2HP blowers.

TABLE 4: MULTI-STAGE AERATOR - GLOUCESTER 1990 BEST OBSERVED RESULTS (13)

feed rate = 40L/min, 2 x 2hp blowers

COMPOUND	FEED ($\mu\text{g/L}$)	TREATED WATER ($\mu\text{g/L}$)	% REDUCTION IN CONC.
1,1 DICHLOROETHENE	395.0	14.7	96.3
TRICHLOROETHENE	511.0	0.17	>99.9
1,1,1 TRICHLOROETHANE	8013.0	0.95	>99.9
TOLUENE	4.11	0.3	92.8
BENZENE	388.0	1.58	99.6
CHLOROBENZENE	10.4	ND	>99.9
CHLOROFORM	255.0	0.84	99.7
1,2 DICHLOROETHANE	102.0	3.52	96.6
TETRAHYDROFURAN	149.0	7.85	94.7

STEAM STRIPPING GLOUCESTER RESULTS

In 1990, the EED steam stripping unit was also set up at the Gloucester landfill (13). Because this was the first time the unit had been set up and run on contaminated water, the main purpose of this trial was to examine the longterm effectiveness of the unit and to work out any of the preliminary equipment problems. The unit was run for approximately 23 hours with runs lasting from one hour to five hours. A total of ten runs were performed. The variables altered included the position of the feed inlet, whether or not the tops were refluxed and the times in which the samples were taken.

As with the air stripper, the feed to the steam stripper was pretreated using pH adjustment in conjunction with either $5.0\mu\text{m}$ filters or $0.2\mu\text{m}$ microfiltration. In order to provide the boiler with clean softened feed water, the bottoms stream from the steam stripper was passed through a mobile reverse osmosis unit.

Throughout the runs the feed flowrate remained between 30 and 33L/min. The volume ratios of steam to feed and waste steam to feed both varied between 10 to 15%. Because of the low concentrations of the contaminants in the water there was no phase separation present in the decanter.

In general, all VOCs, except trichloroethene, showed the greatest reduction in concentration when the concentrate stream was refluxed, regardless of whether the feed stream is fed midway or at the top. Benzene generally showed the greatest concentration reduction, followed by toluene.

In most cases the concentrations of the compounds in the bottoms stream were below the gas chromatograph detection limits and the remediation targets set by Ontario Ministry of the Environment. The only cases where compounds were over the remediation targets were runs without reflux.

The best results were obtained with the steam stripper when the feed was fed midway and the waste stream was refluxed. Using these operating conditions the steam stripper was able to reduce the concentration of all VOCs analyzed, to greater than 99.9%. This case is shown in Table 5. The percent reduction in concentration, in this table, is calculated from the feed and waste stream concentrations because almost all of the treated water streams were below the detection limits.

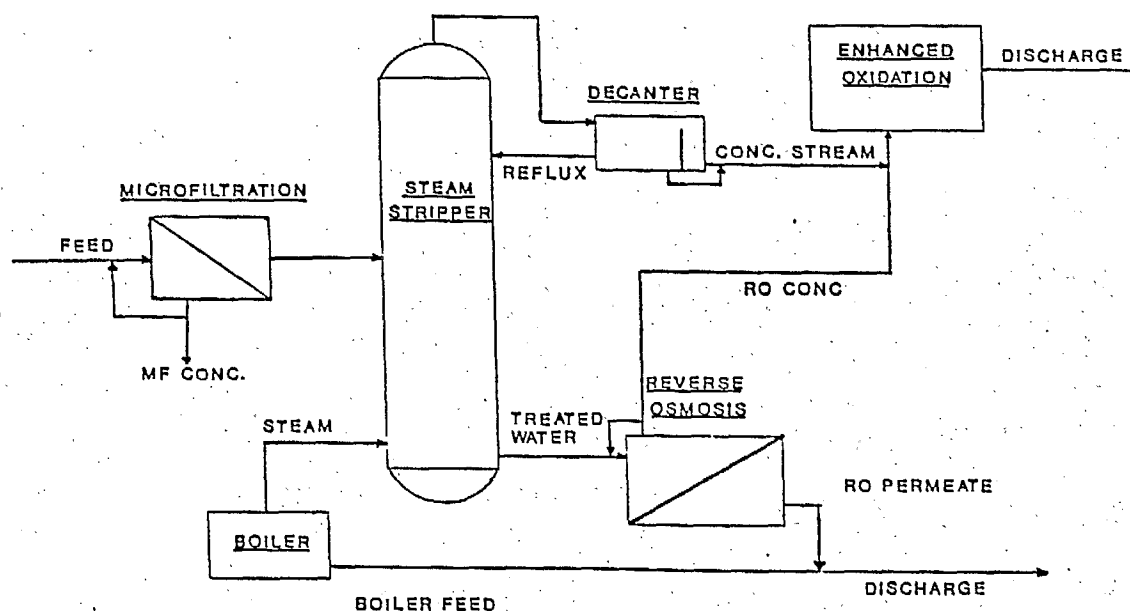
TABLE 5: STEAM STRIPPER - GLOUCESTER 1990 RESULTS (13)
feed rate = 33.3L/min steam/feed = 7/100

	FEED (ug/L)	WASTE STREAM (ug/L)	% REDUCTION IN CONCENTRATION
TRICHLOROETHENE	2800	65060	> 99.9
TOLUENE	0.83	305.3	> 99.9
BENZENE	1.78	12060	> 99.9
CHLOROBENZENE	31.7	3205	> 99.9
CHLOROFORM	157.8	4501	> 99.9
1,2 DICHLOROETHANE	24.0	1104	> 99.9
TETRAHYDROFURAN	836.9	18750	> 99.9
ETHER	76.2	2342	> 99.9

With a dilute feed stream, such as the Gloucester water, refluxing is required to further increase the concentration in the waste stream. It is therefore not surprising that the best results were obtained with reflux and a midway feed. Feeding midway allows the waste stream to be further concentrated in the top part of the column and the feed to be stripped in the bottom part of the column.

The highly concentrated waste stream resulting from the steam stripping process was passed through an enhanced oxidation unit which was able to destroy the contaminants to below discharge limits. It was shown that the combination of the enhanced oxidation unit and the steam stripper had the potential to completely remove and destroy the contaminants in the groundwater. Figure 4 provides a schematic of the process train used at the Gloucester landfill.

FIGURE 4: STEAM STRIPPER PROCESS TRAIN AT GLOUCESTER



LABORATORY ANALYSIS

The samples for both air stripping evaluations and the steam stripping evaluation were analyzed by gas chromatography. The steam stripping results were analyzed in EED's lab using a Hewlett Packard 5830 gas chromatograph (G.C.) with a 7675 purge and trap and a flame ionization detector. The 1990 air stripping samples were analyzed by a Hewlett Packard 5890 G.C. with direct headspace injection (model HP 19395A) and both an electron capture detector and a flame ionization detector. The 1986 air stripping samples were analyzed using purge and trap and flame ionization detection. (3,13)

DISCUSSION OF GLOUCESTER RESULTS

In comparing the results from the air stripping and the steam stripping runs presented above, it can be seen that in all cases the technologies were able to significantly reduce the concentration of the VOCs found in the groundwater. All the compounds shown have relative volatilities within the known removal range for both steam stripping and air stripping, so it is not surprising that both air stripping and steam stripping were able to remove these compounds.

