Effectiveness of Subsurface Treatment Technology at Alberta Sour Gas Plants

Phase IIA:

Assessment of Subsurface Contamination and Remediation at Alberta Sour Gas Plants

Report to
Canadian Petroleum Association
and Environment Canada

February 1992

Prepared by
Piteau Engineering Ltd.

Printed on Recycled Paper

Funding for this project was provided by the Environmental Research Advisory Council of the Canadian Petroleum Association and Environment Canada Resources supplied by the Federal Panel for Energy Research and Development (PERD)

ACKNOWLEDGEMENTS

This report is the result of the efforts of many contributors. Piteau Engineering wishes to thank all of the members of the project team for their good work and enthusiastic support. Shiela Legget of Jim Lore and Associates Ltd. wrote the sections on sulphur pad reclamation, in-situ vitrification, and sulphur recycling, and assisted in ranking of soils technologies. Dr. Fred Farley of Biodyne Inc, in Florida contributed the sections on biotreatment on soils. Dr. Ian Forrester of Gemini Biochemical Research of Calgary contributed material on in-situ bioremediation of groundwater. Carl Mendoza of the University of Waterloo wrote the sections on soil vapour extraction. Joseph Wells of Integrated Environments Ltd, Calgary, contributed the section on excavate and treat methods for contaminated soils, and assisted with ranking of soils technologies. Dr. Jim Mercer of Geotrans Inc, in Virginia, contributed to the overall technology reviews and was part of the selection panel. Mr. Stan Feenstra of Applied Groundwater Research in Mississauga, Ontario, contributed in the area of LNAPL contamination and remediation, and was a member of the panel. Dr. Istavros Papadopulos of SSP&A in Maryland assisted in the selection of technologies. Throughout the report, the work of the individual team members is also referenced.

Piteau acknowledges the support and participation of the members of the CPA Project Steering Committee: Mr. R. Creasey, Mr. W. Ceroici, Mr. B. Goliss, Ms. L. England, and the project co-chairmen - Mr. P. Weeks and Mr. R. Scroggins. Through frequent meetings during the course of the project, the committee members contributed valuable ideas and direction to the study. The views expressed in this report do not represent the views of CPA or Environment Canada.

EXECUTIVE SUMMARY AND
GUIDE TO USING THE REPORT

1. BACKGROUND

This report represents the second part of a multi-phased study into remediation of subsurface contamination at Alberta Sour Gas Plants (ASGPs) sponsored by the Canadian Petroleum Association (CPA) and Environment Canada. Phase I, completed in 1990, reviewed all soil and groundwater data submitted to Alberta Environment by sour gas plants in accordance with the Clear Water Act (1971). From these data, the most common contamination situations at ASGP's were identified.

The findings of the Phase I study provided the necessary foundation for a comprehensive examination of subsurface treatment technologies suitable for Alberta sour gas plants.

The main purpose of this report (Phase IIA) is the identification and selection of the most appropriate remediation/treatment technologies for the main types of contamination situations present at Alberta sour gas plants.

This assessment of available and promising new remediation technologies is undertaken within the context of conditions prevalent at Alberta sour gas plants: geological, hydrogeological, climatic, and economic. Proven technologies as well as new and innovative remediation methods are reviewed and considered.

2. CONTAMINATION SITUATIONS CONSIDERED

Based on the results on Phase I, eighteen individual contamination situations, representing the most common and important subsurface conditions at sour gas plants, were identified for consideration, as shown in Figure E.1.

FIGURE E.1
CONTAMINATION SITUATIONS CONSIDERED

DESCRIPTION	CODE	CONTAMINANTS		
		CONDENSATE (A)	INORGANICS (BC)	LOW pH (D)
soil/us zone				
high K	S1	S1A	S1BC	S1D
low K	S2	S2A	S2BC	S2D
surficial aquifers				
high K	T1	T1A	T1BC	T1D
low K	T2	T2A	T2BC	T2D
bedrock aquifers				
high K	R1	R1A	R1BC	R1D
low K	R2	R2A	R2BC	R2D

3. METHODOLOGY

A general overview of the study methodology is provided in the form of a flow chart, shown in Figure E.2. First, the specific contamination situations to be considered were reviewed and detailed information on each assembled. Next, a comprehensive review of available and emerging subsurface remedial technologies was undertaken by members of the project team. For each contamination situation and relevant sub-group, generally applicable remediation technologies were then identified.

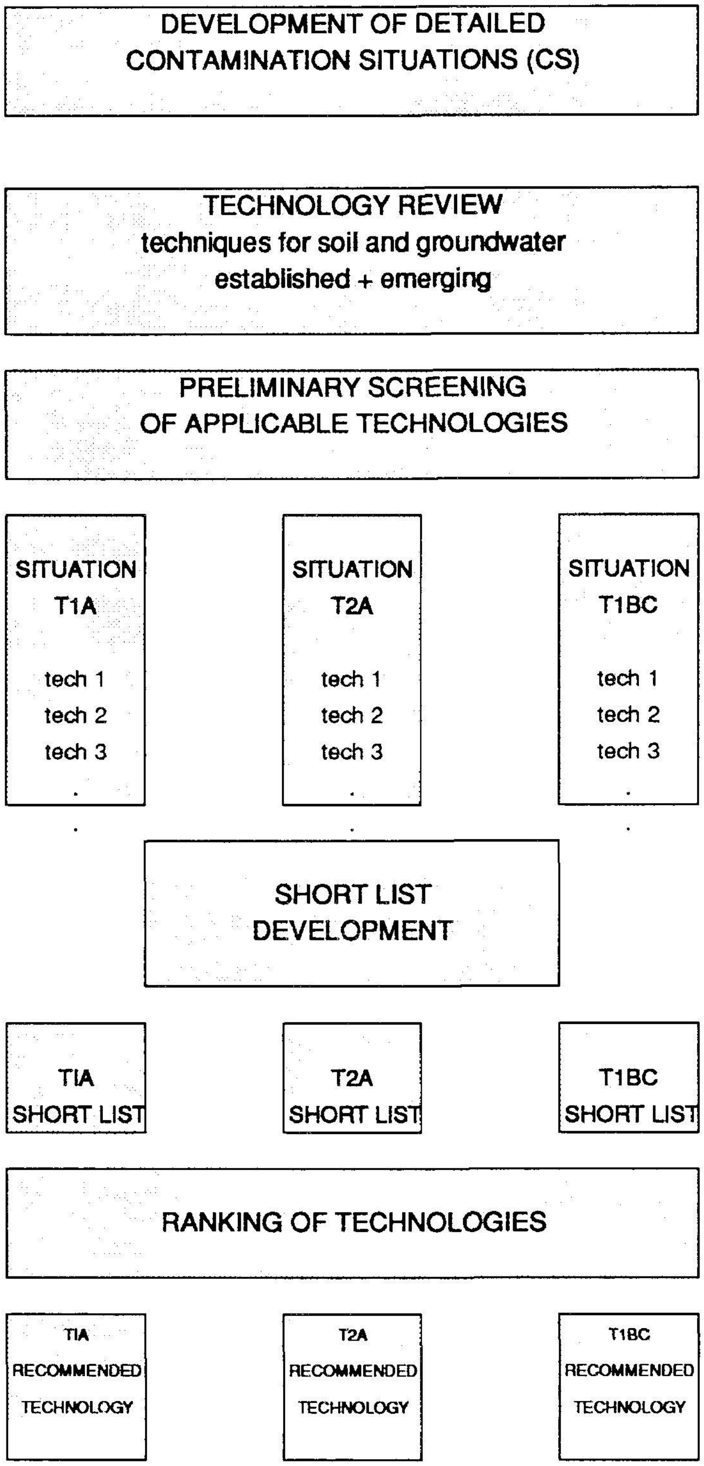
From this information, short lists of appropriate established and promising new/innovative technologies were assembled, and technologies prioritized. Ranking of choices was accomplished by a special panel of five experts, each of whom has broad experience in site remediation. The panel was provided detailed case histories which encompassed all of the contamination situations, and asked to rank choices based on a number of specific criteria. New and innovative technologies which hold promise for remediating contamination at sour gas plants were also assessed.

Next, detailed reviews of each of the recommended technologies were prepared.

4. PROJECT TEAM

The project team assembled for this study included experts in the areas of groundwater remediation, sour gas plant hydrogeology and geology, soil vapour extraction and off-gas treatment, soil remediation technology, soil microbiology, groundwater bioremediation, groundwater in fractured media, organic chemistry, and geotechnical engineering/subsurface structures. The team included the principals and selected associates staff of two major US environmental consulting firms, senior American and Canadian experts in bioremediation technology, and subsurface contamination remediation specialists from Canadian Universities and industry. Considerable Alberta-based expertise was also drawn upon.

FIGURE E.2
PROJECT METHODOLOGY



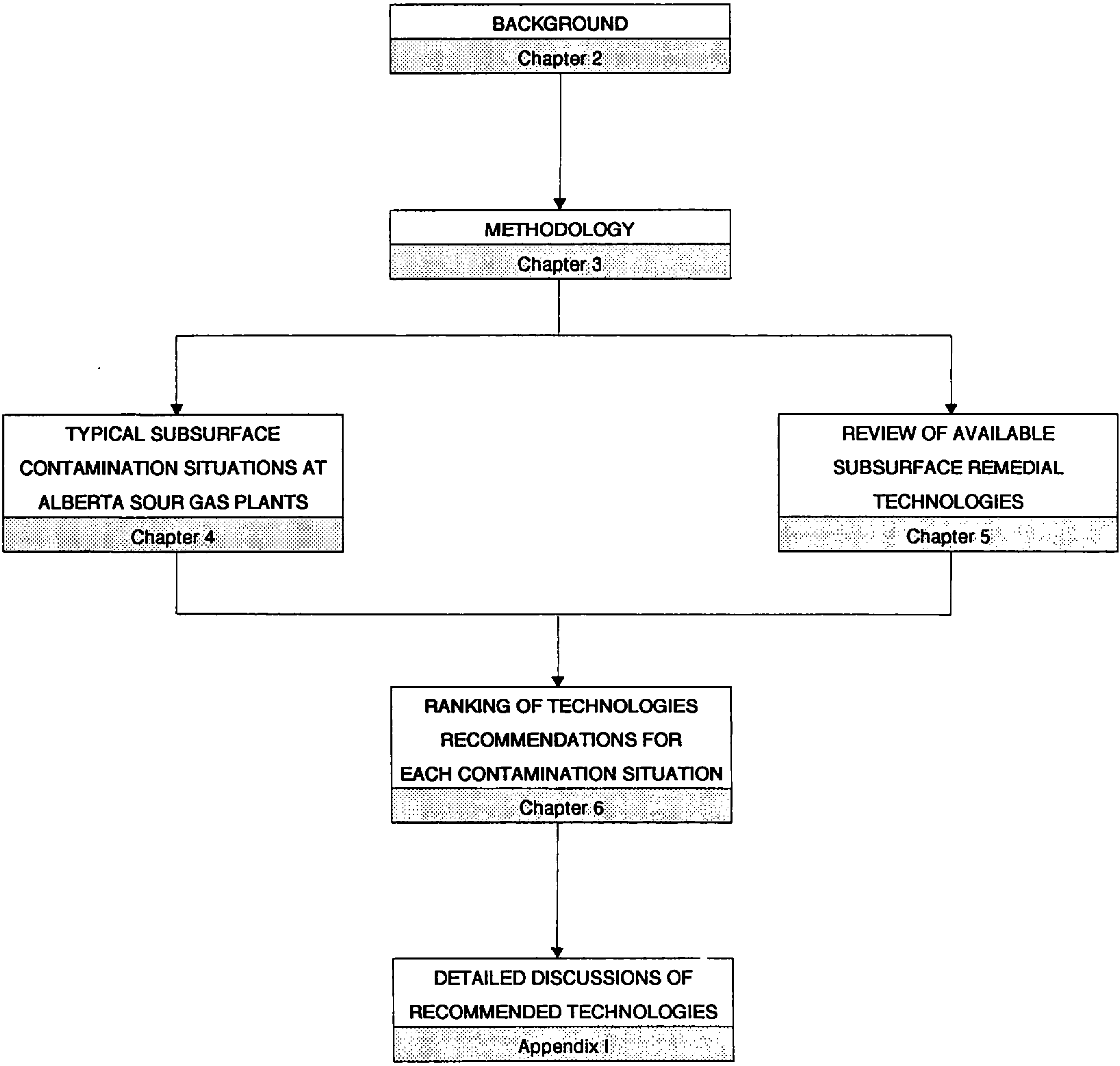
Each member of the team provided expertise in their respective areas of specialization, and senior specialists were selected to provide overall experience and a familiarity with the entire spectrum of remedial options in order to allow critical comparison and ranking of methods. The five senior members of the team formed a panel charged with the final ranking and selection of technologies.

5. ORGANIZATION OF THE REPORT

This document covers a wide range of topics in considerable detail, and takes the reader through a series of decision and ranking steps to arrive at a list of recommended treatment technologies for particular situations. The report is organized in a logical decision making sequence as shown in Figure E.3; first the problems to be considered are discussed in detail; then an overall review of available solutions is completed, and each assessed for general applicability to the problems. The next section considers a short-list of technologies for each contamination situation, compares and ranks them according to a uniform set of criteria. Recommendations are provided for each contamination situation. The following section provides a detailed review of each of the recommended technologies, discussing advantages, limitations, theory and practical application, case histories, remedial efficiency and cost-effectiveness.

Each section, however, is designed to act as a stand-alone reference. If the reader is interested in a general overview of available treatment technologies for soil or groundwater, Section 5 will provide this. Solutions to particular contamination situations are discussed in detail in Section 6 - the reader can, for instance, turn to contamination situation R1A (condensate in highly fractured bedrock), and find a comparison of applicable remedial methods, discussions of their relative strengths, and the approach recommended by the expert panel. For a detailed review and discussion of particular recommended technologies as applied to Alberta sour gas plant conditions, turn to Appendix I. Figure E.4 outlines how the report can be used to find recommended solutions to specific contaminant problems.

FIGURE E.3
REPORT ORGANIZATION



6. TECHNOLOGY RECOMMENDATIONS

For each contamination situation common to ASGP's, the most applicable established technology or approach was identified, and the new/innovative technologies most worthy of future development were identified. The technology recommendations for the various contamination situations are summarized in Table E.5. For each of the recommended technologies, a detailed description is provided in Appendix I of this report. Information presented includes costs, demonstrated efficiencies, case histories, and design and implementation information. It is stressed that there can be no substitute for individual site assessment for selection of the appropriate remedial strategy. Final choice of remedial technology will always depend on the goals of remediation, the unique characteristics of the site, and time and economic constraints. This report should be seen as a starting point for technology selection, and not as a definitive final recommendation.

7. FUTURE OBJECTIVES

Subsurface contamination at sour gas plants in Alberta is characterized by a wide variety of potential contaminants, complex subsurface conditions, and severe climatic conditions. To date, little work has been done to address the considerable challenges of remediating such contamination, and hence the general level of technology and sophistication which has been applied to these problems is low. This situation presents considerable opportunity not only for development and testing of appropriate solutions for the specific problems discussed, but also for the advancement of research into specific treatment technologies.

The present study identifies technologies and approaches applicable to the particular situations present at Alberta sour gas processing facilities and thus worthy of field demonstration. It is planned to demonstrate some of these technologies at one or more gas plant sites to be selected in 1991. At such time, the Canadian Petroleum Association and Environment Canada will be seeking to contact groups interested in participating in field demonstrations of appropriate remedial technologies. The results of the planned field demonstrations will be invaluable to the sour gas processing industry and the cause of environmental protection in general.

FIGURE E.4
USING THE REPORT TO FIND RECOMMENDED SOLUTIONS TO SPECIFIC PROBLEMS

1 Find Appropriate Contamination Situation (Chapter 4)

- Note special considerations

2 Look up Recommended Technologies (Chapter 6)

for the specific contamination situation

3 Refer to Appropriate detailed discussion (Appendix I)
of the Recommended Technology

Note: These steps provide only a guide to recommended technologies. All remedial programs, however, must be approached on a site specific basis. Final decisions on technology selection, design and implementation must be made on the basis of a sound understanding of site conditions.

FIGURE E.5
TECHNOLOGY RECOMMENDATIONS

CONTAMINATION SITUATION		TECHNOLOGY RECOMMENDATION	
	DESCRIPTION	ESTABLISHED	NEW AND INNOVATIVE
S1A	Condensate in permeable soils	• Soil vapour extraction (SVE) with air injection; off-gas treatment	• enhanced SVE with waste heat from plant; bioventing • in-situ bioremediation
S2A	Condensate in less permeable soils	• SVE for lower permeability materials • Excavate hot spots; low temperature thermal volatilization or bioreactor treatment	• Detoxifier system
S1BC/S2BC	Inorganic contaminants in soils	• In-situ soil washing and leachate collection • Deep tilling in less permeable soils • Capping + excavate and treat for hot spots	• None recommended
S1D/S2D	Low pH soils	• Liming and revegetation	• Re-cycling of sulphur-contaminated soil as fertilizer
T1A	Condensate in permeable surficial aquifers	• Pump and treat, dual-pump skimming of mobile product • SVE extraction for residual product • In-situ aerobic bioremediation as polishing step, if required	• Use of waste heat to enhance SVE; and use with subsurface volatization and vapourization (SVVS)
T2A	Condensate in less permeable surficial aquifers	• Pump and treat, skim mobile LNAPL • SVE to remove residual product	• Use waste heat to improve SVE • Trencher technology
T1BC/T2BC	Dissolved contaminants in surficial aquifers	• Risk assessment • Pump and treat, reinject/flush as required	• None recommended
T1D/T2D	Low pH conditions in surficial aquifers	• Source removal • Risk assessment - natural dissipation? • Pump and treat or flush, as required	• None recommended
R1A/XA/R2A	Condensate in fractured bedrock aquifers	• Pump and treat to control dissolved plume, skim mobile product • Remove residual LNAP with SVE and in-situ bioremediation	• Subsurface volatilization and vapourization • surfactants
R1BC/R2BC	Dissolved contaminants in bedrock aquifers	• Risk assessment • Natural dissipation? • Pump and treat, and reinject/flush	• None recommended

FIGURE E.5
TECHNOLOGY RECOMMENDATIONS

CONTAMINATION SITUATION		TECHNOLOGY RECOMMENDATION	
R1D/R2D	Low pH conditions in bedrock aquifers	• Risk assessment • Pump and treat or flush with buffering solutions	• None recommended
ORGANICS IN GROUNDWATER	BTEX in produced groundwater	• Air-stripping • GAC polishing as required	• Advanced oxidation processes (AOP) • Use of waste heat to enhance air-stripping
INORGANICS IN GROUNDWATER	Cl and SO4 in produced groundwater	• Dilute and reinject • Ion exchange if treatment required	• Freeze crystallization
OFF-GAS TREATMENT	Volatile hydrocarbons from air-stripping and SVE	• Knock-out liquids • Catalytic oxidation for high concentrations (SVE) • Carbon adsorption (air-stripping)	• To plant flare system • AOP systems

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1. INTRODUCTION

1.1 BACKGROUND

There are at present over 150 sour gas processing plants operating in Alberta (Oilweek, 1987). Sour gas processing plants produce a wide variety of products and wastes which have the potential to impact the subsurface, including process chemicals such as amines, glycol and sulfinol used to remove H2S from the gas stream, sulphur and sulphur products, hydrocarbon liquids and their dissolved components (such as BTEX), and produced saline waters and brines. These substances can be delivered to the subsurface in many forms by a number of mechanisms, and all have the potential to seriously degrade soil and water quality.

Recognizing the potential impacts of sour gas plant operations on the subsurface environment, the Canadian Petroleum Association (CPA) and Environment Canada have launched this multi-phase study focusing on demonstrating remedial technologies for soil and groundwater contamination at these facilities. The first phase was completed in 1990, and consisted of a comprehensive review of all soil and groundwater monitoring data submitted to Alberta Environment by sour gas plants in accordance with the Clean Water Act (1971). The review indicated that all but one of 45 sour gas plants reviewed exhibited some form of impact on soil and groundwater quality (Piteau Engineering Ltd, 1990; Hardisty et al, 1990). The study identified the most frequently occurring contamination situations at 45 plants, and classified them according to sources and types of contaminants, and the hydrogeological characteristics of the geologic host. The phase I report has been published by the CPA, and is now available.

1.2 PROJECT OVERVIEW

The results of the phase I study provided the first step in an investigation of subsurface remedial technologies applicable to the unique environmental, hydrogeological, climatic, and economic conditions found at Alberta sour gas plants (ASGP's). The new climate of public concern and regulatory and industry commitment to the environment has spurred developments of numerous technologies for clean-up of contaminated soil and groundwater. Some have been available for several years, and are widely used in the USA and parts of Europe and Canada, while others are relatively new and have not undergone rigorous field trials. The purpose of this phase of the study is to select the remedial technologies most appropriate for the most common contamination situations at Alberta sour gas plants, and thereby provide a framework for implementation of one or more pilot subsurface remediation demonstration projects. A parallel goal is to identify new and innovative technologies which show promise for application at these sites and are worthy of further field or bench-scale testing.

In tandem with this study of appropriate remedial technologies, another consultant is presently engaged in the task of soliciting formal support for the implementation of field demonstration projects in the near future. Phase I of the study identified seven sour gas plants in Alberta whose subsurface contamination situations and level of site characterization were suitable for field demonstration purposes. The operators of these seven plants are being approached; two or three will be selected for the demonstration phase of the project, based on their willingness to participate in all aspects of the project.

The technology study and operator selection phases will be completed simultaneously. At that time it is planned to match recommended technologies with appropriate sites, and solicit support for demonstration projects of selected technologies. One of the most important goals of the overall project is to provide opportunities for research into subsurface remediation systems suitable to the unique conditions and contamination situations found at sour gas plants and other petroleum industry installations in Alberta.

1.3 TERMS OF REFERENCE

A request for proposal for the phase II study was received from CPA in September of 1990. The objectives of this second phase of the study, as outlined in CPA's request for proposal were to "Identify and assess the applicability of conventional, new and innovative subsurface remediation technology or technology combinations for field demonstration at a site(s) identified as a result of Phase I review".

The request for proposal also includes the following objective for Phase II: "Develop a detailed design and cost estimate for the field demonstration project given a specific contamination situation(s) and a short list of remediation options." However, the scope of work of the RFP document did not contain any reference to this work. Upon consultation with project co-Chairman Mr. Weeks, Piteau was informed that this task was not to be included in the phase II study.

1.4 SCOPE OF WORK

The scope of work described in the request for proposal (RFP) consisted of six main tasks:

TASK 1: Collect and review relevant literature related to subsurface contaminant treatment and containment technology with emphasis on recent technology reviews in the area of in-situ remediation, pump and treat, soil venting/off-gas treatment and excavation and treatment techniques.

TASK 2: Identify and assess the applicability of conventional, new and innovative subsurface remediation technology or technology combinations to treat and/or contain contaminants in the twelve situations below:

Generic situation: Till with moderate K values (10E-3 to 10E-6 cm/sec) overlying fractured bedrock.

1. Inorganic contaminants in till zone only;
2. Low pH water contamination in till zone only;
3. Combined dissolved organics and inorganics in till zone only;
4. Combined dissolved organics and inorganics, with free phase condensate in till zone only;
5. Inorganic contaminants in fractured bedrock;
6. Low Ph water contamination in fractured bedrock;
7. Combined dissolved organics and inorganics in fractured rock only;
8. Combined dissolved organics and inorganics, with free phase condensate in fractured rock;
9. Inorganic contaminants in till and underlying bedrock;
10. Low Ph water contamination in till and underlying bedrock;
11. Combined dissolved organics and inorganics in till and underlying bedrock;
12. Combined dissolved organics and inorganics, with free phase condensate in till and underlying bedrock;

TASK 3: For each contamination situation, establish a short list of treatment and/or containment technologies or technology combinations with the greatest remediation potential.

TASK 4: For short listed technologies, discuss the following:

- expected contaminant removal efficiency;
- estimated capital costs for installation;
- estimated annual operating costs (demonstration-scale);
- any relevant historical field demonstrations;
- equipment availability

TASK 5: Identify technology (especially new and innovative) which has significant potential for treating the contaminant situations above but requires further bench-scale of field-scale research prior to field demonstration.

TASK 6: Providing justification, prioritize the technology recommended for demonstration for each contamination situation.

In addition to the above task, Piteau Engineering suggested an additional task be included in the study. This task, which was accepted by the committee, consisted of provision of information pertinent to the proper design and field implementation of recommended technologies.

TASK 7 (ADDITIONAL): For each technology recommended for demonstration, identify and discuss the site assessment data required for its proper design and implementation; and provide a summary of recommended design criteria and practices".

1.5 ORGANIZATION OF THE REPORT

This document covers a wide range of topics in considerable detail, and takes the reader through a series of decision and ranking steps to arrive at a list of recommended treatment technologies for particular situations. The report is organized in a logical decision making sequence: first the problems to be considered are discussed in detail; then an overall review of available solutions is completed, and each assessed for general applicability to the problems. The next section considers a short-list of technologies for each contamination situation, compares and ranks them according to a uniform set of criteria. Recommendations are provided for each contamination situation. The following section provides a detailed review of each of the recommended technologies, discussing advantages, limitations, theory and practical application, case histories, remedial efficiency and cost-effectiveness.

Each section, however, is designed to act as a stand-alone reference. If the reader is interested in a general overview of available treatment technologies for soil or groundwater, Section 5 will provide this. Solutions to particular contamination situations are discussed in detail in Section 6 - the reader can, for instance turn to contamination situation R1A (condensate in highly fractured bedrock), and find a comparison of applicable remedial methods, discussions of their relative strengths, and the approach recommended by the expert panel. For a detailed review and discussion of particular recommended technologies as applied to Alberta sour gas plant conditions, turn to Appendix I.

2. STUDY OBJECTIVES

2.1 PHASE I FINDINGS

2.1.1 Impacts on Groundwater

The first phase of the overall study was based on groundwater monitoring data provided by Alberta Environment, and consisted of documents submitted to the Standards and Approvals Division by plant operators pursuant to the Alberta Clean Water Act. In all, information was obtained for 54 Class B sulphur-recovering sour gas plants. The quality and completeness of information contained in the reports were quite variable. Of the 54 plants considered, sufficient data for adequate appraisal of subsurface contamination situations were available for 32. Information from 13 of the remaining plants allowed partial contamination assessment only.

The available data for each gas plant were reviewed and where possible groundwater contamination situations identified. Contamination situations were classified based on the source and types of contaminants, and the physical properties of the geologic host. For the purposes of this study, groundwater contamination was defined as " the presence of any chemical substance whose concentration exceeds background or which is not naturally present in the environment" (Environment Canada, 1984). No assessment of the seriousness (or the perceived need for clean-up) of the various contamination situations was undertaken, as in the majority of cases insufficient data were available for this task. Current guidelines do not specify provision of evaluations of the fate of contaminants by operators. For a detailed discussion of the assessment techniques and criteria used, see Piteau Engineering Ltd. (1990).

Of the 45 plants for which information allowed assessment of the presence of groundwater contamination, only one showed no signs of impact of plant activities on groundwater quality. Since the initial review, indications of groundwater contamination have also been found at the one plant which was originally classified as having no contamination.

There were sufficient data available at 42 plants to determine sources of groundwater contamination. Thirty-three of the 42 plants (78.5%) had at least one contamination situation originating from the process water/evaporation pond. Other common sources of groundwater contamination were process areas and on-site landfills. The sulphur block area was also identified as a frequent source of contamination. Other sources of contamination which were identified included surface runoff drainage ditches and ponds, injection wells on-site, and product loading areas.

There were sufficient data available at 44 plants to determine the types of contaminants in groundwater. Dissolved inorganic and organic species were the most commonly identified groundwater contaminants; these include chloride and sulphate ions, aromatic hydrocarbons, amines and other process chemicals. Impact on groundwater quality by sulphur products, notably sulphate and in some cases acid seepage waters, was identified at 17 of the 45 plants. Of interest, however, is that wherever monitoring wells were installed downgradient of sulphur blocks and storage areas, contamination was detected (only 17 of the plants surveyed had extended their monitoring systems to include sulphur facilities). Free phase condensate contamination was identified at five plants. Although this number represents only about one-tenth of the plants surveyed, the relative concern attached to this type of contamination makes it of particular interest. Free phase hydrocarbon contamination is difficult and expensive to remediate, and very low levels of hydrocarbon render water unfit for human or animal consumption.

It must be noted that findings were affected by the analytical schedules which the various operators chose to apply to their groundwater samples. If more comprehensive analysis of groundwater quality had been done, additional contaminant types may have been identified. Data with which the location of groundwater contamination could be determined were scarcest in the reports provided by Alberta Environment for this study. In many instances, borehole logs or piezometer construction details were not available, making it very difficult to determine which groundwater-bearing zone was being sampled. As a result, the nature and hydraulic properties of the geologic host of groundwater contamination could be determined at only 33 of the 54 plants in the study group.

Zones were classified according to their average hydraulic conductivity, to provide some indication of the ability of contamination to migrate away from source. Unsaturated zone (soil) contamination was provided a separate classification. The majority of groundwater contamination situations at Alberta sour gas plants seem to occur in zones of moderate hydraulic conductivity (10E-5 < K < 10E-8 m/s), represented by such materials as inter-till clayey sand and silt layers and fractured bedrock, both common in Alberta.

Although directly related to the surficial geology of Alberta, this breakdown did confirm that most groundwater bearing zones which are impacted by sour gas plant operations are not extremely hydraulically conductive. Twenty-six of 32 plants had contamination in groundwater bearing zones whose hydraulic conductivity was less than 10E-5 m/s. This helps to put the situation at Alberta sour gas plants into perspective. In the majority of cases, the estimated advective transport rates of groundwater contamination were not very high, however consideration must also be given to the influences of fracture permeability, contaminant-matrix interactions and the accuracy of hydraulic conductivity data provided in reports. Detailed analysis of contaminant transport rates at the various gas plants was beyond the scope of this study.

2.1.2 Impacts on Soil and the Unsaturated Zone

Soil sampling data were not available in the Alberta Environment records provided for the study. Data from six of the 54 plants were obtained directly from plant operators. Due to the limited database, firm conclusions regarding the extent of soil and unsaturated zone contamination at Alberta sour gas plants were difficult to make. However, many of the mechanisms leading to groundwater contamination at these facilities necessarily involve the downward migration of contaminants through soil and unsaturated horizons towards shallow groundwater. Data reviewed seemed to confirm the general hypothesis that the frequency of occurrence of soil and unsaturated zone contamination at SGP's (sour gas plants) will likely be similar to that for groundwater contamination.

2.1.3 Subsurface Remediation

As part of the first phase of the study, a review of information available regarding subsurface remediation efforts currently being undertaken at Alberta sour gas plants was completed. Information was obtained describing subsurface remediation programs at five facilities. Of these, two were primarily soil remediation operations (plant decommissionings), and three were groundwater remediation schemes currently installed at operating facilities. Up to that time, no other data from remediation programs at sour gas plants have been submitted to Alberta Environment.

Subsurface remediation efforts at Alberta sour gas plants to date have included a variety of techniques. Where geologic conditions were suitable, large diameter passive collection systems have been used to recover free-phase hydrocarbon on the groundwater surface. Attempts to recover free phase condensate in more permeable aquifers using single well pumping schemes have, not unexpectedly, been relatively unsuccessful. application of dual-pump scavenger-type systems to recover free phase condensate and groundwater separately is being tested at several facilities. Traditional pump and treat methods are being applied for the recovery of groundwater with dissolved contaminants, and the control of plume migration. Deep well injection is the favoured method for disposing of contaminated groundwater.

To date little effort has been devoted to field trials or application of on-site treatment technologies for contaminated groundwater removed by pumping, or to rigorous study of the optimization and proper implementation of pump-and-treat techniques, and the many associated options which exist to enhance the effectiveness of pump-and-treat. The available information also indicates that little attention has been given to the assessment or field testing of newer and more innovative groundwater and soil remediation techniques. The number of subsurface remediation operations which are known to be presently underway is relatively small. In many cases, remedial action has been deemed unnecessary due to geologic conditions and relative isolation of plants, far from any nearby groundwater users, water courses or population centres. In some instances, remediation has been deemed impractical due to limitations of easily available and affordable technology. One consideration to date has undoubtedly been the relatively high cost of subsurface remediation and the fact that at present no regulations or guidelines are available for these operations in Alberta.

2.2 GOALS OF PHASE II

The findings of the Phase I study provided the necessary foundation for a comprehensive examination of subsurface treatment technologies suitable for Alberta sour gas plants. The study identified common subsurface contamination problems, and provided an insight into the general level of technology which has been applied to these problems to date. These conclusions not only provided the focus for the present phase II study of applicable treatment technologies, but also clearly demonstrated its relevance to the industry.

The main purpose of this phase of work is the identification and selection of the most appropriate remediation/treatment technologies for the main types of contamination situations present at Alberta sour gas plants. The location of many gas plants in the foothills of the Rocky Mountains dictates that much of the geology at these sites will be complex: dipping, faulted and fractured bedrock are common, overburden may consist of permeable glaciofluvial deposits, or clay-rich till streaked with more permeable water-bearing sandy layers. Near-surface groundwater in Alberta can be plentiful, and remediation schemes may have to deal with potentially large volumes of water, requiring not only treatment but disposal. Topography and climate are also considerations.

Suitably, this assessment of available and promising new remediation technologies is undertaken within the context of conditions prevalent at Alberta sour gas plants: geological, hydrogeological, climatic, and economic. Also, the review of technologies is not unnecessarily constrained by the practices of other industries or political jurisdictions where conditions may be different. For these reasons, the study balances the academic and the practical viewpoints - time-tested proven technologies as well as new and innovative remediation methods are reviewed and considered, all within the Alberta sour gas plant frame of reference.

Philosophy

Over the past few years, numerous technology reviews for subsurface remediation have been conducted, and are available in the literature. Clearly, compilation of yet another is not productive, nor would it contribute significantly towards the cause of remediation at Alberta's sour gas plants. What makes this study useful, and indeed unique, is that it approaches the question from the other side: instead of reviewing technologies and listing cases where they may be applicable, this project considers very specific contamination situations, and identifies the most effective methods to deal with them.

2.3 CONTAMINATION SITUATIONS CONSIDERED

Based on the results of Phase I, twelve individual contamination situations, representing the most common and important subsurface conditions at sour gas plants, were identified for consideration. (Many of the situations have also been broken down into sub-groups to provide an added level of refinement to the selection process).

The specific contaminant types being considered are:

- free phase natural gas condensate liquids;
- dissolved inorganic species (chlorides, sulphates)
- dissolved organic compounds (aromatic hydrocarbons, plant process chemical such as sulfinol, glycols and amine products);
- sulphur products and associated low pH conditions.

The remediation of each of these contaminant groups from the following geologic materials is being examined:

- surficial till deposits (clay-rich, low hydraulic conductivity);
- surficial glaciofluvial materials (sand and gravel deposits, moderate to high hydraulic conductivity);
- fractured bedrock;

Remediation of groundwater and the unsaturated zone are being considered. Detailed descriptions of the contamination situations being considered, along with illustrative case histories, are provided in the Contamination Situations section of this report.

2.4 FUTURE OBJECTIVES

Subsurface contamination problems at sour gas plants in Alberta are characterized by a wide variety of potential contaminants and complex subsurface conditions; dealing with these problems is further complicated by the severe climatic conditions of the region. To date, little work has been done to address the considerable challenges of remediating such contamination, and hence the general level of technology and sophistication which has been applied to these problems is low. This situation presents considerable opportunity not only for development and testing of appropriate solutions for the specific problems discussed, but also for the advancement of research into specific treatment technologies.

The present study identifies technologies and approaches applicable to the particular situations present at Alberta sour gas processing facilities and thus worthy of field demonstration. It is planned to demonstrate some of these technologies at one or more gas plant sites to be selected in 1991. At such time, the Canadian Petroleum Association and Environment Canada will be seeking to contact groups interested in participating in field demonstrations of appropriate remedial technologies. The results of the planned field demonstrations will be invaluable to the sour gas processing industry and the cause of environmental protection in general.

3. METHODOLOGY

3.1 OVERVIEW

A general overview of the study methodology is provided in the form of a flow chart, shown in Figure 3.1. First, the specific contamination situations to be considered were reviewed, appropriate sub-groups identified, and detailed information on each assembled. Next, a comprehensive review of available and emerging subsurface remedial technologies was undertaken by members of the project team. All available sources of information were consulted, including libraries, databases, government agencies, consultant and industry reports, and personal interviews. For each contamination situation and relevant sub-group, generally applicable remediation technologies were then identified.

From this information, short lists of appropriate established and promising new/innovative technologies were assembled, and technologies prioritized. Ranking of choices was accomplished by a special panel of five experts, each of whom has broad experience in site remediation. The panel was provided detailed case histories which encompassed all of the contamination situations, and asked to rank choices based on a number of specific criteria. Criteria included documented successes under similar conditions, expected contaminant removal efficiency, ultimate level of clean-up, capital, operation, maintenance and monitoring costs, equipment availability, ability to operate year-round (in severe winter conditions), and rate of clean-up.

New and innovative technologies which hold promise for remediating contamination at sour gas plants were also assessed on the basis of present status of development/research, published field trials and lab results, theoretical and practical arguments for the suspected suitability of the technology to the particular contamination situation, additional work required to determine applicability, and suggested research options for Alberta sour gas plant applications. For each contamination situation, a list of new and promising technologies requiring further bench or field scale testing was then compiled, and the most promising of each identified.

Next, detailed reviews of each of the recommended technologies were prepared. For each, detailed discussions of the types of data needed for proper design are provided. The discussions include recommended data collection during site assessment, data required from equipment suppliers, and acceptable ranges of uncertainty in the data presented in the context of the applicable contamination situation. In addition, a set of recommended design criteria for the application of the technology are presented, including accepted limits for the system, sizing of components, pre-treating requirements, typical design pitfalls and errors, and rules of thumb for installation and operation.

A detailed discussion of the methodologies and criteria used in each of the above steps is provided in the following sections.

3.2 DESCRIPTION OF CONTAMINATION SITUATIONS

One of the most critical aspects of the project was the proper description and characterization of the particular contamination situations being faced at Alberta sour gas plants. The contamination situations to be considered for this study were provided by CPA, based on the results of the phase I study (refer to the Terms of Reference section of this report), and are fairly general. To benefit from an assembled team of experts, considerable additional information on the **particular conditions found at Alberta sour gas plants** was required, such as regional and local hydrogeology and hydrogeochemistry, surficial geology, bedrock structure and fracturing mechanisms and patterns, specific contaminants associated with sour gas plant operations, climatic conditions and substrate biota information, etc.

For each contamination situation, likely sub-cases were identified based on knowledge of ASGP conditions. For each sub-group, likely ranges of key physical, geological and chemical parameters were determined, and typical contamination scenarios described. Data provided included hydraulic conductivities of materials, chemical and physical properties of contaminants, expected water table depths and ranges of seasonal fluctuation, typical plume sizes and configurations, climatic data, typical hydrogeological settings, and typical background groundwater quality.

For the purposes of the final ranking exercise, project team members agreed that comparative evaluation of technologies required a common datum, preferably one which was representative of **actual conditions** at ASGP's. For this reason, case histories of subsurface contamination problems at three Alberta sour gas plants were compiled, which together encompassed all of the contamination situations being examined. These case histories were then used as models for the comparative ranking and final selection of remedial technologies. This step also helped to ensure that the main objective of the study was fulfilled: to provide recommendations for remedial technologies which would be applicable to the particular types of problems facing the Alberta natural gas industry.

The contamination situations considered for this study, detailed descriptions of sub-groups, and the case histories employed are discussed in detail in the Contamination Situations section of this report. In addition, each of the important types of contaminants present at ASGP's is discussed in terms of their environmental significance, physical and chemical properties, and subsurface behaviour.

3.3 PROJECT TEAM

The project team assembled for this study included experts in the areas of groundwater remediation, sour gas plant hydrogeology and geology, soil vapour extraction and off-gas treatment, soil remediation technology, soil microbiology, groundwater bioremediation, groundwater in fractured media, organic chemistry and hydrogeochemistry, and geotechnical engineering/subsurface structures. The team included the principals and selected associate staff of two major US environmental consulting firms, senior American and Canadian experts in bioremediation technology, and subsurface contamination remediation specialists from Canadian Universities and industry. Considerable Alberta-based expertise was also drawn upon.

Each member of the team provided expertise in their respective areas of specialization, and senior specialists were selected to provide overall experience and a familiarity with the entire spectrum of remedial options in order to allow critical comparison and ranking of methods. The five senior members of the team formed a panel charged with the final ranking and selection of technologies.

3.4 PRELIMINARY TECHNOLOGY REVIEW AND SCREENING

The next major step in the study involved a complete review of all available soil and groundwater remedial technologies, established, emerging and experimental. Lists of all available and known remediation/treatment technologies for contaminated groundwater and groundwater-bearing strata, and soils/unsaturated zone contamination were compiled.

The project team reviewed all available information on each method, drawing on published information, and the considerable experience of its members. As much as possible, the team drew upon the recently completed technology review work done by the GASReP (National Groundwater and Soil Remediation Program) subcommittees on in-situ bioremediation, soil vapour and off-gas treatment, soils/excavation and treatment, and pump and treat. Other sources which were consulted included:

- Computer searches of Canadian university libraries;
- On-line searches of the National Water Well Association (NWWA) On-Line information system, USEPA reports catalogue, and the ATTIC database;
- Waterloo Centre for Groundwater Research library collection;
- Review of relevant technical journals and symposia;
- Consultations with other industry professionals and contacts, equipment suppliers, and sour gas plant personnel.

A short summary review of each technology was then compiled, briefly describing the theory behind its use, applications, design, and history. References are provided for each. Each technology was then assessed for general applicability to the contamination situations being considered. This information is presented in the review and preliminary screening of treatment technologies section of the report.

From this, a preliminary list of remedial technologies for consideration was developed for each contamination situation. Preliminary selections were made based on general applicability of the method(s) to the situation (for instance, excavation was not considered for groundwater contamination in bedrock), and the results of the literature review. At this point, each of the technologies to be considered was graded as established or emerging (new and innovative), based on the findings of the literature review and the experience of the project team.

3.5 ASSESSMENT AND RANKING OF TECHNOLOGIES

For each contamination situation (and sub-group), a detailed assessment of the applicability of each of the technologies listed was undertaken. Project team experts considered technologies and situations in their respective areas of expertise, in close cooperation with Piteau hydrogeologists who have extensive experience in Alberta gas plant geology, hydrogeology, and subsurface contamination.

Assessments were made based on:

- results of the literature survey;
- professional experience of project team members;
- discussions with other experts in Canada, the U.S, and abroad;

and considered such factors as:

- field demonstrated effectiveness under similar or identical circumstances;
- degree of use and testing which has been done, and the results thereof;
- case history reviews and reported successes/failures;
- ability of the method to cope with the special concerns identified in step 1;
- theoretical applicability to the contamination situation;
- promise, as determined from initial studies, modelling, or laboratory results (for new/experimental methods);
- economic considerations, practical limitations;
- suitability to Alberta climatic conditions.

Based on the results of the detailed assessments, technologies under consideration were ranked by the project team from most to least suitable for the particular contamination situation being considered. From this, short lists of two to four treatment technologies with the greatest remediation potential were compiled for each contamination situation and situation sub-group (where applicable). The results of these assessments are discussed in full in the detailed review and selection chapter of this report.

3.6 TECHNOLOGY RECOMMENDATIONS

For each contamination situation, short listed technologies (for both established and emerging categories) were reviewed in detail, compared and contrasted, and then prioritized. Project team members researched each of the short listed technologies in detail as applied to the particular contamination situation, making use of:

- data from literature survey;
- case studies;
- professional experience;
- information from suppliers and manufacturers of equipment;
- discussions with other experienced professionals;
- conceptual models of the technology's application to the specific contamination situation. For the purposes of this exercise, three detailed case histories were developed (using data from actual Alberta sour gas plant) encompassing each of the contamination situations under consideration. The case histories, as provided to the expert selection panel, are provided in Appendix I of this report.

3.6.1 Established Technologies

For established technologies, the following factors were compared:

- expected contaminant removal efficiency, estimated time for clean-up and total expected level of clean-up;
- estimated design, capital, start-up, operation, and maintenance costs (on a demonstration scale and cost per unit basis);
- practical limitations on clean-up;
- expected cost effectiveness;
- equipment availability;
- other special consideration, such as time allowances required for ordering, manufacture, and delivery of equipment, and the need for and cost of special modifications required for winter operation.

- Possible need for pre-treatment facilities, and associated costs (e.g. in many cases, presence of dissolved organics in groundwater tends to result in elevated levels of dissolved iron, which can reduce efficiency of air strippers, and cause severe encrustation and iron bacteria problems in infiltration galleries and re-injection wells).

3.6.2 Emerging Technologies

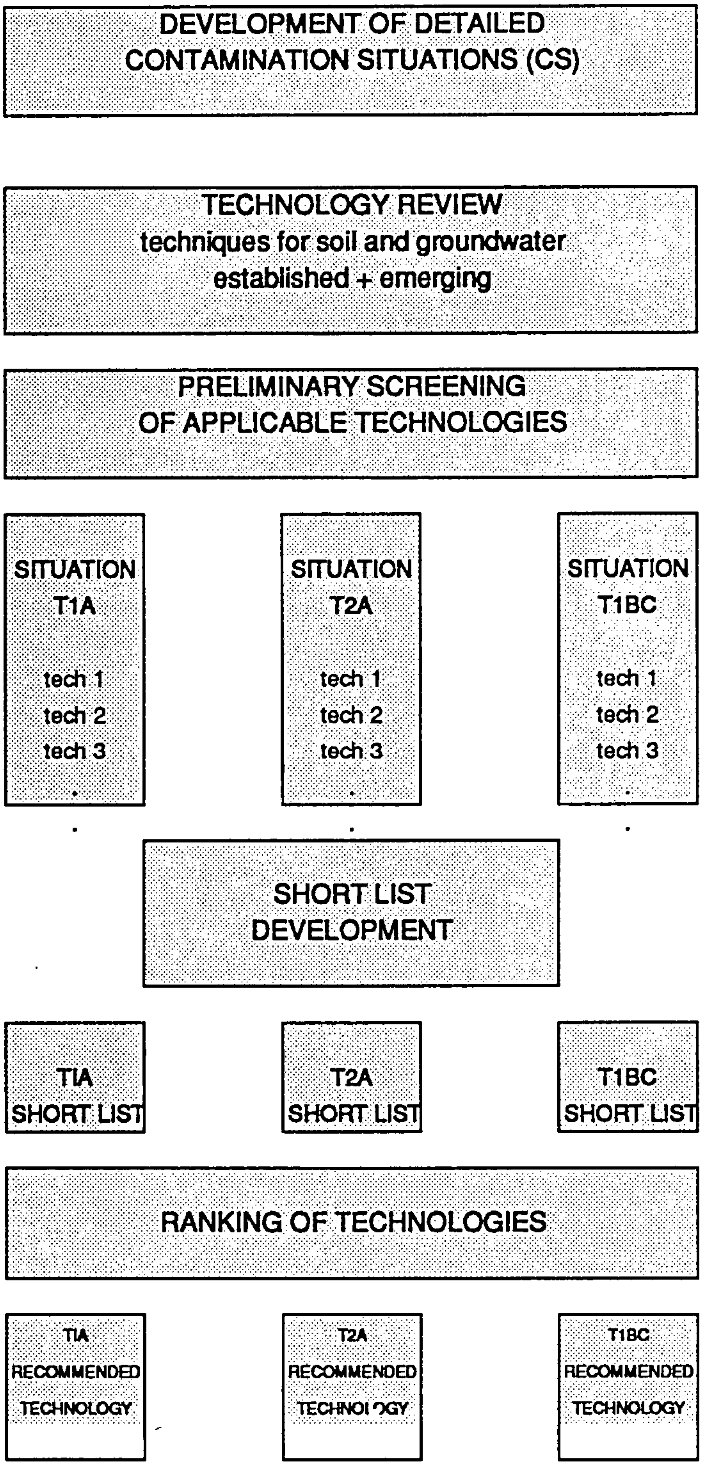
For each short-listed technology classified as "emerging", the following factors were considered:

- present status of development/research;
- published field trials of lab results;
- reasons, theoretical and practical, for the suspected suitability of the technology to the particular contamination situation;
- additional work required to determine applicability;
- suggested research options for Alberta sour gas plant applications.

3.6.3 Selection

The comparative assessments were performed by a panel of five senior members of the project team, each of whom has extensive expertise in subsurface remediation. Each member of the panel was provided with the short-lists, detailed descriptions of each contamination situation, the list of criteria to be considered, available research material on each technology (as required), and the case history-conceptual models. With this information, panel members were asked to independently assess and rank the technologies for each situation, providing separate recommendations for "established" and "emerging" technologies. The ranking process conducted by the individual panel members was based on a number of specific criteria, but no formalized weighting system or matrix was used at this step. A review of ranking/weighting decision systems used in previous technology assessments (Haiges et al, 1990, Lemon and Barker, 1991) revealed that the process is relatively inflexible, does not lend itself well to case-by-case consideration of problems, and does not take full advantage of

FIGURE 3.1
PROJECT METHODOLOGY



expert's knowledge, experience, and "feel" for problems. In addition, a consensus of the project team members was that a formalized weighted-decision-matrix system would be easily manipulated to achieve desired options. As this study required a direct focus on particular problems, an "expert" approach was used instead. Provided with detailed case histories as models, experts were asked to rank technologies/approaches. This process was formalized at a meeting of the panel members held January 15, 1991, to discuss and compare evaluations. This meeting was attended by several members of the project steering committee.

Based on the results of the independent comparative assessments of the panel, and the discussions held at the meeting, an overall ranking was determined for each short-listed technology in each of the "established" and "emerging" categories. Overall final rankings were determined by compiling the independent rankings of each of the panel members, and incorporating the results into a decision matrix system. The ranking-matrix system employed is shown in Table 3.1, and the specific ranking results for each Contamination Situation Classification (CSC) are provided in the Technology Ranking and Selection section of this report.

3.6.4 Recommendations

The top ranked technologies (established and emerging) for each CSC or sub-group were recommended for application/testing/demonstration at sour gas plants. In many cases, the recommended clean-up approach to a particular contamination situation involved the use of two or more individual technologies in parallel, in series, or as parts of a treatment train.

It is interesting to note that in general, panel members agreed very closely in their rankings, particularly for established technologies. In several instances the short-lists of applicable technologies consisted of only one or two truly viable options, and hence the ranking exercise was almost unnecessary. For the emerging/experimental technologies, lack of detailed information made recommendation of a single technology difficult in some cases. When this occurred, more than one was recommended for more detailed study and possible modification to suit ASGP conditions.

3.7 DESIGN CRITERIA DEVELOPMENT

For each of the recommended technologies, once technology rankings were complete, detailed sections on each recommended technology were prepared by project team members most familiar with the particular field. Detailed discussions of the steps required for proper design and implementation technology are provided, including as accepted limits for the system, sizing of components, pre-treating requirements, typical design pitfalls and errors, and rules of thumb for installation and operation. Detailed case histories and cost information are also provided for each technology.

The results of this task are intended to help professionals involved in following phases of this project to design preliminary site assessment and data collection programs at selected demonstration sites, and then use these data to design and implement appropriate remedial systems.

4. CONTAMINATION SITUATIONS

4.1 CLASSIFICATION SYSTEM

The contamination situations to be considered for this report consist of a variety of contaminants (free condensate, process organics, inorganic species and low pH conditions) occurring in soils/unsaturated materials and groundwater. A simple classification system was designed to distinguish between the different contamination situations and sub-groups. The classifications are based on the following designations:

contaminant hosts:

soils and unsaturated zone, moderate permeability (glaciofluvial):	S1
soils and unsaturated zone, low permeability (till):	S2
saturated zone (groundwater), moderate permeability (glaciofluvial):	T1
saturated zone (groundwater), low permeability (till):	T2
saturated zone (groundwater), highly fractured bedrock:	R1
saturated zone (groundwater), slightly fractured bedrock:	R2
groundwater zones in which surficial materials and bedrock are in direct hydraulic connection, (groundwater):	X

The breakdown of contaminant hosts was required to provide additional detail necessary for proper consideration of applicable remedial techniques. Soils/unsaturated zone problems in general require a much different remedial approach, and hence the application of different technologies, than for groundwater problems. In addition, the bulk permeability and geological makeup of soils will affect remedial choices, as will the hydraulic conductivity of the aquifer in question. Hence, subgroups based on the general characteristics of the medium were also used (1 = higher permeability materials, 2 = lower permeability materials). A brief discussion of the geological conditions typically encountered at Alberta sour gas plants is provided in Section 4.3 of this report.

contaminant types:

separate phase natural gas condensate:	A
(dissolved) organic compounds (BTEX, process chemicals):	B
(dissolved) inorganics (chloride, sulphate):	C
low pH conditions:	D

Results of the Phase I study (CPA, 1990) indicated that in more than 90% of cases where dissolved inorganic contamination was detected, organic species were also present. The designation "BC" is used in this report to indicate this scenario. Detailed descriptions of each of the contaminant types under consideration are provided in the following section.

As an example, if free condensate (A) was present in highly fractured bedrock typical of the foothills regions of Alberta (R1), the contamination situation designation would be: R1A. A complete breakdown of the contamination situations considered is provided in Table 4.1.

Detailed descriptions of each contamination situation (as they typically occur at ASGP's) are provided in Sections 4.4 (groundwater contamination situations) and 4.5 (soils/unsaturated zone situations) of this report.

4.2 CONTAMINANTS

4.2.1 Natural Gas Condensate

Chemical and Physical Properties

Natural gas condensate exists as a gas under reservoir temperature and pressure, but upon production reverts to a liquid. Condensate liquids vary in composition but in general are made up of hydrocarbons in the C5 to C30 range (Table 4.2). Partially water soluble components Benzene Toluene Ethylbenzene Xylene (BTEX) can make up to 20% by weight of a given condensate, with a preponderance of xylenes.

The components of the water soluble fraction of a typical gas condensate are given in Table 4.3. Samples of the water soluble fraction of natural gas condensates from a given monitoring

TABLE 4.1
CONTAMINATION SITUATIONS BEING CONSIDERED

GEOLOGIC HOST OF CONTAMINANTS		CONTAMINANTS		
DESCRIPTION	CODE	CONDENSATE (A)	DISSOLVED ORGANICS INORGANICS (BC)	LOW pH (D)
soils/unsaturated zone moderate-high permeability	(S1)	S1A	S1BC	S1D
soils/unsaturated zone low permability	(S2)	S2A	S2BC	S2D
surficial deposits satuated zone moderate-high K	(T1)	T1A	T1BC	T2D
surficial deposits satuated zone low K	(T2)	T2A	T2BC	T2D
bedrock, high K fractured	(R1)	R1A	R1BC	R1D
bedrock, low K slight-no fracturing	(R2)	R2A	R2BC	R2D
bedrock+surficial deposits in hydraulic connection	(RX)	RXA	-	-

EXAMPLE

A contamination situation exists in which free condensate (CONTAMINANT TYPE A) is present in highly permeable glaciofluvial sands and gravels (HOST TYPE T1).