In comparing the best observed results for each technology it can be seen that the steam stripper was able to reduce the concentration of all compounds listed to greater than 99.9%. The concentration reduction for the air stripping runs shown, ranged from 94.0 to 99.8% for the packed column and 92.8% to greater than 99.9% for the multi-stage aerator.

CONCLUSIONS

Both air stripping and steam stripping are effective technologies for removing volatile organic compounds from water. In comparing the operating costs of the two basic technologies, air stripping is considerably less expensive, but recent concerns over the air pollution created by air stripping have resulted in the need to add off-gas treatment. The addition of off-gas treatment, usually carbon with a regeneration system, increases the cost of air stripping substantially, making steam stripping a competitive technology. However, the advancement in new destruction methods for off-gas treatment may increase the favourability of air stripping for VOC removal. When comparing operating and capital costs, it must be kept in mind that steam stripping is a more flexible technology, because it is capable of removing a much wider range of compounds than air stripping.

A full comparison of the technologies should be performed on a case by case basis, because the capital and operating costs will vary with contaminant concentration and contaminant type. It is also recommended that for any VOC or semi-VOC remediation, a series of treatment techniques should be considered to increase the cost effectiveness and decrease the need for off-site treatment of waste streams.

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REMOVAL OF PETROLEUM-DERIVED HYDROCARBONS FROM CONTAMINATED SOILS BY SOLVENT EXTRACTION

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ABSTRACT

The use of solvent extraction for the clean up of oil-contaminated soils has proven to be an effective technology at the bench scale level. Results using a 1,000 g batch system showed extremely high oil removal efficiencies from contaminated sand (up to 98.9%) and peat soil (up to 83.9%). The final oil contaminant concentration for sand varied between 0.06% and 0.39% while that for peat soil varied between 1.52% and 5.21%. The guidelines for the decommissioning and cleanup of sites in Ontario for oil and grease (1 wt.%) were met in all instances for the treated sand. Hexane recovery from diesel contaminated sand and peat soil experiments were approximately 81% and 67% respectively.

INTRODUCTION

The petroleum industry and government agencies are working together to develop technologies for cleaning up oil-contaminated soils. There are many technologies currently available for treating oil-contaminated soil, such as soil vapour extraction, solvent extraction, bioremediation, and incineration. However, many of these technologies are either too expensive to be economically viable or do not clean the soil quickly enough or sufficiently for regulation purposes.

The Emergencies Engineering Division (EED) of Environment Canada initiated a project in September of 1989 involving the removal of petroleum-derived hydrocarbons from contaminated soils by solvent extraction using readily available and relatively inexpensive solvents. This project was jointly funded by EED and the National Groundwater and Soil Remediation Program (GASReP).

BACKGROUND

Solvent extraction is a process whereby a soluble substance is leached from a solid with a liquid solvent. This process has been used effectively in industry for several decades, but it is only recently that it has been applied to the remediation of soils. Most existing soil treatment units employ proprietary solvents resulting in high operating costs. EED chose to evaluate hexane and natural gas condensate (NGC) as solvents because of their low cost and availability at refinery sites, where petroleum hydrocarbon spills are likely to occur. The only drawback to using these solvents is their high flammability which requires an explosion proof facility.

EED has completed laboratory studies employing two solvents (hexane and NGC) for the removal of light crude oil from contaminated soils (sand, peat, and clay). These results suggested that solvent extraction could be an effective technology and efficient process in removing petroleum hydrocarbons from contaminated soils [Hoisak, 1991 and Punt et al., 1991]. Thus further investigation at the bench scale level was recommended prior to designing and building a commercial plant.

The bench scale facility was not complete for testing due to an unexpected delay in obtaining some explosion proof parts and Canadian Standards Association (CSA) approval for the distillation system. This resulted in limited data on the recovery of hexane from the process. Furthermore, NGC could not be evaluated because it had to be pre-distilled to produce a usable solvent.

PROCESS DESCRIPTION

The bench scale process consists of three major steps: solvent washing, settling/decantation/filtration of extract, and solvent recycle. The process uses hexane, a petroleum solvent, which would be available from crude oil processing. The oil-contaminated soil is first contacted with the solvent in a batch multi-stage arrangement within the mixer. The oil/solvent mixture is then decanted from the mixing drum and filtered to prevent solid particles from entering the extract and subsequently hindering the solvent recovery steps. The oil/solvent extract is then distilled for solvent recovery. Whether recovered oil could serve of any use has yet to be determined.

PROCEDURE AND ANALYSIS OF SOILS

Analytical Methods

Initially, freon (1,1,2-Trichlorotrifluoroethane) was used to extract initial and final soil samples in order to determine their percent oil contamination by weight. However, it was discovered, through a few trial runs using dichloromethane (DCM), that this chemical's oil extractive abilities are just as powerful as those of freon. The results using DCM and freon agreed to within 1%. The importance of this discovery is that DCM costs approximately 1/10th the price of freon and therefore DCM was used to extract the remainder of samples in the study.

The percent oil contamination within the sample was calculated as follows:

$$\% \text{ oil contamination} = \frac{\text{weight of oil}}{\text{weight of sample}} \times 100\%$$

The decontamination efficiency was calculated as follows:

$$\text{decontamination efficiency (\%)} = \frac{(\text{initial} - \text{final}) \% \text{ oil}}{\text{initial \% oil}} \times 100\%$$

Preliminary Analysis of Peat and Sand

The average moisture content and fraction of oil present in uncontaminated sand and peat soil are presented in Table 1. The particle size distribution of sand and peat by sieve analysis are presented in Table 2.

Table 1. Average Moisture Content and Fraction of Oil Present in Uncontaminated Soils.

Type of soil	Average Moisture Content (wt. %)	Oil Contamination of Blank Sample (wt. %)
Sand	7.6	0.00
Peat	32.1	0.01

Table 2. Particle Size Distribution of Sand and Peat by Sieve Analysis.

Mesh size	Actual size (micrometers)	Sand (wt. %)	Peat (wt. %)
14	> 1180	28.0	1.8
32	500	27.1	21.9
60	250	21.1	44.0
150	106	21.4	27.9
400	38	2.4	4.4

Soil Contamination and Soil Sample Preparation

Soil samples of between 750 and 1,000 g were used in the bench scale study. The soil samples were added to the mixing chamber along with the desired amount of 24 hour weathered oil. The soil/oil samples were mixed for approximately 10 minutes in a ROSS mixer. This contamination method has two distinct advantages. Firstly, such mixing gives the worst case scenario and therefore the extraction efficiency slightly underscores the project's effectiveness. Secondly, the oil in the soil must be evenly distributed so that a random sample of the contaminated soil will represent the percent contamination of the entire sample.

After mixing the samples, they were allowed to sit for 24 hours prior to their extraction in order that adsorptive and absorptive processes may take place as they would in a real-life oil spill.

Soil Washing

The contaminated sample was added to the mixing container and weighed. The appropriate mass of solvent was added for the first extraction taking into account the desired solvent-to-sample ratio of 2. The slurry was then mixed at the optimum mixing parameters. The mixture was then allowed to settle for 10 minutes prior to decanting through #1 Whatman filter paper. The other extractions were then performed as described above and the extracts were combined.

Centrifugation

The moist extracted solids were then centrifuged in order to remove any more of the oil contaminants and hexane present within the soils. The moist solids were transferred to the centrifuging jars and spun at 4,000 rpm for 15 minutes. Upon completion of the centrifuging process the supernatants atop the centrifuge jars were decanted, filtered through #1 Whatman filter paper and combined with the other extracts from the extraction steps.

Distillation

A simple reflux distillation was employed for separating the oil from the hexane. Once the heating of the hexane extracts began, the temperature of the bottoms increased and then levelled at 69-70°C. The temperature at the top of the reflux condenser stabilized at 68-69°C. The temperature at the top of the reflux column decreased as the solvent fraction in the column diminished. Distillation continued until the temperature at the top of the condenser was between 65.5 and 66.0°C.

Samples of the light ends (tops) and the heavy ends (bottoms) were taken and sent to the chemistry lab for gas chromatography (GC) analysis in order to determine the concentration of hexane in both the distillate and the bottoms. The percent solvent recovery was done on a gravimetric basis and was calculated as follows:

$$\% \text{ hexane recovered} = \frac{\text{weight of hexane recovered}}{\text{total weight of solvent used}} \times 100\%$$

RESULTS

Determination of the Optimum Mixing Parameters for Solvent Extraction

In order to properly assess any engineering process, it is essential that the process be evaluated at optimum experimental parameters. For the solvent extraction process, this means optimizing the mixing time and speed setting along with the number of extractions at the desired solvent-to-sample ratio. A solvent-to-sample ratio of 2 was employed as this was determined to be the optimum based on laboratory results [Hoisak, 1991].

The effect of the number of extractions on the decontamination efficiency of 6% Bunker C-contaminated sand is presented in Table 3. An intermediate contamination of 6% was used since the bench scale study investigated Bunker C-contaminated sand between 2 and 16% and it was known that decontamination efficiency varied with oil contamination.

The decontamination efficiency increases slightly and then levels off with the increase in the number of extractions performed. The optimum number of extractions is 3 as the increased decontamination efficiency observed between 3 and 4 extractions would not justify increased time and labour costs required to perform the additional extraction.

Table 3. The effect of the number of extractions on the decontamination efficiency of 6% Bunker C-contaminated sand samples.

Run No.	No. of Extractions	Oil (wt. %)		Decontamination Efficiency (%)
		Initial	Final	
O-1	1	5.9	0.63	89.3
O-2	2	6.0	0.54	91.0
O-3	3	5.9	0.31	94.7
O-4	4	5.85	0.27	95.4
O-5	5	5.9	0.26	95.6

The next parameters to be optimized were the mixing time and speed. The function of the mixing stage is to provide an adequate combination of agitation and residence time in order to obtain the desired degree of decontamination.

The effect of mixing speed and time on the decontamination efficiency of 2% bunker C-contaminated sands are presented in Tables 4 and 5 respectively. The optimum mixed speed setting and time are 4 (Ross mixer) and 8 minutes respectively as these conditions yield the best decontamination efficiency while minimizing time and power requirements.

Table 4. The Effect of Mixing Speed on the Decontamination Efficiency of 2% Bunker C-contaminated sand. [mixing time: 2 min.]

Run No.	Mixing Speed Setting	Oil (wt. %)		Decontamination Efficiency (%)
		Initial	Final	
O-6	2	1.95	0.24	87.7
O-7	4	1.94	0.19	90.2
O-8	6	1.98	0.19	90.4
O-9	7	1.99	0.19	90.5

Table 5. The effect of mixing time on the decontamination efficiency of 2% Bunker C-contaminated sand. [mixing speed setting: 4]

Run No.	Mixing Time (min)	Oil (wt %)		Decontamination Efficiency (%)
		Initial	Final	
O-10	2	1.94	0.19	90.2
O-11	5	1.97	0.18	90.9
O-12	8	2.08	0.16	92.3
O-13	10	1.95	0.16	91.8

In sum the optimum parameters for Bunker C-contaminated sand are:

Mixing speed: 4 on Ross Mixer
Mixing time: 8 minutes
Number of extractions: 3
Solvent-to-sample ratio: 2

Due to time constraints, these optimum parameters were used for the remainder of bench scale testing regardless of the nature of the soil or the contaminating oil. It should be understood that these parameters may not necessarily represent optimum conditions for all types of soils and oils.

Bunker C-Contaminated Sand and Peat Soil

The results of the hexane extraction of bunker C-contaminated sand and peat soil are presented in Tables 6 and 7 respectively. Decontamination efficiency versus initial oil contaminant concentration in sand and peat soil are plotted in Figures 1 and 2. For the oil concentration range (in sand) investigated, namely from 2.22% to 16.10%, the decontamination efficiency increased from 91.9% to 98.0% while the final oil concentration varied between 0.18% and 0.39%. For the oil concentration range (in peat soil) investigated, namely from 2.5% to 21.0%, the decontamination efficiency increased from 32.0 to 75.2% while the final oil concentration varied from 1.70% to 5.21%.

The extracted soils were quite dark in appearance and were clumped together due to the fact that Bunker C contains a high percentage of heavy ends which cannot be effectively extracted by hexane. [Petti, 1992]

Upon centrifuging the moist solids, the heavy portions of the oil were driven down into the soil. Black pockets of thick viscous hydrocarbons were visible in both the sand and peat soil after centrifuging. It is highly unlikely that Bunker C would be able to penetrate the soils more than a few centimetres in an actual spill due to its high viscosity. Therefore, the extraction efficiency obtained for Bunker C-contaminated soils may substantially underscore the decontamination efficiency since the contacting obtained during sample preparation would not be possible under normal spill conditions. [Petti, 1992]

Table 6. Hexane Extraction of Bunker C-Contaminated Sand at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)
	Initial	Final	
S-1	2.22	0.18	91.9
S-2	4.76	0.30	93.7
S-3	6.70	0.33	95.1
S-4	6.90	0.24	96.5
S-5	7.17	0.39	94.6
S-6	9.62	0.33	96.6
S-7	9.80	0.33	96.6
S-8	14.30	0.36	97.5
Sd-8*	14.21	0.35	97.5
S-9	14.74	0.32	97.8
S-10	16.10	0.32	98.0