The resulting contamination situation type would be: T1A

NOTE: K denotes hydraulic conductivity

TABLE 4.2
NATURAL GAS CONDENSATE
DETAILED COMPONENT SUMMARY

ROCKY MOUNTAIN HOUSE AREA PLANT
SOUR INLET #1 SAMPLE

COMPONENT	BOILING POINT	MOLE FRACTION	MASS FRACTION	VOLUME FRACTION
Nitrogen	-196	0.0000	0.0000	0.0000
Carbon Dioxide	-79	0.0000	0.0000	0.0000
Hydrogen Sulphide	-60	0.0000	0.0000	0.0000
Methane	-162	0.0000	0.0000	0.0000
Ethane	-89	0.0014	0.0004	0.0008
Propane	-42	0.0059	0.0024	0.0035
Iso-Butane	-12	0.0067	0.0036	0.0048
N-Butane	-1	0.0206	0.0087	0.0111
Iso-Pentane	28	0.0274	0.0137	0.0163
N-Pentane	36	0.0841	0.0182	0.0214
Hexanes	69	0.1287	0.0668	0.0748
Heptane	98	0.1338	0.1195	0.1285
Octanes	126	0.0713	0.1390	0.1452
Nonanes	151	0.0708	0.0826	0.0846
Decanes	174	0.0407	0.0898	0.0905
Undecanes	196	0.0231	0.0558	0.0554
Dodecanes	216	0.0113	0.3400	0.0334
Tridecanes	236	0.0053	0.0177	0.0172
Tetradecanes	253	0.0043	0.0087	0.0084
Pentadecanes	271	0.0028	0.0075	0.0072
Hexadecanes	287	0.0013	0.0051	0.0049
Heptadecnaec	302	0.0012	0.0025	0.0024
Octadecanes	317	0.0009	0.0024	0.0023
Nonadecanes	331	0.0008	0.0020	0.0019
Eicosanes	344	0.0007	0.0019	0.0018
Heneicosanes	357	0.0007	0.0018	0.0017
Docosanes	369	0.0007	0.0018	0.0017
Tricosanes	380	0.0007	0.0017	0.0016
Tetracosanes	391	0.0006	0.0016	0.0015
Pentacosanes	402	0.0005	0.0014	0.0013
Hexacosanes	412	0.0005	0.0014	0.0013
Heptacosanes	422	0.0002	0.0005	0.0005
Octacosanes	432	0.0001	0.0004	0.0004
Nonacosanes	441	0.0001	0.0004	0.0004
Triacontanes+	449	0.0005	0.0017	0.0016
Benzene	80	0.0074	0.0053	0.0044
Toluene	111	0.0592	0.0502	0.0425
Xylenes	139	0.1161	0.1134	0.0966
1,2,4-Trimethlybenzene	169	0.0194	0.0214	0.0181
2,2 Dimethylbutane	50	0.0018	0.0014	0.0016
Methylcyclopentane	72	0.0296	0.0229	0.0224
Cyclohexane	81	0.0227	0.0176	0.0166
Methylcyclohexane	101	0.0806	0.0728	0.0694
Totals		1.0000	1.0000	1.0000

well are known to display relative composition with invariance in the concentration of the major components, as shown in Table 4.4. The xylene/benzene ratios were observed to range from 2.5 - 5.1 for water samples collected from a monitoring well at a condensate-contaminated site in Alberta over a three month period. This range is within the precision of the sampling and analytical methodology. The chemical composition of condensates can vary significantly from field to field and over time during production from a given field (Figures 4.1 through 4.4).

Specific Properties of Major Water Soluble Volatile Components (Source Merck Index)

The analysis of volatile organics present in the water soluble fraction of natural gas condensates indicate that this fraction contains the following aromatic hydrocarbons:

- benzene
- toluene
- ethylbenzene
- xylene isomers
- trimethyl benzenes (and isomers)
- tetramethyl benzenes (and isomers)

Chemical and Physical properties of these components are summarized in Table 4.5.

Solubility of gas/liquid condensates

In general the solubility of gas/liquid condensate in water depends on the relative concentration of the components, the water temperature, the gas pressure (or partial pressures for mixtures of gases) and the total solute content.

The solubility of a gas condensate is governed by Henry's law:

$$y = kp$$

where y is solubility of the gas condensate in litres per litre, p is partial pressure, and k is a constant dependent on temperature. The solubility of natural gas condensates will be reduced in the presence of dissolved ions in groundwater.

TABLE 4.3

WATER SOLUBLE COMPONENTS OF GAS CONDENSATE

Peak	Component
1	Hexene
2	Benzene and Hexene
3	Heptene
4	Toluene
5	Ethyl Benzene
6	M/P - Xylenes
7	O-Xylene
8	C_3 substituted benzene
9	C_3 substituted benzene
10	C_3 substituted benzene
11	C_3 substituted benzene
12	C_3 substituted benzene

TABLE 4.4

RELATIVE CONCENTRATION OF XYLENE AND BENZENE FROM A MONITORING WELL

Sample	X/B Ratio
9	2.71
10	2.68
11	2.71
12	3.45
13	2.68
14	2.94
15	5.00
16	3.50
17	3.96
18	2.50
19	4.37
20	4.07
21	4.10
22	3.66
23	3.33
24	5.10
25	3.97

Samples collected over a 3 month period.

TABLE 4.5

PROPERTIES OF AROMATIC HYDROCARBONS IN CONDENSATE

Benzene

C_6H_6 mol_{15} wt 78.11, clear, colourless, highly flammable liquid, characteristic odour. d_4 0.8787.bp 80.1°. solidify + 5.5°, n_{D20} 1.50108. Flash pt. closed cup - 11C sol in 1430 parts water. LD_{50} orally in rats (young adults):3.8 mL/kg.

Human Toxicity:	Acute (from ingenstion or inhalation) - irritation of mucous membranes, restlessness, convulsions, excitement, depression. Death may follow from respiratory failure. Chronic: bone marrow depression and apalasia, rarely leukemia. Harmful amounts may be absorbed through skin. This substance is listed by the EPA as a volatile priority pollutant and carcinogen.

Toluene

C_7H_8 mol wt 92.13. Flammable, refractive liquid; benzene-like odour. d_4^{20} 0.866 solidification -95°; bp 110.6°, n_D^{20} 1.4967. Flash point, closed cup. 4.4°C. Very slightly soluble in water. LD50 orally in rats: 7.53 g/kg.

Human Toxicity:	May cause mild macrocytic anemia but not leukopenia. Less toxic than benzene. Narcotic in high concentrations.

Ethylbenzene

C_8H_{10} mol wt 106.16. Colourless liquid; flammable d_{25} 0.866. bp 136.25°. Freezing point -95.01°. Flash point, closed cup 18°C. Practically insol in water; LD50 orally in rats 5.46 g/kg.

Human Toxicity:	Irritating to eyes, skin, mucous membranes and in high concentrations, narcotic. EPA Priority Pollutant.

Xylene

$C_6H_4(CH_3)_2$ mol wt 106.16. Commercially xylene is mixture of three isomers O-, m- and p-xylene, the m-isomer predominating.

Mobile, flammable liquid, density about 0.86, bp 137-140°. Flash point 29°. Practically insoluble in water. May be narcotic in high conc. Less toxic than benzene. EPA Priority Pollutant.

TABLE 4.5 CONT'D

PROPERTIES OF AROMATIC HYDROCARBONS IN CONDENSATE

m-Xylene

Colourless liquid, d_4^{15} 0.8684. mp-47.4°, bp 139.3°, n_d^{20} 1.4973. Flash pt, closed cup 25°C. Practically insol in water.

o-Xylene

Colourless liquid, d_4^{20} 0.8801. mp-25, bp 144°, n_d^{20} 1.5058. Flash pt, closed cup 17°C. Practically insol in water.

p-Xylene

Colourless plates or prisms at low temp., d_4^{20} 0.86104, mp 13-14°, bp 137-138°, n_d^{20} 1.49575. Flash pt, closed cup 25°C. Practically insol in water.

1,3,5-trimethylbenzene

C_9H_{12}; mol wt 120.19. Liquid; peculiar odour. d_4^{20} 0.8637, mp-44.8°, bp_{760}^{18} 164.7; bp_{100} 98.9; bp_{20} 61°; bp_{10} 47.46; $bp_{1.0}$ 9.6°. n_d^{20} 1.49541. Practically insol in water (100g H_2O) dissolve 0.002g).

1,2,4-Trimethylbenzene

C_9H_{12}; mol wt 120.19. Liquid; d_4^{20} 0.8761, bp 169-171Uo, fp-43.78°, n_d^{21} 1.5044. Practically insol in water LD i.p. in rats - 2.0mL/kg.

Tetramethyl benzenes

Properties similar to trimethyl benzenes.

GAS CONDENSATE CHEMICAL COMPOSITION

SOUR INLET #1 SAMPLE

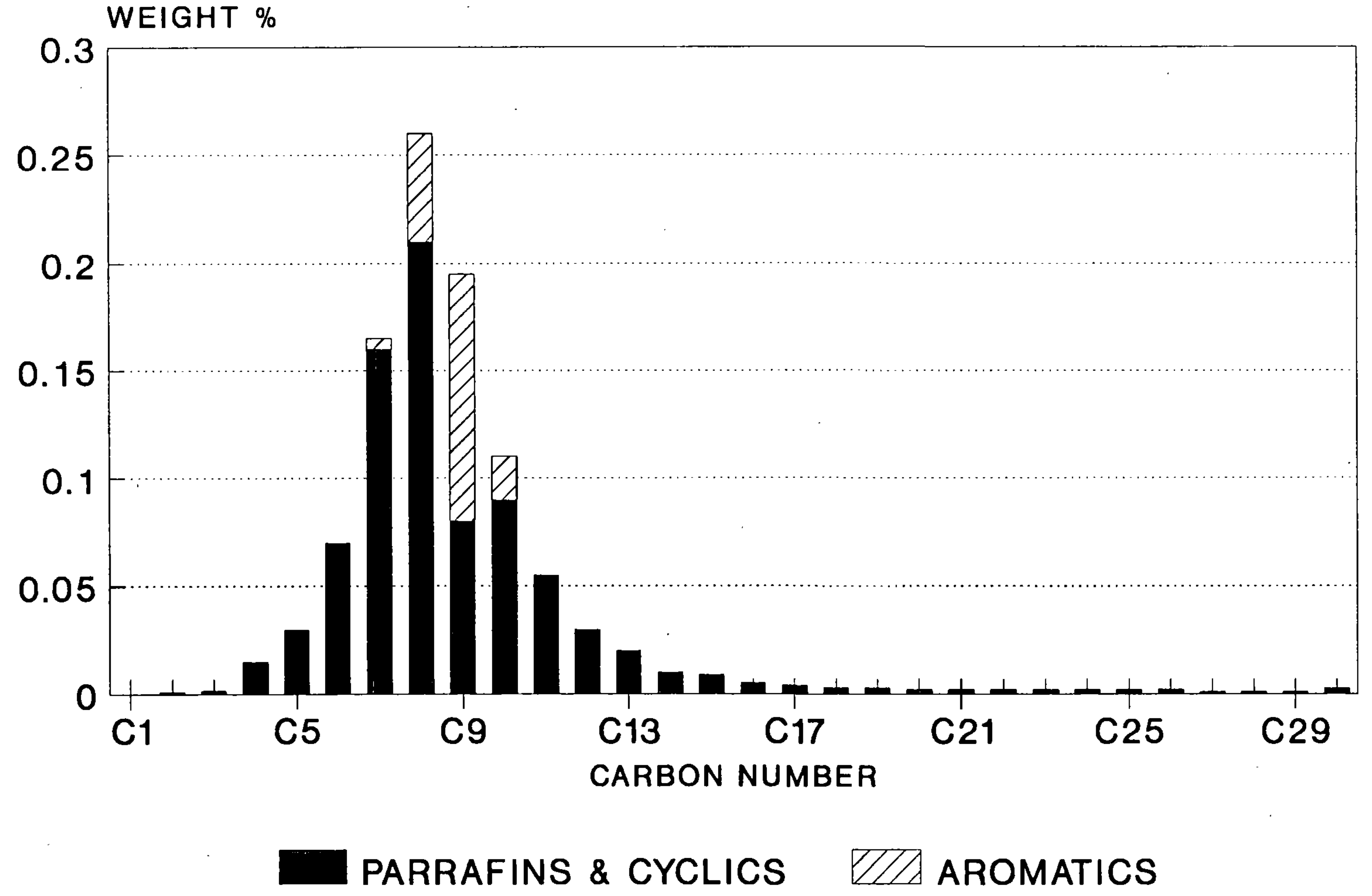


FIGURE 4.1

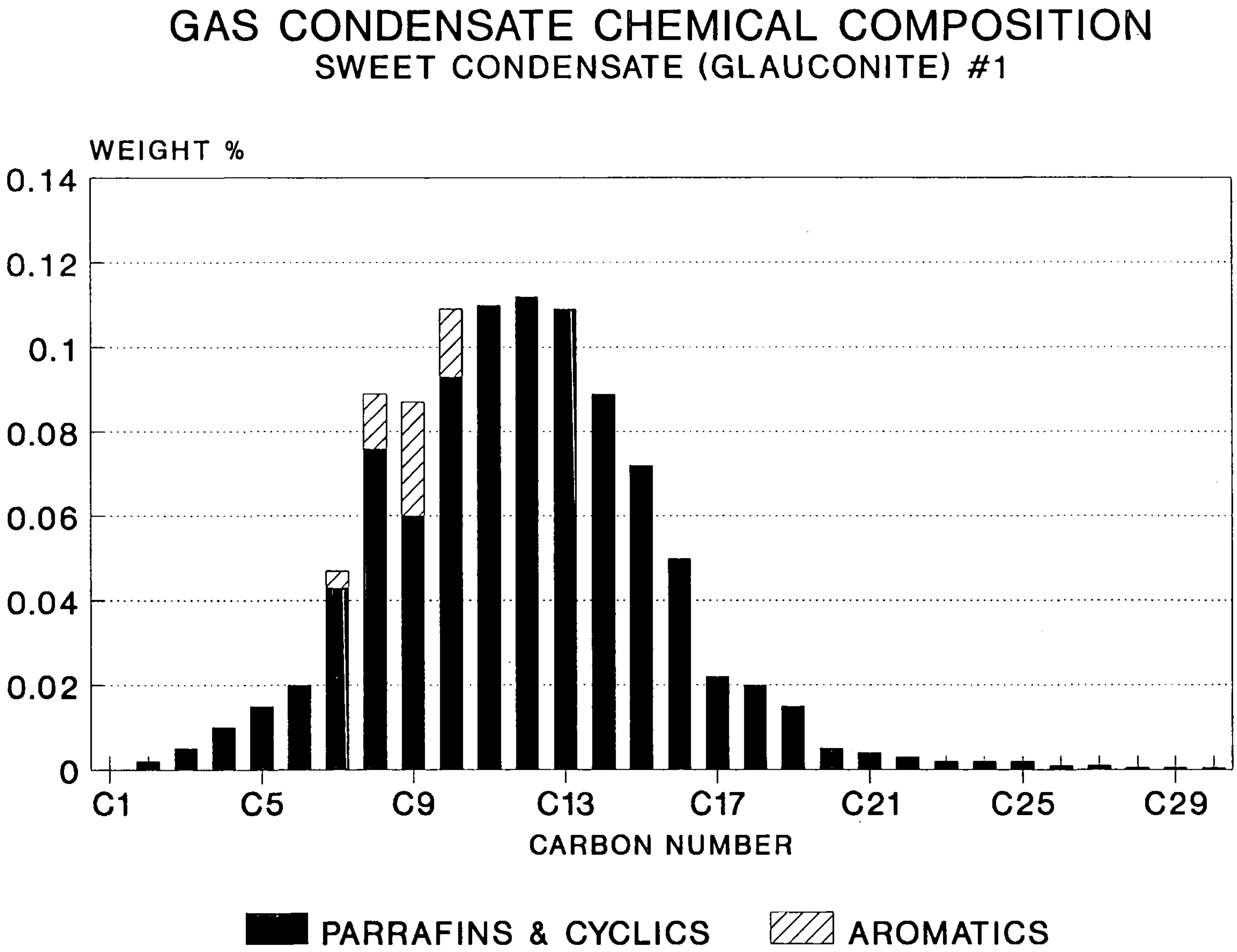

GAS CONDENSATE CHEMICAL COMPOSITION
SWEET CONDENSATE (GLAUCONITE) #1
WEIGHT %
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
C1
C5
C9
C13
C17
C21
C25
C29
CARBON NUMBER
PARRAFINS & CYCLICS
AROMATICS

FIGURE 4.2

GAS CONDENSATE CHEMICAL COMPOSITION

SWEET CONDENSATE (GLAUCONITE) #2

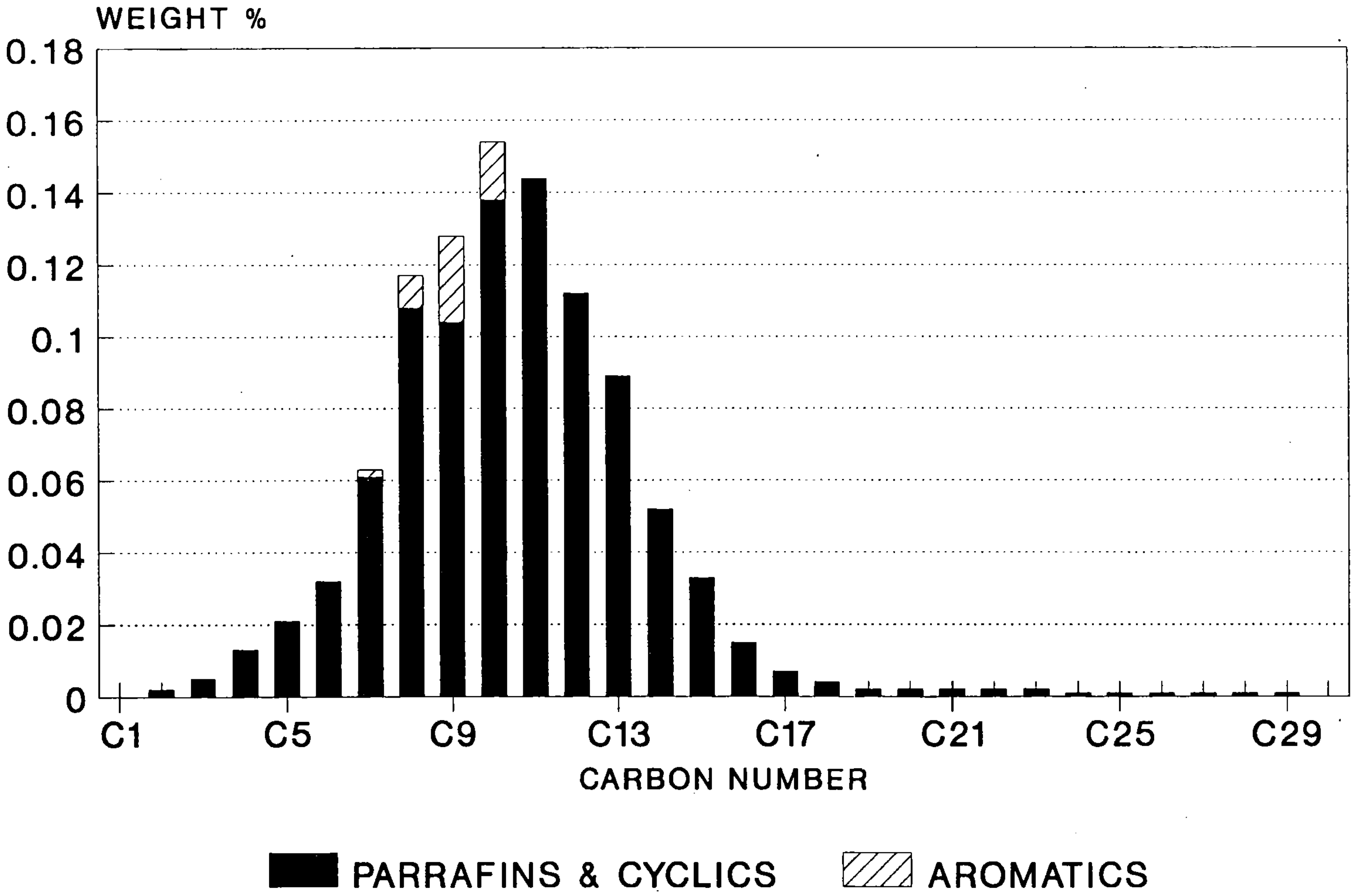
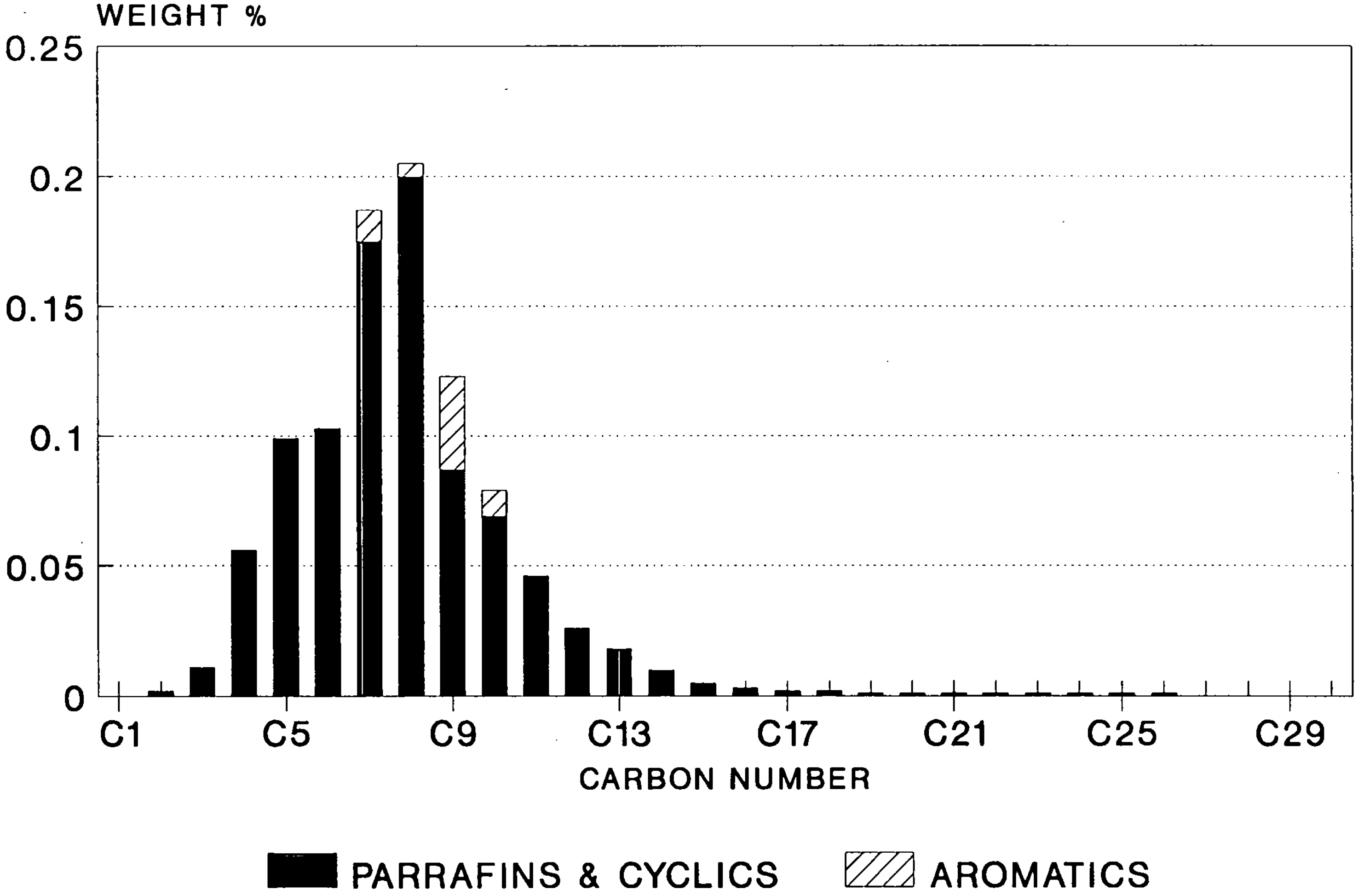


FIGURE 4.3



GAS CONDENSATE CHEMICAL COMPOSITION

SWEET CONDENSATE (GLAUCONITE) #3

FIGURE 4.4

There is little information on volumes of solubility of natural gas condensates in water. Values have been reported for a range of hydrocarbon mixtures at saturation concentrations. For convenience these values are shown in Table 4.6 (Matthess 1982). The chemical composition of natural gas condensates is similar to gasoline and saturation concentrations in water is therefore expected to fall in a similar range, 50 - 500 mg/L. By way of comparison total BTEX levels for water samples collected from monitoring wells at a sour gas plant in Alberta were observed at concentrations up to 57 mg/l.

The components of condensate which pose the greatest environmental concern are the water soluble aromatic hydrocarbons. These include benzene, toluene, ethylbenzene, and xylene isomers (BTEX). Benzene is the most soluble (1780 mg/L at 25 °C), and is a known carcinogen. Even small quantities of BTEX can render water unfit for human or animal consumption, and are toxic to fish and other aquatic species. The maximum acceptable concentration (MAC) of benzene in drinking water is 5 ug/L (ppb), according to the Federal-Provincial subcommittee on Drinking Water (1989).

Monitoring Considerations

Flow of condensate in the subsurface is influenced by the complex relationships of the porous medium-groundwater-condensate system. The relationship between the thickness of condensate in a well (apparent thickness), and the thickness of free condensate in the adjacent porous medium is complex and not well understood (Abdul et al, 1989). When the thickness of free phase in wells is small, the total thickness of condensate in the porous media (mobile and immobile) can be estimated (CONCAWE, 1979).

In the CONCAWE method, an assumption is made of the ratio of condensate in the porous medium to condensate in the well. It is assumed that this ratio is constant. The relationship often used for oil, assuming a density of 0.8, is that the thickness in the well is four (4) times the actual thickness in the medium (based on empirical observations). The same relationship, in the case of condensate, using a density of 0.728 leads to a ratio of 2.7 to 1. At present, several such methods for estimating actual LNAPL (light non-aqueous phase liquids) thicknesses are available, and each provides different results. Recent research has shown that such linear relationships between actual and apparent LNAPL thicknesses are a serious oversimplification, and frequently give erroneous estimates (Kemblowski and Chiang, 1990). All of the methods, however, have been developed for granular media, and no research into their applicability to fractured media has been undertaken.

The presence of condensate at residual saturation in the unsaturated zone is not readily detected since in this state it is maintained in the pores under pressures lower than atmospheric. In these conditions, the condensate will not flow into a monitoring well. In the absence of free condensate in monitoring wells, residual saturation can be indicated by high concentration of volatile organic in the vapour phase of the unsaturated zone (detection of odours in monitoring wells, results of soil vapour surveys), or high concentration of the soluble components of condensate (BTEX) in the groundwater.

Indicator Compounds

BTEX are suitable indicator compounds for monitoring programs and studies to delineate plume characteristics in groundwater. The xylene/benzene ratio can be used to evaluate changes arising from sampling and analytical variance for a given well.

Remedial Considerations

Behaviour of LNAPL Condensate. The subsurface behaviour of LNAPL, especially in fractured media, is notoriously hard to predict (Mercer and Cohen, 1990). Water level fluctuations can alternately trap and remobilize LNAPL, causing fluctuations in apparent thicknesses of product in monitoring wells (Parker and Lenhard, 1987: Kemblowski and Chiang, 1990). This mechanism, known as "smearing", is a function of the low specific gravity of condensate. LNAPL condensate released from a leak will move downwards through the unsaturated zone, fully occupying available air-filled pore space as it goes. If the volume of the spill is sufficient, downward movement will continue until condensate reaches the groundwater capillary fringe. Here, downward movement is halted. Condensate is lighter than water and will "float" on the groundwater surface. The free product accumulating above the groundwater surface will eventually move downgradient in the direction of groundwater flow. Empirical formulae with which to estimate the degree of lateral spreading of free product have been developed (Testa and Winegardner, 1991).

As the groundwater surface fluctuates, either due to seasonal variations in recharge or pumping, free condensate will follow, floating on the surface. As this occurs, LNAPL is redistributed in the pores, or smeared. If fluctuations are large and frequent enough, most or all of a LNAPL spill may be immobilized as residual oil saturation (S_{ro}). Estimates of residual saturation in porous media depend on which phase is being imbibed and which drained, and the physical properties of the medium and the liquids. Once trapped as residual saturation, LNAPL is rendered immobile, and can only be remobilized by altering prevailing conditions (by pumping, dewatering, inducing vapour flow and volatilization, reducing interfacial tension, etc.).

Residual saturation of LNAPL can vary from 0.1 to 0.5 depending on the mechanism of emplacement, physical and chemical characteristics of fluid and medium, and hydraulic history of the aquifer (Mercer and Cohen, 1990).

In view of these facts, water level control during remedial operations will be of prime importance. Mercer and Cohen (1990), state:

> "Large drawdowns ... will create larger dewatered area into which the LNAPL will collect. These areas will have been previously uncontaminated by LNAPL. Substantial amounts of LNAPL will be retained in the aquifer matrix at residual saturation, even after water levels are allowed to recover. Thus recovery systems should maintain recovery while minimizing drawdown."

Condensate Properties and Remediation In general, the aromatic volatile organics which make up the water soluble fraction of natural gas condensates have solubilities below 10,000 mg/L at 25 °C. In simple terms, such compounds will prefer the vapour phase to the water soluble phase. Thus, volatilization techniques are therefore expected to be an excellent treatment option. Groundwater with high brine content or other dissolved salts will promote the displacement of volatile organics into the gas phase. This 'salting effect' can be exploited using enhanced volatilization as a treatment option for subsurface contamination at Alberta sour gas plants. Aspects of condensate remediation are discussed in detail later in this report.

4.2.2 Process Chemicals

Introduction

The processing of natural gas involves removal of undersireable compounds from the influent stream. These compounds include water, carbon dioxide and hydrogen sulphide. Many different methods and process chemicals are used in this process. The resulting wastes are treated and disposed of or discharged as liquids into wastewater ponds and landfills. These sludges are of widely varying chemical composition (Monenco, 1987).

Some effort has been made to characterize gas plant process waste sludges (Monenco, 1985), but to date very little study of the potential for groundwater contamination by process chemicals has been done. This section provides a brief summary of the types of compounds which have been identified in process sludges at Alberta gas plants.

Sources

As described in CPA (1990), three of the most common sources of groundwater contamination at Alberta sour gas plants were the process wastewater ponds, the process area, and on-site landfills. These are also the areas which have been identified as receiving the largest quantities of process sludges, and which were found to exhibit elevated concentrations of inorganic and organic contaminants (Monenco, 1987). Water soluble chemicals present in process water pond, flare pit, sulphur runoff pond and amine system pond sludges may be introduced into groundwater through pond seepage.

Chemical Characterization of Process Wastes

A wide variety of chemicals have been identified in gas plant sludges. These include inorganics, heavy metals, nitrogenous compounds, hydrocarbons and other organics. In many ways it is the water soluble compounds present in process sludges and wastes which are of greatest environmental concern. These are the products which will tend to be mobile in the subsurface, and may be leached and carried toward groundwater. Once introduced into an aquifer, the migration of organic compounds is a function of the groundwater flow velocity and the effects of retardation on the chemicals themselves.

The following water soluble organics have been identified in sludge samples collected from process water pond and flare pit bottoms at gas plants in Alberta (Monenco, 1987):

- benzene
- toluene
- ethylbenzene
- xylenes
- phenols
- monoethanolamine (MEA)
- diethanolamine (DEA)
- sulfinol
- diethylene glycol (DEG)
- diisopropylamine (DIPA)

The subsurface behaviour of aromatic hydrocarbons such as BTEX is relatively well understood. However, the same cannot be said for process chemicals such as DIPA and sulfinol. Additional research in these ares is required to evaluate the potential significance and subsurface mobility of process chemicals.

A variety of other organic compounds have been identified in process sludges. These include (Monenco, 1987):

- saturated aliphatic hydrocarbons
- polyaromatic hydrocarbons such as napthalene and fluorene
- trimethyl benzene
- methyl napthalene
- dibenzothiophene
- ethyl-methylbenzene
- trimethylnapthalene
- methylphenols
- various unidentified organic compounds.

Heavy metals have also been identified in process sludges and pit bottoms.

Implications for Remediation

Due to the wide variety of potential contaminants at ASGP's, careful planning and site characterization are important first steps in remedial system design and selection. Soil and sludge clean-up programs will require detailed information on the types and concentration of contaminants present. Different types of contaminants will require different treatment methods.

Most polyaromatic hydrocarbons have limited aqueous solubilities. The more water soluble components, however, may pose a threat to groundwater quality. Process chemicals such as sulfinol and DIPA have been detected in groundwater at Alberta sour gas plants. More study of the subsurface behaviour of these process chemicals is required to determine their subsurface behaviour, biodegradability, adsorption behaviour, and toxicity. These data will assist in the assessment of associated risks, and in selection of appropriate remedial responses and technologies.

4.2.3 Inorganic Contaminants

Sources of Contamination

Most human activities (municipal, industrial, agricultural) may result in an introduction of inorganic compounds into the subsurface. Many of them, under favourable hydrogeological conditions, may be used as indicators of groundwater contamination (CPA, 1990). Multiple processes which control the behaviour of contaminants in groundwater include:

Physical:	advection-dispersion, filtration and evaporation, gravity effects;
Hydrochemical:	solution-precipitation, acid-base reactions, oxidation-reduction, complexation and sorption, degradation.

Review of the existing groundwater monitoring information indicates that most common sources of groundwater contamination at ASGP's are: burn pit/process water pond(s), surface runoff pond(s), process area, landfill(s) and sulphur storage/forming/loading facilities (CPA, July 1990).

Dissolved inorganic compounds originating from these sources may enter subsurface through:

- seepage from retention structures (eg. burn pit, retention ponds, tanks);
- leakage from buried pipelines, UST's (underground storage tanks) (process area and off-site facilities);
- surface spills in process area, injection well, landfill areas;
- infiltration of contaminated surface runoff from process area, sulphur block and landfill site;
- deposition of particulate emissions (eg. sulphur dust); and,
- infiltration of leachate generated by seasonal saturation of solid wastes disposed of in landfill cells.

Indicators of Groundwater Contamination

Many common salts are associated with the sour gas industry. These include salts containing: chloride, bromide, iodide, sulphate, ammonium, potassium, sodium and other ions. Some of these ions may travel with the same velocity and direction as groundwater, are absent or present only at low concentrations in natural groundwater, do not interact with natural water or soil/rock particles (precipitation, sorption), do not change hydraulic properties of soil/rock, are non-toxic, and are not subject to gravity segregation.

In general, anions are not affected by the groundwater-bearing formation. As such, they are commonly used as indicators of groundwater contamination. Only under low pH conditions and in presence of clay and organic compounds, may anion exchanges occur. Very high ion concentrations may affect clay mineral structure contributing to a change in hydraulic properties.

Cations are more reactive. Through the process of cation exchange they displace other cations from the clay mineral structure and introduce them into solution (eg. sodium, calcium). This characteristic limits the use of cations as indicators of groundwater contamination.

Heavy metals (density greater than 5 g/cm^3) are and/or were commonly used in sour gas industry as catalysts, corrosion inhibitors, wood preserves and in instruments (eg. mercury thermometers, and gauges). Some heavy metals may be released in combustion of fossil fuels. On-site landfills have been identified as potential sources of heavy metals (CPA, 1990). Leachate containing heavy metals may enter groundwater. Produced saline waters and/or brines may contain high concentrations of heavy metals.

Introduction of heavy metals into the subsurface may be associated with sulphur production, storage, handling and loading. As a result of sulphur oxidation in the aqueous environment, sulphuric acid is produced. This strong acid may leach metals from soil/rock matrix, introducing them into solution. Review of hydrochemical data indicates that inorganic compounds (contaminants) originating from Alberta sour gas plant operations are often associated with organic contaminants. Some ions (eg. chloride, sulphate, nitrate) are more persistent/conservative than many of the organic compounds (eg. hydrocarbon products, process chemicals). Determination of main ion concentrations in groundwater is accurate, simple and relatively inexpensive in comparison with organic compounds analysis. Thus, analysis for main ions is often used as a first step in groundwater contamination studies. Once the potential source and nature of contamination are established, more detailed analyses (which may include organic compounds) should be conducted to assess fully the extent and concentration of inorganic and organic contaminants. A brief description of selected main inorganic contaminants often associated with the sour gas industry, and their potential environmental impacts and health concerns is given in the following section.

Common Inorganic Contaminant Types

Chloride

Origin of naturally occurring chloride concentrations in shallow groundwater are often related to:

- solution of evaporites,
- sea water intrusions, and
- connate water.

Background levels in Quaternary and upper bedrock (mostly Tertiary/Upper Cretaceous) deposits in Alberta are very low (less than 10 mg/L) (CPA, 1990). The only exception is the NE part of the province (Ft. McMurray area) where Devonian evaporites are present near the ground surface, resulting in more elevated chloride concentrations.

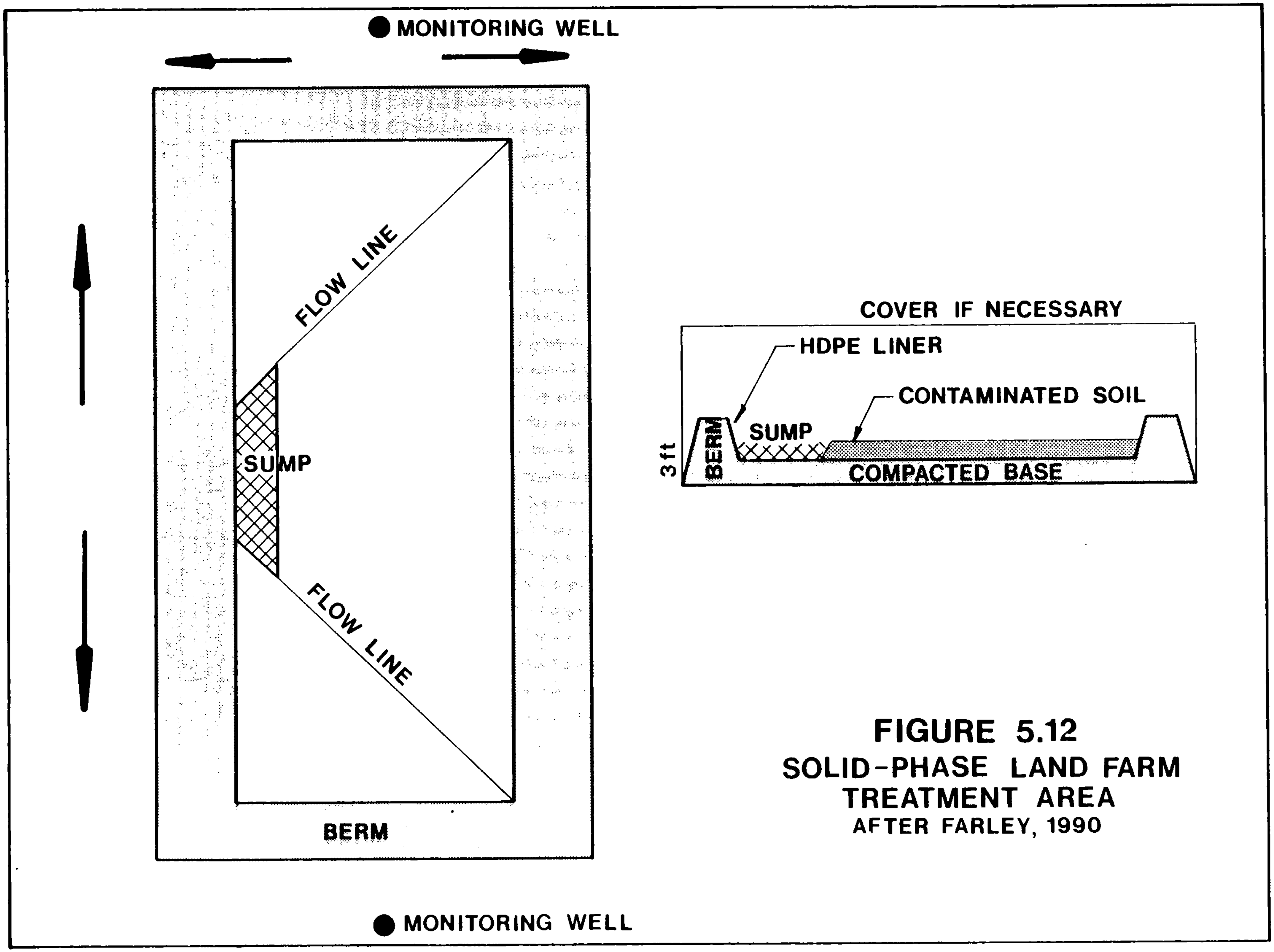


FIGURE 5.12
SOLID-PHASE LAND FARM
TREATMENT AREA
AFTER FARLEY, 1990

The majority of groundwater contamination cases identified at the Alberta sour gas plants involved elevated chloride concentrations (10 to 250 mg/L). In some instances, where saline water or brine was discharged, chloride concentrations in groundwater may exceed 20,000 mg/L. This exceeds chloride concentrations in sea water.

The chloride ion is highly mobile and may only be weakly adsorbed by some soils. Thus it may travel considerable distances without experiencing significant retardation-effects.

No evidence of toxic effects from chloride have been observed in mammals. The maximum acceptable concentration for chloride (250 mg/L) was established on the basis of aesthetic considerations. Concentrations above this level create undesirable taste in water and beverages (Health and Welfare Canada, 1978).

Sulphate

Leaching of gypsum, anhydrite and magnesium-potassium sulphate salts is a main source of sulphate ion present in groundwater. Natural concentrations of this ion in shallow groundwaters in Alberta vary within a wide range, from a few mg/L to several thousand mg/L (CPA, 1990). Under these circumstances, site specific background concentrations should be defined prior to use of sulphate ion as an indicator of groundwater contamination originating from the sour gas plants.

In instances where determination of sulphate origin is of prime importance, sulphur isotope analysis may be used. The sulphur isotope (^{32}S, ^{34}S and ^{36}S) concentrations present in sulphate ions vary considerably depending on their origin. Isotopic composition of sulphate associated with gypsum, pyrite oxidation (present in marine Cretaceous deposits) or elemental sulphur (produced by the sour gas plant) will vary greatly, allowing easy identification of the source of elevated sulphate concentrations in groundwater.

The majority of groundwater contamination cases identified at the Alberta sour gas plants involve elevated sulphate concentrations (200 to 500 mg/L)(CPA, 1990). In some instances concentrations in the order of a few thousand mg/L were encountered. It should be noted that information regarding sulphur production impacts on groundwater chemistry is not well defined. Hydrogeological studies related to sour gas plants conducted during the 1984-1989 period concentrated on process water ponds, process areas and on-site landfills. Additional research into sulphate and sulphur-block derived contamination at ASGP's is required.

The sulphate ion is mobile and relatively non-reactive. Under natural conditions high concentrations of sulphates dissolved in the groundwater-bearing zone may precipitate forming gypsum concretions.

The objective concentration of sulphate ion in potable water is 150 mg/L. This limit was established based on the taste threshold for sodium sulphate. The maximum acceptable concentration of this ion in drinking water is 500 mg/L. This limit is based on health considerations. Ingestion of water with high sulphate concentrations may cause catharsis and gastrointestinal irritation (Health and Welfare Canada, 1978).

Nitrogenous Compounds

Ammonia is produced naturally by the biological degradation of nitrogenous matter present in soil or rock. In aqueous environments ammonia will exist principally as ammonium ion. Nitrates are also produced naturally by complete oxidation of organic nitrogen in oxygenated soil or water. Nitrites may originate from incomplete oxygenation of organic matter or by bacterial reduction of nitrates.

Background concentrations of these ions in groundwater are usually very low. In Alberta however, high ammonia and nitrate concentrations may occur naturally (Hendry, McCready, and Gould, 1984).

Ammonium has high ion exchange capacity. This may reduce its concentrations in groundwater-saturated soil/rock. Elevated and high ammonium concentrations were observed at some sour gas plants in areas adjacent to process waste disposal sites (amine disposal) and ponds where ammonium was used to buffer low pH surface runoff (CPA, 1990).

There is no objective or maximum acceptable ammonia/ammonium concentration established for drinking water. Ammonia has a strong pungent odour that may affect water supplies. The toxic effects of ammonia are mainly on the central nervous system (Health and Welfare Canada, 1978). Nitrate and nitrite anions are subject to oxidation and reduction processes in the underground environment. Nitrate is an essential nutrient for all types of plants. Nitrites are less stable than the nitrate ions, since they are rapidly oxidized to nitrates. Considering the above, concentrations of these ions may change with time and distance from the source of contamination.

Elevated and high nitrate-plus-nitrite expressed as nitrate-nitrogen concentrations were found at several sour gas plants (CPA, 1990). The origin of these ions is not clearly defined, and may be related either to natural conditions or industrial contamination. The total nitrate-plus-nitrite-nitrogen concentration in drinking water should not exceed 10 mg/L. The objective concentration is less than 0.001 mg/L expressed as nitrate-nitrogen (Health and Welfare Canada, 1978).

Total Dissolved Solids (TDS)/Total Filterable Residue (TFR)

This parameter (TDS or TFR) describes mainly the inorganic substances that are dissolved in water. Background levels in Alberta range from a few hundred mg/L in recent alluvial deposits to over 10,000 mg/L in shallow till deposits located in the SE part of the province.

TDS/TFR concentrations elevated above background were detected at nearly all sour gas plants. High mineralization was usually related either to brine spill(s), high sulphate concentrations originating from sulphur storage/handling activities, or from seepage from holding ponds.

The effects of mineralization on drinking water quality depends on the concentration of individual components (eg. chloride, sulphate, sodium, magnesium). A maximum acceptable concentration of 500 mg/L in drinking water has been established on the basis of aesthetic considerations (Health and Welfare Canada, 1978).

Metals

Some metals may occur naturally in elemental form. The majority of metals, however, are widely distributed in minerals, ores, soils, and rock formations. Many metals present in nature are considered toxic, (eg. antimony, arsenic, barium, boron, cadmium, chromium, lead, mercury, selenium, silver, and uranium). In general, dissolved metal concentrations in shallow groundwaters of Alberta are low. The only exception are non-toxic iron and manganese. Elevated and high concentrations of toxic metals in groundwater were found at only a few sour gas plants (CPA, 1990). Sources of contamination were brine, landfill sites and soil leaching by low pH water originating from sulphur block surface runoff pond(s).

Low pH

Groundwater saturating Quaternary and upper bedrock deposits in Alberta is generally either neutral (pH near 7.0) or slightly alkaline ($7.0 < pH < 9.0$). Low pH waters are only locally present in the swampy terrains where organic acids form as a result of decay of vegetation.

Acidic run-off from sulphur storage and handling facilities at sour gas plants may locally contribute to lowering of soil and groundwater pH. The process of elemental sulphur oxidation leading to sulphuric acid production may be described as follows:

$$2S + 3O_2 + 2H_2O \text{ --- } 2H_2SO_4$$

Many soil and rock deposits in Alberta have high carbonate content, and thus have considerable buffering capacity. This may to some extent explain the relatively few cases of serious groundwater acidification identified. However, relatively few exploration programs were conducted in the areas adjacent to sulphur storage/handling facilities, resulting in a negative bias for identification of acidic groundwater and soil conditions (CPA, 1990). Near surface soils downwind of sour gas plants may exhibit pH's as low as 2.0 as a result of acid production/sulphur oxidation.

Low pH (below 6.5) groundwater may corrode metal pipelines and underground storage tanks and may also affect concrete foundations. It may also leach and mobilize toxic heavy metals from soil and rock.

Since pH of water is related to many chemical processes, it has not been possible to determine a direct relationship with human health. Thus a range of 6.5 to 8.5 is considered as acceptable for drinking water (Health and Welfare Canada, 1978).

Remedial Considerations

Inorganic contaminants will be present in groundwater in the dissolved phase. Being quite mobile, and less easily adsorbed, degraded and generally subject to retardation mechanisms then most organic contaminants, inorganic contaminant plumes may be expected to develop more quickly than associated organic plumes.

As discussed, general levels of inorganic contamination at ASGP tend to be relatively low. Under circumstances where background levels are elevated to begin with, (such as for sulphate, at many sites), the need for active remediation must be seriously assessed. In many cases, risk analysis may indicate that source removal alone may reduce inorganic concentrations to acceptable levels within short periods of time. Many of the main inorganic contaminants discussed, however, have been used as general indicators of gas plant contamination, and may be associated with dissolved organic compounds of greater environmental concern (CPA, 1990).

4.3 GEOLOGICAL BACKGROUND

4.3.1 General

The presence of sour gas pools in various Palaeozoic and Mesozoic formations was discovered in two hydrogeological regions of Alberta. These are:

- Cordilleran Region (Rocky Mountains Foothills Subregion), and,
- Interior Plains Region (Cretaceous Subregion and Tertiary Subregion).

Each of these subregions occupies large areas of the Province and is characterized by similar morphological, geological, hydrogeological and climatological conditions. Despite these general similarities, each subregion may be further divided into smaller hydrogeological units.

Complex geological and structural bedrock conditions and variable origin and depositional environment of glacial sediments are common in all hydrogeological regions in Alberta. These factors contribute to considerable differences in groundwater circulation and hydrochemical regimes between hydrogeological units. Often variable groundwater conditions are also observed within the same unit. Variability and presence of complex hydrogeological conditions have been observed during groundwater exploration programs conducted at different Alberta sour gas plant locations.

4.3.2 Cordilleran Region - Foothills Subregion

Bedrock

The Rocky Mountains Foothills form a series of NW-SE trending ridges and valleys. The bedrock is represented by the Upper Palaeozoic (carbonate and clastic sequence), Mesozoic (Jurassic and Lower Cretaceous clastic sequence, Alberta Group clastic sequence) as well as Cretaceous and Tertiary (Brazeau Formation - clastic sequence) sediments (Green, 1970). The bedrock formations are folded and intersected by a series of parallel steely dipping faults. Complex structure contributes to highly variable hydraulic properties of rock and in some instances may control groundwater circulation and contaminant transport patterns.

Hydraulic conductivity of various bedrock formations depends on primary (intergranular) and secondary (structural) porosity. In general fine grained sediments (mudstones, shales and siltstones) will have low hydraulic conductivity (K lower than 10^{-7} m/s). The same deposits, when highly fractured, may become moderately to highly permeable. This has been found to be the case at several gas plant sites investigated by Piteau. Sandstones and conglomerates are expected to have higher hydraulic conductivities (K higher than 10^{-7} m/s). Main structural features (eg. faults or shear zones) may act as high transmissivity conduits or as impermeable barriers when filled with fault gauge (clay).

Bedrock deposits in higher elevation areas are outcropping or are covered by a thin layer of surficial deposits. Thus groundwater recharge during spring break-up or summer heavy rain events may be direct and fast. This may cause considerable seasonal groundwater surface elevations (in order of several meters), which may severely impact remediation operations.

Precipitation infiltrating along ridges and slopes often discharges at springs and seepage zones located near valley bottoms. Within this active groundwater exchange zone, low mineralization (TFR below 500 mg/l) calcium-magnesium-bicarbonate hydrochemical type groundwaters dominate. Mineralization of groundwater depends on many factors including rock-water interactions and residence time in the subsurface.

Quaternary Deposits

Bedrock ridges built by erosion resistant strata are intersected by a number of east-flowing rivers and numerous streams. Some of these major valleys are of glacial origin. The Foothills subregion was affected by at least four Pleistocene glaciations. Various till deposits (clay, clay silt or silt clay) containing carbonate cobbles and boulders originating from the Rocky Mountains are associated with these events.

The till deposits often contain sand and gravel layers of glaciofluvial or fluvial origin. Till deposits exhibit considerable levels of weathering (fractures). Till, depending on grain size composition, may represent a low to moderate hydraulic conductivity medium (less than 10^{-9} m/s to 10^{-6} m/s). Locally present sand/gravel layers and continuous fractures may considerably increase the permeability of these deposits. Glaciofluvial deposits (valley train, eskers and outwash) consisting of permeable sand and gravel sediments (hydraulic conductivity often higher than 10^{-5} m/s) are locally present within valleys, forming terraces or inter till layers. Thicknesses of Quaternary deposits within this hydrogeological subregion may vary from 0 to 10's of meters. In general, however, these units are expected to be less than 20 m thick.

Groundwater circulation in these surficial deposits is controlled by lithology and terrain topography. Maximum flow velocities are expected to reach 100 m/y or more. In most cases, the recorded average groundwater linear flow does not exceed 25 m/year. Surficial deposits often are unsaturated. Seasonally they may be saturated as a result of fluctuations in groundwater surface elevations in the bedrock deposits. Weathered, fractured bedrock may often remain in hydraulic connection with the overlying surficial sediments.

Groundwater chemical composition in surficial deposits is similar to groundwater occurring in bedrock.

4.3.3 Interior Plains Region

Cretaceous Subregion

This hydrogeological subregion occupies a major portion of Alberta and borders with the Devonian Region in the NE, and the Tertiary Subregion in the SW part of the province. Faulted, to gently dipping sedimentary strata of Cretaceous Period are overlain by a variable thickness of Quaternary deposits within this subregion. Cretaceous sediments consist of both marine and non-marine clastic deposits, usually of low hydraulic conductivity. Bedrock aquifers are locally present in sandstone and coal beds. Potable quality groundwater is present at shallow depths generally not exceeding 180 m. Main aquifers are the Milk River Sandstone (South of South Saskatchewan River), the Belly River Formation sandstones in east-central Alberta (Provost-Hardisty area) and coal beds present in non-marine deposits.

Hydraulic properties of Cretaceous aquifers are dominated by fracturing. Matrix porosity is of secondary importance. Since major aquifers are usually separated from the ground surface by lower hydraulic conductivity layers, their recharge is indirect and slow. Thus groundwater flow velocities are generally low (probably less than 10 m/y). Groundwater quality in these aquifers is locally poor. High mineralization (over 1000 mg/l) and high sulphate (over 500 mg/l) concentrations indicate that some Cretaceous aquifers are located below zones of active groundwater exchange. As such, their potential susceptibility to contamination by surface activities is generally low.

Various tills are found within this subregion. Some of them were deposited by the continental ice sheet which originated in the Canadian Shield. Along the eastern margin of the Foothills, tills of Rocky Mountain origin are common. The Lexicon of Canadian Stratigraphy (1990) identifies over twenty till deposits present in this hydrogeological subregion.

Till deposits are characterized by variable mineral composition and grain size distribution, and may represent variable hydraulic properties, which in turn control groundwater circulation and quality. In general, tills are of low to moderate hydraulic conductivity. Despite this limitation many farmers obtain water from wells completed in such units. Such wells are usually marginal producers, with water quality ranging from potable, low mineralization, calcium-magnesium-bicarbonate hydrochemical type to highly mineralized with high dissolved sulphate, nitrate, sodium, iron, and manganese concentrations.

Major river systems flowing from west to east developed during preglacial times eroded broad valleys in Tertiary and Cretaceous sediments. These valleys were filled with sand and gravel derived from the Rocky Mountains. During glaciation, till filled or partially filled these valleys, burying sand and gravel layers. During interglacial periods, younger sand and gravels were deposited within original valleys, or new channels were developed.

In places where buried valley sand and gravels are present and saturated with groundwater, they constitute some of the highest yielding aquifers in the Cretaceous subregion. They are usually confined aquifers containing potable-quality water of calcium-magnesium-bicarbonate hydrochemical type. High dissolved iron and manganese concentrations are common in these deposits.

Glaciofluvial deposits (eskers, outwash plains) locally present on or near the ground surface may contain considerable quantities of groundwater. These aquifers are often utilized as a source of water supply by individual farmers or small communities. Expected groundwater quality is good, low mineralization and calcium-magnesium-bicarbonate. Due to their occurrence at or near the groundwater surface, these aquifers are susceptible to contamination related to gas plant activities.

Alluvial deposits present within major river valleys consist of sand and gravel. These sediments usually have high hydraulic conductivity and have high potential as a source of water. Often sand and gravels have very high silt content. In this instance, intensive development may improve well production. Where hydraulic connection with a river channel is established, well production may be very high (exceeding 25 m^3/hr). Produced water from such wells has chemical composition similar to river water.