* Sd = sand sample duplicate

Table 7. Hexane Extraction of Bunker C-contaminated Peat Soil at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)
	Initial	Final	
P-1	2.50	1.70	32.0
P-2	5.20	2.90	44.2
P-3	6.98	3.19	54.3
P-4	7.67	3.44	55.1
Pd-4*	7.52	3.33	55.7
P-5	9.30	3.50	62.4
P-6	10.26	3.44	66.5
P-7	13.61	3.91	71.3
P-8	18.82	5.01	73.4
P-9	20.13	5.12	74.6
P-10	21.00	5.21	75.2

* Pd = peat soil sample duplicate

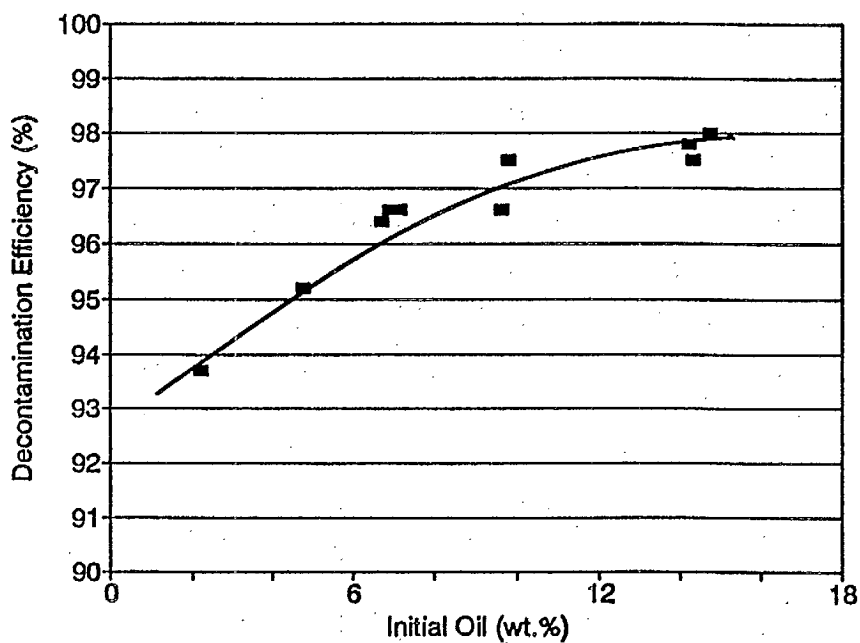


Figure 1. The Effect of Initial Bunker C-Contamination of Sand on Decontamination Efficiency.

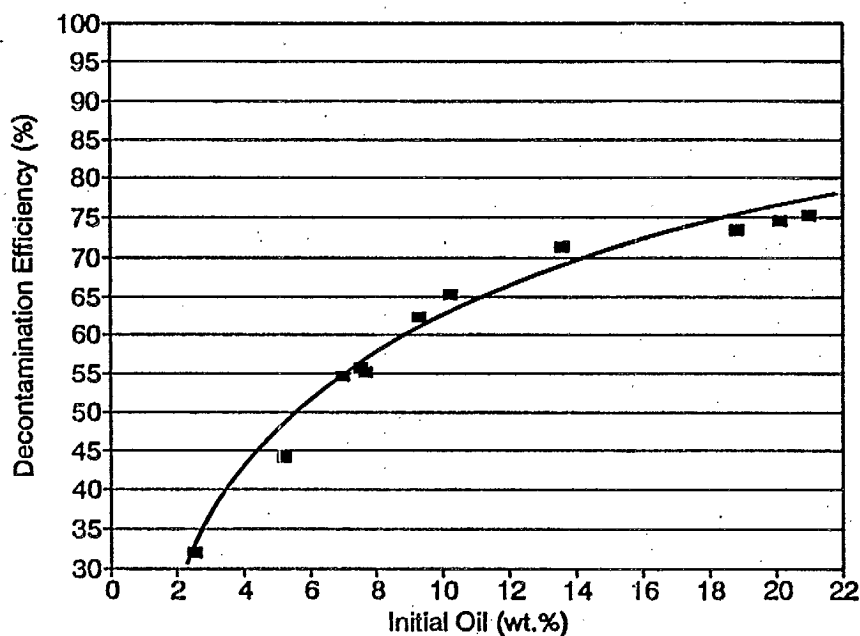


Figure 2. The Effect of Initial Bunker C-Contamination of Peat Soil on Decontamination Efficiency.

Light Crude Oil-Contaminated Sand

The results of the hexane extraction of light crude oil-contaminated sand and peat soil are presented in Tables 8 and 9 respectively. Decontamination efficiency versus initial oil contaminant concentration in sand and peat are plotted in Figures 3 and 4. For the oil concentration range (in sand) investigated, namely from 1.17% to 16.31%, the decontamination efficiency increased from 91.5% to 98.9% while the final oil concentration varied between 0.10% and 0.18%. For the oil concentration range (in peat soil) investigated, namely from 2.57% to 17.23%, the decontamination efficiency increased from 33.9% to 83.9% while the final oil concentration varied between 1.70% and 2.78%.

Light crude oils are complex and variable mixtures of hydrocarbons of different molecular weight and structure and may contain as many as 300 different compounds [Petti, 1992]. It would be unrealistic to assume that hexane would be a suitable solvent for the extraction of all these compounds. When dealing with such a large number of different compounds of different molecular weight and structure, a residual amount of some of the components is expected to remain with the extracted soils.

Table 8. Hexane Extraction of Light Crude Oil-contaminated Sand at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)
	Initial	Final	
S-11	1.17	0.10	91.5
S-12	2.43	0.11	95.5
S-13	2.83	0.12	95.8
S-14	5.16	0.16	96.9
S-15	5.87	0.13	97.8
Sd-15*	6.12	0.16	97.4
S-16	7.41	0.17	97.7
S-17	9.41	0.18	98.3
S-18	11.31	0.14	98.8
S-19	12.44	0.15	98.8
S-20	16.31	0.18	98.9

* Sd = sand sample duplicate

Table 9. Hexane Extraction of Light Crude Oil-contaminated Peat Soil at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)
	Initial	Final	
P-11	2.57	1.70	33.9
P-12	4.41	2.38	46.0
Pd-12*	4.62	2.41	47.8
P-13	6.50	2.40	63.1
P-14	7.84	2.41	69.3
P-15	9.54	2.43	74.5
P-16	10.28	2.43	76.4
P-17	12.11	2.50	79.4
P-18	13.48	2.51	81.4
P-19	14.12	2.70	80.9
P-20	17.23	2.78	83.9

* Pd = peat soil duplicate

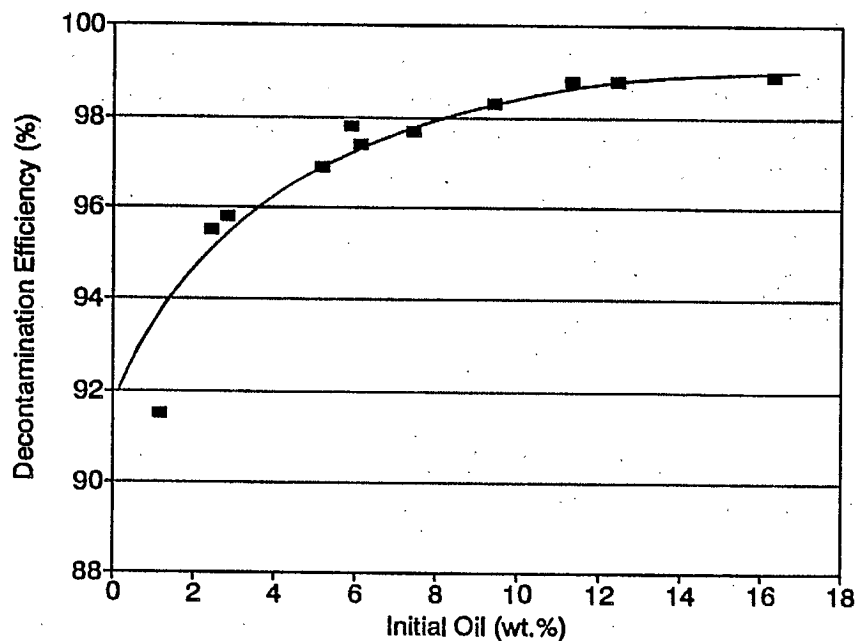


Figure 3. The Effect of Initial Light Crude Oil-Contamination of Sand on Decontamination Efficiency.

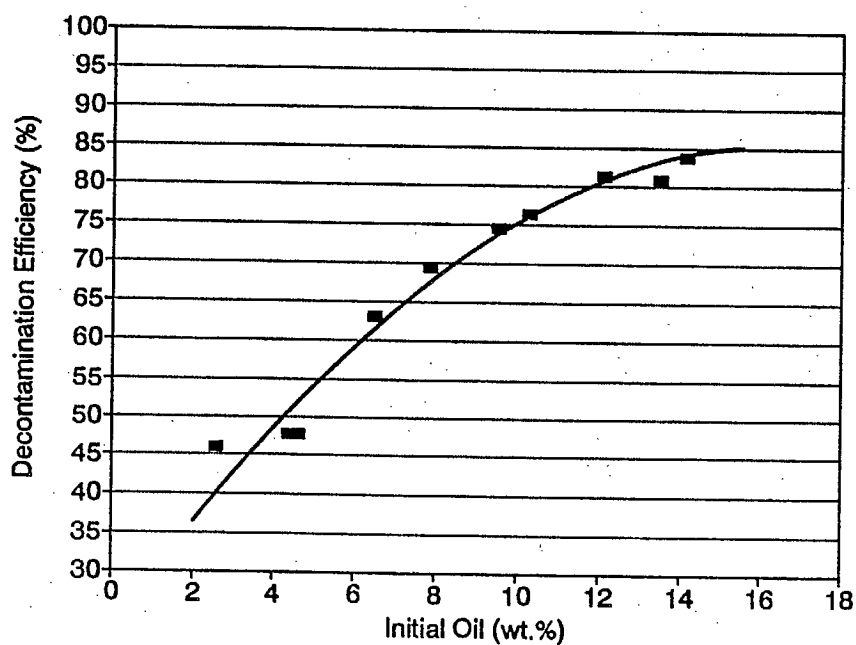


Figure 4. The Effect of Initial Light Crude Oil-Contamination of Peat Soil on Decontamination Efficiency.

Diesel-Contaminated Sand and Peat Soil

The results of the hexane extraction of diesel-contaminated sand and peat soil are presented in Tables 10 and 11. Decontamination efficiency versus initial oil contaminant concentration in sand and peat soil are plotted in Figures 6 and 7. For the oil concentration range (in sand) investigated, namely from 2.42% to 7.83%, the decontamination efficiency remained relatively constant at 97.5% while the final oil concentration varied between 0.06% and 0.19%. For the oil concentration range (in peat soil) investigated, namely from 2.87% to 10.0%, the decontamination efficiency increased from 47.0% to 76.7% while the final oil concentration varied between 1.52% and 2.44%.

Diesel contains a greater amount of light ends as compared to light crude oil. Hexane appears to be a suitable solvent for the extraction of this oil. The extracted soil samples still had a noxious odour even though the residual oil was as low as 0.06% in some extracted sand samples. [Petti, 1992]

The recycling of hexane reduces the cost of the soil treatment and the volume of waste. As previously mentioned, unforeseen delays in obtaining an explosion proof hot plate resulted in obtaining only solvent recovery data for diesel-contaminated soils. Hexane recovery for sand and peat are approximately 81% and 67% respectively regardless of the degree of initial diesel-contamination.

The average percent hexane in the condensate was approximately 99.8%, while a blank run of pure hexane gave a purity of 99.9%. Thus one can conclude that the distilled extract produces a recycled solvent which is suitable for reuse.

Table 10. Hexane Extraction of Diesel-Contaminated Sand at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)	Solvent Recovery (%)
	Initial	Final		
S-21	7.83	0.19	97.6	79.8
S-22	6.42	0.17	97.4	81.3
S-23	4.99	0.13	97.4	79.4
S-24	4.50	0.11	97.6	81.7
S-25	2.42	0.06	97.5	82.0

Table 11. Hexane Extraction of Diesel-Contaminated Peat Soil at the Optimum Mixing Parameters.

Run No.	Oil (wt. %)		Decontamination Efficiency (%)	Solvent Recovery (%)
	Initial	Final		
P-21	10.0	2.44	75.6	66.4
P-22	9.51	2.22	76.7	65.9
P-23	7.16	2.23	68.9	66.8
P-24	5.30	2.00	62.3	67.2
P-25	2.87	1.52	47.0	67.3

COMPARISON TO SOIL REMEDIATION GUIDELINES AND LABORATORY SCALE RESULTS

The guidelines for the decommissioning and cleanup of sites in Ontario for oil and grease set out by the Waste Management Branch of the Ontario Ministry of the Environment (MOE) in February 1989 is 10,000 ppm (1 wt.%). These guidelines were met in all instances for sand contaminated with light crude oil, diesel or Bunker C as the final oil contaminant concentration varied between 0.06% and 0.39%. The final oil contaminant concentration for peat soil varied between 1.52% and 5.21% and thus did not comply with the MOE guidelines. It should be emphasized that these are only guidelines and not regulations.

In general, the decontamination efficiencies at the bench scale are slightly lower but consistent with those at the laboratory scale. Once again, decontamination efficiencies with sand are greater than those with peat and the final oil concentration in sand is less than that in peat.