Tertiary Subregion

This subregion occupies a wide zone between the Foothills and Cretaceous subregions. The bedrock consists of early Tertiary (Palaeocene) Paskapoo Willow Creek and Porcupine Hills Formations. In the southern part of this subregion, approximately between Airdrie and south toward the Oldman River, the Porcupine Hills Formation (Palaeocene) is present (Green, 1970). In the north it overlies and grades laterally into the Paskapoo Formation, while in the south (south of Newton) it grades downward into the Willow Creek Formation.

These Palaeocene Formations consist of a succession of calcareous sandstones, siltstones and mudstones which are lying horizontally. Groundwater occurrence in these deposits is attributed mainly to intense fracturing. The Paskapoo Formation is considered to be a major regional aquifer and is commonly used as a source of water supply by municipalities, industry and farmers. The Willow Creek Formation subcropping east of the Porcupine Hills consists mainly of shales and siltstones and has low groundwater producing potential. The overlying Porcupine Hills Formation has lower hydraulic conductivity than the Paskapoo Formation, thus expected well yields are also lower.

Groundwater circulation in these formations is controlled mainly by fracturing and terrain topography. Presence of large springs within river valleys is common within this hydrogeological subregion. Groundwater surface fluctuations may be considerable (a few meters) as a result of direct infiltration of water during snow melt or heavy rain periods. Flow velocities (controlled by hydraulic gradient, hydraulic conductivity and effective porosity) are expected to be less than 100 m/y. Protection of these aquifers will be a major concern of remediation efforts at ASGP's.

The groundwater contained in these formations is usually of potable quality, with mineralization lower than 1000 mg/l. It mostly represents sodium-bicarbonate hydrochemical type. In areas where groundwater residence time in the subsurface is low (shallow aquifers) calcium-magnesium-bicarbonate groundwaters may also occur.

Quaternary deposits in this subregion are similar to those described in the Cretaceous subregion. It is only expected that content of materials originating from the Rocky Mountains and Foothills will be higher than observed further east.

4.4 GROUNDWATER CONTAMINATION SITUATIONS

4.4.1 General

The following sections provide detailed descriptions of the contamination situations considered for this study. For each, a brief generic description and a detailed scenario typical of conditions at ASGP's are provided. A summary of the situations and assigned codes is presented in Table 4.1.

4.4.2 Situation T1A : Condensate in Till (high K)

Generic Description

Saturated zone, surficial deposits of high hydraulic conductivity, groundwater contaminated with free phase liquid condensate (LNAPL) and associated BTEX dissolved fraction.

Typical Scenario

At a gas plant in the Foothills of Alberta, the saturated zone is contaminated with free phase liquid condensate. Surficial deposits at such an ASGP would consist of glaciofluvial and glacial outwash sands and gravels. These deposits are well graded, with grain sizes varying from silt and clay to large cobbles. Sediments are stratified, with layers of finer and coarser material. Hydraulic conductivity ranges from 10E-4 to 10E-6 m/s. Surficial deposits typically vary in thickness from about 5 to 15 m, and typically lie atop shale and sandstone bedrock which is locally heavily fractured. The depth to groundwater varies from 1 to 10 m below ground surface.

Condensate hydrocarbon contamination occurs floating atop the groundwater surface, and due to seasonal fluctuations of the groundwater surface has been smeared across several metres of the section, existing as residual saturation in both saturated and unsaturated zones.

Typically, the BTEX fractions of the condensate are also present as an aqueous phase plume, typically in levels around the 10 to 20 mg/L range.

At one plant, for example, a broken buried pipe leaked condensate into the ground over several years, creating an extensive plume of LNAPL on the groundwater table. The source point was located inside the plant area, and is very close to several major structures whose foundations are set in the till layer. The plume has migrated downgradient, and is now approximately 1 km in length and 250 m at its widest. Apparent condensate thicknesses measured in monitoring wells vary from 1.5 metres to a thin film. BTEX concentrations in groundwater sampled from below the free phase layer reach 57 mg/L, but vary over the contaminated area.

4.4.3 Situation Code: T2A - Condensate in Till (low K)

Generic Description

Saturated zone, surficial deposits of low hydraulic conductivity, with free phase liquid condensate (LNAPL) and associated BTEX dissolved fraction.

Typical Scenario

Typical geological profile at a plains region ASGP would consist of clay and silt till of low hydraulic conductivity (10E-9 to 10E-11 m/s), with occasional thin water-bearing sandy till layers of higher hydraulic conductivity (10E-6 to 10E-7 m/s). Sandy till layers are usually areally discontinuous, but locally may extend over several hectares. Total thickness of Quaternary deposits does not usually exceed 10 m. Quaternary deposits overlie siltstone/sandstone/shale bedrock.

Condensate leaks from on-site disposal ponds, pipeline leaks, etc. may introduce product into the subsurface, where it eventually collects atop the groundwater surface. At one plant for example, LNAPL contamination has been detected about 100 m downgradient of the pond and has spread over a 25 m lateral distance. Monitoring wells in the centre of the plume have apparent condensate thicknesses in the order of 0.75 m.

4.4.4 Situation Code: T1BC - Dissolved Inorganics and Organics in Till (high K)

Generic Description

Saturated zone, surficial deposits of moderate hydraulic conductivity, groundwater contaminated with dissolved phase compounds:

1) inorganics (Cl, SO4)
2) organics (amines, BTEX, elevated TOC (total organic carbon))

Typical Scenario

At a gas plant in the Foothills of Alberta, the saturated zone is contaminated with dissolved inorganic and organic compounds. Surficial deposits at such an ASGP would consist of glaciofluvial and glacial outwash sands and gravels, as described in the T1A situation in Section 4.4.2., above.

Aqueous phase contamination is present either as inorganic species alone, or as combined organic and inorganic species. Elevated chloride concentrations in groundwater are common, and stem mainly from on-site disposal/produced water ponds and landfills. Background chloride concentrations at ASGP's are usually below 10 mg/L. Typical chloride levels in contaminated groundwater range from 200 mg/L to several thousand mg/L.

Elevated sulphate concentrations in groundwater are often found downgradient of sulphur blocks and sulphur runoff retention ponds. Natural sulphate concentrations in near-surface groundwaters in Alberta are commonly as high as several thousand mg/L. Sulphur isotope analysis is often used to identify the presence of SO4 of industrial origin. A typical scenario might involve sulphate concentrations of 200 to 2000 mg/L, compared to a background level of 100 mg/L.

Inorganic plumes are also often associated with varying concentrations of dissolved organics. Amines and amine degradation products from plant sweetening processes are common (and can be tentatively identified by elevated TKN (total kjeldahl nitrogen) levels), as are dissolved aromatic hydrocarbons (BTEX). Process chemicals such as sulfinol and DIPA may be present at the ug/L range (10 to 1000 ug/L).

4.4.5 Situation Code: T2BC - Dissolved Inorganics and Organics in Till (Low K)

Generic Description

Saturated zone , surficial deposits of low hydraulic conductivity, groundwater contaminated with dissolved phase compounds:

1) inorganics (Cl, SO4)
2) organics (amines, BTEX, elevated TOC)

Typical Scenario

Typical geologic profile at a plains region ASGP would consist of clay and silt till of low hydraulic conductivity (10E-9 to 10E-11 m/s), with an occasional thin water-bearing sandy till layers of higher hydraulic conductivity (10E-7 m/s), as described in situation T2A, above.

At one particular plant, for example, aqueous phase contamination has been detected downgradient of the process water pond. The site geology consists of about 12 m of silt and clay till overburden atop shale bedrock. Two groundwater-bearing sandy till layers occur in the overburden, one at about 6 m depth, the other of slightly coarser-grained sand immediately atop bedrock. Hydraulic conductivities measured for the upper and lower zones were in the order of 10E-7 m/s, but may be locally higher, due to fracturing in till. A plume of dissolved inorganic and organic contaminants has migrated downgradient from the pond in the upper zone for a distance of several hundreds of metres. Chloride concentrations of up to 1930 mg/L and TOC values of 118 mg/L were recorded (compared to backgrounds of 3.6 and 7.3 mg/l respectively. No information on the nature of the organics was available. Samples of water from the pond itself revealed chloride concentrations of 10,950 mg/L and TOC levels of 850 mg/L.

4.4.6 Situation Codes: T1D and T2D - Low pH Conditions in Till

Generic Description

Saturated zone, surficial deposits of both types discussed (T1 and T2).

At some gas plants, low pH conditions in groundwater have been identified, and are attributed to the presence of large quantities of sulphur on-site, stored at sulphur blocks and present in acid water retention ponds. As low pH waters enter the subsurface, they are buffered by the media they pass through. As the buffering capacity of the soil/rock and groundwater becomes exhausted, the zone of acidification grows. The carbonate ion can be used as an indicator of acidification of groundwater, representing depletion of natural buffering capacity.

Typical Scenario

One of the few documented examples of this type of situation is at an ASGP in the foothills region. The pH levels in groundwater downgradient of the sulphur block have been measured to be as low as 2.92. The extent of the plume seems to be limited to a distance of about 500 m from the sulphur block.

4.4.7 Situation Code: R1A - Condensate in highly fractured bedrock

Generic Description

Saturated zone, moderate hydraulic conductivity bedrock, groundwater contaminated with free phase liquid condensate (LNAPL) and associated BTEX dissolved fraction.

Typical Scenario

Typical geologic profile at a SGP in the foothills would consist of interbedded fractured sandstone, siltstone and shale bedrock, dipping at more than 15 degrees. Bedrock fracturing tends to decrease with depth, and as a result the top few metres of bedrock is often in at least partial hydraulic connection with overlying quaternary deposits. Sandstone and siltstone layers are often water-bearing, and exhibit confined/semi-confined behaviour. Hydraulic conductivities of intensely fractured bedrock and permeable sandstone layers are typically in the order of 10E-5 to 10E-7 m/s.

Condensate hydrocarbon contamination occurs floating atop the groundwater surface, and due to seasonal fluctuations of the groundwater surface has been smeared across several metres of the section, existing as residual saturation in both saturated and unsaturated zones.

Typically, the BTEX fractions of the condensate are also present as an aqueous phase plume, typically in levels around the 10 to 20 ppm range. Behaviour of LNAPL in wells completed in bedrock is typically erratic, and apparent product thicknesses may vary widely over time and short distances.

At one particular plant, for example, fractured bedrock dips steeply (45°). A condensate plume has been delineated within a fractured sandstone unit, but is bounded on each side by low hydraulic conductivity shale layers which control condensate migration and distribution. Associated BTEX aqueous phase contamination is present. The groundwater surface is typically 10 to 15 m below ground surface, and fluctuates seasonally.

4.4.8 Situation Code: R2A - Condensate in Bedrock

Generic Description

Saturated zone, low hydraulic conductivity bedrock, contaminated with free phase liquid condensate (LNAPL) and associated BTEX dissolved fraction.

Typical Scenario

Typical lithology at an ASGP in the plains region would consist of almost flat-lying interbedded sandstone, siltstone and shale bedrock. Bedrock fracturing tends to decrease with depth, but in general is much less intense than in foothills areas (R1A). Sandstone and siltstone layers are often water-bearing, and exhibit semi-confined behaviour. Hydraulic conductivities of bedrock sandstone/siltstone layers are typically in the order of 10E-7 to 10E-9 m/s. Bedrock is overlain by 4 to 10 m of unsaturated clay and silt till in many cases.

Condensate hydrocarbon contamination occurs atop the groundwater surface. Typically, the BTEX fractions of the condensate are also present as aqueous phase contamination, typically in levels around the 10 to 20 mg/L range.

4.4.9 Situation Code: R1BC - Dissolved Inorganic and Organic Contamination in Fractured Bedrock

Generic Description

Saturated zone , moderate hydraulic conductivity bedrock, contaminated with dissolved phase compounds:

1) inorganics (Cl, SO4)
2) organics (amines, BTEX, elevated TOC)

Typical Scenario

Geologic profile at an ASGP in the foothills would consist of interbedded fractured sandstone, siltstone and shale bedrock, dipping at 15 to 30 degrees, as described in situation R1A, above.

Aqueous phase contamination is present as inorganic species alone, or as combined organic and inorganic species. Elevated chloride concentrations in groundwater are common, and stem mainly from on-site disposal/produced water ponds and landfills. Background chloride concentrations at ASGP's are usually below 10 mg/L. Typical chloride levels in contaminated groundwater range from 200 mg/L to over 10,000 mg/L. Elevated sulphate concentrations in groundwater are often found downgradient of sulphur blocks and sulphur runoff retention ponds. Natural sulphate concentrations in near-surface groundwaters in Alberta are commonly as high as several thousand mg/L. Inorganic plumes are also often associated with varying concentrations of dissolved organics.

4.4.10 Situation Code: R2BC - Dissolved Inorganic and Organic Contaminants in Bedrock

Generic Description

Saturated zone, low hydraulic conductivity bedrock, contaminated with dissolved phase compounds:

1) inorganics (Cl, SO4)
2) organics (amines, BTEX, elevated TOC)

Typical Scenario

Typical lithology at an ASGP in the plains region is described in the R2A situation, above. In general, it would consist of almost flat-lying interbedded sandstone, siltstone and shale bedrock. Bedrock fracturing tends to decrease with depth, but in general is much less intense than in foothills areas.

Aqueous phase contamination is often present as inorganic species alone, or as combined organic and inorganic species. Elevated chloride and sulphate concentrations in groundwater are common, and range from 200 mg/L to over 10,000 mg/L.

Inorganic plumes are also often associated with varying concentrations of dissolved organics, including dissolved aromatic hydrocarbons (BTEX).

4.4.11 Situation Codes: R1D/R2D - Low pH Conditions in Bedrock

Generic Description

Saturated zone, moderate hydraulic conductivity bedrock, low pH groundwater.

Typical Scenario

Bedrock layers would be typical of foothills (highly fractured - R1) and plains (R2) conditions previously described. Typically, bedrock deposits near surface at ASGP's in foothills regions consist of clastic deposits - carbonate sequences are rare. Carbonate mineral content in these sandstone and shale sequences is usually quite low.

At some gas plants, low pH conditions in groundwater have been identified, and are attributed to the presence of large quantities of sulphur on-site, stored at sulphur blocks, and present in acid water retention ponds. As low pH waters enter the subsurface, they are buffered by the media they pass through. As the buffering capacity of the soil/rock and groundwater becomes exhausted, the zone of acidification grows. Carbonate ion can be used as an indicator of acidification of groundwater, representing depletion of natural buffering capacity.

Documented examples of this type of situation are few; however, such situations are known to exists at a few plants, particularly where the thicknesses of overlying till are small, or where acid water holding ponds have been excavated into or near fractured bedrock. pH levels as low as 2.9 have been identified at ASGP's.

4.5 SOILS AND UNSATURATED ZONE SITUATIONS

4.5.1 Situation Code: S1A - Condensate in High Permeability Soils (Sand and Gravel)

Generic Description

Unsaturated zone/soils, high permeability, contaminated with free phase liquid condensate.

Typical Scenario

Typical lithology at ASGP would consist of glaciofluvial and glacial outwash sands and gravels. Typically these deposits are well graded, with grain sizes varying from silt and clay to large cobbles. Deposits are often stratified, with layers of fine and coarse material.

Condensate hydrocarbon contamination in the unsaturated zone would exist as residual saturation trapped and immobile in pores. Typically areas so contaminated would be inside the plant itself, near large structures etc, close to the original source (broken buried pipeline or leaking tank). Some instances of such contamination can be found in the more accessible areas near flare stack lines (here excavation and ex-situ treatment might be more applicable). Condensate trapped in the zone of natural fluctuation, and exposed by pumping are also considered within this situation.

Case History Information

At a plant in the foothills of Alberta, the unsaturated zone is contaminated with condensate as residual saturation in a glaciofluvial sand and gravel deposit as described above. Measured hydraulic conductivities are in the order of 10E-4 m/s in the saturated zone, and the depth to water table is about 8m from surface, but fluctuates seasonally to about 7m. The glaciofluvial material is capped by a 2 m thickness of clay till. A broken buried pipe leaked condensate into the ground over several years, creating an extensive plume of LNAPL on the groundwater table. The source point is located inside the plant area, and is very close to several major structures whose foundations are set in the till layer. The unsaturated zone is contaminated with condensate at residual saturation at a distance of 2 to 3 metres above the water table across the entire plume area, which covers an estimated 50 hectares.

4.5.2 Situation Code: S2A - Condensate in Till Soils (Low Permeability)

Generic Description

Unsaturated zone/soils, low permeability, contaminated with free phase liquid condensate.

Typical Scenario

Typical lithology at ASGP would consist of a blanket of clay till, occasionally interlayered with thin arealy discontinuous sandy till units. These units are often water bearing. The unsaturated zone consists of clay and silt till of low permeability. Occasionally these tills may be fractured at surface. Typically these deposits are fairly uniform.

Condensate hydrocarbon contamination in the unsaturated zone would exist as residual saturation trapped and immobile in pores. Typically areas so contaminated would be inside the plant itself, near large structures etc, close to the original source (broken buried pipeline or leaking tank). Some instances of such contamination can be found in the more accessible areas near flare stack lines, disposal ponds, and on-site landfills (here excavation and ex-situ treatment might be more applicable).

Case History Information

At a plant in the plains region of Alberta, the unsaturated zone is contaminated with condensate as residual saturation in a clay and silt till as described above. Measured hydraulic conductivities are in the order of 10E-8 to 10E-10 m/s in the saturated zone, and the depth to water table is about 4 m from surface. It is suspected that condensate disposed of into an unlined pond leaked into the ground over several years, creating a plume of LNAPL on the groundwater table. The soils surrounding the source are heavily contaminated by condensate.

The condensate layer floating on the groundwater table now extends downgradient for about 150 m and an associated smear zone of LNAPL in overlying soils has been created by seasonal water table fluctuations. The unsaturated zone has been contaminated in the area of the plume by smearing due to water table fluctuations.

4.5.3 Situation Codes: S1BC and S2BC - Inorganics in Soils

Generic Description

Unsaturated zone/soils, high permeability, contaminated with inorganic contaminants (sulphur, sulphate, high salinity variations).

Typical Scenario

Typical lithology at foothills ASGP would consist of glaciofluvial sands and gravels (S1) and clay till (S2).

Inorganic contamination of soils can occur at ASGP's as a result of contamination from sulphur and/or high salinity. Metals and other contaminants may also be present.

Case History Information

This contamination situation may be rare at ASGP's; however available information does not contain documentation to support this. Little soils data on inorganic contamination of soils were available from Alberta Environment or plant operators.

4.5.4 Situation Code: S1D and S2D - Low pH Conditions in Soils

Generic Description

Unsaturated zone/soils, low pH problem.

Typical Scenario

Typical lithology at foothills ASGP would consist of glaciofluvial sands and gravels (S1) and clay tills of low permeability (S2).

Depressed pH in soils may occur as a result of sulphur dusting and block storage, and the evolution of sulphuric acid, or by other mechanisms.

Case History Information

Soils information for this type of situation was quite scarce (CPA, 1990). At some plants, near-surface soils have been acidified to depths of a few centimetres as far as a kilometre down-wind of sulphur piles and towers. Soil pH near sulphur blocks themselves can be as low as 3.0.

5. REVIEW AND PRELIMINARY SCREENING OF TREATMENT TECHNOLOGIES

5.1 OVERVIEW

The past several years have seen a dramatic increase in concern over subsurface contamination. This fact has been reflected in increased public awareness of problems, more stringent regulatory demands, and a stronger industry focus on all aspects of waste management and clean-up. Particularly in the United States, tough legislation and the risk of litigation have spurred development of numerous technologies designed to control, abate, and remediate subsurface contamination. At present, there exist a myriad of different methods for removing contaminants from soil, air and water. Some are designed for specific contaminants and media, others work equally well on many types of problems. Available technologies range from the tried and tested to the purely experimental, and can vary significantly in cost and efficiency.

In general, remediation of subsurface contamination can be approached in one of the following ways:

1. **In-situ:** soil and groundwater may be treated in-place. A variety of methods have been developed for specific contaminants and specific situations.

2. **Ex-situ:** groundwater or soil may be physically brought to the surface for treatment, and then replaced on-site.

3. **Off-site:** soil and groundwater may also be removed from the subsurface and disposed of or treated at another location. Examples of this technique include excavation of contaminated soil and removal to secure landfill, or deep well injection of contaminated groundwater.

To date at Alberta sour gas plants, the off-site methods, particularly excavate and landfill and deep well injection, have been the most commonly employed techniques (Piteau Engineering, 1990). However, it is important to note that these types of techniques do not destroy or eliminate the contaminants, but simply transfer the problem from one location to another. Over the long term, many of the off-site options will prove unsatisfactory for a variety of reasons, including cost, availability of disposal capacity, transportation problems, and associated liability. It is the opinion of the project team that subsurface contamination is best dealt with on-site. For the purposes of this report, the on-site approaches (in- and ex-situ) are stressed.

A remediation system may remove or control contaminants by one or more of the following means:

1. **Physical processes:** compounds can be made to undergo phase changes, such as from water to vapour, liquid to vapour, or through sorption onto or from soil or organic particles. Immiscible liquids can coalesce from a dispersion in water to a separate liquid phase. Contaminated media may be contained, isolated or encapsulated.

2. **Chemical and biological processes:** examples include chemical precipitation or mobilization of target compounds through oxidation, reduction, and complexing. Microbial metabolism of contaminants in aerobic and anaerobic systems may also be used.

3. **Mechanical processes:** extraction, removal, containment, or replacement of contaminated media is often part of a remediation system. Contaminants may also be removed through mechanical processes such as filtration.

It should be noted that in some cases contaminants may be allowed to dissipate or degrade naturally in the subsurface, if the associated potential risks are found to be low. Similarly, in some instances contaminants may be allowed to remain in place once immobilized or isolated.

Once removed from the host media, contaminants must be captured and treated. Treatment is accomplished in the following ways:

1. **Physical techniques:** typical methods include sorption onto a medium, and separation of immiscible liquids.

2. **Chemical techniques:** thermal destruction and catalytic oxidation are examples of chemical treatment.

3. **Mechanical techniques:** compounds may be filtered, dried, or made to pass through specially designed membranes or separators.

The choice of remedial techniques will depend on a number of factors, including site geology and hydrogeology, contaminants involved, assumed risks associated with the contamination, goals of the remedial project, regulatory concerns, and economics. Each site should be studied individually to determine the most suitable and cost-effective approach. In the majority of situations, the final remedial system selected will consist of a combination of technologies applied in series or to various portions of the site as required.

The following sections provide an overview of available remedial technologies applicable to subsurface remediation of both soils and groundwater. The review encompasses all aspects of the remediation process, from extraction techniques to surface treatment systems and in-situ methods. Established, emerging, and experimental techniques are considered. The individual technologies are discussed briefly, and their general applicability to the specific conditions encountered at Alberta sour gas plants is assessed. In later sections of this report, the generally applicable technologies are assessed in detail and ranked according to their suitability to the most common types of contamination situations encountered at Alberta sour gas plants.

5.2 GROUNDWATER REMEDIATION

5.2.1 General

Most groundwater remediation projects are driven by the need or desire to prevent off-site migration of contaminants towards potential receptors of environmental significance. Common examples of such receptors are rivers, lakes and other surface water bodies, and wells used for domestic or municipal water supply. Around sour gas plants in Alberta impacts to both of these types of receptors are a possibility if contaminants are allowed to migrate unchecked. However, remedial technologies for groundwater developed over the past several years are capable of eliminating or severely reducing such risks, if properly applied.

The first and most important step in remediation of groundwater is the elimination of continued sources of contaminants into the subsurface. Actions which can be taken to prevent contamination include detecting and repairing leaking pipelines and underground storage tanks, lining ponds and lagoons, and controlling sulphur block runoff and dusting. Contaminants bound or trapped in the soils and the unsaturated zone at a site can also be considered as "subsurface sources" of groundwater contamination, as can concentrations of bulk separate phase hydrocarbons. Infiltration of surface runoff and snowmelt may leach contaminants from the soil towards the groundwater surface. Groundwater flowing through LNAPL-contaminated pores will be contaminated by dissolution of water-soluble hydrocarbon components. These "subsurface sources" of contamination must also be dealt with as part of a long-term groundwater remediation strategy.

In this respect "it is appropriate to distinguish between remedial actions which are **control measures** and those which are **corrective measures**. Control measures are directed to the control or containment of dissolved plumes or contaminant sources. In most circumstances, control of the off-site migration of contamination is the most immediate objective of remedial actions. Corrective measures are directed to the restoration of dissolved plumes or the clean-up of contaminant sources. Restoration of dissolved plumes may be to achieve groundwater standards or criteria specified by regulatory agencies or even background concentrations. Corrective measures applied to contaminant sources may be to achieve specific regulatory standards or, more practically, to eliminate the need for perpetual maintenance" (Feenstra, 1991).

From this perspective, the distinction between "established" and "emerging" or "potential" groundwater remediation technologies will depend on the problem to which they are applied, and the goals of the remediation. For example, pump-and-treat technology has been extensively tested and proven as a means of preventing off-site migration of dissolved contaminants and containing plume development, and thus can be designated as an "established" technology for this application. However, pump-and-treat may only be considered as a "potential" technology (one requiring additional research, development and enhancement) for the restoration (complete clean-up) of dissolved plumes (Feenstra, 1991). Furthermore, for the clean-up of LNAPLs such as condensate in the subsurface, it should be considered as an "emerging" technology, requiring substantial study and enhancement before it can be of significant practical value.

In the case of Alberta sour gas plants, it should be noted that very little groundwater remediation has been attempted to date, with a few notable exceptions. This would suggest, in broad terms, that even the most "established" technologies have yet to undergo rigorous testing and evaluation under Alberta sour gas plant conditions, and should be considered as requiring additional study and evaluation.

This caveat, as discussed, applies to the most widely-used and tested groundwater remediation technique: pump-and-treat. Most groundwater remediation schemes will involve some form of pump-and-treat system (be it pumping wells, trenches, or well-points) at some stage in the life of the project (Mercer et al, 1990). Pump-and-treat systems will often serve as an important component for implementation of other remedial techniques. <u>In-situ</u> bioremediation, for example, may require injection of nutrients and oxygen into the aquifer, and the removal of contaminated water downgradient through pumping wells. For the purposes of this report, <u>ex-situ</u> groundwater remediation technologies are those which treat contaminated groundwater recovered from the aquifer. <u>In-situ</u> groundwater remediation technologies are those which serve to contain, immobilize, or degrade contaminants in the aquifer itself - often, a pump-and-treat system will be part of such schemes.

The following sections review the types of groundwater remediation technologies available, and rate their general applicability to the contamination situations being studied.

5.2.2 Technologies for Extraction, Control and Injection of Groundwater

The technologies discussed in this section comprise the mechanical systems with which groundwater and associated dissolved contaminants can be extracted from the aquifer. In essence, they form the "pump" part of the "pump-and-treat" remediation method.Successful implementation of a pump-and-treat system requires a sound understanding of the hydrogeological processes occurring in the subsurface, and a detailed characterization of the distribution, types and concentrations of contaminants. A detailed discussion of pump-and-treat can be found in Mercer et al (1990), and in the Recommended Technologies section of this report.

Conventional Recovery Wells

Conventional recovery wells are the most widely used method of extracting contaminated groundwater from the subsurface. Typically, such wells range from four to twelve inches in diameter, (102 to 305 mm) and are constructed with steel, PVC or ABS pipe depending on the application. Wells can be left as open-hole completions in stable bedrock, or completed with liners designed to allow groundwater to flow into the well while holding back the formation. Depending on the aquifer material in which the well is to be completed, screens or liners may be slotted, perforated or wire-wrapped. In granular aquifers, a filter pack of specially graded inert material (such as silica sand) may be used to prevent aquifer fines from silting up the well.

This type of recovery well is ideally suited for control and clean-up of dissolved phase plumes in moderately or high hydraulic conductivity aquifers (K>10E-7 m/s) which exist at depths beyond the practical limit for excavation (about 3 m). As groundwater is pumped from the well, a "cone of depression" forms in the groundwater surface around it, causing groundwater to flow towards the well. Dissolved contaminants are removed with the pumped groundwater. Clean-up efficiencies and success, as with all groundwater remediation technologies, will be highly dependent on the effects of aquifer heterogeneity and anisotropy, and the behaviour of the contaminants in the subsurface. Detailed discussions of well design and use are found in Driscoll (1986), Mercer et al (1990), and Nyer (1985).

The equipment and materials with which to construct such wells is readily available in Alberta. A typical 10 inch recovery well completed to 15 m depth, with PVC casing and slotted PVC screen, would typically cost in the order of $ 10,000 to $20,000 (1991 dollars), including professional design, supervision, and reporting, drilling and materials costs. Standard submersible pump systems can be easily installed and operated in such wells.

General Applicability: All groundwater contamination situations at ASGP's (T1A, T2A, T1BC, T2BC, T1D, T2D, R1A, R2A, R1BC, R2BC, R1D, R2D).

Status: Established.

Large Diameter Recovery Wells

Large diameter well systems are extensively used for extraction of groundwater from aquifers of low hydraulic conductivity, surficial material or bedrock. Well diameter can range anywhere from one to several feet. Often such wells are about one metre in diameter, and are completed with culvert steel sections. The increased well diameter allows improved flow from the aquifer into the well, and effectively extends the radius of influence of the well. If recharge to the well is slow, it can be pumped on an intermittent basis, or provided with a tailpipe sump which can be pumped out when full.

Typically such wells are slightly more expensive than conventional recovery wells of similar depth. Specialized drilling equipment is required to cut the large diameter holes, and special large diameter pipe or culvert sections must be used for casing. Fortunately, there are numerous oilfield rathole-drilling contractors in Alberta. These firms are equipped for this type of work, and can drill in both surficial materials and bedrock. A 15 m deep well, one metre in diameter, cut half in till and half in fairly hard siltstone-sandstone bedrock typical of the Paskapoo Formation, would typically cost in the order of $20,000 (including professional design, supervision and report, drilling and materials costs).

Large diameter wells are typically fitted with low-volume pumping systems controlled by a float-switch system. As groundwater reaches a certain level in the well, the pump is activated, drawing water from the well. When the water level in the well drops to a pre-set point, the system shuts down, and groundwater is allowed to refill the well. In some circumstances, such fluctuations in the groundwater surface near the well are undesirable (in the case of free product recovery under unconfined conditions, for instance). In these situations, and if flow to the well is very slow, a sealed tailpipe sump may be used to collect contaminated groundwater, and its contents periodically pumped out. Design and use of large diameter recovery wells are discussed in Driscoll (1986) and Testa and Winegardner (1991).

General Applicability: All groundwater contamination situations in low-permeability aquifers where conventional wells would be ineffective (T2A, T2BC, T2D, R2A, R2BC, R2D).

Status: Established.

Trenches

Trenches are an effective method of intercepting and if necessary recovering contaminated groundwater from shallow aquifers. Essentially, a narrow excavation is placed across the contaminated zone, and backfilled with a material more permeable than the surrounding deposits, creating a conduit for flow. Groundwater flows into the trench, either as a result of natural hydraulic gradients (passive interception) or induced gradients (pumping). Once in the trench, groundwater is collected and treated, or removed by pumping. Trenches can be designed with collection pipe, sumps, and geotextile filter cloth backing to prevent LNAPL migration past the trench.

The applicability of trench collection systems at a particular site is limited by the practical depth of excavation. The cost of an excavation will depend on the physical characteristics of the subsurface material (which will determine the need for dewatering, cribbing, etc.), the ability to dispose of contaminated material removed, and the equipment available. Occupational Health and Safety regulations require that any excavation be cribbed or cut back to a 45 degree angle if deeper than 1.5 metres. Typically, trench systems are difficult to construct to depths greater than about 2.5 metres. Trench design and application are discussed in USEPA (1988) and Weston (1988).

Costs of installing trench recovery systems will vary significantly from site to site. A 2 m deep recovery trench recently designed by Piteau Engineering Ltd. for containment and remediation of a gas condensate plume at a sour gas plant in Alberta was estimated to cost approximately $250 per linear metre, and included two collection sumps, slotted PVC piping, fluid level monitoring devices, and geotextile backing.

General Applicability: All shallow (less than 2.5 m) groundwater contamination situations

Status: Established

Injection Wells

Injection wells are often used during pump-and-treat operations to re-introduce produced and treated groundwater into the contaminated aquifer. Injection wells must be carefully designed, based on the type and hydraulic characteristics of the aquifer to be recharged, anticipated flow rate, and the chemical nature of injected and aquifer waters. Systems should be designed to achieve maximum flow with the least hydraulic resistance. Typically, screen lengths should be 50% greater than for pumping wells designed for the same flow rate. In granular materials, use of stainless steel continuous wire-wrap water well screen (such as Johnson) is recommended. A complete discussion of design criteria and parameters for injection wells is provided in Driscoll (1986) and Roscoe Moss (1989). Injection can be accomplished under pressure (forced) or by gravity.

Maintenance is a key aspect of injection well operation. Clogging of well screens due to precipitation of inorganics, or build-ups of biomass, can significantly reduce well efficiency. Wells must often be cleaned or treated periodically to remove encrustation and bacterial buildups.

The advantages of reinjection and reinfiltration (discussed below) are manifold. Upgradient re-injection groundwater can flush contaminants and steepen gradients towards recovery wells, and help provide hydraulic control of plume movement. In some cases, groundwater can be re-injected into the contaminated aquifer after only partial treatment, providing reinjection is done upgradient of pumping wells and complete recapture can be demonstrated. This can save on groundwater treatment costs, while still allowing for flushing and plume control.

Injection well systems can vary significantly in cost, depending on the characteristics of the formation, desired flow rates, and maintenance requirements. Gravity injection wells recently installed to a depth of 10 m in glaciofluvial sand and gravels at a sour gas processing plant in the foothills area of Alberta cost approximately $ 15,000 each (including professional design, supervision and reporting, drilling, materials and testing), and were capable of handling approximately 250 m^3/day of water. The wells were completed with Johnson stainless steel water well screens.

Applicability: Any sites or situations in which pumping and disposal of groundwater is involved. Generally, injection wells are best suited to higher hydraulic conductivity materials.

Status: Established.

Infiltration Galleries

Infiltration galleries can be used at contaminated sites for the same purposes as injections wells: disposal of produced water, plume control, flushing of contaminated zones. Galleries usually consist of a delivery system (pipe network) placed inside a backfilled excavation. Water is pumped through the delivery system, and flows through the permeable backfill and down into the surrounding material under the influence of gravity (Figure 5.1). Galleries are particularly well suited to sites where the near surface materials are permeable and relatively thick. A detailed discussion of the design of infiltration systems is presented in Roscoe Moss (1988). One key design consideration must be the effective winterizing of the system, and the burial of delivery systems below the depth of frost penetration.

Compared to injection wells, infiltration galleries will typically deliver water over a much larger area, and through a greater section of the unsaturated zone. This makes the method ideal for flushing of contaminants from the unsaturated zone, or incorporation as part of an in-situ soil-washing system. Infiltration galleries may be impractical at some sour gas plant sites where space is at a premium, and where saturation of the ground may cause foundation problems. In such cases, injection wells are favoured.

Costs of infiltration systems will depend greatly on the type of geologic materials present at the site. For a given flow rate, more expansive infiltration systems will be required for lower permeability materials. The deeper the system must be installed, the more costly it will be. The practical economic limitations of excavation should also be considered. A preliminary design of an infiltration gallery capable of delivering about 200 m^3/day of water into a glaciofluvial sand and gravel unit was completed by Piteau Engineering Ltd. The cost of

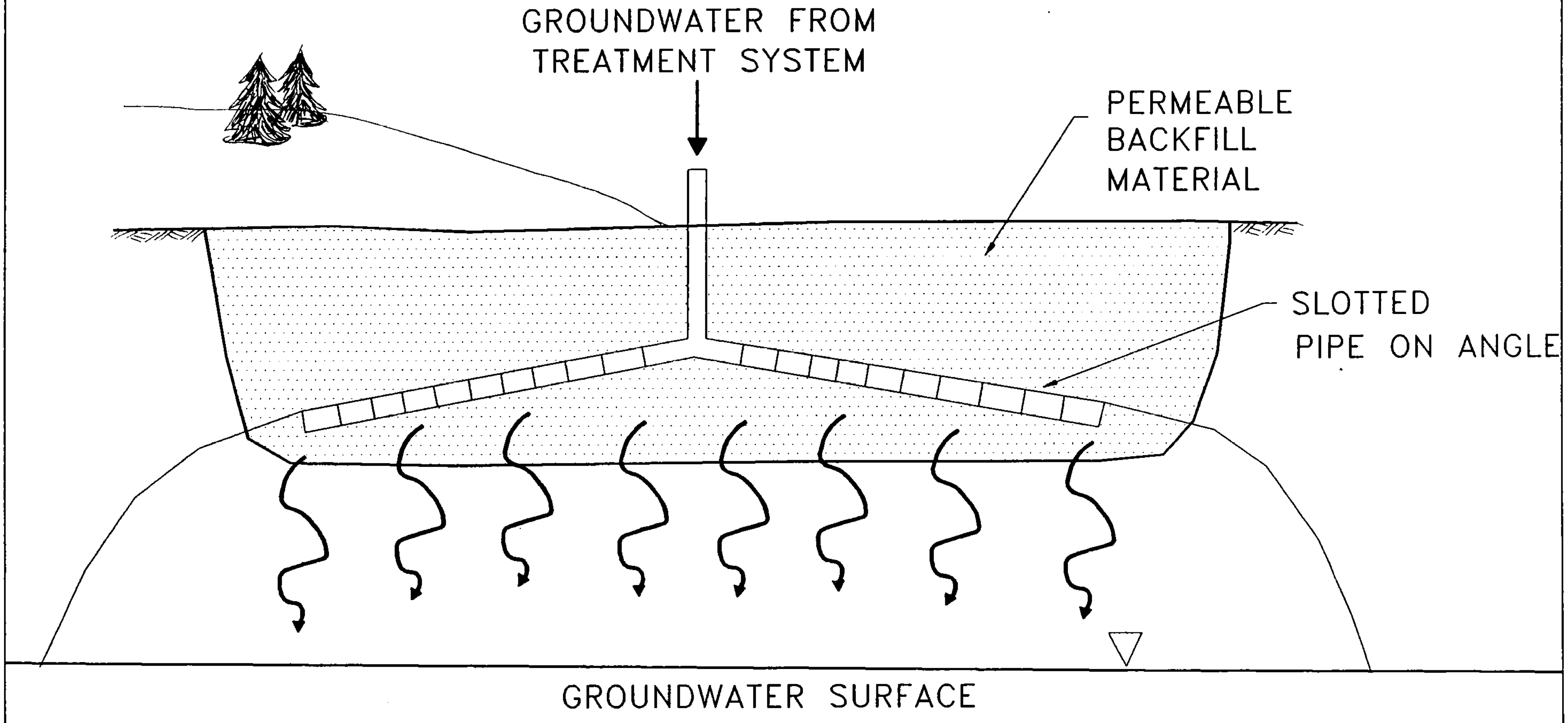


FIGURE 5.1
INFILTRATION GALLERY

excavation was made prohibitive due to the presence of a 2 m layer of relatively low permeability till at the surface, and injection wells were recommended instead. In some situations, spray irrigation can be used as a re-infiltration method, but is limited to spring and summer operation.

Applicability: Reinfiltration back into the subsurface can be applied at any sites where groundwater is being produced, but may be limited by space constraints, and the nature of surficial materials.

Status: Established.

Free Product Recovery Methods

As described in detail in the report section on contaminants, free product (LNAPL gas condensate) can accumulate on the groundwater surface, and migrate in the direction of groundwater flow. Only mobile LNAPL is available for recovery by hydraulic means. Recovery of mobile free product (condensate in this case) can be accomplished in a number of ways. The most commonly used techniques involve the use of trenches and recovery wells. (USEPA, 1988).

Trenches are the most effective method of free product recovery if the depth of the water table does not exceed 1.5 meters. At this depth excavation is relatively simple and not overly costly. Trenches can be used to effectively cut-off and contain plumes (Figure 5.2). Pumping wells of the types described above can also be used for active control of free-product plumes, and are recommended when depth to groundwater exceeds about 5 - 6 m (USEPA, 1988).

Once free product has been drawn into the well or trench, a variety of technologies are available for its removal. These include:

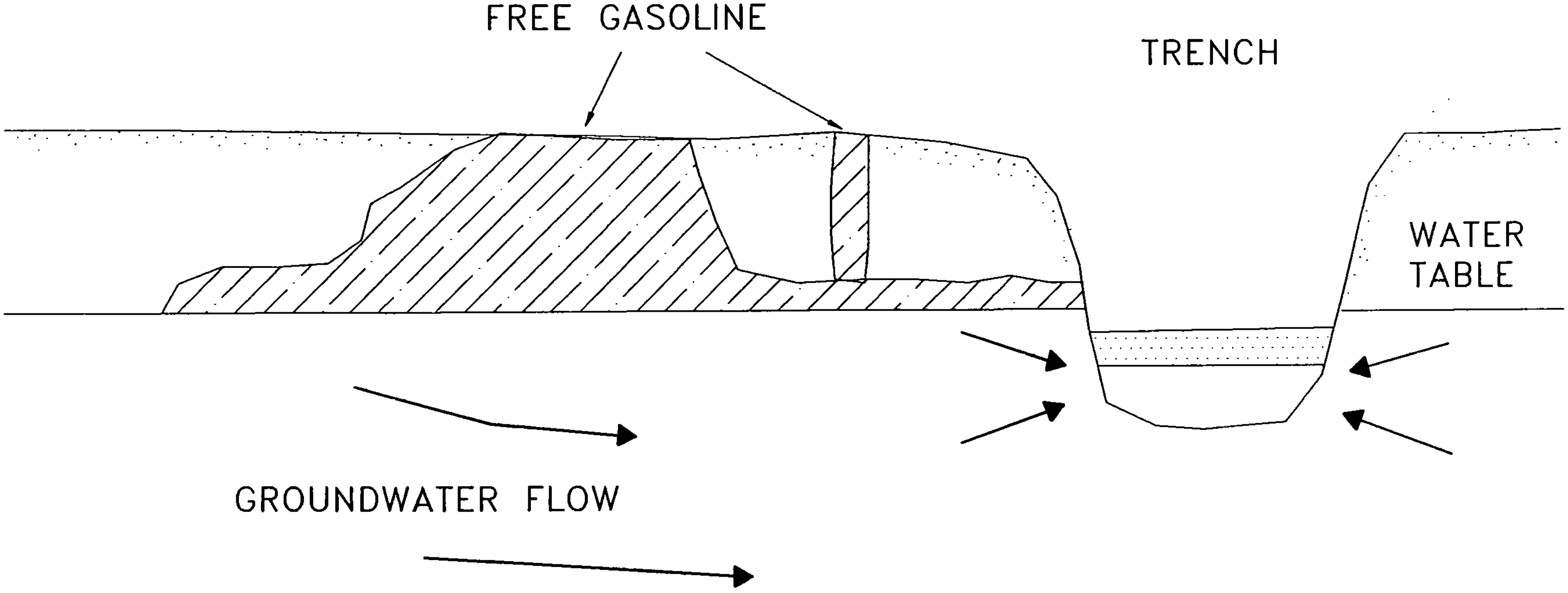


FIGURE 5.2
TRENCH RECOVERY OF FREE PRODUCT

Single Pump Method Both product and water are recovered together and piped to storage tanks or oil-water separators at surface. Disadvantages include increased mixing of water and hydrocarbon, production of large volumes of contaminated groundwater requiring treatment, and inefficient removal of product from the aquifer due to relative permeability and capillary pressure effects. Figure 5.3 shows a typical single pump system.

Dual Pump Method With this technique, groundwater is removed by a water table depression pump which creates a cone of depression around the well. Free product then migrates towards the well, where it is pumped or "skimmed" out with a product pump (Figure 5.4). Product skimmers can remove up to 99% of mobile hydrocarbons floating on the groundwater surface (USEPA, 1988). Filter-scavenger-type pumps use oleophyllic-hydrophobic membranes to skim product down to a thin film. Product pumps can be used alone, or with a water table depression pump, in the same well or in adjacent wells. The dual-pump systems are preferred over single pump systems for most applications as they do not cause mixing of free-product and groundwater. Pure product is pumped directly to a recovery tank, and groundwater to a treatment unit to remove dissolved hydrocarbon components. The USEPA (1988) state: "the cost of recovering free product at a site depends more on the recovery method and equipment required for clean-up than on the size of the spill", and "cost of free product recovery are small compared to the cost of restoring hydrocarbon-contaminated groundwater to drinking water standards."

In case studies reviewed by the USEPA (1988), free product skimming on average recovered only 29 percent of the total volume of spilled product. Cost of recovery ranged from US $3 to $93 per US gallon of product. A detailed discussion of product recovery systems, costs, limitations, and implementation (including case histories) is provided in the Recommended Technologies section of this report.

Applicability: Situations involving free condensate on the groundwater surface (T1A, T2A, R1A, R2A)

Status: Established - but requires further study in complex geological settings such as fractured bedrock.

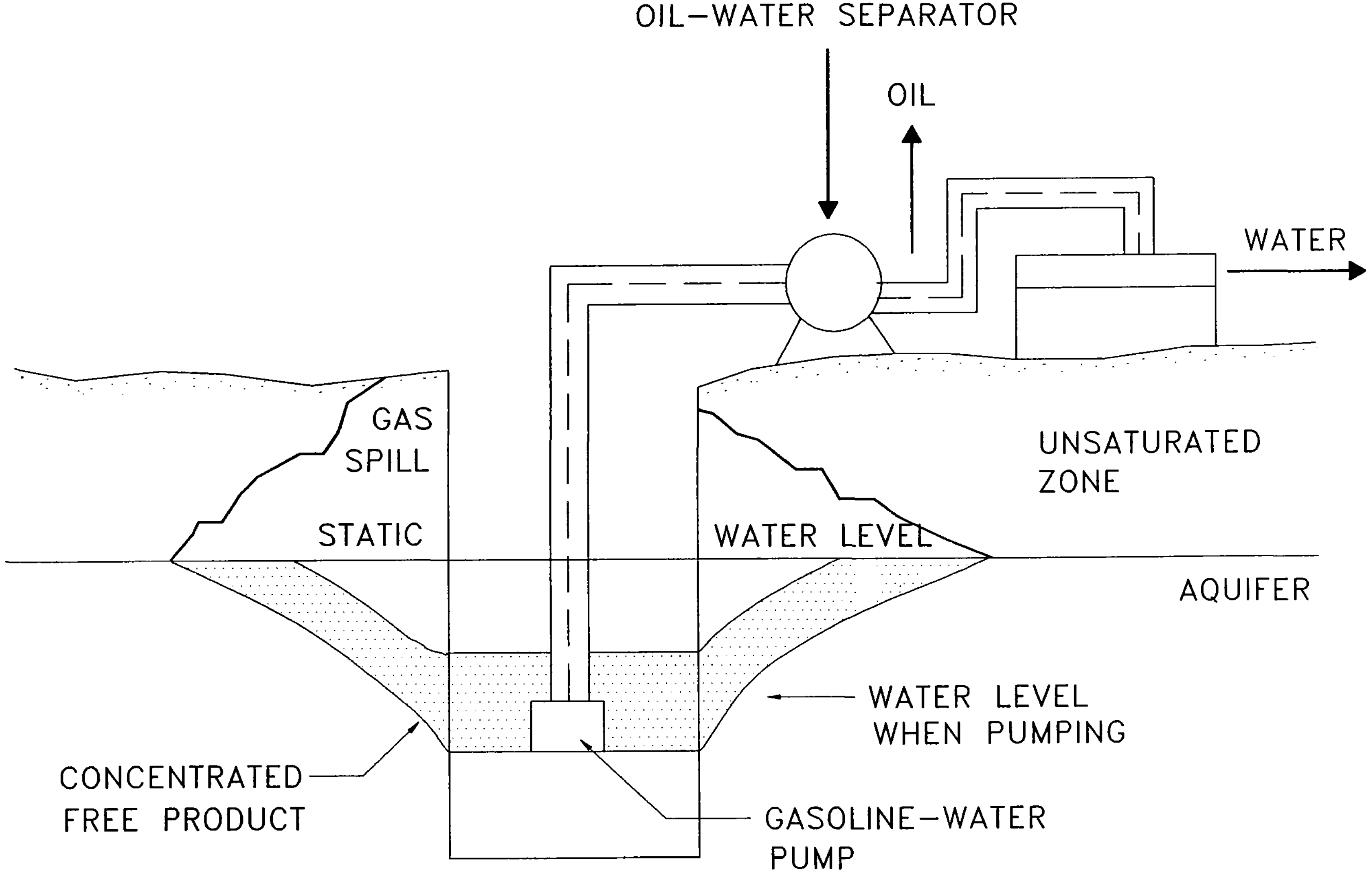


FIGURE 5.3
SINGLE PUMP SYSTEM
FOR FREE-HYDROCARBON RECOVERY

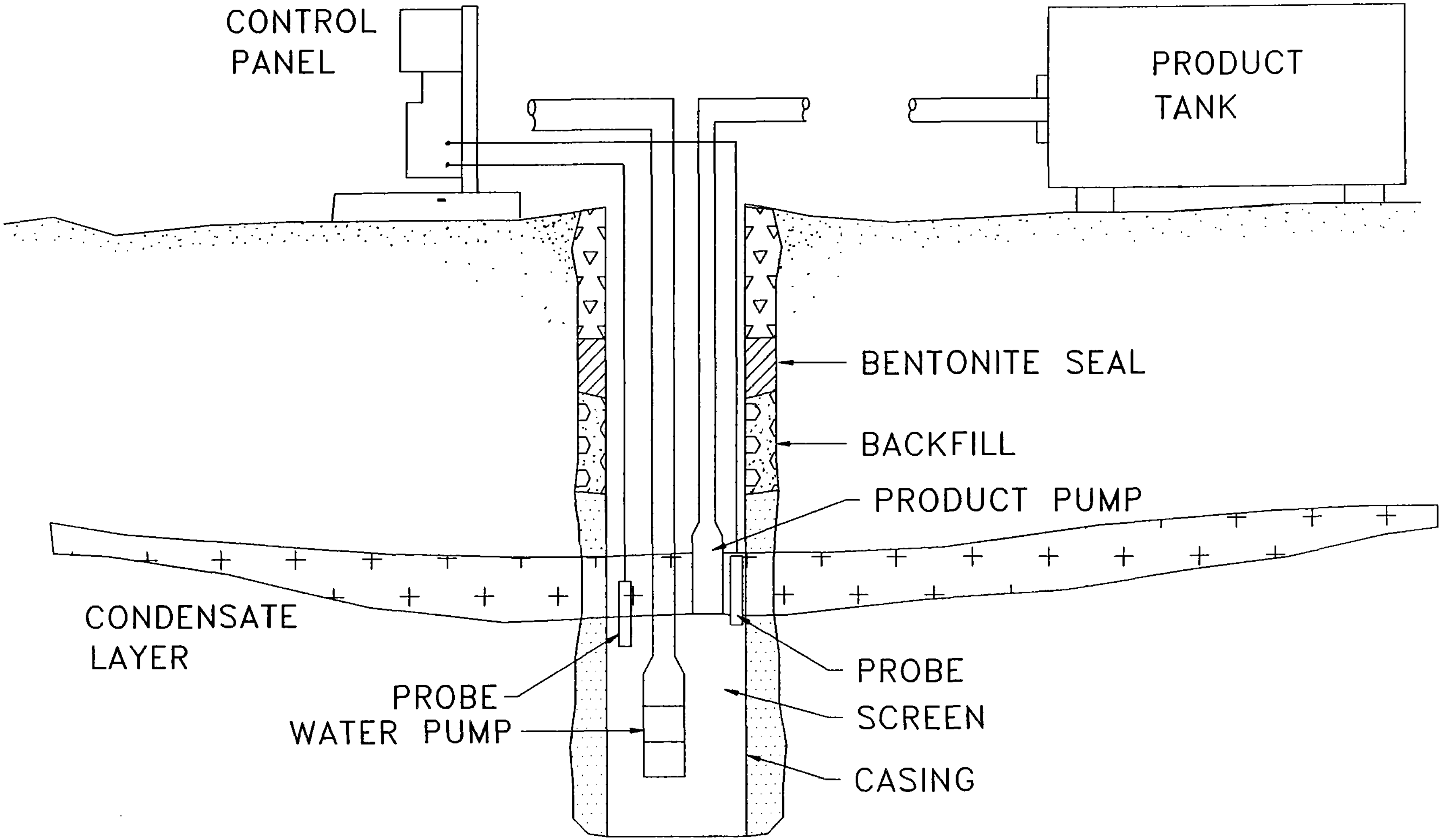


FIGURE 5.4
SCHEMATIC OF A TWO-PUMP SYSTEM USING ONE RECOVERY WELL

5.2.3 Ex-situ (Treatment) Technologies - Organics

Oil-Water Separators

Oil/water separators are used to remove large quantities of immiscible petroleum products from groundwater. This method is applicable if the petroleum products and water exist as separate or emulsified phases. Oil/water separators are available in a variety of designs according to the required removal efficiency. It is possible to achieve effluent oil concentrations below 15 mg/L (ppm) with a design utilizing closely packed sinusoidally shaped plates to enhance the gravity-driven separator of oil and water. The plates collect oil floating to the surface of the water. Other designs preferentially adsorb the hydrocarbon fraction. (The mechanics of the processes were not discussed in the available literature)

When filter type separators are used, spent cartridges will require disposal. Plate-type devices will separate out solids, if any, which require disposal. Product recovery operations have only minor O & M costs and may actually contribute a small source of revenue from recovery of the product (Weston Inc., 1988).

Applicability: Treatment of groundwater contaminated with LNAPL liquids or emulsions.

Status: Established

Aeration

Aeration is a process which brings the contaminated water into intimate contact with air, so that the volatile compounds undergo a phase change from liquid phase to vapour phase. The air then carries off the contamination, leaving the water free from these hazardous compounds. Simple aeration can be accomplished in several ways. These include: aeration tanks, cascade aerators, and spray basins.

The use of aeration tanks is a simple concept whereby compressed air is bubbled through a tank of water. This technique is not generally employed, however, as not enough air can be provided to remove a high percentage of organics (Nyer, 1985).

Cascade aerators are open to the atmosphere, so that there is no operating cost associated with providing an air supply. This process is ineffective due to its low removal efficiency. As with aeration tanks, not enough air-water contact occurs during treatment.

Spray basins is a treatment method which is somewhat more practical than simple aeration or cascade aeration, and has been used in several groundwater cleanup cases. Spray basins operate by spraying a mist of contaminated water over a basin of earthwork or concrete. The water can then be collected in the basin and pumped off. The advantage of this system is its extremely low capital cost, which makes it ideal for a cleanup of a temporary nature. The disadvantages are that large tracts of land are required and that neighbouring properties may be affected by wind driven mists or, in the winter, ice crystals (Nyer, 1985). A packed tower is the most effective means of aeration technology. This method is discussed in more detail in another section.

Applicability: Groundwater contaminated with dissolved BTEX and other volatile organics.
Status: Established, simple aeration techniques have now been largely superseded by packed tower air-stripping.

Air-stripping

This technique is one of the most well established and effective methods for removing VOC's dissolved in groundwater. Air-stripping is an enhanced version of aeration. Water containing dissolved BTEX components (or other VOC's) is run through a counter-current of air, which volatilizes VOC's. Several techniques have been developed to enhance the rate and completeness of volatilization, including the use of packed towers to improve surface contact between air and water, and increase contact time for volatilization. As with all aeration processes, the volatilization of VOC's is controlled by the Henry's Constant (KH), which describes the degree of liquid-vapour phase partitioning of an organic compound.

Air-stripping has been found to provide up to 99.9% removal of dissolved BTEX compounds. The method is cost-effective, however requirements to treat off-gases can increase costs by as much as 100%. The technique is described in detail in the recommended technologies section of this report.

Applicability: Excellent for treatment of groundwater contaminated with BTEX compounds.

Status: Established.

Vacuum Spray Aeration

Vacuum spray aeration is a relatively new adaptation of air-stripping technology, and has been developed primarily to allow volatilization of compounds with relatively low Henry's Constants. The process uses vacuum technology to enhance the volatilization of organic compounds, based on the gas/air relationships. At lower pressures, more volatilization can be achieved at a given temperature. These enhancements, however, add to the cost of the method over conventional air-stripping.

Given the excellent efficiency of conventional air-strippers for removal of BTEX compounds (dissolved components of natural gas condensates), the added expense of the method is not justified for the small potential increases in removal efficiency.

Applicability: Treatment of BTEX in groundwater.

Status: Emerging.

Granular Activated Carbon (GAC)

When present at low levels, some of the water-soluble organic components of gasoline and other products can be more effectively removed by adsorption onto granular activated carbon (GAC) than by air.

The allowable concentration of contaminants for treatment by GAC is in the order of 50 mg/L (Liptak, 1974). Consequently, GAC is often used as a secondary step in groundwater treatment. Other technologies, such as air stripping, biodegradation and oil/water separations, are used initially to remove large amounts of petroleum products from the groundwater. Treatment with GAC then follows as a secondary step to "polish" the treated stream in order to reduce the concentrations to acceptable target levels (Weston Inc., 1988), GAC exhibits a wide range of effectiveness in adsorbing different compounds and generally tends to adsorb high-molecular weight compounds more readily than low-molecular weight substances such as BTEX components. The process of adsorption onto granular activated carbon (GAC) involves contacting the groundwater stream with the carbon. The activated carbon adsorbs the organic constituents by a surface attraction phenomenon in which organic molecules are attracted to the internal pores of the carbon granules. Adsorption depends on the strength of the molecular attraction between adsorbent and adsorbate. The two most significant properties of organic contaminants affecting their adsorption on activated carbon are solubility and affinity. The less soluble the contaminant, the better it was adsorbed. Also the greater the specific attraction of the contaminant to the carbon surface, the greater the potential for adsorption.

Once the micropore surfaces are saturated with organics, the carbon is "spent", and must either be replaced with virgin carbon or be regenerated. The time to reach "breakthrough" or exhaustion is the single most critical operating parameter when deciding on the correct type and volume of carbon for a particular application (Piteau Engineering, 1990). GAC is discussed in more detail in the Recommended Technologies Section of this report under the air-stripping section, as a polishing treatment only.

Applicability: Treatment of BTEX and other organics in groundwater. Costs and carbon treatment/regeneration make it suitable only for low levels of contaminants or as a polishing step.

Status: Established.

Biological Treatment

Groundwater biotreatment usually involves either "pump & flush" in-situ treatment or "pump & treat" ex-situ above ground treatment and discharge. Figure 5.5 depicts a typical ex-situ groundwater remediation design. This treatment design complements biological treatment with a combination of chemical and physical remediation techniques. The groundwater is often pumped from a recovery well to an air stripper when regulations allow. From there the water goes to a bioreactor which has been amended with oxygen, nutrients and inoculum. After

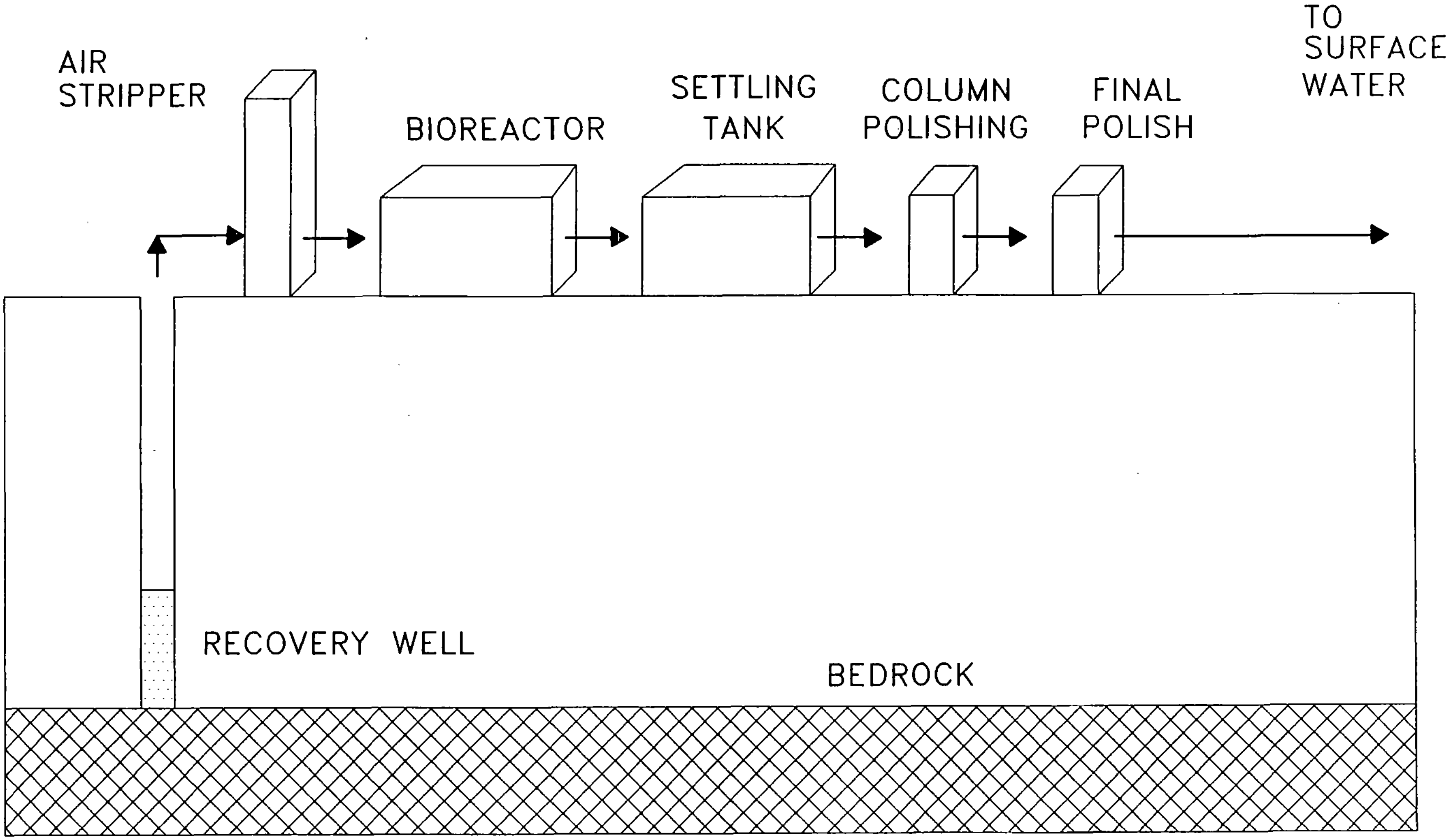


FIGURE 5.5
EX-SITU GROUNDWATER BIOTREATMENT
AFTER FARLEY, 1990

biotreatment, the water is pumped to a settling tank where microbes can be saved and returned to the bioreactor. The supernatant is pumped to either a biofilter tower or a carbon tower for polishing. If complete treatment is required, a second polishing tower may be included. The final effluent may be discharged to surface water.

Applicability: All treatment of biodegradable organics in produced groundwater.

Status: Established for BTEX; experimental for process chemicals whose biodegradability are not known.

Advanced Oxidation Processes (AOP)

This new and promising technology uses various combinations of ultra-violet radiation, catalysts and oxygen sources such as ozone (O_3) and hydrogen peroxide (H_2O_2) to achieve oxidation of dissolved organics. The technique has the advantage of near complete destruction of a very wide range of organics (including BTEX), with water and CO_2 as the only by-products. Unlike some technologies, off-gases are not produced.

Initial pilot tests on AOP systems have demonstrated organic destruction rates as high as 99.9%, at costs which are claimed competitive with conventional air-stripping. To date, there is only one organization in Alberta marketing this technology, but as of yet their systems are still in the developmental stages.

A more detailed discussion of AOP systems, including costs and case histories, as applied to ASGP's is provided in the Recommended Technologies section of this report.

Applicability: Treatment of a wide range of organics (including BTEX and most probably process chemicals) in groundwater.

Status: Emerging.

Ultra-filtration

Ultrafiltration has been used for the separation of emulsions, mainly oil emulsions, from water. The filtrate will still contain all of the surfactant and therefore will require further treatment for groundwater. In industry, both the oil and the surfactants are reused. This is not a widely used treatment method (Nyer, 1985), although some companies such as Canadian Waste Management Ltd. have developed mobile filtration units which are combined with other technologies into a treatment train. These units are designed primarily for treatment of single batches of fluid contaminated with high concentrations of difficult-to-treat compound such as PCB's and pentachlorophenols. This level of sophistication and expense, combined with the relatively low throughput of such units, make the unit generally not applicable to types of contamination situations being considered here.

Applicability: Generally for difficult to treat organics. Not directly applicable to the situations discussed here.

Status: Emerging

5.2.4 Ex-situ (Treatment) Technologies - Inorganics

Overview

The traditional treatment used to remove the more common inorganic contaminants from water and wastewater is aeration (pH adjustment), settling, and filtration. Other treatment methods include ion exchange, membrane separation, and distillation. The amount of research effort which has been devoted to treatment technologies for inorganic contaminants (excluding metals) has been low compared to organic remedial methods. In general, inorganic treatment for anions such as chloride and sulphate are costly and cumbersome.

Chemical Addition/Flocculation

pH Adjustment: The are two main purposes for pH adjustment in the treatment of groundwater. The first is the adjustment of the groundwater to a neutral pH of around 7. The second purpose is the precipitation of heavy metals. In wastewater treatment, the preferred method of pH adjustment is to use two waste products of opposite pH to adjust the pH of both. In most cases this option is not available at ASGP's.

It is very rare for a groundwater to be too alkaline. The main reason for adding acids to a groundwater is for pH readjustment after the water has been raised to a high pH in order to precipitate a metal. A strong acid will be the normal method for this adjustment, because an industrial plant must be nearby in order for carbon dioxide to be a cost effective treatment alternative.

The main reason for pH adjustment is to remove heavy metals from the water. The pH will normally have to be raised above 7 to remove the metals, especially when the metals are held in solution by a chelate. The addition of lime or caustic soda (NaOH) is necessary to reach a higher pH. The main differences between the two compounds are that lime is less expensive and more difficult to use. Lime costs about 40-60% less than caustic. Lime is normally fed as a hydrated lime slurry. The material is stored dry and slurried before it is mixed with the acid groundwater. Lines can become clogged easily, so the slurry must constantly be kept in motion. The slurry should be introduced to the acid groundwater in a completely mixed tank. The slurry will take up to 30 minutes to completely react. This slow reaction time will make pH control more difficult. Also sludge will be formed in the process.

Alternatively, caustic soda can be delivered and stored as a liquid. The reaction time is faster (5-10 min), and the chemical can used in varying concentrations according to the existing pH. Also, less sludge is formed as a byproduct than with the lime slurry process. Following the addition of soda or lime to promote precipitation of a heavy metal, it will be necessary to lower the pH. This can be done by bubbling carbon dioxide in the water or adding a strong acid (ie. HCl, H_2SO_4, etc.). Adding a strong acid is the normal method for this adjustment, because an industrial plant must be nearby in order for carbon dioxide to be cost effective.

Chemical Addition Before Precipitation: Not all metals will precipitate upon an increase in pH. If the metals are being kept in solution by a chelate, they may be less likely to precipitate. Ferrous iron, hexavalent chromium and arsenic will not be removed by a simple increase in pH. These compounds require a chemical addition before they can be precipitated (Nyer, 1985).

Aeration alone is usually effective in the removal of iron when followed directly by filtration, provided that there is little or no manganese present. When both iron and manganese are present, aeration by itself is ineffective as precipitation is not instantaneous. Oxidation is required to convert ferrous iron to the ferric state. Addition of an oxidizing agent such as potassium permanganate is required to promote oxidation. Chlorine or chlorine compounds may also be used, but are not as strong an oxidizing agent, and are more hazardous to use (Kothari, 1988). A detailed discussion of pre-treatment for iron and manganese is presented in the Recommended Technologies section of this report.

Flocculation: From the addition of various chemicals and the adjustment of pH, remaining inorganic species in groundwater exist in the insoluble form. All of the material is now suspended solids that must be removed from the water. These suspended solids are all heavier than water. However, these solids are very fine and will not settle without being made to coagulate. This process is called flocculation.

There are two basic steps to flocculation. The first step is to neutralize particle charge so that the particles can come into contact. Once the particles are in contact, they will not separate unless subjected to high shear forces. Inorganic coagulants (lime, aluminum sulphate, ferric chloride, and others) can be used for this purpose. Coagulant aids include anionic and cationic polyectrolytes.

Settling Equipment: There are several types of settler designs that can be employed to remove suspended solids. These are:

(a) clarifier/thickener
(b) flocculating clarifier
(c) solids contact clarifier
(d) lamella

A clarifier/thickener is the simplest of the four designs. A description of these designs is given in Nyer (1985).

Filtration: Usually, suspended solids will not be removed by a settler. Even the most efficient clarifier will leave 5-10 mg/L suspended solids in water. The simplest form of filtration is to pass the groundwater through a bed of sand. The suspended solids attach to the sand particles, and the water continues through the bed. Two recent filter designs are "Dual Media" and "Tri-Media" filters. A dual media filter consists of a tank with a gravel support bed at the bottom covered with a 1 foot thick layer of fine sand and overlain by a coarser media also 1 foot thick consisting of anthracite coal. The cost of dual media system with a capacity of 10-15 gpm is approximately $25,000. A tri-media bed is similar to the dual media bed except that a layer of quartz sand is used between the fine garnet sand and the anthracite coal layer.

Costs: At a flow rate of 20 gpm, the approximate cost breakdown for a system designed in series using an aerator, clarifier, and sand filter is as follows:

Aerator:	$20,000
Clarifier:	$5,000 (minimum)
Sand Filter:	$5,000

A total cost for such a system (pH adjustment, flocculation, filtration) typically ranges from $30,000 to $50,000, depending on the complexity of the components. The treatment system described above is a multi stage process requiring chemical addition and pH adjustment, followed by removal of suspended solids through flocculation, settling and filtration.

Applicability: Treatment of contaminated groundwater for dissolved inorganics.

Status: Established.

Ion Exchange

The ion exchange properties of soil have been recognized since the 1850s. The largest use of ion exchange technology today is the use of synthetic resin beads for softening of home potable water. Ion exchange involves the exchange of an ion with a high ion exchange selectivity for an ion with a lower selectivity. Any divalent ion will usually have a higher ion exchange selectivity than a monovalent ion. For example, calcium, which is divalent, will replace sodium, which is monovalent, at an exchange site on an ion exchange bead. This is the basis of water softening. The calcium ion, hardness, exchanges with the sodium ion on the ion exchange resin. The calcium is removed from the water and the water has lost the ions that make it "hard". At many sites in Alberta, softening of groundwater will be required as a pre-treatment to prevent scaling problems in air-strippers and other treatment systems.

Heavy metals present in groundwater exist in the divalent or trivalent state, with the exception of hexavalent chrome. A simple sodium exchange unit will remove all of these compounds. However, the process is expensive, and the regeneration brine, with the heavy metals, will still have to be disposed of off site. These two problems severely limit the use of ion exchange as a treatment method for heavy metals. The best use of ion exchange is for very low metal concentrations and for final treatment before potable use.

Heavy metals exist as cations, positively charged. Ion exchange can also be used to remove anions, negatively charged. Chlorides, sulphates, nitrates, etc., can be removed by anion exchange resins (Nyer, 1985). Refer to the attached Figure 5.6 for the ideal resin concentration profiles and breakthrough curves.

Applicability: Treatment of inorganics in groundwater.

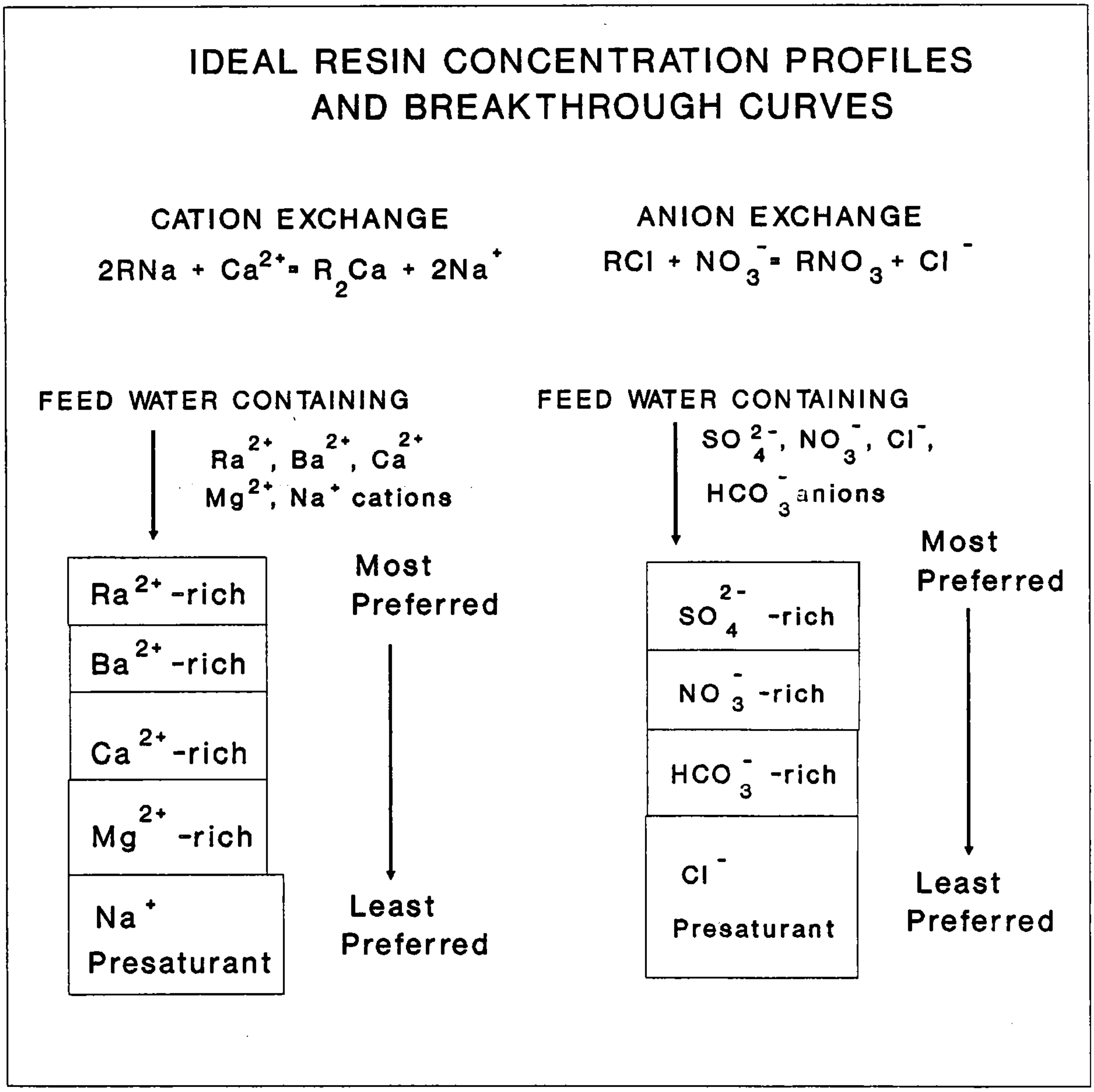
Status: Established, but not tested extensively for groundwater treatment applications.

Reverse Osmosis

Of the many membrane processes available for the separation of ions from solutions, only two, reverse osmosis (RO) and electrodialysis (ED) have reached the practical application stage for the removal of inorganic contaminants from waste water. Both processes remove salt from seawater and thus are commonly classified as desalination processes.

Reverse Osmosis (RO) uses semipermeable membranes and high pressures to force pure water through the membrane. The membrane reflects inorganic material and allows the passage of water. The separation is not perfect. Depending upon how the membrane is prepared, the salt rejection is anywhere from 50% to 99%. Staged systems can accomplish any required removal efficiency.

FIGURE 5.6
(AFTER CLIFFORD AND SORG, 1986)



Low molecular weight organic compounds pass through the membrane at higher rates than inorganics. Reverse osmosis is not a good technology for the removal of organic material. Reverse osmosis systems are readily available, but are expensive to operate due to the high pressures required (100-250 psi). The pH must be maintained between 5.5 and 7.5 to protect the membrane. Great care must also be taken to insure that no precipitation occurs in the RO module.

The advantages of reverse osmosis are that most contaminant ions and most dissolved non-ions are removed; it is relatively insensitive to flow and total dissolved solids level; a low effluent concentration is possible; and bacteria and particles are also removed in the process.

The disadvantages of RO are high capital and operating costs, a high level of pretreatment is required; the membranes are prone to fouling; and the reject stream is 20-90% of the feed flow (Nyer, 1985).

Reverse osmosis has seen limited application in the treatment of industrial wastewater because the membrane's sensitivity to fouling requires elaborate water pretreatment systems. This sensitivity is likewise a problem when RO is applied to the treatment of groundwater. In order to try and overcome some of these fouling problems, the water must be acidified before it enters the RO system, and then brought back to neutral after passage through the system. This complicates the treatment scheme and adds to the operating costs. Reverse osmosis membranes also produce a reject stream of as much as 50% of total flow, with much higher contaminant concentrations. This stream will still require treatment. As with ion exchange, this reject water can sometimes be more difficult to deal with than the contaminated water source (Peck, 1988).

Applicability: Treatment of inorganics in groundwater.

Status: Established.

Electrodialysis

Electrodialysis is a combination of membrane and ion exchange technologies. Electrodialysis uses ion exchangers in membrane form. The driving force across the membrane is provided by electric current. The ions are thus removed from the water and pass through the membrane, attracted by the opposite electric charge on the other side of the membrane.

The advantages of the system are that the residence time controls the amount of dissolved solids removed, and that the system can be run continuously with no regeneration required. The disadvantage of the system is that the water must carry an electric current. The cleaner the water, the more resistance to the current, which increases the cost of operation (Nyer, 1985). This would tend to render the costs of the process excessive at most ASGP situations where concentrations of inorganics are, in general, low. (No case history information or cost was found regarding the use of this technology for groundwater treatment.)

Applicability: Too expensive for ASGP inorganic treatment.

Status: Emerging, for groundwater treatment.

Distillation

Distillation is the evaporation of water followed by recondensation. The inorganics do not evaporate with the water and are left behind. The condensate is purified water. The process requires heating of the water to increase evaporation rates and cooling of the airstream to condense the water vapour. Volatile organics will evaporate and condense with the water.

The cost of heating and cooling the water can be very high. However, new technology in the area has produced multiple-effect distillation. Basically, this process uses the same energy several times in the process. Multiple-effect distillation has had broad applications in the Middle East. Although the technology is readily available, the cost is still relatively high for groundwater treatment.

Applicability: Too expensive for most applications, including the majority of inorganic groundwater contamination at ASGP's.

Status: Untested for groundwater.

Freeze Crystallization

Freeze crystallization is a process which separates dissolved contaminants from water by freezing. The technology is presently being evaluated by the USEPA SITE (Superfund Innovative Technology Evaluation) program, but very little information is yet available on the results of the assessment. The technology may hold promise for application at Alberta sour gas plants, if it can be adapted to take advantage of cold Alberta winter temperatures to assist in the freezing process. This could potentially reduce energy costs significantly. Freeze separation systems will require much additional study, research and adaptation before its utility to ASGP situations can be fully assessed. A complete description of the method is provided in the Recommended Technologies section of this report.

Applicability: Could be developed to treat groundwater contaminated by dissolved inorganics.

Status: Experimental, and promising. However much additional work is required before the method can be adapted to Alberta conditions.

5.2.5 In-situ Technologies

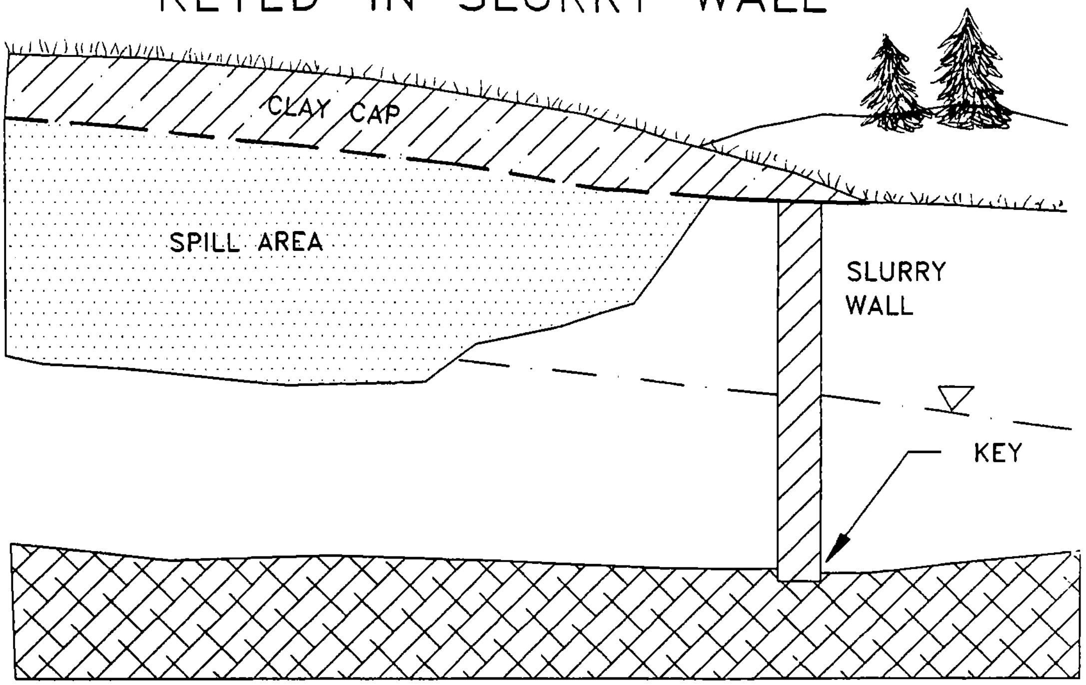
Physical Barriers and Containment Structures

Migration of contaminants in the subsurface can be controlled by low-permeability barriers or wells emplaced within the aquifer. Barriers can be constructed by injection of cement or bentonite slurry into a series of closely spaced boreholes (slurry-wall) or into a trench, or through the use of interlocking sheet-pile (Figure 5.7).

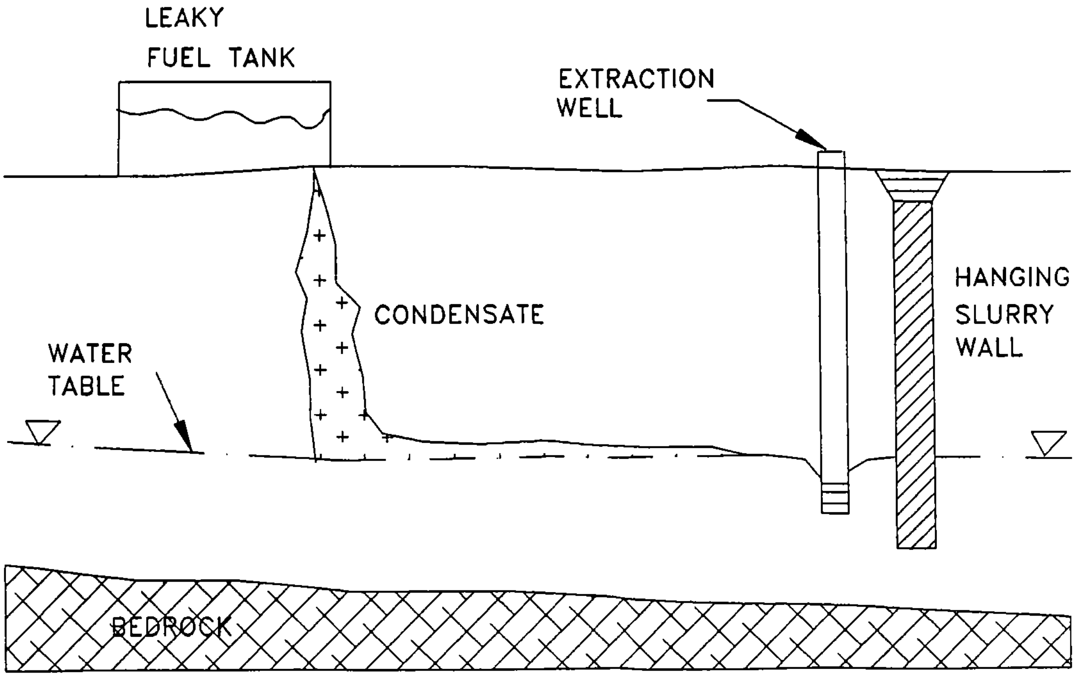
Physical barriers have been employed fairly extensively for this purpose, especially in the United States, with mixed results (Weston, 1988). Barriers are best employed in situations where groundwater flow is naturally restricted to a narrow zone or zones. In these cases, the extent of the barrier can be limited. In most circumstances, physical barriers will be used in conjunction with pumping wells. Specially designed barriers have also been used to assist in the collection and recovery of free product. Figure 5.8 shows a curved barrier used to concentrate free LNAPL towards a recovery well.

FIGURE 5.7

KEYED-IN SLURRY WALL



HANGING SLURRY WALL



(FROM "SLURRY TRENCH CONSTRUCTION FOR POLLUTION MIGRATION CONTROL," EPA-540/2-84-001, 1984)

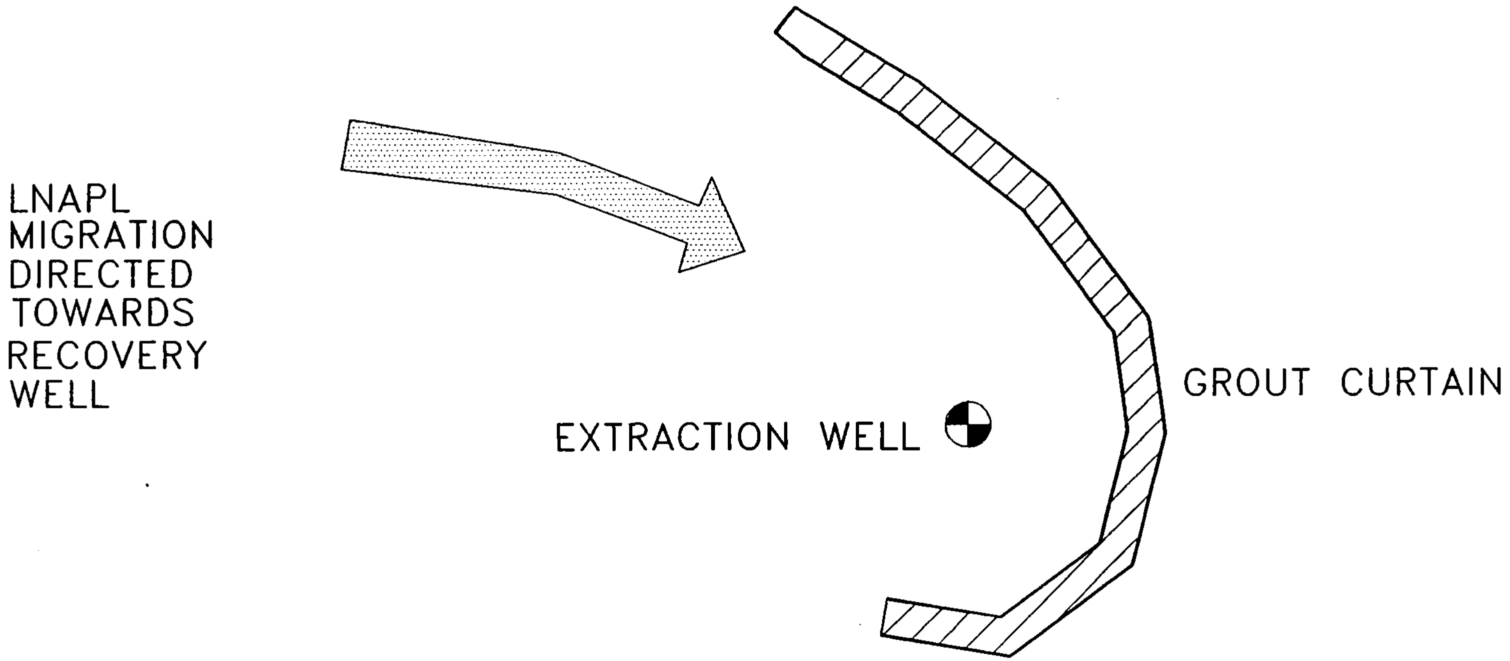


FIGURE 5.8 – CURVED BARRIER

This type of containment system is, in general, quite expensive. Costs will depend on barrier dimensions, reduction in permeability required, and the physical properties of the aquifer into which the barrier is to be placed. A grout curtain designed to prevent migration of contaminated groundwater at a sour gas plant in the foothills region of Alberta has been designed by Komex Consultants Ltd. The hanging curtain is anchored at each end into low-permeability shale units, and design dimensions were 30 m deep x 70 m across. The aquifer consists of fractured, medium grained sandstone of about 15% porosity. The design calls for a bentonite-cement slurry to be injected into three parallel rows of boreholes at 1.5 m spacings. It is estimated that the total cost of the wall could be in the order of $500,000 including engineering, materials and labour.

Applicability: Physical barriers are generally applicable to all groundwater contamination situations, but can only be considered practical in certain very specific situations. Containment of LNAPL is achieved with extreme permeability reductions due to relative permeability effects on LNAPL flow.

Status: Established.

In-situ Bioremediation

In-situ biotreatment is the biological treatment of contaminated soils and groundwater without excavation, usually where contamination is deep in the subsurface or under buildings, roadways, etc. In-situ biotreatment projects utilize various introduction techniques to deliver oxygen, nutrients and inoculum to the contaminated aquifer. Figure 5.9 depicts one delivery adaptation, an in-situ bioremediation project which is utilizing a recharge well as the treatment introduction point. Biological degradation of subsurface contaminants can be accomplished by delivery of oxygenated nutrient solution and inoculum to the zone of contamination. This stimulates indigenous microbes and also introduces known degraders. Contaminated soils above the water table can be treated by artificially raising the groundwater table. Water is cycled through the subsurface using a series of recovery and recharge wells or trenches. Water recharge with recovered groundwater and supplemental makeup water causes groundwater to mound in the water table where the bulk of the contaminants are located. The water is recovered in a down-gradient well or trench and is pumped to surface where it is

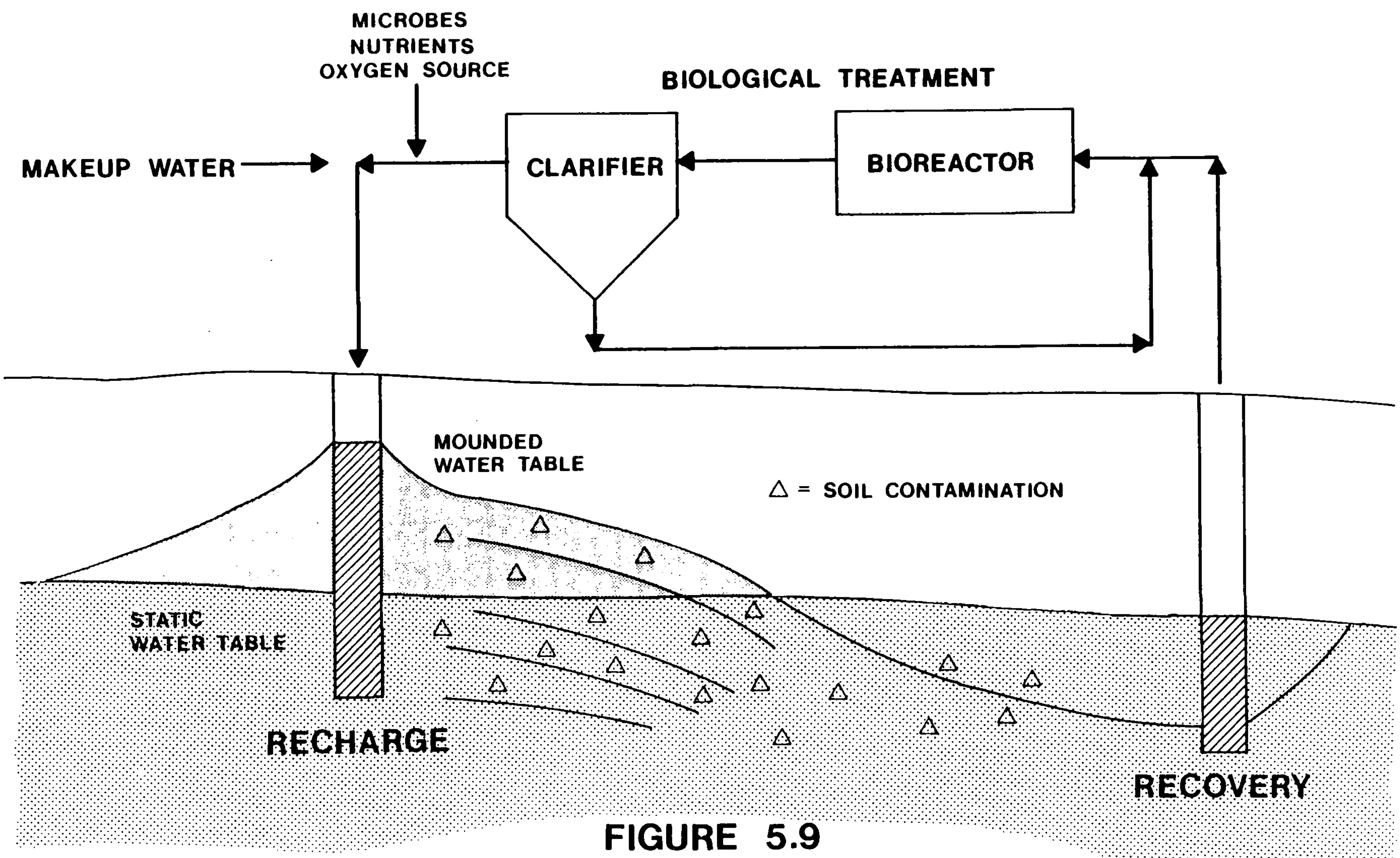


FIGURE 5.9
IN-SITU BIOTREATMENT
(USING RECHARGE WELL OR TRENCH)
AFTER FARLEY, 1990

treated to remove residual contaminants. It may then be amended with nutrients, oxygen and inoculum and reintroduced into the subsurface.

The water may be oxygenated by sparging with air or pure oxygen or by adding hydrogen peroxide which slowly decomposes to oxygen and water. When multiple recharge and recovery wells are used, the system can be cycled be reversing the flow to allow mounding of the groundwater (and biotreatment water) in other areas (Farley, 1991).

In-situ biotreatment involves the controlled management and manipulation of microbial processes in the subsurface. It requires an understanding of the microbiological processes needed to degrade the target contaminants, and the soil's chemical and physical environmental effects on the microbial processes. The engineering of any in-situ bioremediation project is highly dependent on the types of contaminants present, permeability of the aquifer and regulatory constraints. Due to the many variables involved, the costs of in-situ biotreatment vary greatly (Farley, 1991).

Applicability: In-situ bioremediation can be applied to situations involving hydrocarbon/organic-contamination of soils and groundwater (situations T1A/T2A, R1A/R2A).

Status: Emerging, not yet demonstrated at Alberta sites.

Biobarriers

This technology is an extension of "conventional" in-situ bioremediation which takes advantage of the tendency for biota to proliferate and clog aquifer pores. Experimental research has demonstrated that plugging of porous media can be achieved in the presence of high BTX concentrations by adding nitrogen, phosphorous and a primary carbon substrate such as nitrate. Such clogging can be induced in desired areas to build-up what are essentially physical barriers to contaminant migration. The added attraction is that the barriers not only prevent movement of contaminants, but also actively degrade them.

Complete fouling has been found to occur in as little as eighteen days, given proper conditions. The technique has been identified as a potential containment technology by Ortech (1990) as part of a GASReP-funded study. This work was carried out at the laboratory scale, and little is known about the success or costs of field-scale applications. As described in the section on physical barriers and containment structures, the use of barriers to groundwater flow for site remediation applications has in general fallen out of favour in the last five years, due to poor overall performance and cost-effectiveness at numerous sites in the U.S. There are, however, certain conditions where physical or biological barriers may be of great value. These situations are very site-specific, but would tend to involve cases where groundwater flow is severely controlled by natural barriers or structure, and off-site migration control by hydrodynamic means is difficult.

Applicability: Certain site-specific situations may call for the use of barriers to prevent contaminant migration.

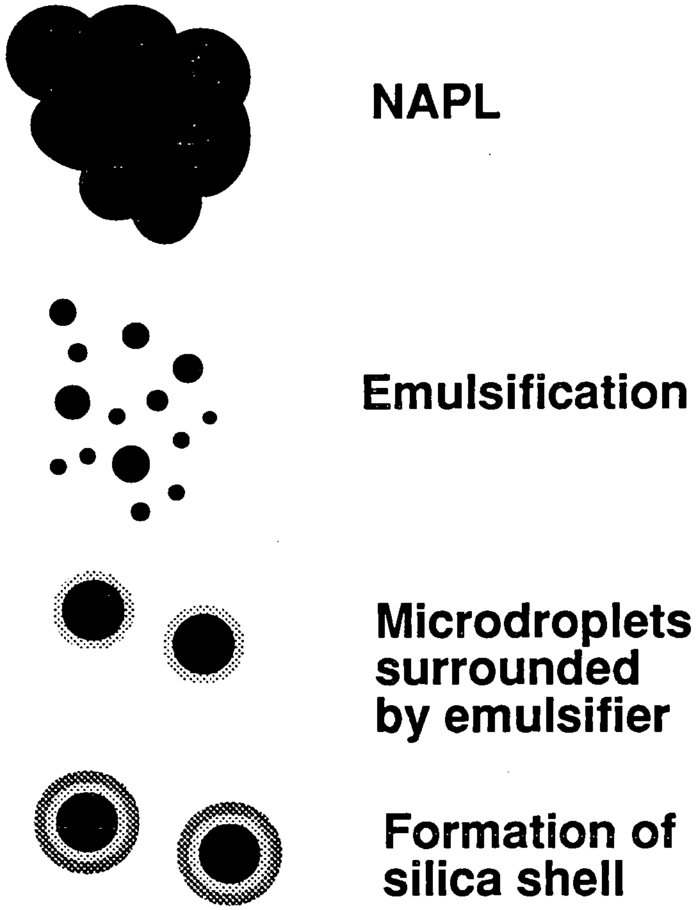
Status: Experimental.

Chemically-Enhanced Solubilization and Surfactants

Chemically-enhanced solubilization is the use of miscible co-solvents or surfactants to increase the solubility of NAPL in groundwater, thereby allowing increased chemical mass removal by groundwater pumping. Miscible co-solvents such as methanol are known to increase the solubility of organic compounds (Rao et al., 1985) but co-solvent concentrations must be in excess of 20% to 30% to achieve increases in solubility greater than a factor of 10. The addition of such solvents is not recommended for use with gas condensates, as the solvents themselves may act as an additional groundwater contaminant.

In comparison, many surfactant compounds are much more effective solubilizing agents. At concentrations ranging from 0.1% to 1%, many surfactants can substantially increase the solubility of organic compounds (Roy and Griffin, 1988). The effectiveness of surfactants depends on the formation of aggregates of surfactant molecules or micelles in solution. Diagrams of surfactant molecules and the formation of micelles are shown in Figure 5.10. Surfactant molecules typically have a hydrophillic end (often ionic) and a hydrophobic end (usually a long hydrocarbon chain). At higher concentrations, the surfactant molecules aggregate. The hydrophobic ends of the molecules prefer to associate with each other rather

FIGURE 5.10
REACTIVE SILICA TECHNOLOGY



than the water, and form micelles. The formation of micelles for a given surfactant occurs at a specific surfactant concentration known as the critical micelle concentration (CMC). The aggregation of the hydrophobic ends of the surfactant molecules creates a concentrated zone of hydrocarbon material which will attract dissolved hydrophobic organic chemicals from water into the micelles. In this way, the mass of chemical in solution (dissolved plus micellar) can be increased above the normal water solubility of the chemical (Feenstra, 1991).

Chemically-enhanced solubilization for NAPL clean-up has been studied at a laboratory scale by Ellis et al. (1985) and McDermott et al. (1988) and is currently being studied by Dr. John Fountain at the State University of New York at Buffalo. Laboratory studies indicate that chemically-enhanced solubilization can be highly effective in the removal of NAPL from soils. Chemically-enhanced solubilization was demonstrated on a pilot scale by Nash (1988) at a site contaminated by solvents and petroleum fuels and was found to be far less effective than suggested by laboratory studies. The ineffectiveness was attributed to heterogeneity of soils. The surfactant solutions introduced into the subsurface followed the zones of highest permeability. Chemical removal in these zones was effective. However, the surfactant solutions did not penetrate lower permeability zones and here chemical removal was minimal. As such, the use of surfactants is likely to be plagued by the same limitations as all pump-and-treat schemes. The effects of aquifer heterogeneity will have a profound impact on remediation levels.

As is the case for surfactant mobilization, the evaluation of a suitable surfactant for chemically-enhanced solubilization must include its potential environmental effects. Surfactants used for chemically-enhanced solubilization will also reduce the interfacial tension of the NAPL, and remobilization of NAPL must also be considered. Laboratory testing of surfactants conducted by Dr. Fountain at SUNY, Buffalo indicates that there are surfactants available from an environmental perspective which reduce interfacial tension by only a factor of 10. Although, a factor of 10 reduction in interfacial tension is modest in comparison to the 100 to 1000 fold reduction by other surfactants, this reduction may still be sufficient to result in further undesired spreading of NAPL (Feenstra, 1991).

Applicability: Surfactants can be used in conjunction with pump-and-treat to improve remedial performance for gas condensates (situations T1A/T2A, R1A/R2A).

Status: Emerging.

Fixation - Reactive Silicate Technology

Encapsulation using reactive silicate technology has been proposed as a technique for in situ immobilization of hydrocarbon contamination. Encapsulation involves emulsification of the LNAPL with a surfactant followed by treatment with a soluble reactive silicate reagent. The silicate reacts with the surfactant surrounding the droplets of emulsified NAPL and forms an insoluble silica shell around the droplet. The LNAPL is thus encapsulated, although a small amount of dissolved chemical from the LNAPL may diffuse out through the silica shell into the groundwater over an extended period of time. This technology has been demonstrated on petroleum hydrocarbons in the laboratory (Feenstra, 1991).

This technology has the same potential difficulties in fractured rock as other technologies which depend on introduction of a chemical agent and alteration of the physical/chemical properties of the LNAPL. The emulsifying agent will invariably lower the interfacial tension of the NAPL and could result in remobilization and worsening of the extent of LNAPL contamination. In addition, depending on the nature of fracture interconnection and NAPL distribution, it is unlikely that chemical agents could be introduced into all zones where LNAPL was present. For this technology it is particularly critical because one encapsulation begins, the encapsulated LNAPL particles will likely plug fractures and restrict further introduction of the chemical agents (Feenstra, 1991).

Applicability: All situations involving condensate (T1A/T2A, R1A/R2A).

Status: Experimental. Only tested to date under laboratory conditions.

In-Situ Air Stripping/ Subsurface Volatilization and Vapourization (SVVS)

This technique is simply an amalgamation of two fairly established remedial methods: soil vapour extraction and air-sparging. Air-sparging, or in-situ air-stripping, is a process whereby air is injected into the contaminated aquifer via an injection well. As air bubbles into the formation, dissolved VOC's such as BTEX are volatilized (in much the same way as a counter-current air-stripper) and carried to the groundwater surface in the vapour phase. Once released into the unsaturated zone, organic vapours are collected by nearby vacuum extraction wells. Systems are usually designed with injection and vapour extraction well pairs.

The technique has been applied successfully at several hydrocarbon-contaminated sites in the U.S., with favourable results. The overall costs of subsurface volatilization systems will be low.

The advantages of these systems include the fact that air-sparging will also significantly increase dissolved oxygen levels in the aquifer, enhancing biological activity. If an in-situ bioremediation system is in-place or is being complemented, a simple coupling of sparging wells with SVE systems would enhance site remediation.

For the problem of residual saturations of LNAPL condensate trapped below the groundwater surface, this system is ideal. If LNAPL is present at significant depths below the groundwater surface, the method of lowering the water table for exposure to SVE is not generally effective. In these cases, in-situ air-stripping provides a remedial solution.

This technology is described in detail, including cost and case history information, in the Recommended Technologies section of this report.

Applicability: Situations involving dissolved hydrocarbons and volatile organics in groundwater (T1BC, T2BC, R1BC, R2BC) and LNAPL condensate, particularly in the saturated zone (T1A/T2A, R1A/R2A).

Status: Emerging. Components, however, are fairly well established.

Chemical Addition / Flushing

In essence, this is not a technology but a remedial approach, and is suited for groundwater affected by low pH conditions. Through a pump-treat-and-reinject system, buffering solutions are flushed through the contaminated aquifer, increasing the pH of the groundwater. This simple method would involve minimal costs over and above a pump-and-treat system. Capital costs would include mixing tanks and dosing equipment. Operation and maintenance costs would include buffering agents ($CaCO_3$), power, and additional injection well maintenance requirements stemming from possible scaling and precipitate problems. No information on the application of this technique was available in the literature.

Applicability: Groundwater with low pH conditions (T1D/T2D, R1D/R2D).

Status: Established.

Buffer - Trenches

Another possible method of preventing migration of low pH groundwater and buffering acid seepage is the use of trenches backfilled with buffering agents. This technique would be suitable for sites where the groundwater table is within 2.5 to 3 metres of the surface. Major costs would be excavation and backfilling. Depending on pH conditions and groundwater flow-rates, buffering materials would have to be periodically replenished. However, once in place, maintenance would be minimal. No information on the application of this technique was available in the literature.

Applicability: Shallow groundwater in surficial materials with low pH conditions (T1D/T2D).

Status: Emerging. Has not been tried at ASGP's.

5.3 SOILS / UNSATURATED ZONE REMEDIATION TECHNOLOGY

5.3.1 General

Overview

Data review from recent reports indicated contamination of soils in and around gas plants resulted from five main components. These were:

- sulphur (as elemental sulphur or sulphate ion)
- hydrocarbon (majority as C5-C14 type condensate)

- metals (leached as a result of low pH)
- anions/cations (brine and process water derivatives)
- sterilants (from vegetation control programs)

Material streams were often commingled either as raw product or as waste streams. As a result, at those facilities where contaminants are present in the unsaturated zone, a mixture of contaminants or their derivatives is regularly found.

Research and development of remediation methodologies for contaminated surficial materials at sour gas plants were initially directed towards sulphur block pads. More recently, experience involving partial or complete decommissioning of sour gas plant sites has generated increased interest in remediation methods for process water pond sludges, hydrocarbon contaminated soils, and brine and metal-contaminated soils. During the 1980's a number of remediation methodologies were tested at sour gas facilities. In many cases on-site remediation was considered too expensive, the success of a methodology was uncertain, or regulatory agencies could not assure companies of process acceptance. In a majority of these cases contaminated soils were removed to an off-site disposal facility such as a regional landfill.

Current criteria established for soil clean-up around sour gas plants have allowed a certain level of organic and inorganic contamination to remain in the unsaturated soil zone. For example at one plant recently decommissioned the lower limit for removal of contaminated soils was 2% total hydrocarbon by weight. This poses an insignificant problem in the upper 30 cm of the aerobic zone. However if contamination extends below this level, biological activity is curtailed and the hydrocarbon continues to be a potential source of organic contamination to groundwater. This problem is of increased concern with contaminants such as sulphur and brine which are not naturally recycled biologically, but are highly soluble and leach readily into the unsaturated zone.

5.3.2 Ex-situ (Excavate and Treat) Technologies

The use of *ex-situ* (excavate and treat) methods of contaminated soil treatment is well established. At Superfund sites in the United States and in Europe several methods have been developed and used successfully for ex-situ decontamination. A recent study conducted by Intera Kenting (GASReP, 1990) provided a review of 45 separate ex-situ technologies for treatment of soils contaminated with hydrocarbons, wood preservatives and chlorinated solvents. Rather than duplicate this extensive computer, literature, and site review the results of this GASReP-funded study have been used wherever applicable. The technology categories that could apply to the contaminant situations at Alberta sour gas plants are:

1. Thermal treatment
    - destructive
    - non-destructive

2. Physical treatment
    - stabilization/solidification
    - soil washing
    - floatation
    - burial and capping

3. Chemical treatment
    - solvent extraction

4. Biological treatment
    - enhanced landfarming
    - surface bioreactor

However, the main problem with the use of ex-situ treatment methods at sour gas plants is the fact that the contaminants have spread from the original source area, increasing substantially the volume of contaminated surficial material. Ex-situ methods are best applied to the source material, such as pond sludges, recently contaminated sites (eg. spills), sulphur pads, and/or landfilled materials.

The purpose of the ex-situ treatment technology review is to establish the applicability and effectiveness of technologies for remediation of soils contaminated by sour gas plant activities.

Applicability and effectiveness are assessed on optimal contaminant removal and treatment unit cost.

Excavation and Material Handling

A major component of ex-situ soil decontamination may involve movement of the material from the site to treatment location and to disposal, or within the site for on-site treatment. This involves excavation, trucking, disposal fees, clean-fill acquisition, and site restoration. These costs increase substantially with the depth of excavation and hauling distances. Without specific site information, an accurate assessment of the cost of a specific technology cannot be undertaken. Even though the unit cost for treatment is attractive, total project costs due to materials handling and site restoration may be prohibitive.