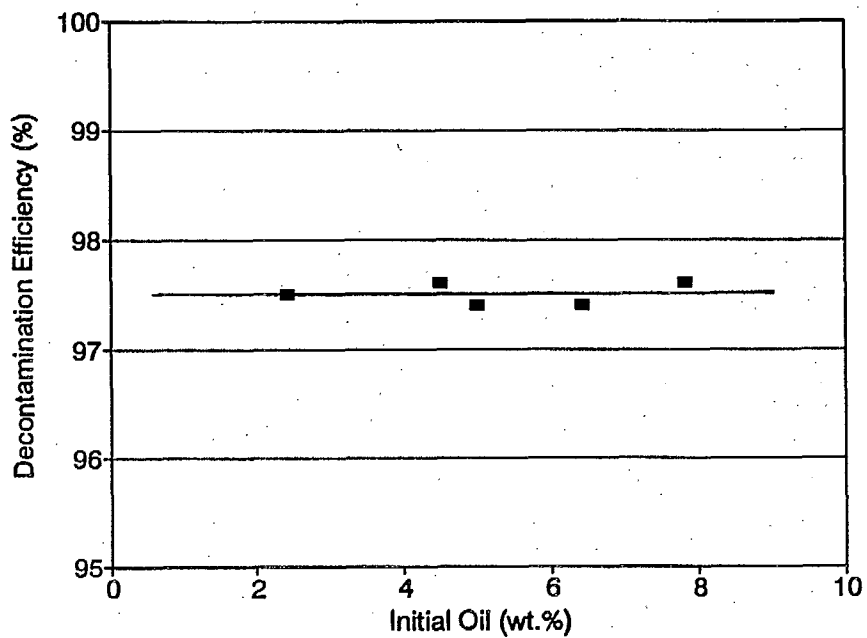


Figure 5. The Effect of Initial Diesel-Contamination of Sand on Decontamination Efficiency.

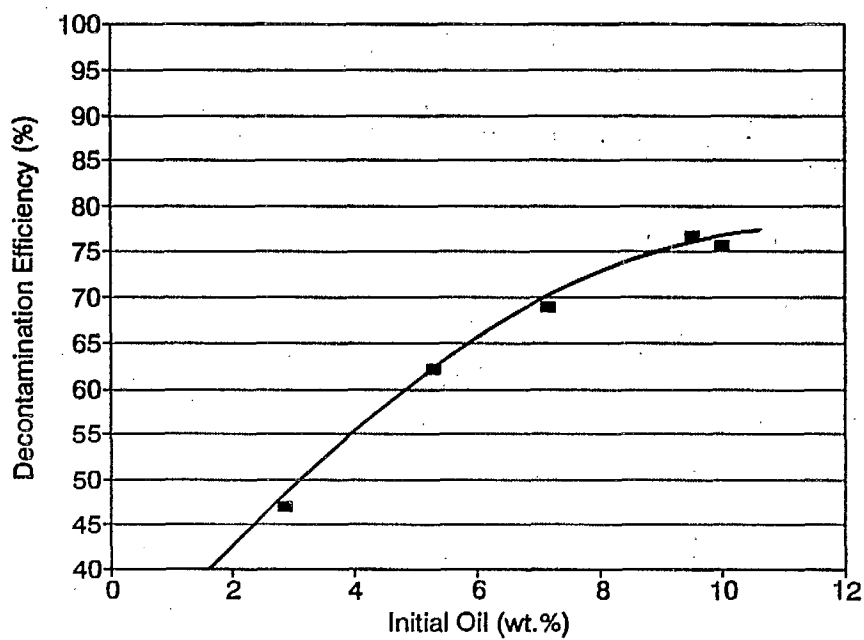


Figure 6. The Effect of Initial Diesel Contamination of Peat Soil on Decontamination Efficiency.

CONCLUSIONS AND RECOMMENDATIONS

Results using a 1,000 g batch system showed extremely high oil removal efficiencies from contaminated sand (up to 98.9%) and peat soil (up to 83.9%). The final oil contaminant concentration for sand varied between 0.06% and 0.39% while that for peat soil varied between 1.52% and 5.21%. The guidelines for the decommissioning and cleanup of sites in Ontario for oil and grease (1 wt.%) were met in all instances for the treated sand but not for the peat soil. Hexane recovery from diesel contaminated sand and peat soil experiments were approximately 81% and 67% respectively.

The solvent extraction process seems to be a promising technology for the treatment of contaminated soils. However, its potential will depend on the environmental regulations and the allowable limits of oil and grease for returning treated soil to its original place. The treated soil may need to be subsequently treated to destroy the residual contaminants or be recycled through the process to meet the environmental regulations at the municipal, provincial, or federal level. Furthermore, as regulations become more stringent, other constituents, such as benzene, toluene, etc. will have to be analyzed.

This treatability study has proven to be very effective for soils that have been in contact with petroleum hydrocarbons for short periods of time. However, this process must be evaluated for soils which have been in contact with petroleum hydrocarbons for longer periods of time resulting in only the heavy, viscous components remaining.

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REMOVAL OF ARSENIC FROM GROUNDWATER USING REAGENT BINDING / MEMBRANE SEPARATION

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A hybrid method incorporating selective polymeric binding and membrane separation was used to remove arsenic from a synthetic solution representing groundwater. Two types of polymers, polyethylenimine (PEI) and poly-diallyl dimethyl ammonium chloride (DADMAC) and an ultrafiltration membrane were used at various concentrations and pH. Bench-scale tests demonstrated a high degree of arsenic removal. The retention of arsenic was also determined in the presence of various background salts such as NaCl, Na₂CO₃, Na₂SO₄, NaNO₃. Retention was found to depend on the concentration and type of anion present in solution.

Introduction

Arsenic contamination in groundwater is a serious problem due to its toxicity and its presence in certain areas of our environment. Arsenic's toxicity varies depending on its oxidation state (+5, +3, 0, -3). Three distinct arsenic forms are most common: metallic As(0), trivalent As(+3), and pentavalent As(+5), the trivalent being the most toxic. Arsenic finds its way into the hydrosphere primarily from mining leachate, the combustion of fossil fuels and the use of herbicides, pesticides and defoliants in agriculture. When combined, these factors cause an annual increase of 110,000 tons [1] in the arsenic level of the hydrosphere.

The increased level of arsenic in water presents a danger for all species existing in our environment, which raises concerns about human health and the salubrity of the environment. In response to the problem of contaminated water and soil, the Canadian government has developed quality criteria intended to provide guidelines for allowable levels of inorganic and organic compounds in surface waters and soil [2]. The remediation criteria set for water are summarized in Table 1.

Table 1. Quality Criteria for Contaminated Sites: Arsenic Concentration in Water.

Freshwater	Irrigation	Livestock Watering	Drinking Water
50 µg/L	100 µg/L	500-5,000 µg/L	25 µg/L

According to these criteria, the concentration of arsenic in fresh water should not exceed 50 ppb. However, the concentration of arsenic in lakes surrounding mines can be in the range of several hundred ppb and as high as several hundred ppm in mining leachate. Arsenic contamination of the hydrosphere is a serious environmental problem since its residence time in lakes is 45 years, while in Oceans it will persist for 60,000 years [1,3]. The persistence of arsenic in a stream is directly affected by water flowrate. In general, lower concentrations of arsenic are observed in streams having higher water flowrates. In such streams arsenic is quickly diluted and less is absorbed by sediments.