Costs for materials handling can vary substantially due to site related factors. However, for the purposes of this study, some unit costs can be assumed. The unit costs presented reflect information from standard engineering texts, recent literature and experience at Alberta sour gas plants (Weston et al, 1989, Calbrese and Kostecki, 1989, Fluter Oilfield Service, 1990). Unit costs used are:

1. Scrapers - \$5.50-\$6.50/m^3
2. Backhoes - \$3.75-\$4.75/m^3
3. Loaders - \$2.20-\$3.20/m^3
4. Trucking - \$2.00-\$3.00/km
5. Site Supervision - \$600.00/day
6. Labour - \$22.00-\$27.00

In addition to material movement to and from the excavation for treatment, the cost of material preparation is frequently (purposefully) left out of the treatment cost when initial project scoping quotations are made. Material preparation can include some or all of the following processes:

- sorting
- grinding
- drying
- blending with additives

Frequently, ex-situ process costs or flow schematics do not include final disposal schemes and costs for disposal of the process by-products. By-products requiring further treatment may include:

- contaminated water
- ash
- concentrated contaminated solids

Thermal Treatment

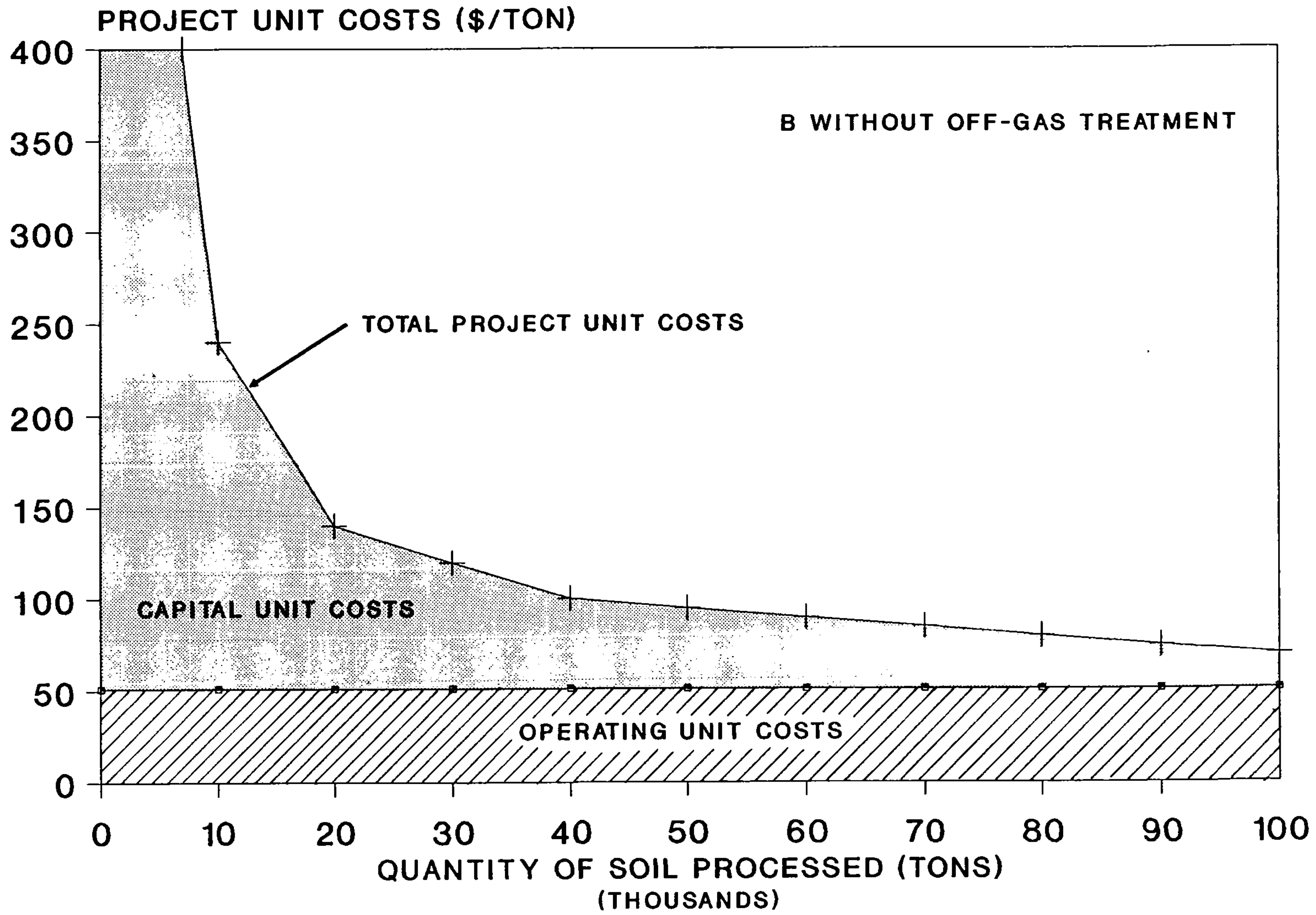
Destruction and/or removal of organic contaminants from excavated soils by thermal treatment is well established in the United States. To date thermal methods have been considered some of the most cost effective methods of treating organically contaminated soils on-site. A variety of incinerators are commercially available using various heat ranges and gas recovery systems. The common types are:

- Rotary Kilns
- Fluidized Beds
- Infra-Red Furnaces
- Pyrolytic Gasifiers
- Low Temperature Direct and Indirect Fired Volatilizers

Each type has advantages and disadvantages depending on the soil/contaminant matrix. The costs for operation range from approximately $100 to $1,700 per tonne of soil depending on the economies of scale and actual contaminant constituents and concentrations. Figure 5.11 shows typical costs for low temperature thermal stripping of different volumes of soil. Alberta has recently promulgated new air pollution regulations which will further restrict the use of thermal treatment due to emission limitations. Emission guidelines increase the equipment necessary for flue gas cleanup, thus increasing capital and operating costs. This does not pose a significant problem if hydrocarbons are the only contaminant. However where contaminant mixtures include sulphur, metals and other inorganic constituents, flue gas cleanup and ash disposal become more significant problems.

FIGURE 5.11

COSTS OF LOW TEMPERATURE THERMAL STRIPPING UNIT



The main organic components present in the unsaturated surficial material at sour gas plants are light hydrocarbons and amine by-products. In most cases the surficial material is primarily clay. For these situations the four most applicable ex-situ thermal treatment units were considered to be;

- portable pyrolyzers;
- portable rotary kilns;
- portable circulating bed combustors; and
- low temperature volatilization;

These systems will manage large cobbles and coarse material found at S1A type sites. Removal efficiency is 99.99%. Taciuk process costs would range from $140-190 per tonne processed. Rotary kiln process would cost between $200-400 per tonne processed. Low Temperature Thermal Processing involves volatilization and recapture of the hydrocarbons. This process allows high volume processing (30-50 tonnes/hr) at a cost of $100-180/tonne. Excavation, handling, and site restoration would cost $20-30 per tonne. Test burn results would need to be supplied to Alberta Environment prior to permit being issued. Test burn sampling costs are $25,000-$75,000 for permit requirements. Low temperature treatment would be most applicable for condensate-contaminated soils.

Applicability: Organic-contaminated soils (situation S1A/S2A; S1BC/S2BC).

Status: Established.

Physical Treatment

Solidification/Fixation

Solidification/fixation has been utilized successfully to stabilize process sludges and underlying contaminated soils, oil and metal contaminated sludges, and landfill sludges and underlying contaminated soils. The fixation methods used have depended on the site specific conditions and contaminated soil properties. The main constituent of solidification mediums is a cement. Various plastic polymer additives have also been used in the process.

Process pond sludges and oily sludges have been solidified with little or no disturbance of the materials surrounding the ponds. Special equipment is used to mix the contaminated materials and fixation additives within the pond. The ponds were then capped and the site revegetated. Other ponds have been excavated and the contaminated materials mixed with the solidifying agents in a special batch mixing unit. The contaminated soils underlying the pond sludges have then been ripped to the required depth and the soils mixed with the solidification agents. The excavated, batched material was then placed into the pond and the site capped and revegetated. One landfill (including the underlying contaminated soils) was excavated and batch mixed with a Portland cement and polymer additive. The cement was then used to construct non-structural items around the plant site such as concrete pads, sidewalks, and drainways. The cleaned landfill was allowed to remain open to allow natural flushing of the site.

The use of fixation agents to contain contaminants within a soil matrix has been extensively used in the United States, Europe and Japan. The process is effective for soils contaminated with a mixture of organic and inorganics. The leaching potential increases as the organic content of the treated soil material increases. A number of solidification projects have been completed at Alberta sour gas facilities in recent years. Solidification tends to be viewed with some distaste since the contaminated material remains on-site and may present a liability. The process could be effective for low level soil contamination that would be considered for on-site disposal if the leaching potential could be reduced to an acceptable level.

Solidification has good potential for the ex-situ treatment of contaminated surficial materials at sour gas plants. The process can deal with commingled waste streams where the contaminant concentration is variable. Potential stabilization/solidification processes applicable to sour gas facilities include:

- portland cement based
- lime based
- silicate based

Soil Washing

Soil washing is a physical transfer process in which contaminants are removed from the soil and become dissolved or dispersed in a fluid such as water, with or without chemical additives such as detergents and surfactant (Offcut et al, 1988).

Soil washing is effective for the removal of a wide range of organic contaminants, and is useful where the removal of inorganics is required. Soils contaminated with hydrocarbon and inorganics are one of the most common situations at sour gas facilities. This process could be used effectively (possibly in conjunction with biological treatments) to reduce cation/anion content and allow microbial activity to proceed uninhibited on the remaining organics. There are presently mobile pilot plants available for site testing from Alberta Solids Treatment Company Ltd., Alberta, Biotron Inc., Minnesota, and Petrocycle Inc., Levis Quebec. These have been used successfully in treating soils contaminated with heavy oils and salts. Biotron Inc. has coupled a bioreactor to treat water produced in the process. Some metals removal can be achieved if the exact type and concentration is known prior to process setup.

Within the Alberta oil and gas industry variations on soil washing are used by most of the oilfield waste reclaimer companies. These companies have not upgraded their processes to maximize removal efficiencies for organic or inorganics. In general this is a result of economic pressure exerted by oil and gas operators.

Applicability: Soils contaminated with organic and organic contaminants.

Status: Established.

Floatation

Floatation has been used by the mining industry for many years. Froth floatation is the main method of separation of base metals. Within the context of this study two processes may be applicable:

- coal particle floatation (Aglo-floatation TM)
- air sparging (Procor Sulphur Systems)

Coal particle floatation was developed to deal with high volumes of hydrocarbon contaminated soil commonly associated with heavy oil developments or coal tar waste dumps. It would have application at sour gas plants only for large volumes of highly contaminated surficial materials.

Status: Emerging.

Air-sparging

Air sparging is being developed by Procor Sulphur Systems Inc. to increase total recovery of sulphur during sulphur block base pad cleanup. Present methods generally reduce total sulphur to approximately 5%. Procor has indicated that the air sparging method will reduce base pad sulphur levels to 1-1.5%. Coupled with present sulphur pad reclamation techniques this will significantly reduce sulphate in the underlying soils and groundwater.

Applicability: Sulphur-contaminated soils.

Status: Established.

Chemical Treatment

Chemical treatment is generally considered to be solvent extraction of organic constituents. It is differentiated from soil washing in that it uses only solvent as the carrier medium. Several patented methods have been developed. Each requires the following site specific information:

- matrix type and grain size
- matrix water content
- contaminant characteristics and concentration

From this information, the ratio of solvent to matrix, and the number of contact cycles required are determined. The processes can use either critical or non-critical fluid solvents.

Solvents used for non-critical extraction are:

- triethylamine (TEA)
- acetone/kerosene

- fluorocarbon-113/methanol
- toluene
- proprietary solvents

Solvents used for critical extraction are:

- carbon dioxide
- propane
- butane

These processes have been successfully employed to remove hydrocarbon and chlorinated organic compounds from soils. They operate most efficiently when a continuous flow system can be established. Propane/butane mixtures have been the most successful extracting hydrocarbons from soil matrices. They do not remove inorganic components such as sulphur, salts and metals.

At gas plants where large volumes of soil must be treated to remove hydrocarbons the critical fluid process may be applicable since propane/butane is generally available. Also the process of working with gases at critical phase is relatively well understood by gas plant operators.

Critical Fluid Extraction

Critical Fluid Extraction may be used successfully at sites involving low permeability soils contaminated with gas condensate (S2A). The CF Systems Process deals with fine grained soils. The treatment method requires that soil be slurried. Plant propane/butane could be used and returned to the process. Extraction efficiencies for condensate type hydrocarbons are 80-99.9%. Costs range from $190-$500/tonne including the cost for handling and slurrying the soils. The slurried soil requires dewatering.

Applicability: Generally applicable to situations involving low permeability soils contaminated with gas condensate (S2A). However, may be expensive.

Status: Emerging.

Biological Treatment

Biological treatment is well known through the development of land-farming operations and biological reactors. Several oil reclaimers and oil refineries have established land-treatment operations and bio-reactors of various types to deal with hydrocarbon contaminated soils. In the past two years, further effort has been applied to assess the effectiveness of bio-inoculation and bio-augmentation to enhance the efficiency of these systems. The use of specific microbial species at high concentrations can in some cases significantly reduce the time required for the maintenance and monitoring of a land-treatment area. Ex-situ biological treatment processes are discussed in detail in the Recommended Technologies section of this report.

Landtreatment

The treatment of certain organic contaminated soils has been tested at sour gas plants. Oily sludges and amine/glycol contaminated sludges mixed with contaminated soils have been treated in this manner. Generally these have been one-time treatment applications completed under approval from the appropriate regulatory agency and where groundwater monitoring systems were established. No permanent land-treatment facilities have been established at Alberta sour gas facilities to deal with contaminated soils or organic wastes.

Land-treatment facility costs vary significantly depending on whether a liner and leachate collection system are required and the extent of groundwater monitoring requirements. Land-treatment can be enhanced through a number of bio-augmentation and bio-inoculation methods.

Enhanced Landtreatment - On-Site

Excavation and land-treatment of contaminated material is a viable remedial alternative in many situations. One consideration is the presence of permeable surficial materials at a given site, which may become contaminated by leachate from the excavated soil. In such a case, a site near the plant offering some protection against infiltration of contaminated fluids would have to be developed. Figure 5.12 shows a diagram of such a site. Cost of site development could be $100,000.00-$150,000.00. Land treatment costs would be $100-$150/tonne for the initial year of treatment. Contaminant removal efficiency would be approximately 70-80%. Excavation, handling, and site restoration would cost $20-30 per tonne. Additional costs would be associated with acquisition of clean fill amounting to $4-$5/tonne required.

Enhanced Landfarming would allow a phased approach to the contaminant removal if the land treatment site were operated over several years. Capital costs would be spread over several operating years. Site disturbance would be longer term but perhaps less disruptive.

Applicability: Can be used effectively to treat petroleum-contaminated soils (PCS) which have been excavated from sour gas plant sites.

Status: Established.

Bioreactors

Bioreactors are vessels, tanks and aerated cells in which biodegradation of contaminants can be controlled and enhanced. They offer advantages over conventional land-treatment such as better process control, improved contaminant availability for microbes, better clay soil treatment, reduced space requirements, and more effective degradation of complex organic. Drum type or slurry phase bioreactors could be employed to deal with hydrocarbon contaminated soils where a landfarm is not available, and/or space and time are limited. Bioreactors allow the soil to be treated and reused as fill for the excavation eliminating the need for clean fill material to replace the landfarmed material. Presently, a Gulf Canada Resources Ltd - led team is engaged in the construction and testing of a bioreactor system for treatment of contaminated soils at the Nevis sour gas plant in Alberta.

Applicability: PCS excavated from sour gas plant sites.

Status: Emerging technology.

Summary

The ex-situ technologies reviewed above have applications for unsaturated zone decontamination in specific situations at Alberta Sour Gas Plants. However, in general, these technologies are not applicable to the remediation of extensive, low level, contamination scenarios. This is true especially where the contamination extends beyond the 2 metre depth. Ex-situ treatment is best suited for localized situations such as pond sludges and underlying contaminated soils, sulphur block base pads, landfills, and high concentration hydrocarbon soil contamination (eg. pipeline breaks, longterm spillage). These "localized" situations, or "hot spots", were shown to be the major contributors to groundwater contamination. However, little or no data was available on the concentration of contaminants laterally and vertically in the soil column (CPA, 1990).

Obviously ex-situ treatment is not applicable for contaminated soils around operating buildings, vessels and piping except for small volumes or problematic materials (eg. TCE spills).

The main requirement for excavate and treat methods of soil remediation is accurate specific knowledge of site conditions, contaminant characteristics, by-product final disposal, and cost of material management. Excavate and treat technologies may be applicable to some situations involving low pH conditions in soil, particularly if organic contaminants are also present.

5.3.3 In-Situ Technologies

Introduction

A great deal of uncertainty presently exists concerning most soil remediation techniques. Understanding of controlling factors, clean-up mechanisms, practical application and optimization of processes remains lacking. In addition, verification of claims of success also require investigation (for instance was a claimed bioremediation success actually the result of biological metabolism of a material, or was volatilization partly responsible?). Many of the newer technologies are not well developed or understood, and many must be considered as experimental (USEPA, 1988).

Enhanced Volatilization

Enhanced volatilization removes volatile organic compounds from soils by contacting contaminated material with air, and inducing transfer of volatile from liquid or adsorbed phases to vapour phase. Exposure of soils to air can be achieved by a number of means:

- Mechanical tillage: near-surface soils are mechanically tilled to increase volatilization rates. This process can continue in layered fashion. Previously tilled soil is removed to a pile, and tilling of a next layer proceeds. Weather and soil-types are factors. Shredding equipment, tractors and similar equipment are widely available. This method is limited to maximum depths of about 1-2 metres, depending on availability of storage space for removed soils. VOC's are released to the atmosphere.

- Enclosed mechanical Serration: soils are excavated and mixed in a rotary drum, releasing volatile organic through volatilization. This system allows collection of off-gases, but is more capital and labour intensive than tillage.

- Low temperature thermal stripping: similar to mechanical aeration, but enhanced through heat transfer to soils. Increased temperatures speed up volatilization and increase efficiency.

- Pneumatic Conveyer systems: use elongated ducts through which contaminated soils are mixed with high speed air currents, stripping VOC's into vapour phase. Similar to air-stripping for groundwater.

Applicability

Of the enhanced volatilization methods, the USEPA (1988) suggests that low temperature thermal stripping systems provides best results for organic compounds with high vapour pressures. Alberta condensates typically contain a large proportion of light volatile hydrocarbon compounds suitable for this techniques.

The technique is generally applicable to contamination situations involving gas condensate in soils. (SIA, S2A)

Costs

Tilling of contaminated soils may be the least costly of the enhanced volatilization methods if sufficient area is available on-site to pile and spread material. In many cases this will not be possible. For the other methods, capital costs are much greater. Overall costs will depend on volume of soil to be treated. The results of an economic analysis performed by Weston Inc. (1986) are summarized as follows:

- For 15-18,000 tons, costs may range from about \$100/m^3 to \$250/m^3 without off-gas treatment. Off gas-treatment is expected to add approximately \$10 to \$25/m' to overall costs.

- For 1000 tons of soil, costs may range from \$70 to \$140/m^3 for most system configurations, with capital costs making up a significant portion of total costs.

- In general, costs for processing less than about 10,000 tons of PCS would be in the order of \$300/m^3.

Detailed case histories of enhanced volatilization are presented in USEPA (1988) which describe 99.99 percent removal of VOC's. Factors affecting treatment effectiveness include temperature, soil type and preparation, residence times in rotating drums, airflow rates, and contaminant types. The method can treat large volumes of contaminated soils on-site.

Status: Established, but specific research still required.

Soil Vapour Extraction

The SVE technique can be used to remediate soils/unsaturated zone contaminated with volatile organic compounds. It is an in-situ technique and does not involve excavation of PCS.

Air-flow is induced in the contaminated areas of the subsurface by means of shallow wells to which vacuum pressure is applied. Air injection to the subsurface can be passive or active. As air moves through the unsaturated zone, VOC's are volatilized and removed through the extraction wells. Vapours can be discharged to the atmosphere or collected and treated. Figure 5.13 shows a schematic diagram of the SVE system.

The technique has been widely applied to treat gasoline-contaminated soils but much uncertainty remains regarding its effectiveness (USEPA, 1988). Under ideal conditions, SVE has achieved removal of more than 99% of bulk volatile hydrocarbon initially present at residual saturation in the subsurface (Hoag et al, 1986; Mendoza 1991).

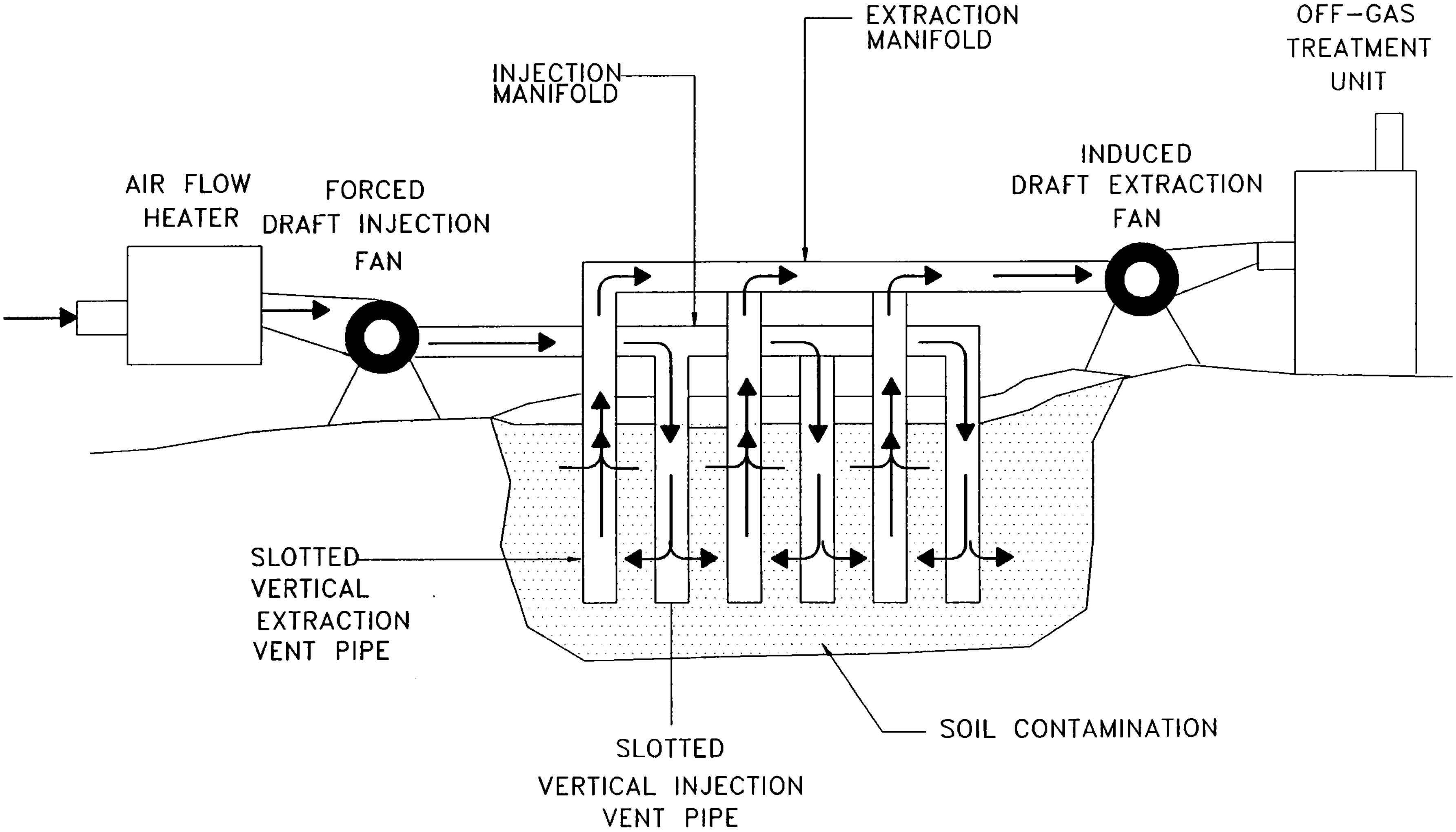


FIGURE 5.13
SCHEMATIC OF VACUUM EXTRACTION SYSTEM

Much information on the SVE technique is available in the literature, including overviews, theoretical discussions, and field demonstrations/case histories. Nyer (1985) and USEPA (1988) present good general overviews of the subject. A comprehensive review of the technique and a review of pertinent case histories are provided in the recommended technologies section of this report and in Mendoza (1991).

Major capital costs for SVE systems are well installation and pump hardware. Off-gas treatment is not presently required in Alberta, but has been found to almost double capital costs of such programs (USEPA, 1988). Overall treatment costs (including O&M) have been estimated at from \$25 to 40/m' exclusive of off-gas system costs.

Major limitations of the SVE method at ASGP's would include the fact that not all components of natural gas condensate are readily volatilized at typical sub-surface temperatures (4-10°C), and geologic heterogeneity of sites. The method works best in high-permeability media such as uniform sands and gravels. However, enhancements to the technique are possible, including the use of sub-surface heating technique to improve rates of volatilization.

Applicability: The method is applicable for the remediation of condensate contamination in the unsaturated zone (S1A; S2A). SVE has also been used to remove bulk LNAPL contamination on the groundwater surface (T1A; T2A; R1A, R2A, XA).

Status: Established. Enhancement of technique and testing at ASGP's on condensate still need to be evaluated.

<u>Air Sparging</u>

Another method of cleanup that is currently being investigated for the capillary fringe is air sparging where air is injected below the water table to volatize contaminants in the saturated zone and transport them into the unsaturated zone. Vacuum extraction systems would usually need to be used in conjunction with sparging to remove the liberated contaminants from the unsaturated zone. To date, this technology has not been proven at the field scale (Johnson et al, 1990).

Radio Frequency Heating (RFH)

Radio frequency heating (RFH) technology may be applicable to enhance the removal of volatile compounds via vapour extraction (Dev et al., 1988). RFH heating was developed in the petroleum industry for the in situ recovery and processing of oil from oil sand and tar sand deposits. RFH involves focusing radio frequency energy into the subsurface at 6 MHz to 2.5 GHz using specifically configured electrode arrays. Temperatures of 200°C to 400°C can be achieved, resulting in the vaporization of the organic compounds. In oil sand and tar sand processing RFH has been demonstrated on a pilot scale in the field for heating volumes of 1 m^3 up to 25 m^3 (Sresty et al., 1986). Heating was found to be effective, although not economical for oil recovery. Because the generation of heat is via radio frequency energy, the effect of geologic heterogeneity on heating of the formation is likely to be less significant than for steam injection where the steam must follow the most permeable pathways. As a result, RFH may be able to effect a more uniform recovery of chemicals.

Capital costs and energy requirements are high for this technology. Costs quoted in pilot studies are about US $125 per ton of soil. The patent for this method is currently held by Weston Inc. (CH2M HILL, 1990).

Applicability: To assist in vacuum-extraction of condensate from soils (S1A/S2A).

Status: Emerging. Expensive.

Steam Injection

Steam injection technology may be also applicable to enhance the removal of volatile compounds via vapour extraction. Steam injection techniques have been used in the petroleum industry for enhanced oil recovery. The theoretical and laboratory evaluation of steam injection for remediation of chemical spill and waste disposal sites has been described by researchers at the University of California at Berkeley (Hunt et al., 1988; Stewart and Udel, 1988). Steam injection is a method of heating the subsurface to vaporize volatile chemicals and increase the mobility of LNAPL such as condensate.

In laboratory column experiments using homogeneous sand, the removal of TCE NAPL was greater then 99.99% after passage of only one pore volume of steam through the column (Hunt et al., 1988). In a column experiment using contaminated sandy silt from a solvent recycling plant, steam passage through the column resulted in removal efficiencies of 99.97% for acetone, >99.92% for 2-butanone, 98.92% for 1,2-dichloroethylenes and 89.33% for xylenes. The relatively high removal efficiency for xylenes is of particular note. The boiling point of xylenes are higher than the steam temperature so that the xylene would not be vaporized as would the more volatile compounds. However, at the steam temperature the vapour pressure of the xylene is substantially increased and this effect likely results in removal of the xylenes. Xylene is the dominant aromatic hydrocarbon component in most Alberta natural gas condensates. This suggests that heating of the subsurface by steam injection may make possible removal of less volatile compounds which would not be removed effectively by vapour extraction alone. These may include the heavier aliphatic hydrocarbons (C_{12} and higher) present in some gas condensates (see the Contaminants section of this report).

A pilot scale field trial of steam injection was conducted at a solvent recycling plant in California (Stewart and Udell, 1989). The basic system is shown in Figure 5.14. A ring of 6 steam injection wells was installed at a radius of 1.5 m around a central recovery well in a shallow sandy silt formation approximately 6 m in thickness. A diverse mixture of high volatility and lower volatility organic solvents were present in the soil. A vapour extraction trial was conducted initially for 40 hours using the central extraction well. This was then followed by a steam injection trial for 140 hours. Approximately 100 kg of solvents were recovered by vapour extraction alone and an additional 250 kg of solvents were recovered by steam-enhanced vapour extraction. Steam-enhanced vapour extraction removed a much higher proportion of lower volatility compounds than did vapour extraction alone. As would be expected, the injected steam followed the more permeable zones and chemical removal in these zones was effective. In lower permeability zones, chemical removal was much less effective.

Application: Situations involving natural gas condensates in soils, and as an enhancement for vapour extraction (situations S1A/S2A).

Status: Emerging.

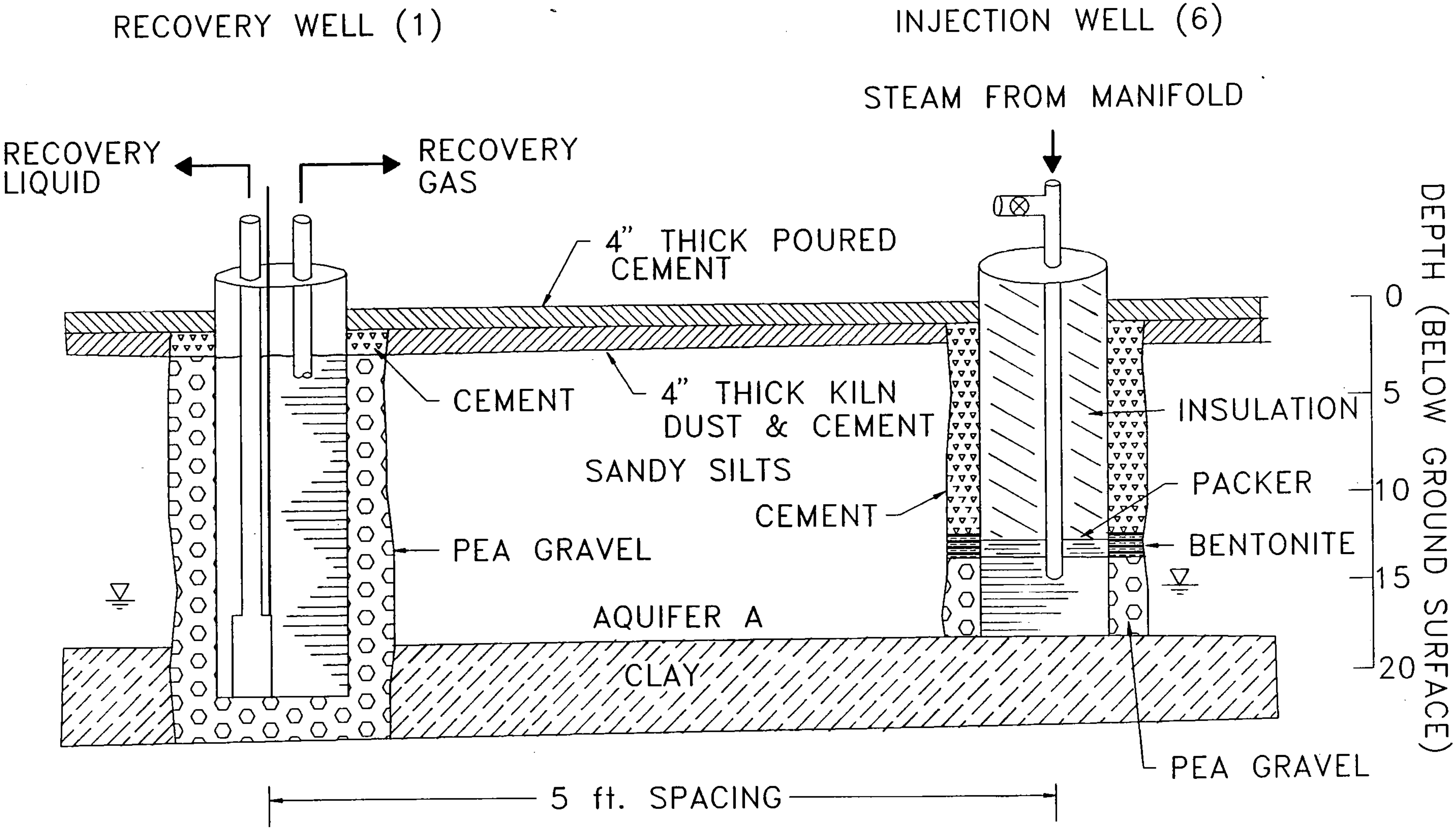


FIGURE 5.14

STEAM-INJECTION PILOT STUDY

(FROM UDELL AND STEWART, 1989)

Enhanced Biodegradation (Bioventing)

It may be possible to promote biodegradation of organic contaminants in the unsaturated zone through vacuum extraction. In essence, aerobic biodegradation requires a supply of nutrients, oxygen for an electron acceptor, water as a medium and an appropriate colony of micro-organisms. They may, given the appropriate conditions, be able to reproduce and consume organic compounds, as water is generally always present as soil moisture. Simply the act of passing air through the unsaturated zone may enhance biodegradation by increasing the supply of oxygen (Johnson et al., 1990). However, it may also be possible to further enhance the rate of biodegradation by supplying additional oxygen, in the form of pure oxygen or ozone, through input wells (GASReP, 1990a).

To date these methods do not appear to have been rigorously applied or tested. As with other vacuum extraction methods, channelling past heterogeneities will likely have important consequences for deliverability.

Application: Soils contaminated with condensate (situations S1A/S2A).

Status: Emerging (but will be a part of most SVE schemes anyhow).

Augering with Steam Injection

An experimental remediation method has been developed where the soil is mixed by augering while steam (or some other appropriate agent) is injected to clean the soil, and vapours are recovered in the off-gases. This method has the advantage of theoretically being able to treat fine-grained soils, but may not be suitable in locations where buildings and services are located. GASReP (1990a) has documented this method in more detail, and report costs of US $150 to US $450 per ton of treated soil. This method borders on being classified as an ex-situ method due to its severe disturbance of the soil. More complete discussions are presented in the Recommended Technologies section of this report.

Applicability: For remediation of shallow condensate contamination in fine-grained soils (S2A).

Status: Emerging.

Fixation / Solidification

Fixation and solidification technologies discussed here refer to methods which are applied directly within LNAPL zones and result in immobilization of the LNAPL. The creation of a low permeability barrier around NAPL zones is considered here as physical containment. Fixation and solidification technologies include:

- Mixing of pozzolanic agents such as cement in the contamination zone to create a low permeability zone from which the contamination cannot escape.
- Encapsulation of the contaminants on a microscopic scale by chemical agents.
- Vitrification of the geologic medium containing the contamination to create a low permeability zone from which the contamination cannot escape.

Mixing of pozzolanic agents with soils may be applicable to in situ immobilization of contaminants such as heavy metals. In soils, the pozzolanic agents can be physically mixed with the soil and upon setting, a solidified, low permeability zone is created. Many pozzolanic agents such as cement also create a high pH in the solidified zone which further immobilizes many heavy metal contaminants. Such methods will have little potential in fractured rock into which the pozzolanic agents can only be introduced by injection directly into the NAPL zone. This would invariably displace much of the NAPL and could worsen the extent of subsurface contamination. In addition, depending on the nature of fracture interconnection and NAPL distribution, it is unlikely that pozzolanic agents could be introduced into all zones where NAPL was present.

In-Situ Vitrification

Vitrification has been proposed for the in situ solidification of heavy metals and radioactive metals in soils by application of sufficient electrical energy to melt the soil. The heavy metals or radioactive elements are thus fixed in the glass matrix of the melted soil. Vitrification will have little potential for NAPL in rock formations below the water table. Rock formations below the water table will require very high energy input. Carbonate rocks such as limestones and dolostones cannot be vitrified because of their low silica content and will decompose with the release of large amounts of carbon dioxide. In addition, most NAPL chemicals are volatile and would be released at much lower temperatures than those required for vitrification.

In situ vitrification (ISV) is a thermal treatment technology which melts contaminated soil and solid material in situ to form an inert glass product. ISV was first conceived in 1980 by scientists at Battelle. Battelle has since formed Geosafe Corporation to provide commercial availability of the technology.

ISV involves the use of electricity for the treatment of organic and inorganic contaminants in soil. Electrodes are inserted into the ground to the desired treatment depth and a conductive mixture of flaked graphite and glass frit is placed among the electrodes to act as a starter path (Schwartz, 1989). An electrical potential is applied to the electrodes, thus establishing a current to the starter path. The resultant power heats the starter path and surrounding soil to 2000° C. Schwartz (1989) reports that the normal fusion temperature of soil ranges between 1100° C and 1400° C. The graphite starter path is eventually consumed by oxidation and the current is transferred to the molten soil. The melt advances at a rate of 1 to 2 inches/hour. Non-volatile elements are incorporated into the vitrified zone and organic compounds are pyrolyzed. The by-products of pyrolysis migrate to the surface of the vitrified zone, where they combust in the presence of oxygen. A hood can be placed over the processing area to confine the resultant combustion gases for off-gas treatment. The result of ISV is the conversion of contaminated soils into a chemically inert, stable glass-like and crystalline material resembling natural obsidian.

According to Schwartz (1989), the melt proceeds at a rate of 7-15 cm/hr. and soils with permeabilities in the range of 10^{-5} to 10^{-9} cm/sec. are considered as candidates for the process even in the presence of groundwater or in the water table. Soils with permeabilities in the range of 10^{-5} to 10^{-4} cm/sec. are considered marginal while soils with permeabilities higher than 10^{-4} cm/sec. are difficult to vitrify without taking preparatory steps such as drawing down the local water table and installing underground barriers (Schwartz, 1989).

The soil melt rate has been estimated at 4-6 ton/hour with an electric power requirement of 12500 - 13800 volts. No pretreatment is required and the residual is a continuous monolith. An array of electrodes can treat 1000 tons and a maximum width of 30 feet. A 20-40% volume reduction will result from the ISV process.

Costs: Cost estimates for the ISV process include five factors (Schwartz, 1989):

a. site preparation
b. equipment or capital recovery
c. operations and labour
d. electrode material
e. electrical power

The amount of moisture in the soil and the cost of electricity are the two factors that most significantly affect total cost. Soil moisture levels directly affect operational time. The electrical energy equivalent of the heat of vaporization for the soil moisture must be supplied and the water boiled off before vitrification can proceed. Librizzi (1990) ranks the cost of ISV relative to other treatment technologies as medium to high. Cost estimates can vary from \$200 - \$300/ton up to \$800 - \$1,000/ton, depending on site factors (Librizzi, pers. comm).

Clean-up efficiency: The resulting structure, following vitrification, is analogous to natural obsidian and is 10 times stronger than concrete. The resulting mass is unaffected by wet/dry and freeze/thaw cycles. In terms of chemical leaching, it passes both the EP-Tox and Toxic Characteristics Leaching Procedure (TCLP) tests and has zero organics present.

Case histories: Three ISV engineering-scale tests have been reported (Timmons, 1990). The first test involved vitrification of a stratified mixture of soil and lime sludge contaminated with mercury, arsenic, aldrin and dieldrin. The second test was conducted on a site contaminated with PCB, while PCBs, lead and cadmium were on the third site. The results of these tests demonstrated the ability of the ISV process to simultaneously destroy aldrin and dieldrin, remove mercury and immobilize arsenic. Results from the two tests involving PCBs showed that ISV results in destruction and removal efficiencies of >99.9999%. TCLP results conducted on the resultant glass showed that it is capable of surpassing EPA leach tests requirements by several orders of magnitude for arsenic, lead and cadmium. The process has also been demonstrated at field-scale level on radioactive wastes at the Department of Energy's Hanford Nuclear Reservation.

Two other sites where ISV is the recommended remedial technique were listed in the 1989 EPA ROD Annual Report. ISV is recommended for a 20 acre municipally owned landfill in the southeast corner of Ionia, Michigan. The principal contaminants of concern are VOC's including vinyl chloride and methyl chloride, other organics and metals including chromium. ISV is also recommended at the Northwest Transformer site which is a 1.6 acre former salvage yard in Whatcom County, Washington. The site was used for transformer storage and salvage and is contaminated with PCBs. The contaminated soil will be treated until PCB concentrations in the remaining residue are less than I mg/kg.

Design and implementation criteria: Key factors involved in determining the suitability of ISV as a clean-up technology include:

a. knowledge of the depth, volume and physical/chemical properties of the contaminant
b. melt chemistry
c. melt temperature
d. dwell time
e. soil properties such as type, moisture and stratigraphy
f. groundwater location
g. structures present
h. degree of overmelting.

The ISV process is limited by:

a. individual void volumes in excess of 150 cubic feet
b. buried metals in excess of 5% of the melt weight or continuous metal occupying 90% of the distance between two electrodes
c. rubble in excess of 10% by weight
d. the amount and concentration of combustible organics in the soil or sludge

These limitations must be addressed for each site.

Areas of concern that have been noted for the ISV process include the 20-40% volume reduction that occurs as a result of the removal of void volume in soil and the vaporization of organics. Another concern is the requirement for the collection and treatment of gases that are released to the atmosphere. Finally there is a concern about potential contaminant movement during treatment as a result of capillary action, convection, molecular diffusion and density differential.

Discussion: ISV is a clean-up process that has been developed relatively recently. To date, its major application seems to be for the containment and encapsulation of highly contaminated, localized areas. From testing carried out to date, the technique appears to be effective and does not present a long term liability in terms of breakdown of the resulting glass-like structure. The costs of undertaking ISV at a site are dependent on a number of factors, with soil moisture levels and the cost of electricity being the most significant.

In summary, the ISV process might be applied to a number of general situations including contaminated soil sites, burial grounds, classified waste that also contains hazardous waste, process sludges and tailings piles.

In-situ Soil Washing

Soil washing can be used to remove a variety of contaminants from the soil matrix by flushing with a washing fluid. The in-situ application of soil washing involves passing a washing fluid through the soil to actively leach out target contaminants. The chemical properties of the washing fluid are chosen based on the types of contaminants present. Water is often chosen to leach out water-soluble organic and inorganic species. The washing fluid is applied to the surface by means of a spray-irrigation system, or possibly through specially built infiltration systems (designed to allow year-round operation). Leachate is then collected via a system of pumping wells designed to capture all leached contaminants, or via an existing pump-and-treat system. Figure 5.15 shows a soil washing system adapted for in-situ biological treatment of petroleum-contaminated soils.

A detailed discussion including case histories is provided for in-situ soil washing in the recommended technologies section of this report.

Applicability: In-situ soil washing is applicable to all soil contamination situations being considered (SIA, S2A, S1BC, S2BC, S1D, S2D). (The ex-situ technique is limited only by the constraints of excavation technology. Excavation is expensive and has practical limitations for contaminants at depths exceeding a few metres.)

Status: Emerging. Study of field application and washing fluid selection required.

In-Situ Bioremediation of Soils

The principal method of in-situ remediation of soils around sour gas plants that are contaminated with hydrocarbons would be the application of some type of bioremediation combined with chemical amendments and physical alteration of the soil. The varieties of remediation would revolve around the types of micro-organisms used and methods of population enhancement and/or introduction. Chemical amendments would involve the addition of adequate nutrient levels, while physical alteration would involve improvement of air and water circulation within the soils.

There have been many studies conducted to investigate the feasibility of degrading various types of organic compounds in soils. The majority of this work is still in the laboratory stage (Ying et al,1990; English and Loehr, 1990) but a few field studies are now being reported (Hinchee et al, 1990; Visscher et al, 1990; Hutzler, 1990; Fu and O'Toole, 1989). The most common type of in-situ treatment involves the biodegradation of contaminants which are adsorbed onto soils within the saturated zone, but in-situ bioreclamation has been used for treatment in unsaturated soils (Torpy et al, 1989).

There is good incentive to develop in-situ technology for the bioremediation of condensate contaminated soils. It eliminates the liability of having to transport and dispose of the material off-site to a landfill or landfarming facility. If the material can be effectively and safely degraded in-situ, problems such as replacement of material that has been excavated and the ultimate disposal of the excavated soil do not need to be addressed. In-situ remediation, once developed, should also be more cost effective than current off-site options.

There has already been some experience with bioremediation of soils in Alberta. Hydrocarbons in soils resulting from pipeline and facility spills have been actively managed and biodegraded throughout much of the province. Experience to date in Alberta and the rest of North America has shown that caution must be exercised when devising these types of remediation programs. Successful bioremediation requires thorough characterization of the amounts and types of organics being degraded and the types of soils being remediated. Environmental factors such as soil type, moisture levels, and temperature are all critical to the program design. In the case of surficial spills, the hydrocarbons are likely within the top 30 cm of soil and the site can be reclaimed by maintaining adequate nutrient levels and cultivating the site frequently. Where hydrocarbons have seeped down through the soil profile and there is also groundwater contamination, additional treatments will be required.

The key to successful bioremediation of condensate contaminated soils in Alberta will be in the development of testing protocols that adequately address the full range of issues. For example, bioremediating muskeg soils in central and northern Alberta will pose different problems than working with Solenetzic soils in southeastern Alberta. Not surprisingly, the microbiology of the soils is a very important aspect of this type of work. Because of the high profile that bioremediation is currently receiving, there has been a plethora of slurries/bug concoctions that have appeared on the marketplace. Bioremediation has been identified as a "inexpensive fix" for a large variety of contaminant situations. It will work in some cases and fail in others. The clean-up of condensate in soils is one case where bioremediation has a high probability of success, but it will not necessarily be an inexpensive solution. Extensive bench scale and field testing will be required before bioremediation can be efficiently applied to contaminant situations.

The microbiology, chemistry and physics of the problem are complex. In-situ bioremediation, as currently practised, has been limited to the degradation of simple hydrocarbon contamination and involves the addition of oxygen and nutrients. Major (1990) also points out that a major limitation to advancing the technology is a better understanding of the microbial response to the process. As with many environmental problems, there is a need for greater co-operation and integration between disciplines such as microbiology, hydrogeology and soil science. Much effort is now being devoted to this technology. For example, a symposium was held on the topic of "In-Situ and On-Site Bioreclamation" in March, 1991. The objectives of the meeting were to promote an exchange of ideas, transfer technology, and integrate scientific research and engineering applications.

Treatment with a calcium amendment and soil flushing with water

It has been assumed that the high salinity conditions would be the result of salt water and/or sulphur contamination. If the degree of contamination is not severe enough to warrant collection of the leachate and the major objective is to reduce the level of inorganic contamination so that plant growth can be supported, the area could be flushed with water and a calcium amendment that would replace any excess sodium in the soil. This would also provide the neutralizing power required to counteract any produced acidity from the oxidation of sulphur. In this case, the best amendment would likely be calcium carbonate (limestone). Soil sampling and analyses would be required to determine the relative degree of each type of contamination. The correct mixture of techniques to flush unwanted salts through the profile, neutralize any existing and/or reserve acidity could then be determined.

Because of the high permeability of the soils, flushing with water once adequate levels of calcium carbonate have been applied, should help to move the inorganic salts out of the rooting zone. Continued irrigation until the salts have moved down a couple of metres should ensure that upward migration will be minimized. Establishment of a plant cover over the site once the soil chemistry will permit it, will encourage the downward percolation of the salts. Soil flushing as a means of reclaiming forested soils contaminated by brine spills has been described by Innes and Webster (1981).

Electro-reclamation

In the case of high levels of metal contamination, another technique which merits further investigation is electro-reclamation. The technique is described, complete with case histories, in Lageman (1990). The information in this brief description has been taken from Lageman (l990). The technique has been used to remove heavy metals and other contaminants from soil and groundwater. It is based on electrokinetical phenomena which occur when the soil is charged by means of one or several electrode-arrays.

Equipment involves the electrodes and their housing. In principle, they can be installed at any depth, either vertically or horizontally. The cathode and anode housings are interconnected but form two separate circulation systems, filled with different chemical solutions. The contaminants captured in these solutions are brought to a connected treatment system.

Liming soils contaminated with sulphur dust

The remediation technology for sulphur dusted soils is fairly well developed and has been practised for at least 15 years. Based on annual soil monitoring programs which are required by Alberta Environment, liming recommendations are drawn up to neutralize the acidity generated by the oxidation of the elemental sulphur. Because the degree of contamination is usually fairly low, application of limestone (calcium carbonate) is straightforward.

Based on chemical stoichiometry, calcium carbonate must be applied at a rate of 3.2 times the amount of total sulphur detected in the soil. This should provide adequate neutralization of both the active and reserve acidity in the dusted soils. Other types of amendments can be used such as calcium oxide or calcium hydroxide, but the drawback to use these chemicals is that it is very easy to apply just a little too much and end up with a soil pH of 10.

The major issue in liming dusted soils is making sure that the limestone reaches the area that requires treatment. Many of the dusted sites are located in forests and aerial applications of the limestone are required. Because the product is being dropped from the air, it must be heavy enough to fall through the forest canopy and not be blown away. However, once it lands on the forest floor, it must be able to break down readily so that neutralization of the acidified areas can occur. Pelletized limestone is available and is a fine powdered limestone that is held together by a "glue". Pelletized limestone will breakdown when it comes in contact with moisture, thus making it available for neutralizing the acidic layers of the forest floor.

Liming soils that are heavily contaminated with elemental sulphur

Soils in close proximity to the sulphur blocks or underlying former sulphur blocks present a different type of remediation problem. These soils have much higher levels of total sulphur. Based on chemical stoichiometry, a soil that contains 15% elemental sulphur, by weight, would require an application of 48%, by weight, of limestone. If you assume that a 15 cm depth of soil taken over a 1 ha area weighs 2.2 million kg, then 1.0 million kg or 1056 tonnes of limestone would be theoretically required to neutralize the area. In reality, most basepad clean-ups are successful in reducing total sulphur concentrations to less than 7-8%. Many sites have less than 5% total sulphur remaining once clean-up operations have been completed.

Even at this level of contamination, application of limestone at the 3.2:1 ratio can cause soil structural and chemical problems. It has been reported that application of limestone can cause soil structural problems due to the fineness of the product and the formation of calcium sulphate during the neutralization reaction (Leggett, 1988). The limestone available in Alberta has some magnesium carbonate present in the product. Despite the fact that the level of magnesium carbonate is less than 5%, significant quantities of magnesium sulphate have been measured on basepad sites that have received repeated applications of limestone. Magnesium sulphate is soluble enough in water to affect soil salinity levels. Consequently, high levels of salinity have been recorded at some basepad sites that are now being actively treated with limestone.

There are two types of acidity within a soil; active and reserve acidity. In a soil that is heavily contaminated with elemental sulphur, a portion of the soil acidity will be reserve acidity due to the presence of unoxidized elemental sulphur. In one experiment, the amount of limestone added using the 3.2:1 ratio was a minimum of 10 fold greater than that required to neutralize the active acidity (Leggett, 1988). Overliming is known to reduce pore space which results in reduced soil water and air necessary for healthy root development.

On the basis of this information, two alternatives are available. The first is that the site is treated with limestone using the 3.2:1 ratio. In the case of soils which are not severely contaminated, this is likely a cost efficient and viable technique. However a different approach may be required for soils with higher levels of contamination. One proposal would be to actively encourage microbial oxidation of the sulphur. The organisms thought to have the greatest oxidizing ability are Thiobacillus spp., which are reported to operate best under acidic soil conditions. Rather than striving to maintain a neutral soil pH, the focus could be shifted to trying to maintain an optimal environment for the sulphur-oxidizing microorganisms, thereby maximizing sulphur oxidation. Surface and drainage water interceptors should be installed to ensure that all water is captured from the site. In essence, this type of approach is the opposite of the technology presently being practised, in that it encourages the oxidation of sulphur, rather than trying to minimize it. Sulphur oxidation will occur at more neutral pH ranges, but the process will take longer and require much longer monitoring periods. This technique would likely work best in the highly permeable soils, but may be appropriate in a wide range of soils.

Re-use of sulphur contaminated soil

The third technique involves the concept of re-use or recycling. In Alberta, large agricultural areas could potentially benefit from an inexpensive sulphur source. It has been estimated that 1.2 million hectares of improved cropland in central and northern Alberta are low in sulphur for cereal and grass production, while 2.5 million hectares in these areas may be sulphur deficient for oilseed and legume production. There exists within the farming community a willingness to use sulphur-contaminated soil as a sulphur fertilizer. Farm demand for the material could make landspreading an attractive and inexpensive method of recycling this material. In addition to supplying present sulphur nutrient demands, this material, comprised of a variety of sulphur particle sizes, could also represent a residual source of crop-available sulphate. Larger pieces of sulphur would oxidize over subsequent seasons, thus providing a longer term source of crop available sulphur.

Preliminary investigations indicate that the costs of landspreading sulphur-contaminated soil would be similar, if not lower, than landfilling (Sonntag & Leggett, in prep.). Costs to farmers were estimated to be approximately 25% of the values of elemental sulphur purchased as fertilizer from a dealer.

Another potential use for this material could be as an inexpensive means of lowering soil pH. Bole(1986) indicated that acidification with elemental sulphur may improve certain soil characteristics in irrigated, calcareous Solenetzic soils. In fact, interest has been expressed by some specialty crop producers in obtaining sulphur-contaminated soil. It is felt the material could provide a cost-effective means of adjusting soil pH for acid-loving crops, such as blueberry.

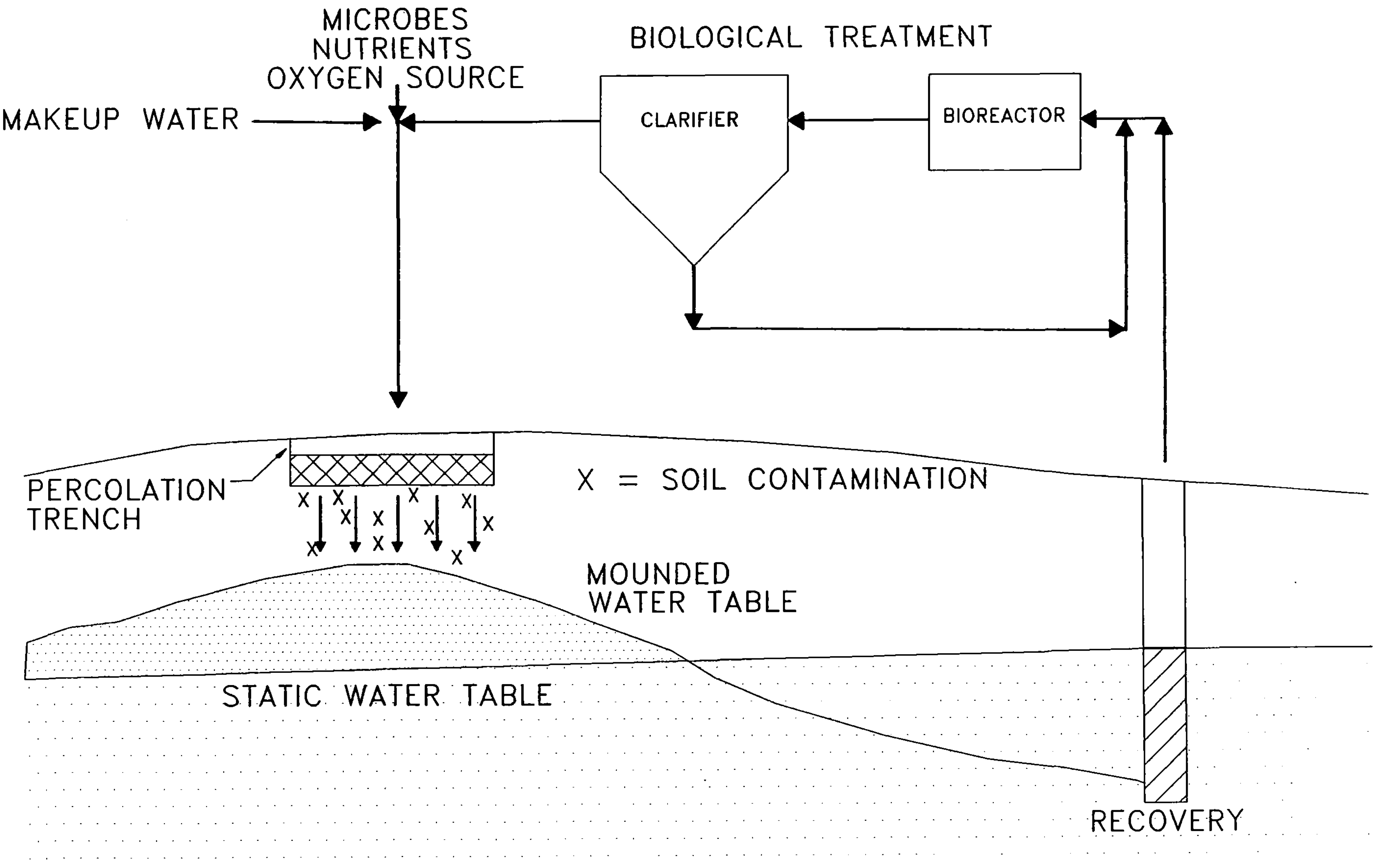


FIGURE 5.15

IN-SITU BIOTREATMENT (USING INFILTRATION)

AFTER FARLEY, 1990

Field trials are required to pursue the options outlined in this section. There would be some capital costs associated with adapting a grinder and a shaker/screener machine to ensure that a reasonably consistent product could be produced. This equipment could be portable and be moved from site to site.

5.4 OFF-GAS TREATMENT

5.4.1 Overview

Air stripping and soil venting are two common remediation techniques which remove VOC's from contaminated groundwater and soil. Presently, in Alberta, these off-gas emissions may be discharged into the atmosphere. Technologies have recently been developed which treat off-gases in order to minimize the emission of volatile organic carbon compounds.

There are five types of technologies which have been successfully utilized in treating the off-gases from air stripping and soil venting installations. These are:

(1) Activated Carbon Adsorption,
(2) Thermal Incineration,
(3) Catalytic Oxidation,
(4) Membrane Separation
(5) Biofiltration

There are several other technologies which are emerging but have not been widely applied in the field. Most of them are commercially available but may require further development. These include:

(6) Flare Incineration
(7) Peat Moss Adsorption
(8) Advanced Oxidation Processes
(9) Carbon Fiber Adsorption
(10) Fixed Film (Bioair)

5.4.2 Established Technologies

Activated Carbon - Vapour Phase Adsorption

Carbon adsorption has primarily been used for water treatment, but has recently been applied to vapour phase treatment. In most cases, activated carbon is extremely effective at removing VOC's from the air stream through adsorption. Commercially available units have demonstrated the effectiveness of the technology. The primary disadvantage of the technology is that contaminants are only transferred from one medium to another (air to carbon), and will eventually require further treatment such as:

(a) Disposal in a secure landfill
(b) Destruction by incineration
(c) Regeneration by steam stripping or dry heat, and destruction of the stripped material. or
(d) Biological regeneration of carbon (discussed below)

The adsorption capacity of carbon is adversely affected by excess moisture (effluents from air-strippers are at 100% humidity). A heater is therefore required between the air stripper and the adsorber to reduce relative humidity to 40-50%. Difficulty has been experienced at several installations with the heater, resulting in a drop in removal efficiency below the design specifications (Radian Corporation, 1987).

If applied to soil venting, there is a risk of bed fires due to the heat of adsorption. Influent concentrations should therefore be kept to 25% of the LEL (lower explosive limit). This is rarely a factor in air-stripping, but may be crucial in soil venting of very heavily contaminated soils (such as zones contaminated with free-phase condensate), especially during start-up. It is important to install a heater which produces low heat, preferably less than 40 degrees C.

This system shows preferential adsorption for some organics. If not properly monitored some organics can be released to the atmosphere at greater concentrations than are in the influent (Radian Corp., 1987). Specific organic types were not identified in the available literature. Further research is required.

Biological Regeneration of Carbon

"Integration of biological treatment and adsorption into a single reactor has been shown to have significant advantages over separate biological and adsorption treatment" (GASReP, 1990b). During periods of high organic loading, adsorption by the carbon will be the predominant treatment mechanism. At times of zero or low organic loading, the micro-organisms will utilize the organics adsorbed on the carbon as a food source, thus regenerating a portion of the carbon.

"The reliability of the biological activation process (BAC) depends on the ratio between the limiting global degradation rate, and the applied mass loading rate of the target compound. When the global biodegradation rate is lower than the influent mass loading rate, breakthrough will eventually occur after all available adsorption sites are exhausted. Biodegradation rates in aerobic BAC processes can be limited by a variety of factors such as the availability of nutrients, and the persistence of many organic compounds. Additionally, when organic loading is high, proliferation of biomass in aerobic BAC units often causes operational difficulties including hydraulic short circuiting and excessive headloss buildup" (GASReP, 1990b).

A system employing biological regeneration was installed at a site processing 300 cfm of off-gas. The cost of the installation was $70,000 (Remedial Systems Inc., 1991).

Cost may be the most limiting factor with regard to carbon adsorption, particularly in the case of soil venting, where very high concentrations of VOC's may be encountered. Thus, this process may be better suited to treatment of air-stripper off-gases, which will be of much lower concentration.

Batch Off-Line Carbon Regeneration

The principal difference between a BAC and batch off-line biological regeneration process is the termination of influent flow to the adsorption column during regeneration. During off-line bioregeneration an exhausted activated carbon column is removed from service, and regenerated by recycling a mixture of nutrients, acclimated bacteria, and dissolved oxygen through the column. This creates an environment favourable to enhancing biodegradation of the adsorbates thereby regenerating a portion of the carbon's adsorptive capacity (GASReP, 1990b).

Batch biological regeneration of activated carbon is applicable to spent carbon from a vapour phase or liquid phase application. However, an additional drying step would have to be incorporated following the biological regeneration if the carbon is to be used for vapour phase applications, which are adversely affected by excess moisture. This would result in some decease in cost effectiveness.

The GASReP study cited used activated carbon saturated with phenol. The parameters varied were time, and the initial amount of added biomass. It was demonstrated that 75% regeneration could be achieved in a four day period, with greater than 60% regeneration occurring in the first 48 hours. It is uncertain whether this process has been carried out under field conditions.

Research on bioregeneration of activated carbon by genetically engineered micro-organisms is currently being undertaken at the University of Waterloo. The engineered microorganism is capable of satisfactory growth between 0 and 10 degrees C.

Thermal Incineration

Thermal incineration is the most complete and most expensive method for destroying volatile organic compounds in off-gases. The VOC's are burned at high temperatures (1100-1400 degrees C) in the presence of excess air and are completely oxidized. In the case of simple hydrocarbons, such as those removed during gas condensate stripping or venting, the final products of oxidation are carbon dioxide and water.

One disadvantage is that this process may require post treatment to remove acidic products. Also, products of incomplete combustion may be formed if the system is not properly optimized or maintained. A supplemental fuel source may be required.

Although thermal incineration is a proven technology for the destruction of liquid or solid hazardous waste, it has rarely been used for the treatment of off-gases. Out of 177 air stripping cases reviewed by EPA, only two incorporated thermal incineration. Performance data is not available for these two cases, although the design efficiencies for both units were stated to be 99.9% or better (Radian Corp, 1987). Given the present state of regulatory affairs in Alberta (off-gas treatment is not required), the high costs of this technology do not make it a practical choice.

Status: Established.

Catalytic Oxidation

The catalytic oxidation of VOC's in air-stripping emissions is carried out for low reactant concentrations (typically <1000 mg/l) with a very large stoichiometric excess of oxygen. These processes are generally net users of heat, as the whole air stream requires heating to reaction temperature, as the added contribution from the heat of combustion of the organics is negligible. A highly active non-selective catalyst and the lowest possible reaction temperature (200-500 deg. C) are required. The catalyst is usually a metal oxide supported on an inert porous medium to allow for maximum surface area. The extremely high humidity of air-stripper off-gas is a factor not encountered in the original industrial process. Its effect on catalyst chemistry has not been established (Kosusko et al, 1988). Additional research is required on the formulation of catalysts, including resistance to poisoning by sulphur compounds, which are commonly found in groundwater at Alberta sour gas plants.

The advantages of catalytic oxidation are that contaminant removal is rapid and the system is able to cope with feed variations. It has been found to achieve 99% destruction when properly designed, and commercial units are available in the United States. Excess heat from gas plant operations could be used to heat the influent air-stream.

The main disadvantages of catalytic oxidation processes are: the high capital cost involved, and the need for further development for more efficient treatment of VOC off-gases. Also, the efficiency of the system will decrease with catalyst fouling. Other problems are similar to those affecting the thermal incineration process: post treatment may be required to remove acidic products, products of incomplete combustion may be formed if the system is not properly optimized or maintained, and a supplementary fuel source may be required.

Case History - Thermal Incineration/Catalytic Oxidation

A gasoline spill of nearly 73,000 litres from an underground storage tank in Burbank, California, was treated by soil venting (Fall, 1989). Since it was expected that the initial concentrations of the gasoline vapour would be in the burnable range (1.3% by volume), a combination incineration/catalytic oxidation unit was utilized. With this system, direct combustion is possible when vapour concentration is high. As recovery progresses, concentrations may drop and require the addition of natural gas to maintain combustion. At very low gasoline levels (approx. 10% of the LEL) this will become uneconomical and the treatment system can be shifted to the catalytic mode.

At the time of publishing, the vapour extraction system had operated for 221 hours and extracted over one million cubic feet of soil gas, destroying about 10% of the original spill volume of gasoline, and it had not yet been necessary to shift to the catalytic mode. It was also calculated that a further 7% of the gasoline had been degraded in place by bacterial action due to enhancement of the oxygen levels in the soil caused by the vapour extraction system.

There are several methods by which the economics of the thermal or catalytic oxidation systems may be improved. The higher the concentration of volatile organics in the off-gas, and the lower the flow rate, then the more economical the system becomes.

Membrane Separation

Membrane vapour separation is a low pressure process for separating volatile organic solvents from air. The contaminated airstream is introduced into an array of membrane modules, each containing a semipermeable composite membrane with a large surface area packed into a small volume. Organic solvents are preferentially drawn through the membrane and the solvent is condensed and removed as a liquid. The purified airstream is discharged or treated again in a second stage.

The system can be configured as:

(a) A single stage unit, usually removing 80-90% of the volatile organics from the airstream, and giving a permeate 5-10 times richer in organics concentration.

(b) A two stage unit where the permeate from the first stage becomes the feed for the second stage. Removal is about the same, but the final permeate is 50-100 times richer in volatiles.

(c) A two step/two stage unit in which both permeate and residue are subjected to a second stage. With this configuration, removals of 95-99% of the organics in the influent airstream can be attained.

The relative costs of these three membrane configurations for treatment of butane, TCA and Treon mixture are shown below:

	Single Stage	Two Stage	2 Step/2 Stage
Feed Flow (scfm)	500	500	500
Capital Cost	282,000	425,000	650,000
Operating Cost/ 1000 scf Feed	0.52	0.76	1.25
Cost/lb of Solvent Recovery	0.68	0.21	0.10
% Removed	77	90	97.5

The advantages of the membrane separation process are: simple operation, can be configured for desired removal efficiency, very efficient for gasoline vapours, and is compact and easily transportable. This is an economical treatment method for streams too concentrated for carbon adsorption or air stripping and too dilute for incineration or distillation. The organic concentrate produced can usually be recycled and the clean water stream is suitable for discharge, recycling or a polishing treatment.

Carbon adsorption costs usually increase sharply with feed airstream concentration while incineration and condensation costs decrease with increasing solvent concentration. As a result, carbon adsorption systems are preferred for very dilute streams containing less than 0.05% solvent while incineration and condensation systems are preferred for very concentrated streams containing more than 5-20% solvent.

As a rule of thumb, capital costs of VaporSep systems are in the range of $400-1000 per scfm of plant capacity. Operating costs can be largely offset by the value of the recovered solvent if feed air solvent concentrations are greater than 0.5 to 1.0%.

Commercially available membrane treatment systems are marketed by Membrane Technology and Research, from Menlo Park, California. They are designed for removal/recovery of chlorinated hydrocarbons, aliphatic hydrocarbons, and benzene and other aromatics, from either air or aqueous streams.

The disadvantage of membrane technology is that it is suited to low-flow, high concentration airstreams. At present, some membrane systems have been installed in pilot scale only. More development will likely be required to ensure that membrane separation is a useful and cost effective technology.

Biofiltration

Another alternative technology for the treatment of off-gas is through the biological degradation of hydrocarbon vapours. Biofiltration is a destructive technology which is accomplished by introducing the contaminated air stream to a filter bed containing an organic media (e.g. composted leaves, peat moss, etc.). As the air stream flows through the biofilter bed, microorganisms degrade the hydrocarbons into water, carbon dioxide, and trace inorganic salts. With proper moisture, nutrient, and pH conditions, removal efficiencies for hydrocarbons can exceed 90% (Kosky et al., 1989).

The biological degradation of hydrocarbons from air streams is roughly analogous to the biological unit processes (e.g. trickling filters, activated sludge units, etc.) which degrade hydrocarbons in water. In both cases, bacteria are provided with both a hospitable environment (in terms of oxygen, temperature, nutrients, and pH) and a carbon source for energy. The bacteria utilize these favourable conditions to metabolize the carbon source to its primary components (ie. carbon dioxide and water). The result is a "clean" air stream.

The types of hydrocarbons which are amenable to treatment using biofilter technology include many commonly encountered compounds, including straight chained hydrocarbons (ie. n-alkanes), branched aliphatics, and aromatics.

Removal efficiencies for selected VOC's under laboratory conditions are summarized as follows:

Compound	Removal Efficiency
Ethyl benzene	92%
Chlorobenzene	69%
Propane, Isobutane, N-Butane	95-99%
Toluene, Acetates	95%

The major components of a biofilter include:

1. An air blower - to push the waste air stream through the filter media;
2. An air distribution system - to provide a uniform air flow to the filter media;
3. A moisturizing system - to maintain proper moisture content in the filter media;
4. Filter media - to provide the habitat for the microorganisms; and
5. An under drain system - to remove excess water (e.g. rainfall) from the bed to prevent waterlogging of the media.

This type of biofilter has been used for several decades with favourable results. However, it has some serious drawbacks. These include uneven air distribution through the filter media, difficult serviceability of the filter media, and low loading rates resulting in a large filter area. There is a new design on the market called "Bikovent" which addresses these limitations.

The Bikovent system is an integrated design consisting of concrete parts. The design consists of an aerated plate that provides uniform air distribution, integrated air supply and drainage ducts, a driveable surface allowing for mechanized installation and maintenance of the filter media, and a non-clogging air escape port. The air loading rates are approximately 5-10 cfm/ft2.

The prefabricated, interchangeable components of the Bikovent system support multi-bed installations, thereby allowing for continued biofilter operation during maintenance periods. Air supply can be made to either biofilter section through controls at the humidification chamber. This chamber is used to moisten the raw gas to allow for uniform, optimal biological activity.

The possible mechanisms for microbial uptake of the organic substrate in biofilters have been extensively reported by Eitner (1984), who found that bacterial uptake of the organic gases occurs through gas molecule diffusion and absorption onto passing water droplets.

Emerging Technology

Flares

Gas plants use flares to burn off waste gases during processing. These are essentially open flames. On at least two sites in the U.S. emissions from air stripping have been piped to existing flares. No performance or operating data are available from these sites, so the efficiency is unknown (Radian Corp., 1987).

In a study by Shareef et al. (1984), the efficiencies of several flare heads were measured, and found to vary from 55-100% over a very large range of air-flow velocities (0.9-7600 cm/sec). The majority were in the very high 90's, especially those with the higher flow rates. Further studies of the flare heads showed combustion efficiencies of 99.74% with a 100% propane feed, and 99.72% with a 50% propane feed, for the same flare head. Therefore, piping the off-gases from an air stripper to the flare may be a practical and efficient method of disposal providing the calorific value of the flare gas is sufficient to compensate for the dilution factor, and that the addition of air will not impede overall performance (GASReP, 1990b).

Discussions with gas plant engineers and field operations personnel have led to the conclusion that this type of technology may indeed be feasible. However, gas plant facilities may not be willing to attempt this type of installation for two reasons. First, there is the safety aspect.

When injecting the off-gas into the top of the flare stack there is the danger that the additional vapours could result in backflow, with the flare moving back down the stack. However, the installation of a flame arrester would protect against this possibility. Secondly, there would be some initial cost involved in setting up such a system for experimentation.

Peat Moss Adsorption

Peat moss can be used for off-gas treatment in a similar fashion to the activated carbon process discussed above. Comparative studies of peat vs. activated carbon were carried out by Soniassy (1974). The main difference between peat moss and carbon was in bulk. Although the moss adsorbed 80-97% of the amount that would be adsorbed by an equal weight of carbon, to make up for its lower density a peat moss adsorber would have to be five times the size of one containing carbon.

Because peat moss is an abundant, naturally occurring material, it could potentially become a cost-effective treatment method vs. activated carbon. However, the effect of humidity on the adsorptive performance is not yet known. To date there have be no pilot-scale installations on VOC's using peat moss.

Advanced Oxidation Processes - UV/Ozone/Catalyst

Advanced oxidation has been used to date primarily for aqueous treatment. In many cases, however, some of the incompletely oxidized components are stripped from the gaseous effluent from the aqueous stream by the partially used ozone. The gaseous effluent is then treated using UV/Oxone/Catalyst. Using conventional UV lamps, a destruction rate of 75% has been achieved. However, some products of incomplete oxidation are of concern (Ashworth et al., 1987).

A recent development, which is now becoming commercially available is a catalyst formulation first developed by a British firm, using titanium dioxide supported on a glass-fibre matrix. This promising technique may soon lead to considerable technological advancement in this area.

(A company called Purus Corp. in San Jose (408-453-7804), is the only firm presently marketing UV/Ozone/Catalyst technology.)

Carbon Fiber Adsorption

Carbon fibres are similar to the carbon adsorption system discussed earlier, but are sufficiently different to be discussed as a separate technique. The technique operates in a continuous adsorption/desorption cycle instead of the normal batch mode. The regenerant hot air stream contains 5-15 times the VOC's of the influent stream.

The carbon fibre system (called KF) was developed in Japan as a superior method for recovery and re-use of solvents. It has been particulary useful for the recovery of corrosive or reactive solvents, because of its short desorption cycle (8-10 min.). For industry its advantages over conventional carbon beds are:

(1) Higher quality of recovered solvent
(2) Less system corrosion problems
(3) Greatly reduced risk of bed fires
(4) More compact and lighter systems

The commercial system contains two cylinders of which at any time one is in the adsorption mode, and the other is in the desorption mode. This system is claimed to be cost competitive with the standard carbon adsorption technique for solvent recovery, and to give a much purer end product due to a very short adsorption and desorption time. It is fully automated. It has also been marketed as a tandem carbon adsorption/desorption and incineration process. Its applicability to off-gas treatment has not been discussed in the literature.

Fixed Film

Fixed film is a new technology developed in 1989 to deal with hydrocarbon contaminated air from soil venting operations. The treatment unit, called "Bioair", consists of a sump which is attached to a tower containing a 5 m high plastic fixed media bed. To operate the system, a biological population was established in the sump, then circulated to the top of the tower, and allowed to cascade down through the media. Simultaneously, air was forced up through the tower. Once a stable population of bio-growth was established on the media, the air stream from the vapour extraction system was introduced into the Bioair unit.

Preliminary results showed there was a significant removal of BTX (from 30%-80%) (GASReP, 1990b). The disadvantages of this process are that it is very slow, and cannot handle large flow rates. Also, the process is difficult to maintain and handles single contaminants better than mixtures. The technology is still under development. The research was being conducted by Detox Inc., which is no longer in business.

Costs and Efficiencies

Some typical removal efficiencies of processes for off-gas VOC's are:

- Thermal incineration	99.9%
- Catalytic oxidation	95-99.9%
- Advanced photo oxidation	95-99.8%
- Membrane separation	
2 Stage	90-99%
1 Stage	50-90%
- Conventional UV/Ozone	75%
- Biofiltration	92-99%

An overall ranking of the various treatment processes cannot be made, as the composition of off-gases being treated by each technology varies widely. However, some generalised comments can be made as follows:

Soil venting of hydrocarbon contaminants. Until recently, the cheapest form of treatment/destruction was a two phase process. Direct combustion was used until the concentration dropped to very low levels, after which catalytic oxidation was required. In some cases attempts were made to recover the fuel, either by the use of a condenser on the off-gas stream or a carbon adsorption followed by steam stripping (GASReP, 1990b).

Biofiltration using the Bikovent design may be currently the most economical treatment technology. Membrane separation technology may soon be a cost effective technology as well. The system requires less maintenance than combustion/incineration, and the recovered solvent can be recycled to offset the cost of the installation if the feed solvent concentrations are greater than 0.5-1.0%. However, this technology has only been installed in pilot scale projects to date.

Carbon adsorption is not feasible for high VOC concentrations due to the expense of regeneration or disposal of the carbon. Also, there is a high risk of bed fires when applied to with soil venting operations.

Off-gases from air-stripping of groundwater. The calorific value of these off-gases is usually so low that thermal oxidation of the VOC's is not economical. Traditionally carbon adsorption has been used, but it requires disposal or regeneration of the carbon. Future developments may shift the emphasis towards the use of catalytic oxidation processes (GASReP, 1990b).

An EPA report estimated air emission treatment costs at four remedial sites by three different treatment systems: thermal incineration, catalytic oxidation, and activated carbon adsorption (including the cost of carbon replacement). These costs are shown on Table 5.1. Stripping efficiency was 99% or better (Radian Corp., 1987). The cost/scfm for each technology, each applied at four different sites, is summarized as follows:

Technology	Cost/scfm (US$)
Carbon Adsorption	11,510 - 59,846
Thermal Incineration	58,490 - 99,231
Catalytic Oxidation	31,563 - 66,231

There are two other technologies which may be viable alternatives for the treatment of off-gases from air strippers. Firstly, membrane separation technology appears to be a very efficient and cost effective treatment method. The promotional literature states that the cost of a large VaporSep membrane system is approximately $170,000 US which can handle 200 scfm. Annual maintenance costs are approximately $50,000.

The use of flares at a gas plant facility to burn off waste gases is also a potentially feasible treatment method. However, there appears to be reluctance on behalf of gas plant personnel in designing such a flow system from the air stripper to the flare stack. This is caused by potential safety concerns and design costs.

TABLE 5.1
COMPARATIVE COST ESTIMATES FOR DIFFERENT AIR-STRIPPER OFF-GAS TREATMENT ALTERNATIVES (IN $ U.S.)
(RADIAN CORP., 1990)

SITE	(A)	(B)	(C)	(D)
Water Flow Rate (g/m)	1400	155	1900	3600
Air Flow Rate (cfm)	8000	1300	5500	19200
Air/Water Ratio	42.7	62.7	21.7	39.9
Total Aqueous Organics (ppb)	4300	1500	38	200
Organics in Air Phase (ppb)	100.6	23.9	1.8	5.0
Organic Emmissions/year (g)	11500	440	140	1400
Carbon Adsorption				
Control Efficiency (%)	80	NR*	74	90
Installed Cost ($)	150000	152000	223000	500000
Direct Operating Cost	50400	31300	62700	120000
Total Annualized Cost	96400	77800	124000	221000
Cost/1000 cfm ($)	12050	59846	22545	11510
Cost/g Adsorbed Organics	8.38	176.82	885.71	157.86
Thermal Incineration				
Control Efficiency	98	98	98	98
Installed Cost ($)	318000	187000	285000	432000
Direct Operating Cost ($)	432000	86800	303000	1047000
Total Annualized Cost ($)	492000	129000	358000	1123000
Cost/1000 cfm ($)	61500	99231	65091	58490
Catalytic Oxidation				
Control Efficiency	95	95	95	95
Installed Cost ($)	307000	134000	251000	586000
Direct Operating Cost ($)	210000	51600	151000	508000
Total Annualized Cost ($)	269000	86100	201000	606000
Cost/1000 cfm ($)	33625	66231	36545	31563

* NOT REPORTED

6. TECHNOLOGY RANKINGS AND SELECTION

6.1 OVERVIEW

6.1.1 Ranking Procedure

This section covers the ranking and selection of treatment technologies for the specific contamination situations at Alberta sour gas plants (ASGP). For each of the situations being considered, a short list of generally applicable established and new/innovative technologies was developed. These short lists were then studied by the members of the expert review panel, who were asked to rank the technologies based on a number of specific criteria (including effectiveness, cost, and applicability to ASGP conditions) (See the Methodology Section of this Report). Ranking criteria and procedures are discussed in detail in the methodologies section of this report. Separate rankings were provided for established and new/innovative/emerging technologies. As described in the Methodology section of this report, the rankings of individual panel members were done separately, and followed an expert approach, rather than a formalized weighted ranking technique. Individual rankings were then compiled, and final recommendations produced based on a ranking-matrix system.

The intent of the ranking exercise for established technologies was to provide recommendations for systems which could be effectively applied today at sour gas plant sites, and which had the best potential for showing positive results.

The following sections provide full details on the results of the ranking and selection exercise for each of the contamination situations being considered. Each of the technologies recommended in this section are discussed in full in the Recommended Technologies section of this report (Appendix I).

6.1.2 General Observations

Despite differing experience and areas of specialization, the members of the project team voiced a few fundamental observations. As expected, the consensus among professionals involved with subsurface remediation is that there is no substitute for assessment of each site individually. A study such as this is useful insofar as it narrows down the possible choices for remediation, but it must be followed with detailed site assessment to allow final selection and detailed design and optimization of the system. To date, as discussed above, very few rigorous attempts at remediating subsurface contamination have been undertaken at sour gas plants in Alberta, and virtually no details of such undertakings are available in the literature. From this perspective, the study provides technical guidance for subsurface remediation efforts at Alberta sour gas plants. Demonstration of selected technologies will provide a valuable core of research data on which the industry as a whole can base its approach to remediation.

Another commonly held conviction amongst the team was the superiority of on-site treatment of contamination problems, despite the present prevalence of deep-well injection and excavate-and-remove methods. Removal or transfer of contaminated material from one site or medium to another is not seen as a viable long-term solution, either from the regulatory or environmental perspectives. However, the disposal of contaminated water in secure deep formations must remain a practical alternative, and the economics of this method should continue to be assessed against other alternatives, where practical. It is also evident that most solutions to subsurface contamination problems at Alberta sour gas plants will involve several technologies, used either in series or in parallel, or sequentially to move from one level of clean-up to another. The rankings presented reflect all of these findings.

6.2 SITUATION S1A: CONDENSATE IN PERMEABLE SOILS

Based on the results of the literature review and preliminary screening of technologies, a short-list of technologies for remediation of condensate in permeable soils (typically sand, silt and gravel deposits) was compiled. As for all the short-lists in this section, separate categories were provided for "established" and "emerging" or new/innovative technologies. The short-listed candidates are shown in Table 6.1.

TABLE 6.1

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: S1A

DESCRIPTION: Soil/unsaturated zone
High to moderate permeability materials
Free condensate liquids and associated dissolved organics

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Soil vapour extraction (SVE) with off-gas treatment; possible enhancements include:
    - passive air injection;
    - forced aeration enhanced biodegradation
2. In-situ soil flushing techniques; possible enhancements/additions:
    - water, surfactants, washing fluids;
    - collection of flushed water through groundwater pumping or underlying drainage systems;
3. In-situ biological remediation, culturing of native organisms and nutrient and oxygen additions; approaches include:
    - trench systems or injection wells, raise groundwater table and cycle through recovery wells, surface bioreactor, additions of nutrients and oxygen.
4. Excavate and treat, various possible on-site treatments.

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. In-situ ozone treatment - oxidizes organics in place.
2. Detoxifier
3. Enhancements to SVE - waste heat from plant - to increase volatilization.
4. RF heating + SVE

6.2.1 Factors of Concern

The chief factors affecting clean-up of gas condensate from more permeable types of soils typically found at ASGP's were identified as:

Subsurface behaviour of condensate
LNAPL spilled at surface or in the unsaturated zone will migrate downwards under the influence of gravity towards the groundwater surface, as long as there is sufficient volume of LNAPL to completely saturate available pore space. If the volume of the spill is small, the LNAPL may stop moving before it can reach the zone of saturation. The vertical migration of condensate liquids will also be affected by soil heterogeneities. Layers of less permeable clay, for instance, may redirect the liquids, or form perched LNAPL layers in the unsaturated zone. As with all remediation, a firm understanding of the site geology will be required.

Physical and Chemical Properties of Condensate
As discussed in the Contaminants subsection of this report, the chemical composition of gas condensates is quite variable. Some may have a preponderance of lighter, more volatile fractions, other of heavier (C12 +) molecular weight. This makeup will have a bearing on the effectiveness of volatilization methods such as soil vapour extraction.

Size and Volume of Spill
Larger spills may have to be treated differently than small spills. Volume will affect depth of infiltration of LNAPL, and the likelihood of the presence of free LNAPL on the groundwater surface.

Presence of LNAPL on the Groundwater Surface
Once the LNAPL reaches the groundwater surface, it will tend to accumulate on the capillary fringe, eventually depressing the groundwater surface by its accumulated weight, and move off in the direction of groundwater flow. As described in the Contamination Situations Section (Section 4 of this report), seasonal fluctuations of the groundwater surface will tend to smear LNAPL as residual saturation across the unsaturated zone, resulting in considerable additional volume of LNAPL-contaminated unsaturated material.

LNAPL as a Source of Dissolved Groundwater Contaminants

Condensate in the soils/unsaturated zone will act as continuous source of dissolved BTEX contaminants to groundwater. The same applies to free phase floating on groundwater.

6.2.2 Ranking

Ranking of remedial technologies for this situation focused on the premise that the LNAPL condensate in the soils would act as continuous source of BTEX to groundwater. Pump-and-treat of dissolved BTEX contaminants in groundwater, without remediation of the "subsurface source" of contaminants, has been shown to be cost inefficient, and ineffective in the long-term. In fact, allowing condensate to remain in soils will create a situation of perpetual maintenance at the site, no matter what technology is used to remediate groundwater. From this perspective, it is the water-soluble fraction of condensate (BTEX and other aromatics) that is of most concern.

Table 6.2 shows the results of the technology ranking for both established and new/innovative techniques.

6.2.3 Discussion

Established Technologies

All panel members agreed that soil vapour extraction, enhanced by passive or active injection of air to the vadose zone, was the most appropriate choice among established technologies. This system can be expected to remove up to 90% of typical Alberta condensates under these conditions, and do so more rapidly than the other listed technologies. Another advantage is that it is the volatile components of condensate, and in particular the water soluble aromatics, which will be removed first and most completely. This in effect eliminates the LNAPL as a "subsurface source". Remaining high molecular weight components are of much lower environmental significance.

Cost is also an important consideration. Compared to the construction of extensive caps or isolation structures, implementation of a soil washing scheme, or elevating the water table to

TABLE 6.2

TECHNOLOGY RANKING MATRIX

SITUATION S1A - CONDENSATE IN PERMEABLE SOILS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Soil vapour extraction	1	1	1	1	1	50
Excavate and treat	3	4	3*	3	4	19
Soil flushing	2	3	2	2	3	34
Caps, covers, barriers	-	2	5	-	-	07
In-situ bioremediation by elevating water table	4	5	4	4	2	15
EMERGING						
In-situ bioremediation of soils	2	3	2	2	1	30
In-situ ozone treatment	-	-	-	-	4	02
detoxifier	3	2	-	-	2	21
enhancement of SVE with heat	1	1	1	1	3	43

* Excavate "hot spots"

POINT SYSTEM:

RANKING	POINTS
1	10
2	08
3	05
4	02
5	01
-	declined to mention

NQ = Not Questioned

improve the effectiveness of in-situ bioremediation, soil vapour extraction is expected to be more economical. A detailed breakdown of costs for soil vapour extraction systems is presented in the Recommended Technologies part of this report.

With proper winterization, the technique can operate year-round. The technology is simple to install and operate, unlike other short-listed technologies such as in-situ bioremediation. Excavate and treat was deemed impractical for most large-scale problems, and far too expensive when compared to SVE.

Off-gas treatment is not presently required in Alberta. However, the off-gases produced by vapour extraction of large volumes of condensate will have significant hydrocarbon concentrations. Some form of treatment is recommended. Off-gas treatments are discussed later in this section.

New and Innovative Technology

Of the emerging technologies short-listed, enhancements to SVE were selected as the most promising and worthy of further development and study. The demonstrated effectiveness of conventional soil vapour extraction techniques for this situation, and the availability of large quantities of waste heat from gas plants influenced the majority of panel members to select this option. The introduction of waste heat into the unsaturated zone may be expected to increase contaminant removal rates and efficiencies up to four-fold (Feenstra, 1991), by increasing vaporization and volatilization. An associated benefit to this technique is that biological activity in the unsaturated zone is also expected to increase, further accelerating remediation.

The complexities of harnessing this waste heat, and successfully introducing it into the unsaturated subsurface are many, and include the effects of moisture on vadose zone permeability and air deliverability, and the mechanical systems required to duct heat to the system and effectively introduce it to the subsurface. All of these aspects will require extensive study and field testing.

The "detoxifier" steam augering system was ranked third amongst the emerging technologies, but is more applicable to finer-grained soils where SVE is less efficient.

6.2.4 Recommendation

For contamination situations involving condensate in permeable soils, the following technologies are recommended:

Established Technology: Soil vapour extraction with passive air injection. Off-gas treatments discussed in a following section.

Emerging Technology: Enhanced vacuum extraction / Bioventing, using injection of waste heat from gas plant operations to improve volatilization and biodegradation rates.

6.3 SITUATION S2A: CONDENSATE IN LESS PERMEABLE SOILS

The short listed technologies considered applicable for contamination situations involving condensate in low permeability unsaturated zone materials are shown in Table 6.3.

6.3.1 Factors of Concern

In general, the factors affecting remediation and technology selection for this case were similar to those outlined for more permeable soils (S1A). The physical and chemical properties of LNAPL condensate and its subsurface behaviour will play significant roles in the distribution and ease of remediation of the problem. As with the case involving more permeable soils, condensate trapped in soils or floating atop the groundwater surface will act as a long-term source of dissolved contaminants to groundwater. Any effective remedial strategy will have to consider removing this threat at some point, or face the consequences of perpetual maintenance. As with all situations, however, a detailed assessment of the risks to groundwater associated with the contamination should be initiated before decisions on remediation are made. In cases involving lower permeability materials particularly, risk assessment may show that the impact on groundwater quality is very small, and extensive remediation is not required.

TABLE 6.3

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: S2A

DESCRIPTION: Soil/unsaturated zone
low permeability materials (till)
Free condensate liquids and associated dissolved organics

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Soil vapour extraction, small spacings for low k materials, with off-gas treatment;
2. Biologically enhanced water infiltration/flushing during summer months;
3. Excavate and treat, various possible on-site treatments;
4. In-situ biological remediation, culturing of native organisms and nutrient and oxygen additions; approaches include:
    - trench systems or injection wells, raise groundwater table and cycle through recovery wells, surface bioreactor, additions of nutrients and oxygen.

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. "Detoxifier" system, steam-enhanced volatilization of VOC's using soil augering technique - estimated cost $150 to $450/T;
2. Radio frequency heating (RFH) as an enhancement to vacuum extraction - some pilot studies have quoted costs in the order of $150/T.
3. In-situ ozone treatment - in-place oxidation of organics.
4. Enhancement of SVE with waste heat from plant.

6.3.2 Ranking

Ranking of remedial technologies for this situation, as was the case with the situation involving more permeable soils, focused on the premise that the LNAPL condensate in the soils would act as continuous source of BTEX to groundwater. Pump-and-treat of dissolved BTEX contaminants in groundwater, without remediation of the "subsurface source" of contaminants, has been shown to be cost inefficient and ineffective in the long-term. Again, it is the water soluble fraction of condensate (BTEX and other aromatics) that are of most concern.

Table 6.4 shows the results of the technology ranking for both established and new/innovative techniques.

6.3.3 Discussion

Established Technologies

Four of five panel members agreed that soil vapour extraction, enhanced by passive ventilation of the unsaturated zone, was the most appropriate choice among established technologies. In lower permeability materials, however, soil vapour extraction systems are generally less efficient. Application of the technique under these conditions will require smaller extraction well spacings, or the use of vapour extraction trench systems. This system can be expected to remove up to 90% of typical Alberta condensates under these conditions, and do so more rapidly than the other listed technologies (except excavation). Another advantage is that it is the volatile components of condensate, and in particular the water soluble aromatics, which will be removed first and most completely. This in effect eliminates the LNAPL as a "subsurface source". Remaining high molecular weight components are of much lower environmental significance.

Other proven technologies ranked lower overall than SVE. Other methods are also hampered by low permeability conditions, notably in-situ bioremediation and soil washing, but their remedial effectiveness has not been well documented.

TABLE 6.4

TECHNOLOGY RANKING MATRIX

SITUATION S2A - CONDENSATE IN LESS PERMEABLE SOILS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Soil vapour extraction	**1**	**1**	**1**	**1**	**2**	**48**
Excavate and treat	2*	2*	2*	2	4	34*
Soil flushing	4	3	3	3	3	22
In-situ bioremediation	3	4	4	4	1	21
EMERGING						
Detoxifier	**1**	**2**	**1**	**1**	**1**	**48**
RF heating and SVE	4	4	4	-	4	08
Enhancement of SVE with heat	2	1	2	-	3	29
In-situ ozone treatment	-	-	5	-	-	01
In-situ bioremediation of soils	3	3	3	-	2	17
* Excavate "hot spots"						
POINT SYSTEM:	RANKING	POINTS				
	1	10				
	2	08				
	3	05				
	4	02				
	5	01				
	-	declined to mention				

Again, excavate and treat was considered to be too costly for general application. However, excavate and treat was identified by the panel members as suitable for treatment of isolated small "hotspots" of hydrocarbon-soil contamination. LNAPL migration rates will generally be slower in low permeability materials, so the overall occurrence of small hotspots is likely to be greater. Excavated soils could be treated on-site using low temperature volatilization techniques, or fed into experimental bioreactors of the type presently being tested by Gulf Canada at Rimbey Gas Plant, Alberta.

Off-gas treatment is not presently required in Alberta. However, the off-gases produced by vapour extraction of large volumes of condensate will have significant hydrocarbon concentrations. Some form of treatment is recommended. Off-gas treatments are discussed later in this section.

New and Innovative Technology

For lower permeability materials, the "Detoxifier" steam augering system was identified as holding most promise for remediation of relatively shallow (<10m) LNAPL soils contamination. This method was considered very appropriate by all panel members. Use of plant waste heat to enhance soil vapour extraction effectiveness was ranked second, but in cases of large contaminated areas at residual saturation (especially due to water table fluctuation LNAPL smearing), SVE would again be the preferred choice. One potential problem with the detoxifier system is that contaminants may be remobilized and introduced to the groundwater. The effectiveness of this system should be investigated under field conditions.

6.3.4 Recommendation

For less permeable soils contaminated with natural gas condensate, the following technologies are recommended:

Established Technology: Soil vapour extraction with passive air injection, design adjustments for lower permeability materials. Off-gas treatments discussed in a following section. For small isolated hotspots no deeper than about 4 m, excavation and treatment through low temperature volatilization (established) or bioreactor systems(emerging) is recommended.

Emerging Technology: Detoxifier steam augering system for volatilization of hydrocarbons from lower permeability materials.

6.4 SITUATIONS S1BC/ S2BC - INORGANIC CONTAMINANTS IN SOILS

A variety of inorganic contaminants may be found at ASGP's. The most common of these anions are such as chlorides and sulphates, and elemental sulphur from sulphur blocks. Heavy metals have been identified only at a few plants, and are not included in this discussion. The short-list of remedial technologies considered generally applicable for these situation are listed in Table 6.5 (permeable soils) and Table 6.7 (lower permeability soils).

6.4.1 Factors of Concern

A thorough review of the literature and available case histories of subsurface contamination revealed that the general level of effort which has been devoted to the study of remediation of inorganics (other than metals) from soils is quite low. This seems to have been due to the relative lack of concern with which such problems are viewed, especially in relation to the problems of contamination by toxic and carcinogenic organic compounds so prevalent in the US.

Soil contamination by chlorides and sulphates at Alberta sour gas plants is not well documented (CPA, 1990), but may provide a source for continued groundwater contamination. The general level of concern attached to these problems will, in general, be low compared to those involving organics, metals, and hydrocarbons. For this reason, technologies short-listed for consideration are in general simple and relatively inexpensive.

6.4.2 Ranking

If situations involving soil contamination by inorganics are of concern at a sour gas plant site, in-situ soil flushing is the recommended method of treatment for permeable and less permeable soils (Tables 6.6 and 6.8), particularly if a pump-and-treat system is already in place to deal with associated groundwater contamination. Infiltration may be assisted by deep

TABLE 6.5

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: S1BC

DESCRIPTION:	Soil/unsaturated zone high - moderate permeability materials inorganic contaminants; sulphur, sulphate, high salinity

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Chemical ammendments to treat specific inorganics (e.g. calcium carbonate additions to neutralize acid soil conditions from high sulphur content in soils), revegetation with specific plant species - for upper metre of soil.
2. In-situ soil flushing with water, shallow leachate collection or capture in groundwater pump-treat and reinfiltration system;
3. Excavate and treat, various ex-situ treatments.
4. Capping of sources, use of barriers for isolation.

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. Immobilization - stabilization with binding agents; work required to determine longevity of binding agents; literature quotes estimated costs of $40-80 /T.
2. Electroreclamation - in-situ method using electrode arrays, has been tested primarily on metal contamination problems, may be suitable for other contaminants.

TABLE 6.6

TECHNOLOGY RANKING MATRIX

SITUATION SIBC - INORGANIC CONTAMINANTS IN IN PERMEABLE SOILS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Chemical ammendment	4	-	4	-	1	14
In-situ soil flushing	**1**	**1**	**1**	**1**	**2**	**48**
Excavate and heat	2*	2*	2*	2	3	37
Capping/barriers	3	3	3	3	-	20
EMERGING						
Immobilization (in-situ binding)	-	-	-	-	-	-
Electroreclamation	-	-	-	-	-	-
* Excavate "hot spots"						

POINT SYSTEM:	RANKING	POINTS
	1	10
	2	08
	3	05
	4	02
	5	01
	-	declined to mention

TABLE 6.7

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: S2BC

DESCRIPTION:	Soil/unsaturated zone low permeability materials (till) inorganic contaminants; sulphur, sulphate, high salinity

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Chemical ammendments to treat specific inorganics (e.g. calcium carbonate additions to neutralize acid soil conditions from high sulphur content in soils), revegetation with specific plant species - for upper metre of soil.
2. Soil flushing with water, shallow leachate collection or capture in groundwater pump-treat and reinfiltration system; deep tilling could help infiltration rates in low K soils.
3. Excavate and treat, various ex-situ treatments.

NEW AND INNOVATIVE TECHNOLOGIES:

1. In-situ vitrification. Some field-scale pilot testing has been done, seems to be fairly expensive and only suited to small volumes.

TABLE 6.8

TECHNOLOGY RANKING MATRIX

SITUATION S2BC - INORGANIC CONTAMINANTS IN LESS PERMEABLE SOILS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Chemical ammendment	3	-	-	-	2	13
Soil flushing/deep filling	**1**	**1**	**1**	**1**	**1**	**50**
Excavate and treat	2*	-	2*	-	3	21
EMERGING						
In-situ vitrification (metals)	metals	-	-	-	metals	metals
* Excavate "hot spots"						

POINT SYSTEM:	RANKING	POINTS
	1	10
	2	08
	3	05
	4	02
	5	01
	-	declined to mention

tilling or ripping in the case of less permeable soils. If the problem is considered serious enough to require remediation, it will usually be as a result of a threat to groundwater quality. In these circumstances, groundwater extraction wells may already be in place downgradient of the spill site. Particular hot-spots could be excavated or capped with an impervious liner to prevent infiltration. The final choice of technology should be made depending on the results of risk assessment, and considering the areal extent and concentrations of the contaminated zone.

Based on the considerations outlined, development of a new/innovative technology was not seen as a priority, nor particularly worthwhile, by the project team. The methods short-listed (immobilization, electroreclamation, and in-situ vitrification) are extremely expensive, and are applicable mainly to metals problems.

6.4.3 Recommendation

For soils contaminated with inorganics (excluding metals), the following treatment technologies are recommended:

Established Technology: In-situ soil washing combined with a pump-and-treat system to collect leachate. For less permeable soils, deep tilling or ripping may help infiltration. Treatment technologies for inorganics in groundwater are discussed later in this section. Capping of spill sites or excavate and treat methods may be used for small, isolated, highly concentrated zones of contamination.

Emerging Technology: No emerging technologies are recommended for testing or development for this application.

6.5 SITUATION S1D/S2D - LOW pH CONDITIONS IN SOILS

The short-list of technologies which were considered for application at sour gas plants experiencing low pH (acidic) conditions in soils, primarily due to the oxidation of sulphur, are shown in Table 6.9.

TABLE 6.9

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: S1D/S2D

DESCRIPTION: Soil/unsaturated zone
Low pH soils , usually due to the presence of varying concentrations of elemental sulphur.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Liming and revegetation with appropriate plant species - a widely used technique at present. Additions of calcium carbonate depend on sulphur concentration in soils.
2. Excavate and treat or remove. Costly.
3. Soil flushing and collection of leachates, or flushing with buffering solutions, used in conjunction with pump-treat and reinfiltrate system for groundwater (if applicable), or underdrain system.

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. Removal and recycling of S-contaminated soils - to be used as fertilizer for Alberta farms; preliminary research shows costs would be similar to landfilling. A market for sulphur as a fertilizer appears to exist in Alberta.
2. Enhanced bacterial oxidation of sulphur - longer term process, works best under acidic soil conditions, effort required to maintain optimal conditions for the organisms;

This is one of the more prevalent problems at Alberta SGP's at present, due to the large amounts of sulphur which are produced and stored at many sites.

6.5.1 Factors of Concern

The presence of acidic soil conditions at gas plants is of concern to operators for several reasons. Low pH soils are detrimental to the development of vegetation, and may create "kill" zones around sulphur blocks or downwind of sulphur stacks as a result of sulphur dusting. Sulphur contamination concentrations in soils underlying sulphur blocks can be as high as 15% (Legget, 1991). Low pH conditions are discussed in detail in the Contaminant Situations section of this report (Section 4).

A main consideration in the remediation of this type of contamination must be the elimination of sources of soil acidity. Hence, removal of bulk elemental sulphur contamination will be of prime importance. Again, results of risk assessments will be of great value in determining the appropriate level of effort to be applied to a particular situation.

6.5.2 Ranking

Established Technologies

The results of the ranking exercise for this contamination situation are presented in Table 6.10. Of the established techniques, liming and revegetation of sulphur-contaminated soils has been widely tested, and has shown good success over the years (Legget, 1991). In terms of cost, simplicity and effectiveness, continued development of this method was seen as the most appropriate course. Other short-listed techniques such as soil flushing and excavation were deemed more complex, more expensive, and less effective overall than liming. A complete discussion of the liming and revegetation technique is provided in the Recommended Technologies section of this report.

Emerging Technologies

Two new and promising techniques for dealing with sulphur and low pH contaminated soils were considered. Each was very different, and could prove useful under different

TABLE 6.10

TECHNOLOGY RANKING MATRIX

SITUATION S1D/S2D - LOW pH CONDITIONS IN SOILS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Liming and revegitation	**1**	**NQ**	**1**	**1**	**1**	**40**
Excavate and treat	3*	NQ	3	-	3	15
Soil flushing	2	NQ	2	-	2	24
EMERGING						
Removal and recycling	**1**	**NQ**	**1**	**1**	**1**	**40**
Enhanced bacterial oxidation	2	NQ	-	-	2	16
* Excavate "hot spots"						

POINT SYSTEM:	RANKING	POINTS	NQ = Not Questioned
	1	10	
	2	08	
	3	05	
	4	02	
	5	01	
	-	declined to mention	

circumstances. The panel rated recycling of sulphur-contaminated soils for agricultural fertilizer as a very attractive solution worthy of future research. The philosophical elegance of solving one problem by solving another was attractive to the project team. Cost benefits to both operators and farmers purchasing fertilizer material are anticipated.

Degradation of sulphur by sulphur-oxidizing bacteria was also considered worthy of further study, although the potential increases in acid production caused by the process, the need to collect all drainage from the site, and the relatively long times required for oxidation made this option less favourable.

6.5.3 Recommendation

For remediating soils with low pH conditions and high levels of sulphur, the following are recommended:

Established Technology: Liming and revegetation.

Emerging Technology: Re-cycling of sulphur-contaminated soil as a fertilizer material for Alberta farms.

6.6 SITUATION T1A - CONDENSATE IN PERMEABLE SURFICIAL AQUIFERS

The short list of technologies which were considered as solutions to situations involving gas condensate LNAPL and associated dissolved aromatic hydrocarbons in groundwater is shown in Table 6.11. The variety of technologies which have been developed over the past several years for just this sort of application is considerable. This reflects the environmental concern attached to these types of problems. It must be stressed here that despite the grouping of technologies into "established" and "emerging" categories, the remediation of LNAPL hydrocarbon from groundwater is still a poorly-understood process. In the case of Alberta sour gas plants, complex geological conditions and the scarcity of information on the behaviour of gas condensate as a contaminant, dictate that all techniques be considered as emerging or experimental, and requiring significant additional study and field demonstration.

TABLE 6.11

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: T1A

DESCRIPTION: Saturated zone - surficial deposits
High to moderate hydraulic conductivity, sand and gravels typical
Groundwater contaminated with free phase condensate (LNAPL) and associated dissolved organics.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Pump-and-treat, using separate phase skimming systems; with various possible enhancements to the extraction system including:
    - reinfiltration/reinjection of treated water,
    - reinjection of heated water;

   Various possible treatment technologies for water contaminated with emulsified and dissolved hydrocarbons.
2. Soil vapour extraction; to assist in LNAPL residual removal.
3. In-situ bioremediation, surface bioreactor for native bacteria operating at low temperatures (10-15C), nutrient and oxygen additions, coupled with a pump-and-treat system to remove free hydrocarbon.

Combinations of the above

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. In-situ intercedent biological barriers - development of biofouling cultures to reduce medium permeability and simultaneously biodegrade dissolved organics. Experimental - lab testing showed good results.
2. In-situ sorption barriers - addition of cationic surfactants to increase sorption of organics by aquifer matrix. Experimental - no field or pilot tests founded in literature.
3. Use of large quantities of steam and waste heat available at gas plants to reduce LNAPL viscosity and improve mobility, and to increase volatility.
4. Subsurface volatilization and vapourization system (SVVS); bubbling of air through the saturated zone, combined with vacuum extraction of unsaturated zone. Possible enhancements include dry steam injection.
5. Use of surfactants to mobilize additional LNAPL in conjunction with Pump-and-Treat.

6.6.1 Factors of Concern

The key factors affecting the choice of technology at a particular site will include the subsurface behaviour of LNAPL condensate and its dissolved fraction, the hydrogeological conditions at the site, and the results of risk analysis. As with LNAPL-contaminated soils, the presence of mobile or residual LNAPL at, above or beneath the groundwater surface will severely complicate and lengthen remedial operations. Such LNAPL is considered as a "subsurface source" of dissolved contaminants to groundwater. Remedial efforts must focus not only on containment of the plume, but on removal of bulk LNAPL from the aquifer. Technology ranking proceeded under this assumption.

6.6.2 Ranking

Established Technology

The results of the technology rankings are shown in Table 6.12. The method advocated by all panel members was the initial implementation of a pump-and-treat system using dual pump systems to remove mobile LNAPL from the groundwater surface and control dissolved plume migration. In permeable homogeneous aquifers, this method can be expected to achieve recovery of up to 99% of free mobile product (USEPA, 1988). This method is recommended by the USEPA (1988) for similar situations. Skimming will not, however, significantly remediate residual saturations of LNAPL. As a second step of action, once the plume has come under control and the bulk of mobile condensate has been skimmed, is to implement a vapour extraction scheme in the unsaturated zone immediately above the now-depressed water table. SVE is recommended for situation S1A (condensate in the unsaturated zone).

Other short-listed techniques, including bioremediation and the use of physical or biological barriers, would also require implementation of pump-and-treat, and thus will add considerably to overall project costs. In-situ aerobic bioremediation could be considered as a polishing step after SVE had reached an asymptotic recovery point, if more complete clean-up were required.

TABLE 6.12

TECHNOLOGY RANKING MATRIX

SITUATION T1A - CONDENSATE IN PERMEABLE SURFICIAL AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Pump and treat	1	1	1	1	NQ	40
SVE	2	2	2	2	NQ	32
Barriers	4	4	4	4	NQ	08
In-situ bioremediati	3	3	3	3	NQ	20
In-combination	yes	yes	yes	yes	NQ	yes
EMERGING						
Biobarriers	4	4	-	-	NQ	04
Use of waste heat	1	1	1	1	NQ	40
SVVS	2	3	2	2	NQ	29
Suffactants	3	2	3	3	NQ	23

POINT SYSTEM:	RANKING	POINTS	NQ = Not Questioned
	1	10	
	2	08	
	3	05	
	4	02	
	5	01	
	-	declined to mention	

Pump-and-treat, hydrocarbon recovery methods, soil vapour extraction and in-situ bioremediation are discussed in detail (including costs and case history information) in the Recommended Technologies Section of this report.

Emerging Technology

Of the emerging technologies or techniques considered, the use of waste heat and steam to enhance the recovery of condensate LNAPL in both saturated and unsaturated zones was recommended by all panel members. The chief justification for this approach was the cost effectiveness of making use of this on-site resource, and the expected large increases in condensate volatilization and vaporization rates resulting from increased temperatures. For soil vapour extraction (situation S1A), this has been discussed and recommended. Introduction of steam or heated air into the aquifer via sparging-type wells as part of an enhanced subsurface volatilization-vaporization system (SVVS) was also ranked high. In essence, these recommendations are complementary.

The use of surfactants and biobarriers both hold promise for this type of situation, but were ranked lower due to higher anticipated costs, and the lack of detailed information on practical applications under similar circumstances. The use of surfactants may pose additional concerns through the introduction of additional contaminants (the surfactants themselves). The use of in-situ biological barriers may be applicable to such situations, but in general the use of barriers is recommended only for specific conditions where particular high hydraulic conductivity zones which control groundwater flow can be readily sealed.

6.6.3 Recommendation

For remediation of condensate LNAPL in permeable surficial aquifers, the following are recommended:

Established Technology: Pump-and-treat with dual pump systems to contain dissolved plume and skim mobile LNAPL, followed by soil vapour extraction to remove residual LNAPL in the unsaturated zone (including material exposed by water table depression). In-situ aerobic bioremediation could be applied as a final polishing step, using existing wells for nutrient and oxygen addition.

Emerging Technology: The use of waste heat from the plant, either as steam or for heating air should be investigated for enhancement of SVE, and for use with subsurface volatilization and vaporization techniques (SVVS).

6.7 SITUATION T2A - CONDENSATE IN LESS PERMEABLE SURFICIAL AQUIFERS

As with the previous situation (T1A, above), a wide variety of technologies were available for consideration. The short-list of technologies considered is presented in Table 6.13.

6.7.1 Factors of Concern

As with the high hydraulic conductivity situation (T1A), the main factor of concern for selection of remedial design was considered to be the potential for long-term groundwater contamination represented by residual phase LNAPL condensate on, below and above the groundwater surface. The long-term cost effectiveness of source removal was considered extremely important.

6.7.2 Ranking

Established Technologies

The recommended approach to this situation was similar to that chosen for the more conductive aquifer type (T1A), except that individual systems would be designed for low hydraulic conductivity conditions. Ranking results are shown in Table 6.14. Pump-and-treat systems would make use of large diameter wells or trenches, and be fitted with dual pump systems for skimming mobile condensate. Soil vapour extraction systems designed with close spacings should be applied, if necessary, as a next step. For low hydraulic conductivity conditions, the applicability of in-situ bioremediation was considered to be limited, based on case history information. Again, the use of several technologies in tandem or sequence was

TABLE 6.13

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: T2A

DESCRIPTION: Saturated zone - surficial deposits (e.g. till)
Low to moderate hydraulic conductivity
Groundwater contaminated with free phase condensate (LNAPL) and associated dissolved organics.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Pump-and-treat, using separate phase skimming systems, adapted for low K conditions - large diameter wells, close spacings; with various possible enhancements to the extraction system including:
    - reinfiltration/reinjection of treated water,
    - reinjection of heated water;

   Various possible treatment technologies for water contaminated with emulsified and dissolved hydrocarbons.