Several methods have been developed to extract arsenic from aqueous solutions. Three main techniques are currently employed, namely reagent precipitation, ion exchange on polymeric resins and sorption on inorganic sorbents [4]. Reagent precipitation is currently the most widely used technique on an industrial scale. Table 2 summarizes various precipitation agents used and the recovery obtained for each.

Table 2. Percentage of arsenic removed using various precipitating agents.

precipitating agent	% removed
ferric sulfate	80 - 99
ferric chloride	81 - 100
ferric hydroxyde	94 - 96
alum	85 - 92
sulfide	80

As shown in Table 2, FeCl_3 can achieve a higher percentage of arsenic removal, but $\text{Fe}(\text{OH})_3$ is still considered to be the most efficient and economical precipitant. Although it is very effective, precipitation by $\text{Fe}(\text{OH})_3$, cannot reach the low concentration of arsenic imposed by Canadian environmental standards.

Ion exchange is a technique which has been developed initially for use with a stationary resin. This method is effective reaching 100% removal provided that the concentration of background salts remains at a low level. Sorption on inorganic sorbents can also be very effective with 95% rejection but the process is relatively slow and can take as long as several hours or even days to achieve the saturation of a sorbent. None of the existing technologies for arsenic removal is ideal and universal. Improvement of existing methods and the development of new techniques is, therefore, an environmental necessity.

The combined method of polymeric binding and membrane separation has been used for wastewater treatment [5], for the selective concentration of microcomponents from seawater [6], for analytical [7] and other purposes. The technique involves the addition of a water-soluble polymer to a contaminated aqueous solution. Target ions bind selectively with the polymer and ultrafiltration is performed to remove the polymer from the solution. The technique has also been used in the past to remove arsenic with limited success [8]. Knowing that groundwater is a multicomponent system where many constituents can interact with the binding agent, we assumed that the polymeric binding agents used in ref. [8] did not possess sufficient selectivity towards arsenic.

The main objective of this work was to investigate the applicability of the polymeric binding / membrane separation method for the purposes of arsenic removal using agents having a greater selectivity for arsenic. The effect of solution composition (components, concentrations, pH) on the efficiency of the separation was studied.

Experimental

Synthetic groundwater was produced by preparing solutions containing anions found in groundwater. A total of eight synthetic ground water solutions were prepared using the following salts, NaCl, Na₂CO₃, Na₂SO₄, NaNO₃. A 1,000 mg/l solution of pentavalent arsenic was then added to these solutions yielding spiked solutions of arsenic containing 0.3 to 30 ppm of arsenic. Commercially available polyelectrolytes, polyethylenimine (PEI) and poly-(diallyl dimethyl ammonium chloride) (DADMAC) were used as binding agents. The physico-chemical properties of these polymers were described by Mangravite [9]. PEI and DADMAC were selected for arsenic binding since it was documented that water soluble polymers, which have similar chemical structure and properties as solid polymeric resins, possess an affinity towards arsenic [4,10].

All tests were performed using standard ultrafiltration equipment. Polyethersulphone membranes Bioken (Bioken Separations, Inc.) with a molecular weight cut-off of 10,000 daltons were employed. Polymers tested in this work were completely rejected by the membrane.

The retention of arsenic on the high pressure side (feed side) of the membrane (R_{As}) was used to characterize the efficiency of arsenic removal. It was reported in Volchek, Legault and Keller [11] that metal retention in the case of the polymeric binding / membrane separation process could be found as a product of polymer retention (R_p) and the degree of binding of a metal by a polymer (β). If a polymer is completely retained by a membrane ($R_p = 1$), the metal retention is simply equal to its binding degree, i.e. $R_{As} = \beta$.

Arsenic concentrations were determined by atomic absorption spectrophotometry. A hydride generator was used to enhance the sensitivity of the apparatus at low metal concentrations.

Results and Discussion

In the first set of tests, the relative effectiveness of polymers as binding agents was studied. Selected results are presented in Table 3.

Table 3. Retention of arsenic in the presence of polymeric binding agents.
Feed concentration [As] = 0.3 ppm; Transmembrane pressure: 40 psi.

pH	Arsenic Retention (R_{As})			
	DADMAC		PEI	
	1ppm	10ppm	1ppm	10ppm
3.5	0.20	0.46	0.43	0.79
7.0	1.00	1.00	0.55	0.74

At higher pH, DADMAC was a more effective binding agent than PEI. This fact may be explained as follows: DADMAC is a chemical analog of strongly cationic ion exchange resins, whereas PEI is an analog of weakly cationic resins. Strongly cationic resins possess higher affinity towards arsenic [1]; therefore, DADMAC should be a stronger binding agent. The experimental results justify this hypothesis.

It was also found that a decrease in pH resulted in a decrease in arsenic retention by the membrane. This observation was more evident in the case of DADMAC. In the case of PEI, however, the change in arsenic retention was less significant. This can be explained by the fact that arsenic in groundwater is present predominantly as As(V) forming several species: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} [12]. The presence of each species depends on the pH level of the solution as demonstrated by Figure 1. Calculations were carried out using data presented by Pascal [12]. The arsenic anions can interact with positively charged groups of resins (or polyelectrolytes) forming metal-polymeric compounds, whereas the neutral form H_3AsO_4 is inactive. All four forms of As(V) are in a chemical equilibrium while at lower pH this equilibrium shifts favoring the formation of the neutral form. At a pH above 4.5 a greater amount of arsenic is accessible for binding.

In the case of PEI, this polymer is capable of binding arsenic when it possesses positively charged ammonia groups. This takes place when the concentration of protons in a solution is high enough, i.e. at pH values below neutral. In this case, the change in pH affects both arsenic and PEI.

In the second series of tests, the effect of background salts on the arsenic retention was studied. It was found that an increase in the salinity level of water resulted in a decrease in arsenic retention. The magnitude of this effect being different for each salt (see Figure 2). This phenomenon may be explained from the point of view of competitive binding.

Naturally occurring groundwater is a multicomponent system. Many components, including all anions, can interact with a polycation. Greater stability constants and higher concentrations of an anion result in a higher degree of binding with a polymer [11]. It is known that strongly cationic resins containing ammonia groups have the following affinity towards anions: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$ [10]. Also, when an anion with a lower affinity is present at much higher concentrations it can block the binding of a more affine anion. Therefore, the binding of arsenic in groundwater has a competitive character. At lower concentrations, background salts do not affect arsenic binding substantially since the anions of these salts possess less affinity towards DADMAC. At higher concentration, however, they block arsenic binding which results in a deterioration of arsenic retention. Varying magnitudes of arsenic retention obtained in the presence of these salts can be explained as a result of the different stability constants of the DADMAC with the anions of these salts.