2. In-situ bioremediation, surface bioreactor for native bacteria operating at low temperatures (10-15C), nutrient and oxygen additions, coupled with a pump-and-treat system to remove free hydrocarbon.

Combinations of the above

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. In-situ intercedent biological barriers - development of biofouling cultures to reduce medium permeability and simultaneously biodegrade dissolved organics. Experimental - lab testing showed good results.

2. In-situ sorption barriers - addition of cationic surfactants to increase sorption of organics by aquifer matrix. Experimental - no field or pilot tests founded in literature.

3. Use of large quantities of steam and waste heat available at gas plants to reduce LNAPL viscosity and improve mobility, and to increase volatility.

4. Subsurface volatilization and vapourization system (SVVS) adapted to low K conditions, closer spacings; bubbling of air through the saturated zone, combined with vacuum extraction of unsaturated zone. Possible enhancements include dry steam injection.

5. Use of surfactants to mobilize LNAPL, in conjunction with pump-and-treat.

OTHER:

1. New trencher technologies allowing one-step excavation, collection system installation

TABLE 6.14

TECHNOLOGY RANKING MATRIX

SITUATION T2A - CONDENSATE IN LESS PERMEABLE SURFICIAL AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Pump and treat	1	1	1	1	NQ	40
SVE	2	2	2	2	NQ	32
Barriers	3	3	3	3	NQ	20
In-situ bioremediation	?	-	-	-	NQ	-
EMERGING						
Use of waste heat	1	1	1	1	NQ	40
Biobarriers	2	2	-	-	NQ	16
SVVS	3	-	-	-	NQ	05
Trenchen systems	yes	yes	yes	yes	NQ	yes
* excavate "hot spots"						

POINT SYSTEM:

RANKING	POINTS
1	10
2	08
3	05
4	02
5	01
-	declined to mention

NQ = Not Questioned

seen as the best approach. Phasing-in of enhancements or improvements over the life of the project could increase overall long-term costs by slightly increasing clean-up time, but the added flexibility and ability to modify systems is of definite benefit.

Emerging Technologies

As with situation T1A, study of the use of waste heat to improve volatilization and vaporization was recommended by the panel. The use of air-sparging systems and SVVS was not however recommended for use in low permeability materials. A specific technology that may be investigated for application is the "trencher" machine, which will simultaneously excavate a narrow trench, lay pipe, and backfill. Biobarriers were seen as being of limited applicability in low permeability materials where groundwater flow velocities would be fairly slow to begin with.

6.7.3 Recommendation

For remediation of gas condensate in less permeable surficial aquifers, the following are recommended:

Established Technology: Pump-and-treat with dual pump systems to contain dissolved contamination and skim mobile LNAPL, using trenches or large diameter wells as applicable. This to be followed by soil vapour extraction to remove residual LNAPL in the unsaturated zone and the area exposed by water table depression.

Emerging Technology: The use of waste heat from the plant, either as steam or for heating air should be investigated for enhancement of SVE. Trencher technologies may be used to quickly and cost-effectively construct interception trenches.

6.8 SITUATIONS T1BC / T2BC - DISSOLVED CONTAMINANTS IN SURFICIAL AQUIFERS

As described in the contamination situations section of this report, and in CPA (1990), groundwater contamination by dissolved inorganics (primarily chloride and sulphate), was found to be a common occurrence at ASGP's. In many cases where such inorganic plumes were sampled for dissolved organics, compounds such as BTEX and low levels of process chemicals such as sulfolane and DIPA also were detected (CPA, 1990). A complete discussion of process chemicals from gas plant operations and wastes is presented in the Contamination Situations section of this report. At present, the extent of the process chemicals problem at ASGP's is not known, and clearly requires more study.

The technologies short-listed for application to this contamination situation are shown in Table 6.15. No emerging technologies are discussed. Due to the types and concentrations of contaminants involved, most of the new and innovative technologies developed for in-situ treatment of organics are not applicable.

6.8.1 Factors of Concern

The appropriate remedial response for this contamination situation will depend on the presence, types and concentrations of process chemicals and BTEX in the inorganic plume. Unless present in very high concentrations, sulphate and chlorides alone are not of extreme environmental concern. However, the presence of BTEX and/or process chemicals will significantly affect the results of a risk assessment.

The selected remedial approach in most cases of this type will be dictated by the perceived need to prevent plume migration towards receptors of environmental significance. In some cases, plume clean-up will be desired. Of course, the obvious (but too often neglected) first step should always be to remove the source of further contamination. Process water ponds, for instance could be decommissioned or reconstructed with impermeable liners and leak-detection systems. Ranking was based on the premise that plume containment and eventual clean-up were required, and that the presence of low levels of process chemicals and possibly BTEX were the driving forces behind that decision.

6.8.2 Ranking

The results of the ranking exercise are shown in Table 6.16. Each of the panel members recommended that in the majority of the cases described at ASGP's involving dissolved contaminants, concentrations of inorganics were so low (chlorides typically from 150 to 500 mg/L) that the option of allowing natural dissipation of the plume should be seriously

TABLE 6.15

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODES: T1BC/T2BC

DESCRIPTION: Saturated zone - surficial deposits
Groundwater contaminated with dissolved inorganic and inorganic compounds.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Pump-and-treat. Treat and reinfiltrate/reinject water for flushing. Various treatment methods for dissolved inorganic species. Provides clean-up and hydraulic control of plume migration.
2. Physical barriers.
3. Passive barriers/collection systems such as trenches. Treatment of contaminated water.
4. Passive dissipation if results of risk assessment allow.

TABLE 6.16

TECHNOLOGY RANKING MATRIX

SITUATION T1BC/T2BC - DISSOLVED CONTAMINANTS IN SURFICIAL AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
<u>ESTABLISHED</u>						
Pump, treat and reinject	2	2	2	2	NQ	32
Passive dissipation	1	1	1	1	NQ	40
Flushing only	1-2	1-2	1-2	1-2	NQ	36
Barriers	-	-	-	-	-	-
Source removal	yes	yes	yes	yes	NQ	yes

POINT SYSTEM:	RANKING	POINTS
	1	10
	2	08
	3	05
	4	02
	5	01
	-	declined to mention

NQ = Not Questioned

considered, especially where no receptors are close by and dissolved organic concentrations are low. A risk assessment exercise through the use of predictive hydrogeological modelling would provide estimates of expected plume concentrations and distributions in the future.

In cases where active control or remediation would be required, the pump-and-treat technique is ideal. After treatment or dilution, produced groundwater could be reinjected up or down gradient of the plume to provide flushing and additional plume control. Treatment methods for this type of inorganic/organic contamination are discussed later in this section. In cases where simple plume dilution will achieve the required goals, the aquifer could be flushed with clean water from another supply. These recommended approaches were chosen for their practicality, simplicity, and cost effectiveness.

6.8.3 Recommendation

For situations involving dissolved inorganics and organics in surficial aquifers, the following are recommended:

Established Technology: Risk assessment to determine if natural dissipation will suffice. If active remediation is required, flush aquifer, or pump-treat-and-reinject.

6.9 SITUATION T1D / T2D - LOW PH CONDITIONS IN SURFICIAL AQUIFERS

The short list of applicable technologies for these situation is shown in Table 6.17. Due to the comparative rarity of acid seepage conditions at industrial sites, very little work on new and innovative remedial technologies for these problems has been conducted to date. In most instances, however, such problems at ASGP's are typically local in extent, due to the large natural buffering capacity of soils and groundwater (CPA, 1990).

6.9.1 Factors of Concern

Acid seepage waters from sulphur block runoff have been documented at only a few gas plants (CPA, 1990). Case history P-2 exhibits such an example. In general, the natural

TABLE 6.17

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: T1D / T2D

DESCRIPTION: Saturated zone - surficial deposits
All ranges of hydraulic conductivity
Low pH groundwater conditions, acid water seepage associated with sulphur contamination, and seepage from sulphur runoff ponds.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Remove/isolate source of acid, allow natural dissipation of acidity (depending on natural buffering capacity of soils, volumes being considered, and groundwater flow velocities).
2. Flushing with buffered water, via infiltration galleries or wells.
3. Pump-and-treat to control plume migration and remove acid waters, surface treatment and reinjection to flush zone.
4. Interception by buffering trenches, buffering materials cycled through downgradient trench system.

In the context of ASGP's, all methods are essentially new, as no work on this problem has yet been attempted.

TABLE 6.18

TECHNOLOGY RANKING MATRIX

SITUATION TD/T2D - LOW pH CONDITIONS IN SURFICIAL AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Natural dissipation w. source removal	1	1	1	1	NQ	40
Pumps & treat & inject	2-3	2-3	2-3	2-3	NQ	26
Flush with buffering solutions	2-3	2-3	2-3	2-3	NQ	26
Buffer Trenches	4	4	4	-	NQ	6

POINT SYSTEM:

RANKING	POINTS
1	10
2	08
3	05
4	02
5	01
-	declined to mention

NQ = Not Questioned

buffering capacities of soil and bedrock in Alberta will likely prove sufficient to attenuate acidic conditions within a few metres of the source. One related problem may be the mobilization of heavy metals. This situation was identified at one sour gas plant during the phase I study (CPA, 1990). The likelihood of extensive migration of low pH plumes in groundwater in surficial aquifers is not considered high.

6.9.2 Ranking

The results of the ranking exercise for this situation are shown in Table 6.18. As with situations involving relatively low concentrations of dissolved inorganic compounds, natural dissipation after source removal may be sufficient to control and eventually eliminate the plume. A simple hydrogeological or hydrogeochemical model could be used to determine likely plume behaviour, migration and buffering. If the results of the risk assessment indicate that active remediation is required, a pump-treat-and-reinject system can be installed. A system to flush the aquifer with a buffering solution may also be applicable. These solutions are simple, effective and relatively inexpensive. The need for development of new technologies for this problem was not recognized by the panel.

6.9.3 Recommendation

For situations involving low pH conditions in groundwater in surficial aquifers, the following is recommended:

Remove source. Based on risk assessment, allow passive dissipation, flush with buffering solutions, or pump-and-treat to control plume. Level of effort to depend on severity of problem.

6.10 SITUATIONS R1A / XA / R2A - CONDENSATE IN FRACTURED BEDROCK AQUIFERS

As with the previous contamination situations involving groundwater hydrocarbon remediation, the number of different technologies available is large (conventional and experimental). This is reflected in the short list, presented in Table 6.19.

TABLE 6.19

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: R1A / XA /RZA

DESCRIPTION: Saturated zone - bedrock, and bedrock in hydraulic connection with high K surficial materials.
Matrix and fracture permeability,
Groundwater contaminated with free hydrocarbon and associated dissolved organics.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Soil venting.

2. Pump-and-treat, using seperate phase skimming; treatment of contaminated groundwater, reinfiltration of water. Possible enhancements to help remove residual hydrocarbon saturation in unsaturated and saturated zones:
   - surfactants,
   - dry steam,
   - HC degrading bacteria and nutrients,

3. In-situ bioremediation.

4. Physical barriers (in applicable cases only).

NEW AND INNOVATIVE TECHNOLOGIES FOR CONSIDERATION:

1. In-situ intercedent biological barriers - development of biofouling cultures to reduce medium permeability and simultaneously biodegrade dissolved organics. Experimental - lab testing showed good results.

2. In-situ sorption barriers - addition of cationic surfactants to increase sorption of organics by aquifer matrix. Experimental - no field or pilot tests founded in literature.

3. SVVS system; air injection into saturated zone coupled with vacuum extraction. Possible enhancements.

4. Use of surfactants to mobilize LNAPL as part of a pump-and-treat sustem.

OTHER:

1. Use of large quantities of steam and waste heat available at gas plants to reduce LNAPL viscosity and improve mobility, and to increase volatility. Use of other methods of substrate heating, including low energy RF heaters).

6.10.1 Factors of Concern

Several factors will control the effectiveness of remedial techniques for LNAPL gas condensate in fractured bedrock. Most conventional hydrocarbon recovery systems have been developed for use in granular materials. The presence of fractures will in general reduce clean-up efficiencies and prolong remedial programs. LNAPL may be trapped in dead-ends and cutoffs. In dual-porosity aquifers, where rock of significant matrix porosity and permeability is also fractured, fractures may be swept preferentially and LNAPL preferentially retained in the matrix. For all of these reasons, the remediation of LNAPL gas condensate in fractured bedrock must be considered as "experimental" at best (Feenstra, 1991). Very little work has been done in this area to date. The effectiveness under these conditions of even the most well-understood technologies (such as pump-and-treat) have to be explored in detail. Panel members all expressed caution in their selections for these situations, and stressed the need for further research before definitive conclusions could be drawn. On this basis, the rankings should be seen as a guide for continuing study rather than a definitive recommendation.

6.10.2 Rankings

Established Technologies

The rankings for these situations are shown in Table 6.20. Pump-and-treat was selected as the most appropriate first step in controlling migration of dissolved contaminants and skimming of mobile LNAPL condensate. If practical, LNAPL smeared above the groundwater surface can be removed with soil vapour extraction systems. As a polishing step, in-situ bioremediation enhanced by oxygen and nutrient additions could be applied. For this situation, a combination of technologies was seen as the best approach. Simple skimming and plume control was not considered sufficient for these situations, as residual LNAPL would act as a permanent source of dissolved BTEX. This combination of steps has been applied at several sites with good success. These and other case histories are discussed in the Recommended Technologies section of this report.

TABLE 6.20

TECHNOLOGY RANKING MATRIX

SITUATION R1A/XA/R2A - CONDENSATE IN FRACTURED BEDROCK AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Pump and treat	1	1	1	1	NQ	40
SVE	1	1	1	1	NQ	40
In-situ bioremediation	2	3	2	2	NQ	29
Barriers	3	2	3	Don't Use	NQ	18
EMERGING						
Bio-barriers	3	3	3	3	NQ	20
SVVS	1	2	1	1	NQ	38
Surfactants	2	1	2	2	NQ	34
Sorption barriers	4	4	-	-	NQ	8
NOTES						
Subsurface source (?) removal	YES	YES	YES	YES	NQ	YES
Skim free product (?)	YES	NO	YES	YES	NQ	YES

POINT SYSTEM:	RANKING	POINTS
	1	10
	2	08
	3	05
	4	02
	5	01
	-	declined to mention

NQ = Not Questioned

Emerging Technologies

Given the complex nature of contaminant behaviour and groundwater flow in fractured bedrock, it was recognized that the much-discussed limitations of pump-and-treat would also apply to other technologies which depend on transport through the aquifer to achieve contaminant removal or contact. These techniques would include in-situ bioremediation, surfactant addition, soil vapour extraction, in-situ air-stripping (SVVS), and others. Both the SVVS / air-sparging system and the use of surfactants were identified as being worthy of study and field demonstration at Alberta sour gas plants. Again, however, their dependence on pump-treat-reinject systems reinforces the need for research into pump-and-treat in fractured bedrock conditions.

6.10.3 Recommendations

For condensate LNAPL contamination of fractured bedrock aquifers, the following technologies are recommended:

Established Technology: Pump-and-treat to control dissolved plume. Skim free condensate with dual pump systems. Remove source residual LNAPL using soil vapour extraction and in-situ bioremediation.

Emerging technology: Subsurface volatilization and vaporization (SVVS) and the use of surfactants are recommended for additional study.

6.11 SITUATION R1BC / R2BC - DISSOLVED CONTAMINANTS IN BEDROCK AQUIFERS

The short list of technologies considered for this contamination situation are listed in Table 6.21. As with other situations involving low concentrations of dissolved organics and trace levels of organics such as BTEX and process chemicals, the available options are limited. Recent research into techniques for remediating these types of problems has been sparse.

TABLE 6.21

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: R1BC / R2BC

DESCRIPTION:	Saturated zone - bedrock, sandstone and siltstone; or fractured bedrock; Range of hydraulic conductivities, Groundwater contaminated with dissolved inorganics and organics.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Pump and treat. Reinfiltration of treated water upgradient to flush contaminants; combined water treatment trains using technologies suited to types of contaminants found.
2. Physical barriers / containment.
3. Passive dissipation, based on results of risk assessment (elimination of sources assumed).

* No promising new technologies were found which are suitable to this type of situation.

TABLE 6.22

TECHNOLOGY RANKING MATRIX

SITUATION R1BC/R2BC - DISSOLVED CONTAMINANTS IN BEDROCK AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Pump & treat & inject	2	2	2	2	NQ	20
Barriers	3	3	3	3	NQ	32
Climinate source and natural dissipation (if possible)	**1**	**1**	**1**	**1**	**NQ**	**40**
NOTES						
Study into process chemicals in groundwater requried?	YES	YES	YES	YES	NQ	YES

POINT SYSTEM:	RANKING	POINTS	NQ = Not Questioned
	1	10	
	2	08	
	3	05	
	4	02	
	5	01	
	-	declined to mention	

6.11.1 Factors of Concern

The main factor of concern in selecting a remedial alternative for this type of problem is the associated risk. If organics of concern (BTEX, process chemicals) are present at significant levels in the plume, active remediation may be required. Additional research into the extent of process chemicals contamination at Albert sour gas plants is required.

6.11.2 Ranking

As with similar contamination situations in surficial materials (T1BC/T2BC), source elimination and natural dissipation was seen by the panel as the first, most simple, and least expensive option. Risk assessment techniques can be used to help make decisions of this nature. If the results of such assessments dictate the need for active remediation, pump-and-treat-and-flush systems should be able to provide complete plume capture, control and remediation in most cases. Treatment alternatives for inorganic contaminants are discussed later in this section. No need for development and testing of new and innovative remediation technologies for this type of problem was identified by the panel. Ranking results are shown in Table 6.22.

6.11.3 Recommendation

For situations involving dissolved contaminants (primarily inorganics) in bedrock aquifers, the following is recommended:

Depending on results of risk analysis, remove source and allow natural dissipation of plume. If active remediation is required, implement a pump-treat-and-flush system.

6.12 SITUATION R1D / R2D - LOW pH CONDITIONS IN BEDROCK

The short list of technologies considered for this situation is shown in Table 6.23. As with other situations involving low pH conditions, relatively few applicable technologies were considered. Little research and development into this type of problem has been done to date.

TABLE 6.23

TECHNOLOGY SHORT LIST

CONTAMINATION SITUATION CODE: R1D/ R2D

DESCRIPTION: Saturated zone - bedrock, sandstone and siltstone; or fractured bedrock;
Range of hydraulic conductivities,
Low pH groundwater associated with sulphur contamination, acid seepage from sulphur runoff ponds.

APPLICABLE TECHNOLOGIES/APPROACHES:

1. Source elimination / isolation, allowing natural dissipation and buffering to eliminate plume over time (based on results of risk assessment).

2. Pump and treat. Reinfiltration of treated water upgradient to flush contaminants; could be coupled with reinjection of water with enhanced buffering ability. In cases of rapid migration of acid water through zones of high hydraulic conductivity (such as fractures) and little natural buffering capacity (clastics), active hydraulic control may be required.

3. Flushing of aquifer with water, or with buffering solutions, no recovery;

6.12.1 Factors of Concern

The main factors affecting the choice of remedial technology for this situation are similar to those described for acidic conditions in surficial aquifers (T1D / T2D). One important difference should be considered, however. The potential for migration of low pH water over long distances through bedrock fractures does exist. Large fractures in clastic bedrock with low carbonate content could form conduits for rapid off-site migration of acidic waters. Minimal surface contact and low buffering capacity of the rock could combine to produce relatively serious acid water migration. Detection and delineation of fractures is difficult and expensive. However, regional techniques (such as air-photo interpretation) can be used to determine if the area in question has a good probability of being heavily fractured. In cases involving large continuous sources of acid water (large sulphur blocks), active remediation may be the prudent course.

6.12.2 Ranking

If source removal is possible, the option of allowing the plume to dissipate and buffer naturally should be investigated. If remediation is required, or if intensive fracturing in clastic rock is suspected, a pump-treat and flush system is recommended. Flushing with buffering solutions could speed up remediation considerably. The potential effects of fracturing on pumping and injection effectiveness should be investigated during the design phase. The recommended methods should provide simple, quick and relatively cost-effective remediation of acid seepage problems. The ranking results are shown in Table 6.24.

6.12.3 Recommendation

For situations involving low pH conditions in bedrock aquifers, the following is recommended:

Assess risks associated with contamination. If risks warrant, implement pump-treat and flush system.

TABLE 6.24

TECHNOLOGY RANKING MATRIX

SITUATION R1D/R2D - LOW pH CONDITIONS IN BEDROCK AQUIFERS

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Pump & treat & reinject	2	2	2	2	NQ	32
Flush with buffering solutions	2	2	2	2	NQ	32
Source removal and passive dissipation (if possible)	**1**	**1**	**1**	**1**	**NQ**	**40**

POINT SYSTEM:

RANKING	POINTS
1	10
2	08
3	05
4	02
5	01
-	declined to mention

NQ = Not Questioned

6.13 TREATMENT OF DISSOLVED ORGANICS IN GROUNDWATER

The short list of treatment technologies for groundwater contaminated with dissolved organics (primarily targeted at BTEX compounds associated with gas condensate contamination) is found in Table 6.25. Over the past several years, many new technologies for the treatment of organics have been developed, including methods providing complete destruction of organics.

6.13.1 Factors of Concern

Factors considered during the comparative assessment included treatment level (using BTEX in the 20 to 50 mg/L range as a datum) , cost, and availability of equipment. The ability of systems to treat relatively large flows (up to 2000 L/min) was also a factor. The ability to treat low levels of process chemicals was not examined directly, as more research into these compounds is required for a proper comparative analysis.

6.13.2 Ranking

Established Technology

The panel selected conventional air-stripping as the treatment technology presently most applicable to treatment of BTEX - contaminated groundwater (Table 6.26). The technology has been widely tested, including at a large sour gas plant site in Alberta, where removal efficiencies of 99.9% were achieved for BTEX from condensate-contaminated groundwater. Air-strippers are readily available, relatively easy to set-up and operate, and are less expensive (capital and O&M) than other options considered, for the same level of clean-up. The air-stripping process could also be readily enhanced by heating influent with plant waste heat. At present off-gas treatment for air-strippers is not required in Alberta, but is recommended. Air stripping is discussed in detail in the Recommended Technologies Section of this report.

GAC alone was found to be far too expensive over the long term, and spent carbon poses additional problems of disposal or regeneration. If surface water release is required, the use of GAC could be considered as a polishing step after air-stripping. In this capacity, the system would be effective, and carbon replacement would be much less frequent. Surface bioreactors

TABLE 6.25

TECHNOLOGY SHORT LIST

TREATMENT METHODS FOR GROUNDWATER CONTAMINATED WITH DISSOLVED ORGANICS

Most Common dissolved organics: BTEX, 1,2,4 trimethyl benzene, can be associated with emulsified free phase gas condensate; process chemicals such as sulfinol, sulfolane, amines, diisopropyl amine (DIPA), and glycols (e.g. ethylene glycol).

TREATMENT METHODS - TESTED AND ESTABLISHED

1. Air stripping with off-gas treatment; possible enhancements include heating influent, with off-gas treatment by:
   - flaring
   - catalytic oxidation
   - incineration
   - AC filtration

2. Granular activated carbon filtering (GAC)

3. Biotreatment; enhanced surface bioreactor systems;

4. Oil-water separators, for removal of free product/emulsion; common, advanced designs available.

TREATMENT METHODS - REQUIRING ADDITIONAL TESTING

1. Advanced oxidation processes (AOP); H_2O_2, Ozone, UV systems; high destruction efficiency, no by-products for disposal. Some field-scale pilot test done in USA - costs claimed to be similar to air-stripping and AGC. Requires a "clean" feed (no free hydrocarbon). In use at three superfund sites.

2. Steam stripping, using stripping tower technology with steam from gas plant operations; good for higher concentrations of influent organic concentration.

3. Vacuum spray aeration technologies.

TABLE 6.26

TECHNOLOGY RANKING MATRIX

TREATMENT OF ORGANICS (BTEX) IN GROUNDWATER

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Air-stripping	1	1	1	1	NQ	40
Activated carbon	3	3	3	3	NQ	32
Simple aeration	2	2	2	2	NQ	20
EMERGING						
Advanced oxidation	1	1	1	1	NQ	40
Steam stripping	2	4	3	2	NQ	23
Vaccum spray aeration	4	3	4	4	NQ	9
Surface bioreaction	3	2	2	3	NQ	26

POINT SYSTEM:	RANKING	POINTS
	1	10
	2	08
	3	05
	4	02
	5	01
	-	declined to mention

NQ = Not Questioned

were deemed to be too experimental and requiring of additional research to recommend as an established technology.

Emerging Technology

Of the emerging technologies considered, the panel overwhelmingly endorsed advanced oxidation processes (AOP) as worthy of research and demonstration at ASGP's. This technology was seen as having the advantages of complete destruction of organics, at a cost claimed to be comparable to air-stripping. As an added attraction, AOP has been shown to be effective on a wide variety of complex and difficult-to-treat organics, and could be used to simultaneously treat process chemicals in groundwater. These advantages made AOP the clear choice of the panel as the recommended emerging technology. A complete discussion of AOP, including case histories and cost information, is provided in the Recommended Technologies Section.

6.13.3 Recommendation

Established Technology: Air-stripping to remove BTEX, and GAC polishing if surface water quality disposal is required. Off-gas treatment recommended but not required.

Emerging Technology: Advanced oxidation processes for complete destruction of a wide variety of process chemicals, potentially including process chemicals.

6.14 TREATMENT OF DISSOLVED INORGANICS IN GROUNDWATER

The short-list of treatment technologies considered is provided in Table 6.27. Many traditional treatment technologies used in the wastewater industry are available, and sophisticated desalinization processes have also been developed.

6.14.1 Factors of Concern

The typical inorganic constituents in dissolved phase plumes at Alberta sour gas plants were found to be chlorides and sulphates. The concentrations of these anions in contaminated

TABLE 6.27

TECHNOLOGY SHORT LIST

TREATMENT METHODS FOR GROUNDWATER CONTAMINATED WITH DISSOLVED INORGANICS

Most Common dissolved inorganics: chlorides, sulphates

TREATMENT METHODS - TESTED AND ESTABLISHED

1. Reverse osmosis (RO) systems;
2. Ion exchanged and filtration methods.
3. Chemical precipitation - through pH adjustment and oxidation-reduction reactions. Must be desinged for specific contaminants.
4. Dilution and reinjection (for lower elvels of dissolved inorganics).

TREATMENT METHODS - REQUIRING ADDITIONAL TESTING

1. Freeze crystallization - takes advantage of the cold winter temperatures and uses freezing of water as a way to remove dissolved inorganics (experimental).

groundwater at ASGP's are typically quite low, ranging from 100 to 5000 mg/L (CPA, 1990). These levels do not, in most circumstances, pose a serious environmental or health hazard. Associated concentrations of dissolved organics may be of much greater concern. These considerations were considered to be very important be panel members. Alone, such concentrations of inorganics are difficult and expensive to treat, and in many cases treatment may not be required. Technology ranking proceeded on this basis.

6.14.2 Ranking

Established Technologies

Of the technologies discussed, the use of ion exchange was identified as most worthy of further consideration and research with regard to removing inorganic anions such as chlorides and sulphates. An alternative solution, and the one which was recommended by the panel, would be to combine the effluent stream, after organics removal, with clean water from pumping wells on-site. The combined water would have a decreased concentration of inorganics and could then be reinjected upgradient of the contaminant plume on a continuing basis to help flush contaminants and dilute plume concentrations. This approach would provide an effective and relatively inexpensive remedy. The rigorous removal of such low levels of inorganics was not seen as worthwhile, other than in special circumstances. Systems such as reverse osmosis are expensive, not always effective, and work best on highly saline influents. Ranking results are shown in Table 6.28.

Emerging Technologies

Of the emerging technologies, freeze crystallization and separation technologies were selected as having the best potential for further development. At present, very little is known about the applicability of the technique to treatment of groundwater, particularly for relatively low concentrations of inorganics found at ASGP's. The panel found the potential use of cold temperatures particularly attractive, and suggested that development of the technology might be appropriate. A detailed discussion of freeze crystallization is provided in the recommended technologies section of this report.

TABLE 6.28

TECHNOLOGY RANKING MATRIX

TREATMENT OF INORGANICS IN GROUNDWATER

	PANEL MEMBER					POINT TOTAL
	1	2	3	4	5	
ESTABLISHED						
Remove trace organics and dilute	1	1	1	1	NQ	40
Ion exchange & filtration	2	3	2	2	NQ	29
Reverse osmosis	-	-	-	-	NQ	-
Chemical precipitation	4	-	-	-	NQ	2
Deep well injection	3	2	3	-	NQ	18
EMERGING						
Freeze crystallization	1	1	1	-	NQ	30

POINT SYSTEM:

RANKING	POINTS
1	10
2	08
3	05
4	02
5	01
-	declined to mention

NQ = Not Questioned

6.14.3 Recommendation

Established Technology: Treat recovered groundwater for organics, dilute with clean groundwater and reinject to flush and dilute plume.

Emerging Technology: Freeze crystallization techniques should be investigated as a possible treatment method for inorganics in groundwater.

6.15 TREATMENT OF OFF-GASES

A number of treatment methods for off-gases have been developed, mostly in the US where air-emission standards and regulations are quite strict. In Alberta at present there are no requirements for off-gas treatment. The short-listed technologies considered are shown in Table 6.29

6.15.1 Factors of Concern

One of the main decision making criteria for selection of treatment technologies is cost. The lack of regulations requiring off-gas treatment in Alberta makes the use of all such systems difficult to justify at present. All the short-listed should be expected to at least double the cost of the chosen remediation technology. Other factors influencing the choice of remediation technology would include the concentration of organics in the off-gases, and the presence of sensitive neighbours downwind. The use of complete destruction technologies such as AOP for treatment of VOC-contaminated groundwater will eliminate the need for off-gas treatment.

6.15.2 Ranking

Due to the limited amount of data available it is was not possible to generate accurate comparisons between the various methods for treatment of the same off-gas. A further complication was the fact that each off-gas varies in concentration and composition not only with treatment site, but often over time. For instance, treatment of offgases from a SVE system at a site contaminated with large volumes of free condensate would be expected to produce high concentrations of VOC vapours for the first several months of operation. This would decline with time. A site contaminated with low levels of a heavier condensate would generate soil vapour off-gases of lower concentrations and different composition.

TABLE 6.29

TECHNOLOGY SHORT LIST

TREATMENT METHODS FOR OFF-GASES FROM AIR-STRIPPERS AND SVE SYSTEMS

Treatment for volatile components of natural gas condensates: BTEX and lighter aliphatic hydrocarbons. Concentrations are expected to be much higher from soil venting than from air-stripping.

TREATMENT METHODS - TESTED AND ESTABLISHED

1. Activated carbon adorption
2. Thermal incineartion
3. Catalytic oxidation
4. Membrane separation
5. biofiltration

TREATMENT METHODS - REQUIRING ADDITIONAL TESTING

1. Flaring through adaptation of existing gas flare tsacks at sour gas plants.
2. Advanced oxidation systems
3. Peat moss adsorption
4. Carbon fibre adsorption
5. Fixed film (bioair)

Established Technologies

The established technologies considered all possessed pros and cons regarding potential applications. Also, flow conditions and VOC concentrations will affect choice of technology. For SVE systems, the use of knock-out devices is recommended as the first step in treatment of heavily contaminated off-gases. This will allow recovery of condensate liquids from SVE systems at heavily contaminated sites. For secondary SVE off-gas treatment of air-stripper off-gas treatment, catalytic oxidation processes are likely the best choice. Capital costs are higher than for activated carbon systems, but carbon systems O&M costs for high VOC concentration off-gases would be considerable. Thermal incineration has been only rarely applied for off-gas treatment in the US, and is the most expensive of the available systems. The other main advantage of catalytic oxidation is that contaminants are completely destroyed (unlike carbon which must be regenerated or disposed of). Removal efficiencies for catalytic oxidation systems are above 95%.

For air-stripper off-gases, however, carbon adsorption systems become the best choice. Much lower VOC influent concentrations for treatment mean carbon lasts longer. Carbon adsorption costs per unit volume of off-gas treated from air-strippers has been shown to be at least three times cheaper than for thermal incineration and catalytic oxidation.

Emerging Technologies

Of the emerging off-gas treatment methods, the one with the most promise at ASGP's was deemed to be the use of existing gas flaring systems for the flaring of condensate vapours. Initial discussions held with plant engineers at sites in Alberta indicated that this was possible. The obvious advantage is the tremendous potential cost savings over all other conventional and emerging treatment systems. Of the self-contained treatment technologies, the use of advanced oxidation (UV) processes were thought most worthy of research. These systems can provide complete destruction of organics, and have shown excellent potential for becoming cost-competitive with more established technologies.

6.15.3 Recommendation

For the treatment of off-gases from soil vapour extraction systems and air-strippers, the following technologies are recommended:

Established Technology: For treatment of high-concentration SVE off-gases, use a preliminary knock-out system for liquids, and then take off-gas to a catalytic oxidation system. For air-stripping off-gases, use carbon adsorption (but recognize that development of AOP treatment methods for VOC-contaminated groundwater will eliminate this need altogether).

Emerging Technology: Both use of on-site flaring systems, and AOP for off-gases are worthy of study and future development for application at ASGP's.

6.16 SUMMARY

The selections and recommendations discussed in the previous sections were designed to provide the most cost-effective and efficient solutions to particular contamination situations which have been identified at Alberta sour gas plants. The selection and ranking method employed relied on the experience of senior members of the project team. It is interesting to note that an independent study of appropriate remedial technologies presented in the Hazardous Waste Consultant (1990) supports the conclusions drawn by this study. Using a formal ranking system based on technical feasibility, treatment level, innovation, adverse impacts, cost, and time considerations, the aforementioned study ranked the following technologies as generally most appropriate:

- For contaminated soils:
  1. In-situ bioremediation
  2. Soil washing

- For free product recovery:
  1. Dual pump systems

- For treatment of contaminated groundwater:
  1. Thermal vacuum spray aeration
  2. AOP

- For in-situ groundwater treatment:
  1. Aerobic bioremediation

These results, although determined as part of a broad, general study focusing on industrial contamination in the US, reinforces the validity of the general selections and approach of this study of gas plant related situations.

Again, the need for research into all aspects of sour gas plant-related subsurface contamination must be stressed. In particular, the following areas should be targeted for study:

- The nature, occurrence and subsurface behaviour of process chemicals; and treatment technologies suitable for their remediation;

- The behaviour of LNAPL gas condensate in the subsurface, and particularly in fractured media. Specific areas of concern include monitoring and site characterization techniques, remedial concerns, biodegradability of condensate, and the interactions between liquid, vapour and aqueous phases;

- Analysis and optimization of pump-and-treat techniques in fractured bedrock under remediation conditions;

- Association of dissolved organics of potential environmental concern with dissolved inorganic groundwater plumes from produced water ponds and other sources;

- the use of in-situ biological techniques at sour gas plants, and under relatively cold winter conditions;

- The practicality of harnessing waste heat from plant operations to enhance various treatment techniques such as air-stripping, SVE, SVVS, and bioremediation.

7. REMEDIAL SYSTEM DESIGN

7.1 OVERVIEW

The approach to any remediation project must be based on a few fundamental concepts. As with any major undertaking, the problems to be solved must first be precisely determined. What exactly is the nature of the problem being faced? Where are the contaminants, what types and concentrations exist, and how do they behave in the subsurface? What are the potential risks associated with these contaminants, now and in the future? The answers to these questions can only be answered by a detailed and thorough site investigation. Data obtained can be used to undertake an analysis of the risks posed by the contamination. If the risks are considered sufficient to warrant action at the site, decisions must then be made on the goals of the remedial actions. Will simple containment of the contamination and prevention of off-site migration suffice, or will a more involved effort be required to remove "subsurface sources" of contamination? The goals of remediation should be clearly defined, as they will have a profound influence on the design of the remediation system and the choices of technologies. The economic and practical consequences of the remedial goal decisions should also be carefully considered. Simple containment of contaminant plumes, without removal of sources of continued contamination can lead to a situation of perpetual maintenance.

Once goals have been defined, a pilot-scale remedial program should be implemented to test chosen remedial technologies and systems on a small scale. The advantages of a pilot program are numerous, including the opportunity to observe subsurface behaviour of contaminants under actual remediation conditions, and the chance to field test clean-up equipment on a small scale before committing to full-scale resource expenditures. The pilot program will provide technical and managerial staff with an added degree of assurance and comfort in proceeding to full-scale remediation. Data collected during the pilot phase should then be used to design the full-scale remedial system. Optimization should be preformed to ensure that the remedial system design achieves all of the goals of clean-up for the minimum expenditure (capital and O&M). Once the design is implemented, it should be recognized that continued regular monitoring of the system is crucial. Monitoring will allow the progress and efficiency of the remediation to be assessed, and will indicate the need for adjustments and modifications. Removal of contaminants from the subsurface is a dynamic process. Conditions are continually changing as contaminant concentrations and distributions change. Under these conditions all remedial systems will, by their very nature, require frequent periodic modifications.

The cost implications of each of these steps and decisions should be clearly weighed before launching a remediation program. The following sections discuss each of these key aspects of remedial system design in more detail.

7.2 SITE CHARACTERIZATION

7.2.1 Requirements

A proper detailed site characterization program is the essential first step towards a successful remediation program. The site investigation at a sour gas plant is best carried out using a phased approach, and should be designed to provide the data required to answer the following questions:

- What type of contaminants are at the site, where are they now, and where are they expected to go?
- What are the factors which will influence contaminant movement and concentrations?
- Are there any features of concern nearby which may be adversely impacted by the contaminants?
- What risks does the contamination pose to humans and the environment?

To answer these and other questions adequately, a site characterization program should strive to provide a detailed understanding of the following:

- the geological and hydrogeological conditions at the site, including geological units, structure, stratigraphy, fracturing, groundwater flow directions, patterns and gradients within and between all units of concern, and hydraulic conductivities of units of concern;
- background hydrogeochemistry at the site for each unit of interest;

- nature, type, concentrations and distribution of contaminants;
- factors controlling contaminant movement in the subsurface, including geological controls, contaminant retardation, and effects of plant facilities such as disposal ponds, water supply and disposal wells, etc.;
- sources of contaminants;

A proper investigation will provide decision makers with the information necessary to assess the risks associated with the contamination, and thus allow definition of appropriate remedial goals.

7.2.2 Techniques

Standard characterization techniques for contaminated sites are discussed in USEPA/NWWA (1988). This guidance document published by the US Environmental Protection Agency (USEPA) provides a complete discussion of recommended techniques and practice, including design and installation of groundwater monitoring wells, sampling and analysis of groundwater, and the use of non-invasive techniques. Site characterization should only be performed by qualified personnel.

7.3 GOALS OF REMEDIATION

The first step in the design of a groundwater remediation program is to define the goals of remediation. Objectives can vary considerably, from complete clean-up to background conditions, to temporary control of plume migration, to deferment of action supported by the results of risk assessment.

7.3.1 General Considerations

According to Canter and Knox (1985):

> "Specific strategies to achieve the goal(s) will be dictated, for the most part, by physical, chemical and monetary constraints. This decision making process includes four (4) different goals: prevention, abatement, cleanup and restoration. Prevention, as the name implies, means that pollution is not allowed to occur. Abatement means "putting an end to". Hence, abatement of groundwater pollution will include the

> cessation of pollutants moving into groundwater, and the curtailment of the movement of pollutants having already reached groundwater. Cleanup refers to elimination of pollutants through removal or treatment or in-situ immobilization or treatment. Restoration will include those measures that attempt to return the aquifer to its original state."

They continue:

> "It should be noted that these goals are not totally independent of each other. More specifically, a truly effective "clean-up" strategy may also include prevention and abatement measures".

Only after the goals of a remedial program are defined, can selection of appropriate technologies and system design proceed. When considering the objectives of remediation, the long term economic implications of the decision should be considered in detail. The following factors will determine the overall project cost:

- **time frame of remedial operations;** the longer operations proceed, the greater the final project cost. Remedial goals will have a profound influence on the length of operations. Abatement or containment, without source clean-up, will in many cases require perpetual maintenance. Immediate clean-up will significantly shorten operations, all other things remaining equal.

- **technologies selected:** Selection of the most efficient and cost effective technologies will generally reduce clean-up costs and times.

- **site hydrogeology:** In general, the more complex the conditions, the longer remediation will have to proceed, the more sophisticated the equipment required, the longer the time frame involved, and the lower the ultimate clean-up levels achieved.

- **remedial system design:** Proper system design is crucial to the long term success of remediation efforts. System design involves selection of appropriate methodologies, sizing, design, placement and operational specification of chosen technologies, monitoring, and forecasting. Ideally, the design phase will seek to provide optimal recovery (or other goals) with respect to cost, while achieving all specified goals. In essence, careful design will ensure the most clean-up for the fewest dollars. The first step in the design procedure is implementation of a pilot phase.

- **regulatory constraints;** Depending on the regulations which may apply, the level of clean-up required may be specified by a regulatory body. At present in Alberta there are no clean-up guidelines for sour gas plants.

7.3.2 Contaminant Control vs. Clean-Up

The goals of preventing further migration of contaminants and cleaning up bulk condensate are inextricably linked. The presence of potential "subsurface sources" of contamination should be considered during the determination of goals. Free condensate, for instance, which may exist as residual LNAPL saturation in the subsurface contains about 15 to 20 % of water soluble BTEX compounds. Due to relative permeability effects, groundwater will tend to move much more quickly through the subsurface than will free condensate LNAPL (generally from 5 to 10 times faster). As groundwater flows past free product, BTEX compounds will dissolve into the groundwater and move away down-gradient. In a similar fashion, precipitation and snowmelt will flush BTEX compounds into the groundwater. Free product trapped and immobile as residual saturation in the saturated and unsaturated zones, and mobile free product atop the water table, act as a continuous source of groundwater contamination. In fact, many researchers refer to accumulations of LNAPL in the subsurface as "sources" of contamination. Controlling the migration of the dissolved BTEX can be achieved by pumping the aquifer at a sufficient rate to ensure complete capture of the plume. After sufficient time, and with proper well placement, the dissolved phase plume emanating from the LNAPL "source" can be virtually eliminated. However, as soon as pumping is stopped, the plume will begin forming anew. This situation is often referred to as "perpetual maintenance'. To achieve the goal of contaminant containment, pumping must continue indefinitely.

Cleaning up the LNAPL in the subsurface will remove the "source" of dissolved contaminants, and indirectly prevent plume migration. Attacking the free product is initially more expensive, and requires a more concerted engineering effort. However, the annual operation and maintenance costs of a hydrodynamic control system will accumulate over time. Containment without source clean-up becomes even more uneconomic if, as is often the case, clean-up is eventually required anyway. Under these circumstances, the costs incurred during the years of plume control are essentially wasted. Under most circumstances, plume control is achieved as a part of clean-up operations. The only circumstances where plume control alone should be considered are when regulatory pressures force premature action.

7.4 REGULATORY CLIMATE

The present regulatory climate in Alberta is quite fluid. New general regulations on environmental protection are expected to become law in 1991. However, new guidelines and criteria for remediation and site monitoring are not yet available. It should be expected that remedial goals may change significantly over time as regulations become stricter. Other provinces such as Ontario, Prince Edward Island and Quebec presently have stricter regulation and clean-up criteria in place than does Alberta. On this basis alone, it is very likely that Alberta's regulations will become stricter in the near future. Indeed, formulation of the new Contaminated Sites Remediation Guidelines is underway at Alberta Environment. Remediation planning should proceed with this in mind.

7.5 PILOT PHASE OF REMEDIATION

7.5.1 Purpose of a Pilot Program

The main purpose of a pilot program is to test ideas and equipment on a small scale before committing significant resources to a full-scale program. This type of preliminary test phase is considered absolutely essential by most workers in the field of aquifer remediation (Testa and Winegardner, 1991; Mercer, 1991; Papadopulos, 1991; Feenstra, 1991). A pilot program provides investigators with an opportunity to learn about the field-scale behaviour of the system, and to test various techniques and technologies, without committing to the considerable expense of a full-scale program. Often, the results of a pilot phase will show that a modification of the initial remedial concept is required. Sometimes, they will indicate that the proposed approach is unsuitable. In these cases, necessary adjustments can be made before significant resources are committed to the project.

7.5.2 Objectives

The objectives of a pilot program will vary depending on the specific nature of the contamination situation at the plant. However, pilot schemes will usually share the following basic objectives:

1. To characterize the hydraulic behaviour of the aquifer system at the plant site. Determine hydraulic parameters (transmissivity, storativity, hydraulic conductivity), effective base of the aquifer, vertical and areal interconnection of units, effective area of influence of wells (for groundwater problems);
2. to determine the types, concentrations and distribution of contaminants in the soil and groundwater;
3. to assess the behaviour of contaminants in the subsurface during remedial operations, and our ability to remove, recover or otherwise clean-up the subsurface material;
4. to select, design, construct and test groundwater and soil treatment technologies applicable to the specific conditions at the site;
5. to test options for disposal of recovered water and soils (if applicable);
6. to refine overall understanding of the behaviour and movement of groundwater contaminants at the site, and provide the information required for the design and implementation of an effective and cost efficient aquifer remediation program.

7.5.3 Groundwater Remediation Considerations

Some of the most important considerations in designing an aquifer remediation program are:

- the presence, concentrations and distribution of dissolved phase hydrocarbons in groundwater. Knowledge of the expected types and concentrations of contaminants is required to select and design water treatment technology;

- the expected long-term behaviour and hydraulic characteristics of the aquifer. This information is crucial to the proper design and optimization of a pump-and-treat system, and provides estimates of groundwater pumping rates, volumes of water to be treated, areas of well influence and capture radii, and well spacings required to achieve various goals (such as maintenance of a steady water level over time, containment of contaminants, etc.);

- the behaviour of the free phase condensate liquids. The presence of a separate phase contaminant in the subsurface complicates aquifer remediation significantly. Mobility of contaminants is dictated by relative permeability considerations, pore geometry, capillary pressure and saturation effects, and fluid properties. The field scale behaviour of LNAPL during remedial programs has been shown to be erratic and unpredictable. A pilot program can provide some idea of the mobility of product to wells and allows recovery equipment to be field-tested.

- Any pump-and-treat operation can produce significant volumes of groundwater requiring treatment and disposal. Part of any pilot program should be devoted to identifying and testing methods of treating contaminated groundwater, and disposing of it in a fashion acceptable to regulatory agencies and beneficial to the remedial project. This aspect of a remediation program can be very costly. Time taken to study the problem and refine system designs before full-scale implementation can result in very significant savings over the life of a project (Nyer, 1985).

Over the past few years, significant advances have been made in development of technologies for cleaning up contaminated aquifers. However, the applicability and effectiveness of the vast majority of these techniques is still under investigation. Also, much of the information available to date in the literature deals with recovery operations in relatively uniform granular media - not complex heterogeneous and fractured aquifers. For these reasons, a preliminary pilot phase is strongly recommended before moving into full scale clean-up operations.

7.5.4 Soil Remediation Considerations

The many advantages of pilot operations also apply to soil remediation efforts. In the same way as for groundwater, pilot operations allow remediation technologies to be tested in the field under actual site conditions on a small scale. If modification are found to be required, these can be made easily, without having to incur the major expense of changing or abandoning a full-scale system. All of the soil remediation technologies discussed in this report are amenable to pilot-scale field testing.

Soil vacuum extraction systems, for instance, should always be tested on the pilot scale before moving into a full-scale operation (Mendoza, 1991). Recommended pilot tests and implementation are discussed in the recommended technologies section (Appendix I) of this report. In a similar fashion, small scale field trials on in-situ soilwashing and soil bioremediation can and should be attempted before proceeding to more ambitious scales.

7.6 SYSTEM OPTIMIZATION

Once the site characterization has been done at a site, the problem identified, and potential remedial technologies tested on a pilot scale, the full-scale design of the remediation system may proceed. The remedial system should be designed in such a way that it achieves all of the goals set for it, but does so for the lowest capital and operational costs. In many cases, the faster the clean-up, the lower the ultimate clean-up costs. Design optimization procedures should be used to objectively determine the most efficient way to implement the clean-up program.

To achieve the desired remedial goals at the lowest possible cost, the remediation system should be **optimized.** This process uses detailed hydrogeologic and economic modelling techniques to determine the best use of resources to achieve maximum benefit. For a pump-and-treat system, for instance, each pumping well installed will have associated with it a capital cost and a fixed annual O&M cost. In addition, each well will produce a certain volume of water requiring treatment and eventual disposal. Over the life of a project, the elimination of a single well from the system design can save hundreds of thousands of dollars.

Hydrogeologic modelling techniques are commonly used as a tool in designing remediation programs (Mercer et al, 1990; Canter and Knox, 1985; Taylor et al, 1989). These tools allow the hydrogeologist or groundwater engineer to determine the effects a particular combination of pumping and injection wells will have on the contaminant plume. Different well configurations pumping at different rates can be modelled, and the effects on the plume simulated. During optimization, the goal is to reduce the number of pumping wells and the volume of water produced as much as possible, while still achieving complete plume capture. This procedure can significantly lower the eventual costs of clean-up by eliminating unnecessary pumping and injection wells, lowering time for clean-up, and reducing demands on water treatment facilities.

7.7 OPERATION, MONITORING AND MODIFICATIONS

The need for continued operation, monitoring and periodic modification of any remedial system must be clearly recognized at the onset of the project. Unfortunately, sub-surface remediation is not an area where once the equipment is set up and running, the problem is solved. Due to the changing nature of subsurface conditions as contaminants are removed, remedial systems must be continually monitored and adjusted. Nyer (1985) and other workers indicate that operation and monitoring costs can account for the majority of total costs over the life of a typical remediation project. Estimates for O&M must be built in up-front.

8. CONCLUSIONS

1. A complete review of subsurface remedial technologies was completed, and the most applicable technologies for the specific problems identified at Alberta sour gas plants (ASGP) determined. For each contamination situation common to ASGP's, the most applicable established technology or approach was identified, and the new/innovative technology most worthy of future development was identified.

2. The technology recommendations for the various contamination situations are summarized in Table 8.1.

3. For each of the recommended technologies, a detailed description is provided in Appendix I of this report. Information presented includes costs, demonstrated efficiencies, case histories, and design and implementation information.

4. It is stressed that there can be no substitute for individual site assessment for selection of the appropriate remedial strategy. Final choice of remedial technology will always depend on the goals of remediation, the unique characteristics of the site, and time and economic constraints. This report should be seen as a starting point for technology selection, and not as a definitive final recommendation.

9. RECOMMENDATIONS

1. On the whole, all remediation technologies are "new and innovative" at Alberta sour gas plants, as very little in the way of rigorous study and application of clean-up programs has been done to date at these facilities. For this reason, even the technologies rated as "established" should be considered for demonstration and further study under Alberta conditions.

2. Further study of the nature, prevalence and subsurface behaviour of sour gas process chemicals is required. At present there is very little information available on this subject.

3. The subsurface behaviour of LNAPL gas condensate requires additional study. At present there is a scarcity of information available, especially concerning its behaviour under recovery operations (pump-and-treat, soil vapour extraction, etc) and in fractured media.

4. The harnessing and use of waste heat and steam from gas plant operations should be investigated. This resource has the potential to enhance several remediation processes, including air-stripping, soil vapour extraction, in- and ex-situ bioremediation, and others.

5. The field demonstration at Alberta sour gas plants of one or more of the technologies recommended by this study is endorsed.

10. REFERENCES

Al-Ekabi, H. and Safarzadeh-Amiri, A. 1990. Advanced technology for destruction of organic pollutants by photocatalysis. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

American Petroleum Institute, 1991. Groundwater Remediation: A Statistical Evaluation Method. (In Press, 1991).

Ardito, C.P. and Billings, J.F., 1990. Alternative remediation strategies: the subsurface volatilization and ventilation system. Proc. NNWA/API conference on Hydrocarbons and Organic Chemicals in Groundwater. Houston, 1990.

Arvin, E., and Bronholm, K. 1991. Toxic effects of chlorinated aliphatic hydrocarbons to methanotrophic bacteria. Proceedings International Symposium on In Situ and On Site Bioreclamation. March, San Diego.

Ashworth, R.A., Pallazzolo, M.A., and Tichenor, B.A. 1987. "Destruction of Organic Contaminants by Catalytic Oxidation." EPA/600/D-87/224. PB87-212916.

Baehr, A.L. and M.F. Hult, 1988. Determination of the air-phase permeability tensor of an unsaturated zone at the Bemidji, Minnesota, research site. In, USGS Toxic Substances Hydrology Program-Proceedings of the Technical Meeting, Phoenix, AR, September 26-30. Edited by G.E. Mallard and S.E. Ragone. (USGS Water Resources Investigative Report 88-4220).

Baehr, A.L., G.E. Hoag and M.C. Marley, 1989. Removing volatile contaminants from the unsaturated zone by inducing adventive air-phase transport. J. of Contaminant Hydrology, 4, pp. 1-26.

Barbaro, J.R., Barker, J.F., and Lemon, L.A. 1991. Nitrate addition as an alternate electron acceptor for the remediation of anaerobic BTEX contaminated groundwater. Proceedings, 1st Annual Groundwater and Soil Remediation R,D & D Symposium. January, 1990. Ottawa.

Barcelona,M.J., Gibb, J.P., Helfrich, J.A. and Garoke, E.E., 1985. Practical Guide to Groundwater Sampling. USEPA and RSKERL.

Bernardin, F.E.Jr., 1989, Treatment of dissolved organics with UV/hydrogen peroxide. Presented at NWWA Focus Conference on eastern regional groundwater issues, Kitchener Ontario.

Bird, R. B. Stewart, W.E. Lightfoot E.N.; 1960 Transport Phenomena. Whiley & Sons, New York.

Blake, D., Magrini, K. and Webb, J., 1990. Solar detoxification of water. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

Bolton, James R., 1990. Mechanism of the photochemical degradation of organic pollutants on TiO^2. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

Brewer, I. 1990. "Literature Review and Research Scoping Study on the Treatment of Volatile Organic Carbon Compounds in the Off-Gas from Contaminated Groundwater and Soil Remedial Technologies." Draft report prepared for GASReP.

Brooks, R.H. and A.T. Corey, 1964. Hydraulic properties of porous media. Hydrology Papers, 3, Colorado State University, Fort Collins.

Brown, R.A., Tribe, R., and Duquette, A. 1989. Bioreclamation: the three R's of product losses - response, regulation, remediation. Water and Pollution Control.

Brown, R.A., 1989. Oxygen sources for biotechnological application. Paper presented at Biotechnology Work Group. Feb. 21-23, 1989. Monterey, California.

Canter, L.W., and Knox, R.C., 1985. Groundwater Pollution Control. Lewis.

Carey, J.H., 1990. Introduction to advanced oxidation processes (AOP) for destruction of organics in wastewaters. Lakes Research Branch, National Water Research Institute, Canada Centre for Inland Waters, P.O. 5050, 867 Lakeshore Road, Burlington, Ontario.

Cater, S.R., Bircher, K.G. and Stevens, R.D.S., 1990. RAYOX: a second generation enhanced oxidation process for groundwater remediation. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

CH2M Hill Ltd and Solar Chem Environmental Systems, 1989, Elmira, the groundwater remediation. Hazardous Material Management Magazine, June 1989.

Clifford, D. and Sorg, T. (1986) "Removing dissolved inorganic contaminants from water", Environmental Science and Technology, V.20.

Cooper, W.J., Nickelsen, M.G., Waite, T.D. and Kurucz, C.N., 1990. High-energy electron beam irradiation: an advanced oxidation process for the treatment of aqueous based organic hazardous wastes. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

CPA, 1990. Effectiveness of Subsurface Treatment Technology at Alberta Sour Gas Plants. Phase I: Assessment of Subsurface Contamination and Remedy at ASGP's. Report by Piteau Engineering Ltd., Calgary.