Conclusions

The evaluations performed to date have demonstrated that the combined method of polymeric binding / ultrafiltration can be used for the removal of arsenic from contaminated water. The presence of anions strongly affects the efficiency of the process. Water soluble polymer DADMAC can be considered suitable for arsenic removal. Results indicate that the proposed technique could be used as a single step method for water treatment or as a post-treatment step after reagent precipitation.

Acknowledgement

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concentration (mmol/L)

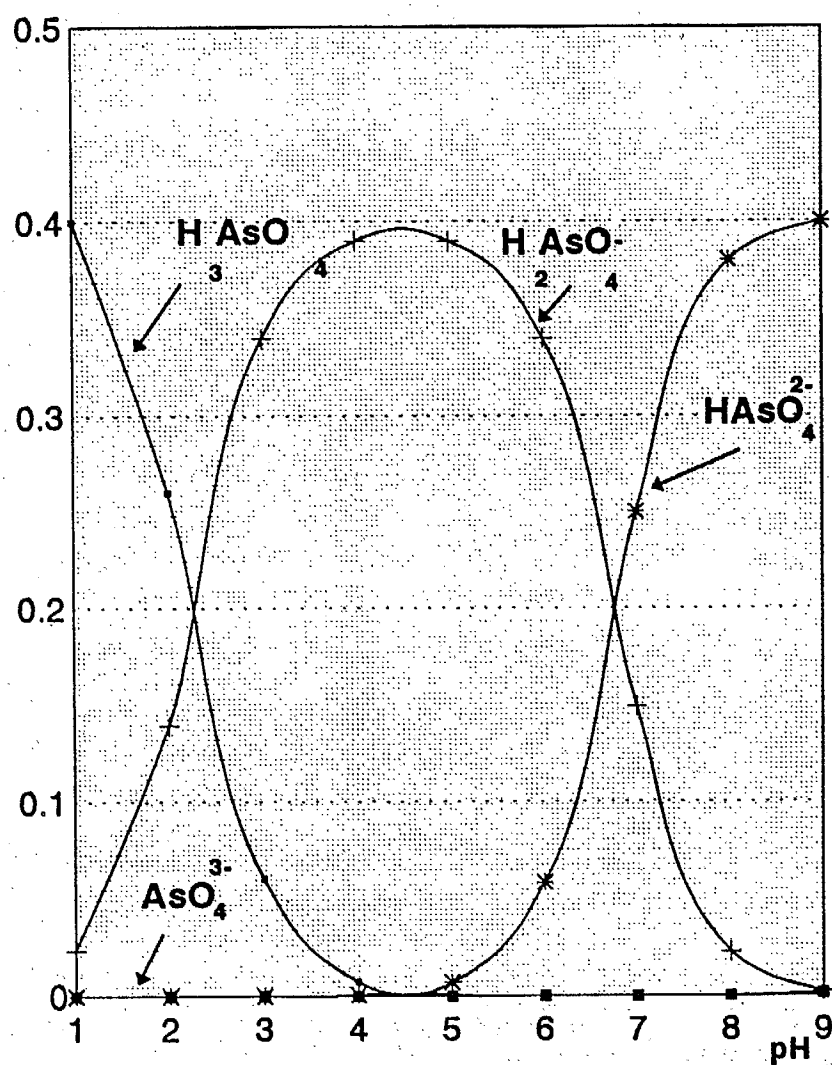


Figure 1. Concentration of Arsenic Compounds at Various pH.

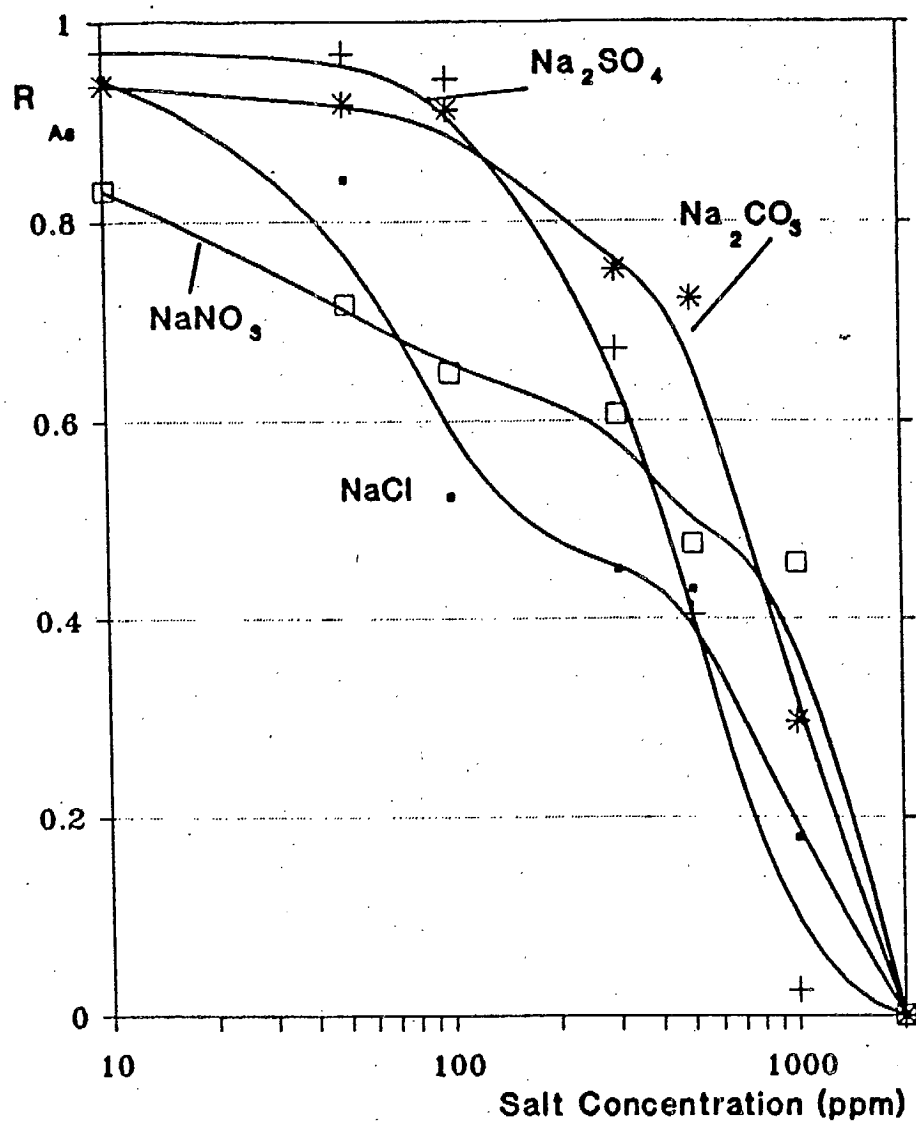


Figure 2. Retention of arsenic (R_{As}) in the presence of DADMAC and background salts: $NaCl$, $NaNO_3$, Na_2SO_4 , Na_2CO_3 .
 Feed concentrations: $[As] = 30$ ppm; $[DADMAC] = 3,000$ ppm;
 Transmembrane pressure: 40 psi.

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