Dawson, G.W. and Mercer B.W., 1986. Hazardous Waste Management, Wiley Interscience, New York.

Dean, J.A., (ed.), 1985. Lang's Handbook of Chemistry, 13th edition. McGraw-Hill, New York.

Dev, H., P. Condorelli, J.E. Bridges, C. Rogers and D. Downey 1988. In situ radio frequency heating process for decontamination of soils. American Chemical Society Symposium on Solving Hazardous Waste Problems. ACS Symposium Series 07.

Driscoll, 1986. Groundwater and Wells. Johnson Filtration Systems Inc., St. Paul. Minnesota, 55112.

Dworkin, D. and Cawley, M., 1988, Aquifer Restoration: Chlorinated Organics Removal Considerations in Proven vs. Innovative Technologies. Environmental Progress, May 1988, Vol.7, No.2.

Eastcott, L., W.Y. Shiu and D. Mackay, 1988. Environmentally relevant physical-chemical properties of hydrocarbons: A review of data and development of simple correlations. Oil and Chemical Pollution, 4, pp. 191-216.

Ellis, W.D., J.R. Payne and G.D. McNabb, 1985. Treatment of Contaminated Soils with Aqueous Surfactants. US Environmental Protection Agency Report, EPA-600/2-85/129.

Environment Canada, 1984. National Guidelines for Decommissioning Industrial Sites. Monenco, Ottawa.

Fall, E.W. 1989. In-situ Hydrocarbon Extraction: A Case Study. The Hazardous Waste Consultant. January.

Farley, F.E., 1990. Report on CPA Sour Gas Plant Remediation Study. Report to Piteau Engineering Ltd. Unpublished.

Feenstra, 1991. Comments on Remedial Alternatives for Sour Gas Plant Study. Report to Piteau Engineering Ltd. Unpublished.

Forrester, I. 1990. In-Situ bioremediation of hydrocarbon contaminated sites with special reference to natural gas processing plants. Report to Piteau Engineering Ltd. Unpublished.

Forrester, I. 1990a. Evaluation of native microbial population and commercial microbial material for in-situ bioremediation of hydrocarbon contamination. Report to Piteau Engineering Ltd. Unpublished.

Freeze, R.A. and Cherry, D.A., 1979. Groundwater. Prentice Hall, New Jersey.

Freeze Technologies Corporation, 1990. Remediation and Treatment of Superfund and RCRA Hazardous Wastes by Freeze Crystallization. Raleigh, N.C.

Froelich, Emery M., 1990. The perox-pure™ oxidation system - A comparative summary. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

GASReP, 1990. Report on Current and Innovative Excavate and Treat Technologies for the Remediation of Contaminated Soils. Prepared for the National Groundwater and Soil Remediation Program (GAS ReP), Excavate and Treat Technical Sub-Committee.

GASReP, 1990b. Report on In-situ Intercedent Biological Barriers for the Containment and Remediation of Contaminated Groundwater. Prepared for the Petroleum Association for The Conservation of the Canadian Environment.

Gosset, N.W. and Harries, R., 1990. Technology evaluation: advanced oxidation processes vs. conventional treatment technologies for aqueous contaminants. CH2M Hill Engineering, Ltd., Suite 600, 180 King St. South, Kitchener, Ontario.

Green, R., 1970. Geological Map of Alberta, Scale 1:1,267,000. Alberta Research Council. Reprinted in 1982.

Green, D.W., (ed), 1984. Perryl's Engineer's Handbook, 6th edition. McGraw-Hill, New York.

Hall, C.W., 1988. Practical limits to Pump-and-Treat technology for aquifer remediation. In Groundwater Quality Protection Pre-conference workshop proceedings, Water Pollution Control Federation, 61st Annual Conference, Dallas, 1988.

Hardisty, P.E., T. L. Dabrowski, L.S. Lyness, R. Scroggins and P. Weeks, 1990. Nature, occurrence and remediation of groundwater contamination at Alberta sour gas plants. Presented, IAH conference on Subsurface Contamination by Immiscible Fluids, April Calgary.

Hardisty, P.E. and Headley, J.V., 1991. Behaviour of Natural Gas Condensates in Groundwater. In preparation.

Heist, J.A. May 7, 1979. Freeze crystallization. Chemical Engineering.

Hincher, R.E. and Downey, D.C. 1988. The Role of Hydrogen peroxide and Enhanced biodegradation proceedings. WWWA.AP1 conference of P.H.C. and Org. Chem G/U Houston.

Hoag, G.E., Marley M.C and Bruell C.J. 1986. Soil venting of gasoline contaminated soils. ASCE.

Hunt, J.R., N. Sitar and K.S. Udell, 1988. Nonaqueous phase liquid transport and cleanup 2. Experimental studies. Water Resources Research, v. 24, no.8, p. 1259-1269.

Hurling, S. and Bledsoe, B. 1991. Enhanced bioremediation using hydrogen peroxide as a supplemental source of oxygen: A lab and field study. Proceedings International Symposium on In Situ and On Site Bioreclamation. March, San Diego.

Johnson, P.C., C.C. Stanley, M.W. Kemblowski, D.L. Byers and J.D. Colthart, 1990. A Practical approach to the design, operation, and monitoring of in-situ soil-venting systems. Ground Water Monitoring Review, 10(2). pp. 159-178.

Keely, J.F., 1984. Optimizing Pumping Strategies for Contaminant Studies and Remedial Actions. Groundwater Monitoring Review, Summer 1984.

Keely, J.F., 1989. Performance Evaluations of Pump-and-Treat Remediations. Report to RSKERL, USEPA. Report #EPA/540-14-89/005.

Kosusko, M., Mullins, E.M., Ramanathan, K. and Rogers, T.N. 1988. "Catalytic Oxidation of Groundwater Stripping Emissions." Environmental Progress. Vol. 1, No.2.

Kothari, N. (1988). "Groundwater, Iron and Manganese: An Unwelcome Trio," WATER/Engineering and Management, February, pp. 25-26.

Kruseman, G.P. and DeRidder, N.A., 1989. Analysis and Evaluation of Pumping Test Data. International Institute for Land Reclamation and Improvement. Netherlands.

Kwader, T., 1986. The use of geophysical logs for determining formation water quality. Groundwater, v. 24.

Lee, M.D., Thomas, J.M., Borden, R.C. et al. 1988. Biorestoration of aquifers contaminated with organic compounds. CRC critical reviews in environmental control. vol 18.

Leitzke O. and Whitby, G.E., 1990. The combined application of ozone and UV irradiation for the treatment of water. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air, June 4&5, 1990, Toronto Canada.

Lemon, L.A. and Barker, J.F., 1991. Site Selection for Demonstration and Evaluation of Technologies for Remediation of Gasoline Spills. In proceedings, 1st Annual Groundwater and Soil Remediation R,D&D Symposium, Ottawa.

Lenzo, F., 1988. Air Stripping Teases VOC's from Groundwater, Water Engineering and Management, February 1988.

Lewis, N., Kirankumar, T. Welshans, G. and Foster, R., 1990. A field demonstration of the UV/Oxidation technology to treat groundwater contaminated with VOCs. Journal of the Air & Waste Management Association Vol. 40, No 4, April 1990.

Lewis, R., 1991. pers comm. Bioremediation specialist, Risk Reduction Engineering Laboratory, US EPA, Cincinnati, OH.

Lexicon of Canadian Stratigraphy, 1990. Volume 4. Western Canada, Including Eastern British Columbia, Alberta, Saskatchewan, and Southern Manitoba. Canadian Society of Petroleum Geologists, Calgary, Alberta. Editor D.J. Glass.

Liptak, B. (editor) 1974. Environmental Engineers' Handbook: Water Pollution, Volume 1. Chilton Book Company, Radnor, Pennsylvania. 2018 pages.

Lyman, W.J., W.F. Reehl and D.H. Rosenblant, 1982. Handbook of Chemical Estimation Methods. MacGraw-Hill, Toronto.

Mackay, D.M. and Cherry, D.A., 1989. Groundwater Contamination: Pump-and-Treat Remediation. Environmental Sci. and Technology. Vol. 23, No. 6.

Mackay, D. and W.Y. Shiu, 1981. A critical review of Henry's Law constants for chemical of environmental interest. J. of Physical and Chemical Reference Data, 10(4), pp. 1175-1199.

Major, D. 1991. The current state-of-the-art of *in situ* bioremediation: considerations, limitations, potential, and future directions. Proceedings, 1st Annual Groundwater and Soil Remediation R,D & D Symposium. January, 1990. Ottawa.

Major, D., 1991b. pers comm.

Massmann, J.W., 1989. Applying groundwater flow models in vapour extraction system design. J. of Environmental Engineering, 115(1), pp. 129-149.

McDermott, J.B., R. Unterman, M.J. Brennan, R.E. Brooks, D.P. Mobley, C.C. Schwartz and D.K. Dietrich, 1988. Two strategies for PCB soil remediation: Biodegradation and surfactant extraction. American Institute of Chemical Engineers Spring Meeting, March, 1988, New Orleans, Louisiana.

McFarland, W., 1989. Air Stripping Removes Petroleum from Groundwater. Water Engineering and Management, May 1989.

McWhorter, D.B., 1990. Unsteady radial flow of gas in the vadose zone. J. of Contaminant Hydrology, 5, pp. 297-314.

Mercer, J.W. 1990. Treatment technologies for Alberta sour gas plants. Report for Piteau Engineering Ltd. Unpublished.

Mercer, J.W. and Cohen, K.M., 1991. A review of immiscible fluids in the subsurface: properties, models, characterization and remediation. Journal of Contaminant Hydrology, v6.

Mercer, J.W., Skipp, D.C., and Giffin, D. 1990. Basics of pump-and-treat ground-water remediation technology. USEPA project EPA-600/8-90/003.

Mendoza, C.A., 1991. In-situ remediation of organic in the unsaturated zone: Vacuum extraction and other technologies. Report to Piteau Engineering Ltd. for Sour Gas Plant remediation Technology Study, sponsored by the Canadian Petroleum Association and Environment Canada.

Millington, R.J. and J. P. Quirk, 1961. Permeability of porous solids. Transactions of the Faraday Society, 57,pp. 1200-1207.

Milne-Home, W.A., 1988. Interpretation of pumping tests in fractured aquifers: from theory to routine field analysis. Proceedings, 4th Canadian American Conference on Hydrogeology. Banff.

Nash, J. 1988. Field Studies of In Situ Soil Washing. US Environmental Protection Agency Report, EPA-600/S2-87/110.

NWWA/USEPA, 1986. RCRA Ground Water Monitoring Technical Enforcement Guidance Document. Published by NWWA, Dublin, Ohio.

Nyer, E. 1985. Groundwater Treatment Technology. Van Nostrand Reinhold, New York, p. 188.

Nyer, E., 1988. Treatment of BTEX Compounds at Low Flow Rates. Groundwater Monitoring Review, Spring 1988.

Nyer, E. and Montgomery, J. "Would the Real Air Stripper Please Stand Up?", Groundwater Monitoring Review, Fall 1989.

O'Brian & Gere Engineers Inc., 1988. Hazardous Waste Site Remediation, Van Nostrand Reinhold, New York.

Palmer, I.D. and Veatch, R.W. Jr., 1988. Insights into formation fracturing from analysis of Step-rate tests. Proceedings, 4th Canadian American Conference on Hydrogeology. Banff.

Papadopulos, S.S., 1991. Personal communication.

Peck, G. and Uhrich, K., 1988. Electrochemical Method For Heavy Metal Removal From Groundwater. Presented at On-Site Groundwater and Soil Remediation Seminars.

Peyton, G.R., 1990. A comparison of the advanced oxidation processes. Aquatic Chemistry Section, Illinois State Water Survey, Champaign, Illinois 61820.

Piteau Engineering Ltd., 1990. Confidential Report for a Gas Plant Remediation Study, Unpublished.

Radian Corporation. 1987. Air Stripping of Contaminated Water Sources - Air Emissions and Controls. EPA-450/3-87-017. PB88-106166/AS.

Rao, P.S.C., A.G. Hornsby, D.P. Kilcrease and P. Nkedi-Kizza, 1985. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. Journal of Environmental Quality, v. 14, no. 3, p. 376-383.

Remedial Systems Inc., 1991. Personal Communication.

Roscoe Moss Co. Ltd., 1990. Handbook of Ground Water Development. John Wiley and Sons, New York.

Roy, W.R. and R.A. Griffin, 1988. Surfactant and Chelate-Induced Decontamination of Soil Materials: Current Status. Open-File Report of the Environmental Institute for Waste Management Studies, University of Alabama.

Satkin, R.L. and Bedient, P.G., 1988. Effectiveness of Various Aquifer Restoration Schemes under Various Hydrogeologic Conditions. Groundwater, vol. 26 (4).

Savage, G.M., et al. 1985. Biological treatment of organic toxic wastes. Biocycle, vol 26(1).

Schaffner, R., Lee, Y., Holdaway, B.H., Seeley, R., Mayo, A.L., Borup, M.B., 1990. Bacterial pore clogging as a primary factor in limiting the enhanced biodegradation of highly contaminated aquifers. Proceedings, Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, October, 1990, Houston.

Schmelling, S.G., 1991. USEPA Ground Water Initiative: improvement of pump-and-treat remediation. Proceedings, 1st Annual Groundwater and Soil Remediation R, D & D Symposium, Ottawa, 1991.

Shareef, G.S., Miles, A.J., and Post, B.K., 1984. Hazardous/Toxic Air Pollution Control Technology: A Literature Review. EPA-600/2-84-194. December. PB85-137107.

Skala, P., Whittaker, H., Al-Ekabi, H., Robertson, M., Safarzadeh-Amiri, A. and Henderson, B., 1989. Technology transfer conference, Ontario Ministry of the Environment, Analytical Methods Proceedings, Invited paper, 171-193.

Soniassy, R.N., 1974. Adsorption of Odours by Peat Moss. CIM Bulletin. August.

Sresty, G.C., H.Dev, R.H. Snow and J.E. Bridges, 1986. Recovery of bitumen from tar sand deposits with the radio frequency process. Petroleum Engineering Journal, January 1986, p. 85-94.

Staps, S.J., 1990. International Evaluation of in-situ biorestoration of contaminated soil and groundwater. USEPA, report EPA/540/2-90/012.

Stewart, M., Layton, M. and Lizanec, T. 1983. Application of surface resistivity surveys to regional hydrogeologic reconnaissance. Ground Water, v. 21.

Stewart, L.D. and K.S. Udell, 1988. Mechanisms of residual oil displacement by steam injection. Society of Petroleum Engineers Reservoir Engineering, p. 1233-1242.

Sullivan, K. and Lenzo, F., 1989. Groundwater Treatment Techniques. US/USSR Conference on Hydrogeology, July 1989.

Testa, S.M., and Winegardner, D.L. 1991. Restoration of petroleum contaminated aquifers. Lewis.

Watergroup Inc., 1990. Profile of the Cav-Ox™ Process and The Watergroup Inc.

Thomas, J.M., Ward, C.H. 1989. In situ biorestoration of organic contaminants in the subsurface. Environ. Sci. Technol. Vol 23, No. 7.

Turcotte, D.L. Fractals in Geology and Geophysics. In Fractals and Geophysics. Bukhauser, Germany.

Udell, K.S. and L.D. Stewart, 1989. Field Study on In Situ Injection and Vacuum Extraction for Recovery of Volatile Organic Solvents. University of California Berkeley, Sanitary Engineering and Environmental Health Research Laboratory, UCB-SEEHRL Report No. 89-2.

USEPA, 1988. Cleanup of Releases from petroleum USTs: selected technologies. US EPA Office of Underground Storage Tanks, Washington. EPA/530/UST-88/001.

USEPA, 1989. Evaluation of Ground-Water Extraction Remedies; vol. 1. Prepared by CH2M HILL.

Washington, D.C. Report PB90-183583.

van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America J., 44, pp. 892-898.

Water and Earth Science Assoc. Ltd., 1988. Biorestoration methodologies for the clean-up of gasoline contaminated groundwater. Carp, Ontario, Canada.

Weast, R.C., (ed.), 1987. CRC Handbook of Chemistry and Physics, 68th edition. CRC Press, Boca Raton.

Weston, R.F. Inc., 1985. Remedial Technologies for Leaking Underground Storage Tanks. Lewis, Michigan.

Weston, R.F. Inc. 1986. Economic evaluation of low temperature thermal stripping of volatile organic compounds from soil. US Army toxic Hazardous Materials Agency Report No. AMXTH-TE-CR 86085.

Westray, M.S., Brown, R.A., and Norris, R.D., 1985. in Groundwater Microbiology and Pollution Control, FMC Aquifer Remediation Systems, Princeton, N.J..

Willey, B. and Williams, R., 1986. Ways to Tackle the VOC Problem. Water Engineering and Management, May 1986.

Yaniga, P.M., 1982. Alternatives in decontamination for hydrocarbon-contaminated aquifers. Proceedings of the 2nd National Symposium on Aquifer Restoration and Ground Water Monitoring. NWWA, Worthington, Ohio.

Zeff, J.D., and Barich, J.T., 1990. UV/oxidation of organic contaminants in ground, waste and leachate waters. Proceedings of the symposium on advanced oxidation processes for the treatment of contaminated water and air. June 4&5, 1990, Toronto, Canada.

APPENDIX I

APPENDIX I

RECOMMENDED TECHNOLOGIES

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APPENDIX I
RECOMMENDED TECHNOLOGIES

The following sections provide detailed reviews of technologies recommended as suitable for application to contamination situations at Alberta sour gas plants. Both established and new and innovative/emerging technologies are presented. For each, a detailed description of theory and practical application, cost considerations, and case history information is provided. The focus of these reviews is towards typical ASGP conditions.

I.1 GROUNDWATER REMEDIATION - ESTABLISHED TECHNOLOGIES

I.1.1 PUMP-AND-TREAT

1. Introduction

1.1 General

The technique consisting of extracting groundwater and treating it at the surface is referred to as pump-and-treat. Pumping alters the flow field to control the migration of miscible contaminants in groundwater and creates a water table depression to control the migration of immiscible contaminants less dense than water. In most cases of groundwater contamination, a form of pump-and-treat technology is used, alone or in conjunction with other remediation techniques. In the case of deep groundwater contamination problems, it may be the only option available. Depending on site specific limitations and level of effort considered, pump-and-treat can be used for contamination plume containment or plume remediation. For any of these selections, the remedial objectives have to be stated clearly, a monitoring program should be implemented to verify that the goals are met and contingency plans should exist to provide new options if they are not. In this section, the data required to decide on the applicability of a pump-and-treat system to a site and for the design of such a system are reviewed. The limitations of the technique and the efficiency and cost in different cases are discussed, with reference to ASGP contamination situations for which pump-and-treat is recommended. This section will focus on the techniques, mechanisms, and limitations of contaminant removal from the subsurface. Treatment technologies for recovered groundwater are discussed in following sections. Good overviews of the pump-and-treat method can be found in Mercer et (1990), Keely (1989), USEPA (1989), and Mackay and Cherry (1989).

1.2 Applicability

Pump-and-treat was found to be a critical component of the recommended remedial approaches for all of the groundwater contamination situations considered. Specifically, pump-and-treat was recommended as:

- A primary control measure for migration of dissolved phase BTEX contamination associated with free phase condensate in surficial and bedrock materials (T1A/T2A; R1A/R2A), and as a first step in recovery of mobile free product from the groundwater surface. Pump-and-treat will also provide groundwater surface fluctuation control to prevent smearing and trapping of LNAPL, and expose residual LNAPL in the unsaturated zone to enhanced vapour extraction by lowering the water table.

- As the primary method of controlling downgradient migration of dissolved inorganic plumes (which are commonly associated with low levels of process chemicals), and remediating groundwater (T1BC/T2BC; R1BC/R2BC). Use of reinjection/reinfiltration techniques is also recommended in these cases to provide flushing of dissolved contaminants and increasing flow gradients.

- As a method of delivering buffering agents and controlling/remediating low pH groundwater originating from sulphur block seepage and runoff, in cases where natural buffering is not sufficient (T1D/T2D; R1D/R2D).

Depending on the specific application, pump-and-treat systems will be designed differently. However, all pump-and-treat systems share some fundamental requirements for successful application: a thorough understanding of site conditions and the behaviour of target contaminants under those conditions.

2. Data Requirements

Whether a pump-and-treat system is planned to contain or clean-up a groundwater plume, or is intended to function as part of a larger remediation system, a solid conceptual model of the site contamination problem is required. This model should incorporate the hydrogeology of the site, and the mass, types and distribution of the contaminants involved. This information will allow a critical assessment of whether or not pump-and-treat is indeed an appropriate measure at the site. If it can be used, the information will then help determine **how** best it can be used.

2.1 Hydrogeological data

The hydrogeological information necessary to make these decisions, and then to develop an appropriate conceptual model covers three main aspects: geology, hydraulics and groundwater use. A water supply well pumped near a contaminated site might have drastic effects on the migration of a plume of contaminated groundwater. The identification of nearby groundwater users is important for a complete understanding of the flow system and to protect the users. The main geological information required consists of the type of water-bearing units present, their thickness, areal extent, type of porosity, the presence or absence of impermeable units, and the depth to the water table. The hydraulic factors of influence are the hydraulic properties of the water-bearing units, the pressure conditions in these units, the characteristics of groundwater flow (direction, horizontal and vertical gradients, rate), groundwater-surface water interactions and seasonal variations of groundwater conditions. All these information are required to characterize the dynamics of the groundwater flow system and thus the behaviour of contaminants in this system under natural flow conditions.

2.2 Contaminant data

To design appropriate pumping and treatment systems, key information on the contaminants themselves is also required. Data required include the nature, duration and location of the input of contaminants (often difficult to determine), and the types, concentrations and spatial distribution of the contaminants in the system. Chemical data required includes hydrogeochemical makeup of groundwater, presence of trace organics of concern, concentrations of dissolved hydrocarbons (BTEX plus), and the chemical makeup of LNAPLs present.

Data on movement of non-reactive and reactive solutes in groundwater are also required. Dissolved contaminants move in the subsurface primarily by advective transport, and to a lesser extent by dispersive processes such as mechanical mixing and molecular diffusion. Advective transport causes the plume to move in the direction and at the rate of groundwater flow, while the dispersive mechanisms tend to cause the plume to expand and its concentration to decrease (Mercer et al, 1990; Freeze and Cherry, 1979). The transport of reactive solutes will be affected by processes such as sorption, chemical reaction, and biological degradation. These transformation processes will in many cases retard plume migration, and attenuate plume concentrations. This is the case for many organic solutes (such as BTEX compounds). However, these retardation processes may increase the clean-up times required during pump-and-treat. Data collection activities should provide the data necessary to quantify solute transport and retardation processes. In particular, data on the following should be available:

- aqueous solubilities of target contaminants: In general, the more soluble a compound, the lower its sorption tendencies. Sour gas plants process chemicals such as DIPA and sulfolane, for instance are very soluble.

- Henry's Law constant (K_H): Compounds with high K_H will tend to partition out of the aqueous phase and into the vapour phase. Dissolved phase plumes of these types of compounds may be retarded significantly by volatilization, and may be readily delineated by soil vapour survey techniques. Benzene has a K_H of 5.59E-03 atm-m^3/mol, and is readily volatilized from the aqueous phase. In contrast, amine compounds typically have Henry's constants in the 10E-6 to 10E-9 atm-m^3/mol range, and are much more water soluble. These differences will have profound effects on the relative distributions of contaminants within a plume, and care should be taken when assessing plume migration and distribution based on individual indicator parameters. Conservative solutes such as chloride, which usually are not subject to retardation effects, will provide a worst-case picture of plume behaviour.

- Organic carbon partitioning coefficient (K_{oc}): This indicates the chemical's tendency to sorb onto organic soil matter. High K_{oc} values mean a contaminant is hydrophobic and will tend to sorb onto the soil. This will tend to retard the movement of the compound in the plume. Benzene has a K_{oc} of 83.0 mg/L, and will sorb to organic material in the subsurface. Xylene has a K_{oc} of 240.0 mg/L, and will tend to sorb more strongly.

- Biodegradability: These data will help determine the persistence of the chemical in the subsurface. In general, condensate and dissolved hydrocarbon species are readily biodegradable, and as such will be good targets for enhanced bioremediation in conjunction with a pump-and-treat system. Amine products and associated process chemicals are not readily biodegraded.

Data on solute behaviour may be obtained from reference material such as Lyman et al (1982), Mercer et al (1990) and Eastcott et al (1988).

The presence of LNAPL gas condensate at the site (or indeed any other NAPLs) will have a profound influence on the effectiveness of pump-and-treat, the way in which it is applied, and the overall behaviour of contaminants at the site. As discussed in the section on condensate (Section 4 of this report), LNAPL behaviour in the subsurface is complex and hard to predict. Water table fluctuations and excessive pumping drawdowns can smear LNAPL and trap it as residual saturation in both the unsaturated and saturated zones. Data on the thicknesses of mobile free product, extent of smearing, residual saturations, and the relationship between liquid and dissolved phases of hydrocarbon contaminants are required for remedial design. If possible, the following data should be collected:

- physical and chemical properties of the condensate or other NAPL, such as density, viscosity, and chemical composition;
- physical relationships between LNAPL and porous medium, such as relative permeability curves, and capillary pressure-residual saturation relationships;

Detailed discussions of NAPL characteristics, properties, subsurface behaviour, and remediation are presented in Mercer and Cohen (1990), and Testa and Winegardner (1991).

3. Data Collection

Some of the data required for proper selection and design of a pump-and-treat system can be obtained from the literature. However, the bulk of necessary data must be acquired through detailed site investigation and characterization. Design and implementation of a detailed site investigation is a vital first step in any remedial operations (Mercer et al, 1990; Canter and Knox, 1986; R.F. Weston, 1989). A comprehensive guide to the site characterization procedures recommended by the USEPA is presented in NWWA/EPA (1986).

Site investigation techniques appropriate for sour gas plants include properly designed and constructed monitoring wells and piezometers (see Driscoll,1986; NWWA/EPA, 1986); soil vapour surveys (see Devitt et al, 1987), geophysical methods including borehole logging and electromagnetic surveys (see Kwader, 1986; and Stewart et al, 1983), soil sampling, and aquifer tests (see Kruseman and De Ridder, 1989).

For fractured media common at Alberta sour gas plants, site characterization and design of pump-and-treat systems are considerably more complicated. Fractures impart strong anisotropy and heterogeneity to the system, making accurate predictions of system performance difficult. Additional data collection measures which may be useful in fractured rock include coring, fracture trace analysis (Lattman and Parizek, 1964), the use of geophysical techniques such as borehole telemetry, and specialized analysis of aquifer tests (Palmer and Veatch, 1988; Milne-Home, 1988).

Groundwater quality data from samples collected from site piezometers will provide important information for the design, operation and monitoring of pump-and-treat systems. The use of proper sampling techniques is critical to ensure the quality and reliability of these data, on which so many important decisions will be based. A comprehensive treatment of recommended groundwater sampling procedures is given in Barcelona et al (1985).

4. Design Considerations

The design of a pump-and-treat system involves several key steps, including technology selection, system design and optimization, and setting of operational parameters. Data collected during the site investigation is important to all of these tasks.

4.1 Technology Selection - Extraction Methods

The most appropriate technology must be selected for extraction of contaminated groundwater and possibly LNAPL. The groundwater can be extracted with drains in the case of a formation with a low hydraulic conductivity, however the use of extraction wells is usually preferred if the situation allows it. When the groundwater is fairly shallow (less than two metres below surface) collection trenches may be used. For deeper groundwater contamination, conventional recovery wells are often the only solution (Mercer et al, 1990). In low hydraulic conductivity materials such as clay till or even inter-till sand and silt lenses of hydraulic conductivity in the 10E-07 to 10E-09 m/s range (T2), large diameter recovery wells are preferred. The advantages and relative costs of the various extraction methods are discussed in the Technology Overview section of the report.

4.2 Technology Selection - LNAPL Condensate Recovery Methods

Many methods have been devised for the recovery of free mobile hydrocarbons which pool atop the groundwater surface, including single pumps, dual pump systems, and filter-scavengers. Each of the various methods is discussed briefly in the Technology Overview section of this report. Dual pump recovery systems, incorporating a water table depression pump to induce flow towards the well and a separate product skimming pump (deployed in the same well or a nearby well), were recommended for use in ASGP contamination situations involving free condensate (T1A/T2A; R1A/R2A). According to the USEPA (1988), the technique is capable of removing up to 99% of free mobile condensate from the groundwater surface, but not LNAPL trapped as residual saturation.

In cases where the groundwater table is relatively near the surface, and trenches are used, condensate can be recovered in a similar fashion, using floating product skimmers. Trenches should be fitted with an impermeable membrane placed on the downgradient side to prevent flow of condensate back into the aquifer.

Product recovery systems are available from numerous suppliers in Canada and the U.S.. Generally, these fall into a few general categories:

> **Floating Skimmers:** These units are designed to float on the water, and will automatically skim off product floating on the surface. The most effective units are equipped with sensors which activate the pump when product is detected. Such equipment is generally easy to deploy and operate, and is available in various sizes and capacities. Units typically cost in the order of $8,000 to $11,000.
>
> **Filter separators:** These units are similar to skimmers and float on the water surface. The equipment uses an oleophyllic-hydrophobic membrane which allows oil to pass, but rejects water. The filter floats so that the membrane is positioned at the water-product interface. In this way, the equipment is capable of removing condensate LNAPL down to a thin film. The cost of the units is comparable to skimmers. These units should be employed in situations involving relatively small thicknesses of product (less than 2 cm).
>
> **Product pumps:** Product pumps are designed to work in conjunction with a water table depression pump, which induces a flow of LNAPL towards the well. The two pumps are set at least 1.5 m apart in the same or adjacent wells, to ensure that product does not enter the water table pump. Each pump is equipped with its own sensors, and is usually operated independently. At depths beyond about 6 m, submersible pumps are required (although these are typically about 20% more expensive than surface-mounted pumps). Installation and operation of dual-pump systems requires some effort, however. The product pump should be set in a position which will keep it in contact with the product in the well. During remedial operations, water table fluctuation should be reduced as much as possible, but over the course of a year many adjustments of pump settings will usually be required. Units are available

in various sizes, and can be fitted with sensors to accommodate different thicknesses of product.

Table I1.1 provides a summary of available product recovery equipment for use in trenches, shallow (less than 6m) and deeper wells.

4.3 Technology Selection - Groundwater Treatment

Next, the most appropriate treatment systems must be chosen. Several options are available to handle the recovered contaminated groundwater and the choice is often based on the level of effort. In the first phase of a remediation program, when the remediation program focuses on recovery of the bulk of the contaminant mass, the recovered groundwater could be reinjected upgradient of the extraction wells after a minimal level of treatment. The water reinjected thus reduces the amount of clean water required to flush the contaminants. Another option would be to treat the recovered groundwater to bring it back to surface discharge standards.

Treatment technologies for groundwater produced during pump-and-treat operations are available for various types of contaminants, and range from simple and inexpensive, to sophisticated and costly. An overview of technologies for dissolved organics, inorganics, and immiscible phase liquids is provided in the Technology Review Section of this report. Recommended treatment technologies for dissolved hydrocarbons (BTEX), process chemicals, and inorganic salts are discussed in detail later in this section.

4.4 Design Considerations

Once technologies have been decided upon, an assessment of the most efficient and effective deployment of the groundwater extraction systems is called for. For example, if pumping wells with dual skimmer pumps for LNAPL recovery are the selected technology, the locations, completion details, construction, and operating parameters of the wells must be determined. In most cases, a pump-and-treat system will involve several extraction and injection points. In many instances, "it is advantageous to have multiple extraction wells pumping at small rates versus one well pumping at a large rate" (Mercer et al, 1990). Modelling techniques then become very useful for optimizing well locations and pumping rates, and estimating clean-up times (Mercer et al, 1990; Keeley, 1989). Such techniques allow a variety of recovery and

TABLE I1.1
PRODUCT RECOVERY EQUIPMENT
TRENCHES

COMPANY/PRODUCT	DYNAMIC HEAD (ft.)	PUMPING RATES (gal/min)	DEGREE OF OIL/WATER SEPARATION	ADVANTAGES	DISADVANTAGES	APPROXIMATE COST
ORS Scavenger	<20	<5	Sheen	Lightweight, portable, passive filter separator (does no require energy inputs for separation), automatic product pump	Maximum pumping distance 20 ft.	$8,905
ORS Tramp Oil Scavenger	<70	<2.8	99%+	Pumps product automatically, can be operated manually or deployed permanently, pneumatic pump can pump thick oil grit		$8,905
SHALLOW WELLS (WATER TABLE < 20 ft.)						
ORS Scavenger	<20	<5	Sheen	Lightweight, portable, passive filter separator (does no require energy inputs for separation), automatic product pump	Requires 24–in well, maximum pumping distance is 20 ft.	$8,905
ORS Probe–Scavenger	15–80	8–38	99%+	Smaller than Scavenger, submersible, greater pumping capacity	Requires 8–in well	$8,775
ORS Shallow Well	20–90	5–35	99%+	Can be used in wells as narrow as 3 1/2 in., submersible		$8,775
EMTEK –VP–1075–VCP	6–50	74–10	99%+	Can withstand advese pumping conditions, can be used in wells as narrow as 6 in.		$8,528
NEPCCO Petropurge	5–85	40–0.5	99%+	Submersible, minimum well size is 4 in.		$7,735
ORS Probe/Pump	15–35	70–10		Submersible, designed for Probe–Scavenger		$5,135
ORS Stainless–Steel Water Table Depression Pump	50–10 (1/2 hp) 50–125 (3/4 hp)	50–12		Can be exposed to saltwater, maintains uniform depression	Requires 8–in well	$6,305

TABLE I1.1
PRODUCT RECOVERY EQUIPMENT
TRENCHES

COMPANY/PRODUCT	DYNAMIC HEAD (ft.)	PUMPING RATES (gal/min)	DEGREE OF OIL/WATER SEPARATION	ADVANTAGES	DISADVANTAGES	APPROXIMATE COST
ORS Shallow Well Water Table Depression Pump	15–26	30–10		Can fit in 3 1/2–in well, can be used in corrosive environment surface–mounted	For shallow water table only	$5,395
EMTEK-WP-1075 (3/4)	6–50	74–10		Surface–mounted, can withstand adverse pumping conditions, minimum well size is 6 in		$4,857
NEPCCO HP 1–9	93–190	7–1		Submersible, minimum well size is 4 in		$5,135
NEPCCO HP 4–6	60–130	28–10		Submersible, minimum well size is 4 in		$7,735

DEEP WELLS (WATER TABLE > 20 ft)

COMPANY/PRODUCT	DYNAMIC HEAD (ft.)	PUMPING RATES (gal/min)	DEGREE OF OIL/WATER SEPARATION	ADVANTAGES	DISADVANTAGES	APPROXIMATE COST
ORS Probe/Pump	15–35	70–10		Submersible	Maximum pumping distance is 40 ft	$5,135
ORS Stainless–Steel Water Table Depression Pump	50–150	60–25 (2 hp) 100–5 (3 hp)		Can be exposed to saltwater, submersible	Requires 8–in well	$9,035
EMTEK-WP-1075-SHH	80–160	28–11 (3/4 HP)		Submersible, multistage certified pump, can withstand corrosive environments	Requires 8–in well	$4,279
NEPCCO HP 1–9	93–190	7–1		Submersible, minimum well size is 4 in	Low pumping rates at high heads	$5,135
NEPCCO HP 4–6	60–130	28–10		Submersible, minimum well size is 4 in		$5,428

injection well patterns to be simulated, and the relative clean-up plume capture efficiencies compared. In this way, a pump-and-treat system can be optimized to provide the most clean-up with the fewest wells and the lowest volumes of groundwater for treatment. Pump-and-treat optimization has been conducted for the design of remedial systems at several Alberta sour gas facilities by Piteau Engineering Ltd. Mathematical models suitable for this type of work include the USGS MODFLOW, MOC and SUTRA codes, Waterloo Hydrogeologic Software FLOWPATH, and Environmental Technologies' MOFAT and ARMOS mutiphase codes, although many others are available. The extraction and injection well design, location and pumping/injection rates have to be carefully selected. Heterogeneity, anisotropy and preferential flowpaths have large impacts on the influence of wells. Anisotropy and the occurrence of specific heterogeneities can be used to optimize the location of recovery wells. Examples in the literature of the use of modelling to design pump-and-treat recovery systems include Satkin and Bedient (1988), Keeley (1984), and others.

Groundwater extraction can be conducted on a continuous basis if the focus is to maintain a hydraulic gradient towards the well. Pulsed pumping can be used in some cases to optimize the removal of contaminants. Recovering groundwater at a high rate increases the flow velocity inside the area of influence and may disturb solubility equilibrium, reducing clean-up efficiency. The pumping rate and pumping schedule (continuous or pulsed) must be carefully selected. Extraction can also be combined with some form of containment to minimize the amount of clean water recovered.

When dealing with free condensate, care should be taken to design recovery and monitoring wells. Capillary barrier problems may result from improper selection of screen size, filter pack material, and construction materials (Mercer et al, 1990). Screens should be placed so that they cover the range of anticipated water level fluctuations, and allow passage of mobile LNAPL.

5. Efficiency and Limitations

The pump-and-treat technique has been widely applied over the last several years in an attempt to remediate contaminant plumes in groundwater, and control contaminant migration. In the latter it has proved relatively successful, but in the former limitations have been

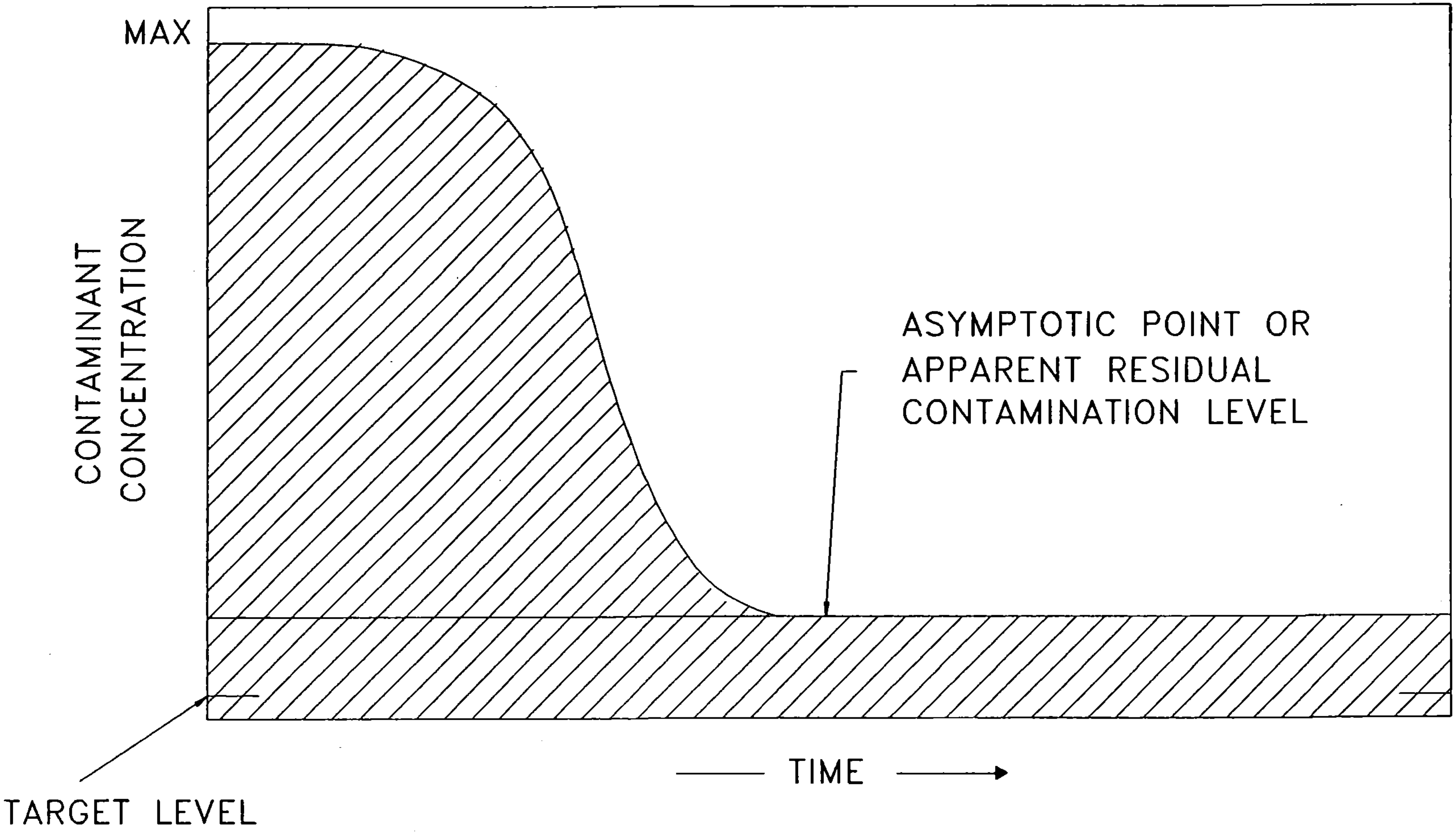


FIGURE I1.1
APPARENT CLEAN-UP
BY PUMP-AND-TREAT REMEDIATION

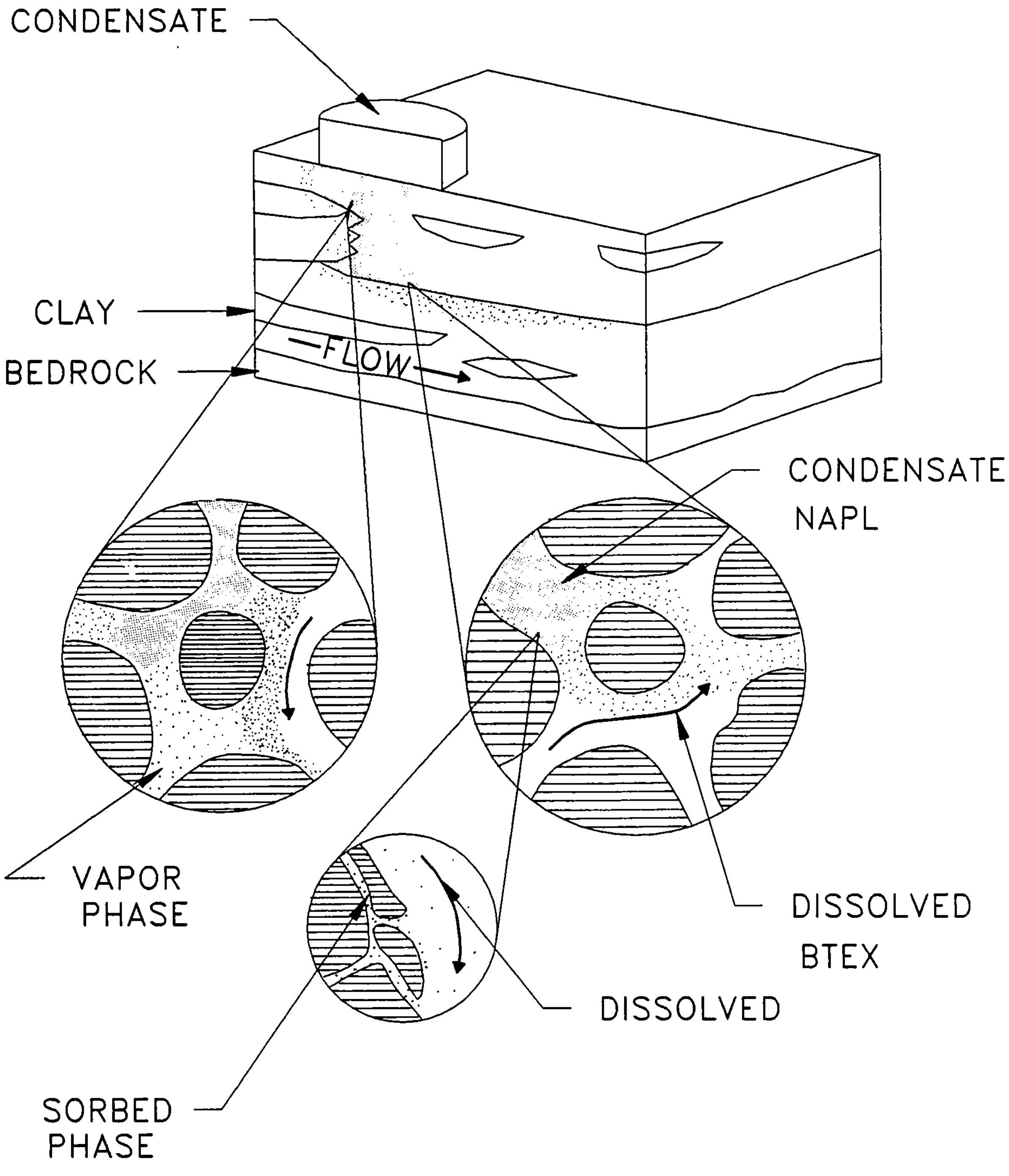


FIGURE I1.2
SCHEMATIC OF
GRANULAR SUBSURFACE ENVIRONMENT

recognized (Mackay and Cherry, 1989; Keeley, 1989; Feenstra, 1991). Three main factors control the degree of success (level of clean-up and time to accomplish clean-up) of the pump-and-treat technique: presence of contaminant sources, the physical and chemical properties of the contaminant and its behaviour in the subsurface, and the hydrogeology of the site.

Conventional pump-and-treat systems will often involve continuous operation of one or more extraction and reinjection wells. In many documented cases, these systems achieve a dramatic reduction in contaminant levels measured at monitoring wells in a relatively short time (often a year or less). However, after the initial sharp decrease in concentrations, low levels of contamination persist for long periods of time (Figure I1.1). This point is often referred to as the apparent residual contamination level. Beyond this point, continuous pumping of the aquifer will achieve only small reductions in contaminant levels, even over long periods. When this situation occurs, clean-up efficiency drops dramatically, as large volumes of water must be pumped and treated to remove small amounts of contaminant (Keeley, 1989). Once this asymptotic phase has been reached, however, concentrations of contaminants may remain above target clean-up levels indefinitely.

5.1 Factors Affecting Pump-and-Treat Efficiency

Contaminant Desorption and LNAPL Residual Saturation. This type of asymptotic response, in the case of contamination by organics and free condensate (BC and A - type contaminants), is the result of residual contamination adsorbed onto soil/aquifer particles or trapped in pores or fractures as NAPL. Groundwater initially extracted during pump-and-treat may have been in contact with the adsorbed and trapped contaminants for a significant period of time, and equilibrium between adsorbed, liquid and dissolved phases may have been fully or partially achieved. During the initial high efficiency period of operations, this groundwater is removed, and contains elevated levels of dissolved contaminants. As pumping continues, however, dissolution of contaminants is limited by the rate of contaminant desorption and the effects of aquifer heterogeneity (Figure I1.2). Present understanding of the relative mobility and sorption/desorption of organic contaminants in the subsurface is limited, but is sufficient to state that "field retardation varies among contaminants for a given site and among sites for a given contaminant" (Mackay and Cherry, 1989; Mercer and Cohen, 1990). The greater the retardation, the more time will be required for contaminant removal.

In the case of contamination by light non-aqueous phase liquids (LNAPL) such as condensate, the presence of a "subsurface source" of dissolved contaminants greatly increases the degree of difficulty in site remediation. Free flowing LNAPL can be recovered relatively easily. However, an LNAPL release leaves in its path a zone of LNAPL in the subsurface at residual saturation (up to 50% of the available pore space (Mercer and Cohen, 1990). LNAPL at a saturation equal or lower than residual saturation will not flow, as its relative permeability at that point is by definition zero. Water table fluctuations can cause vertical smearing of LNAPL, resulting in additional aquifer volume contaminated with LNAPL at residual saturation. The zones of residual saturation will act as sources of dissolved contaminants until they are removed, and greatly limit the efficiency of a pump-and-treat remediation.

The primary challenge in groundwater clean-ups is to remove the mass of organic contaminants that act as "subsurfaces sources" of dissolved contaminants. The use of pump-and-treat to continually remove dissolved contaminant mass is, compared to source removal, extremely cost and time-inefficient (Mackay and Cherry, 1989). This scenario has been described as one of perpetual maintenance.

Process chemicals have been detected in groundwater at ASGP's only at relatively low levels (a few mg/L at most), and only in the dissolved phase (CPA, 1990). Little information is available in the literature regarding the subsurface behaviour of process chemicals such as DIPA and sulfinol. Research into these areas is required to determine the potential effectiveness of pump-and-treat for process chemicals aquifer clean-up.

Geologic Complexity and Heterogeneity. Another important factor which limits the effectiveness of pump-and-treat is aquifer heterogeneity. This, in turn, is one of the key reasons why detailed site investigation is so important to the success of any remediation program. The design of each remediation program will be very site specific (Mercer et al, 1990; Mackay and Cherry, 1989). The geology at Alberta sour gas plants is typically complex and heterogeneous (Hardisty et al, 1990), characterized by interbedded clay-rich till units, discretely layered glaciofluvial and outwash sand and gravel deposits, and folded fractured interbedded sandstone-siltstone-shale bedrock units. Aquifer heterogeneity and anisotropy will to a large extent control the patterns of groundwater flow in both steady state and transient conditions.

During pump-and-treat, groundwater being pumped towards recovery wells will flow preferentially through zones of higher hydraulic conductivity, such as clean sand and gravel units, fractures, and fracture zones. Contaminants initially present in these zones will be drawn quickly towards recovery wells, while contaminants (adsorbed, trapped and dissolved) in the less permeable zones will be affected much less. In the extreme, the pumping wells will simply be circulating water continually through the same permeable areas, bypassing more contaminated zones. Under these circumstances, contaminant removal has essentially moved into a diffusion-limited phase, as mass is transferred from the less to more permeable zones by diffusion only.

Figure I1.3 shows hypothetical examples of contaminant removal from aquifers of differing complexity, and the effects on pump-and-treat. It is anticipated that the limitations of pump-and-treat discussed herein will be especially apparent at the majority of Alberta sour gas plant sites where organics and gas condensate contamination are a problem.

Fractured Rock Aquifers. Clean-up of LNAPL condensate in fractured bedrock (R1A/R2A) poses a myriad of special problems for pump-and-treat, and indeed for all other remedial approaches. Fractured rock is generally characterized by open discontinuities, fissures and cracks across a variety of scales, from regional to local to microscopic. As such, fracturing has been described as a fractal process (Turcotte, 1989). Fracturing on different scales will have different effects on aquifer behaviour and the ability to recover contaminant and achieve plume control with pump-and-treat. Regional fracture systems may provide boundaries to flow, or signal abrupt changes in geological units, especially in the Foothills region of Alberta. Local fracture networks may impart strong anisotropy to flow systems, and influence contaminant transport pathways and distribution. On the pore scale, fractures can trap LNAPL in "dead-ends", and affect distribution and concentrations of LNAPL residual saturation and degree of smearing. All of these factors make clean-up of fractured aquifers a difficult and time-consuming undertaking. "When attempts are made to clean-up such aquifers by pumping water, major improvements in water quality are exceedingly slow because little or no water flushes through dead-end fracture segments or through the porous but impervious rock matrix"

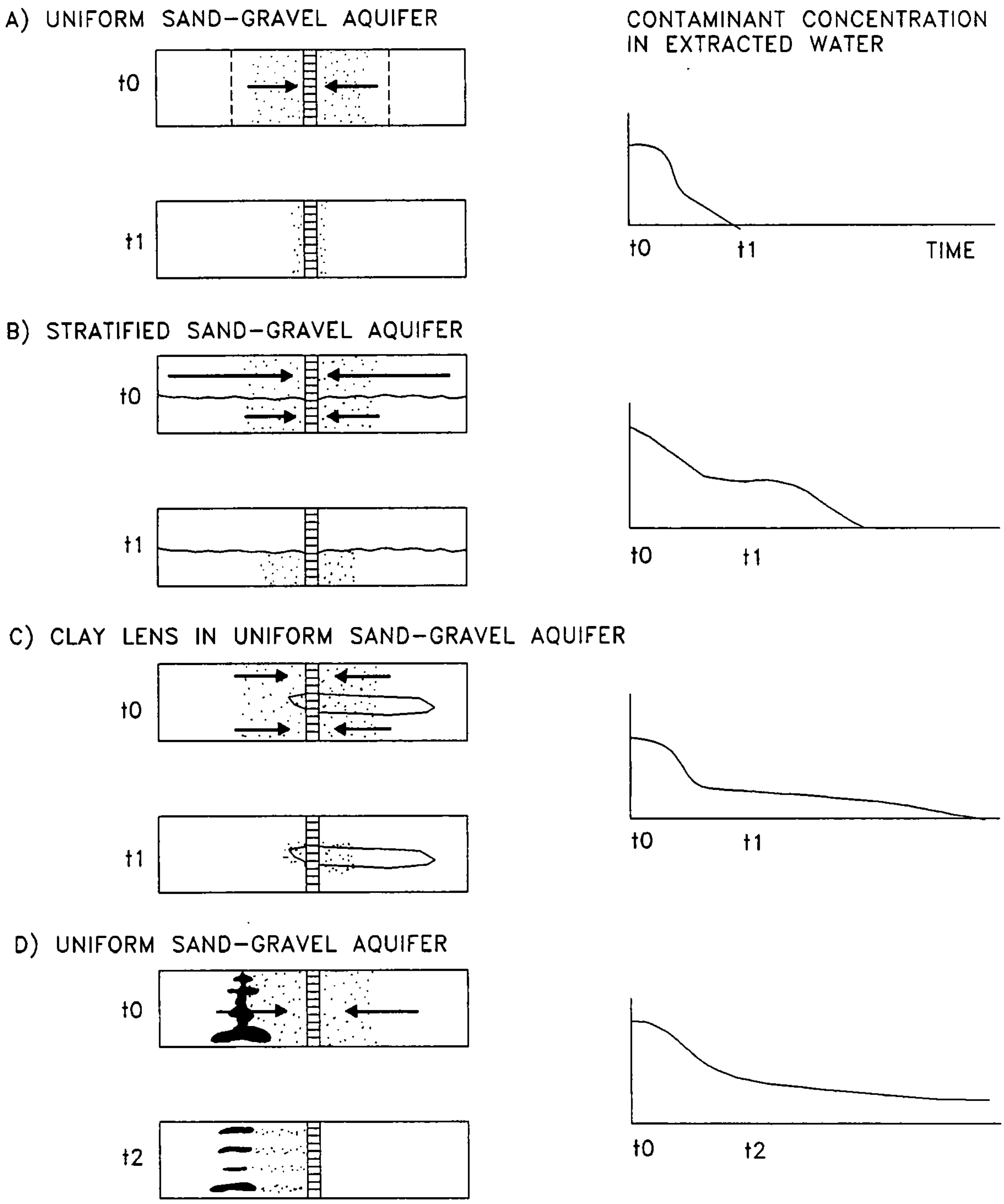


FIGURE 11.3
HYPOTHETICAL EXAMPLES OF
CONTAMINANT FROM AQUIFERS
A(AFTER MACKEY AND CHERRY, 1989)

(Mackay and Cherry, 1989). Even in situations involving fractured rock of fairly high porosity and matrix permeability which have been observed in core from sour gas plant sites in the Foothills region, flow through fractures may predominate, by-passing bulk contamination in the rock matrix.

Much further research and study of the effectiveness of pump-and-treat in fractured rock are required. In particular, the distribution, behaviour and monitoring of LNAPL condensate in fractured rock is an area on which little study has been done. The success of pump-and-treat and most other remediation methods will depend on an improved understanding of these mechanisms, and our ability to accurately assess and measure remedial performance (Mercer and Cohen, 1990). The remediation of LANPL-contaminated fractured rock aquifers at Alberta sour gas plants will likely require a combination of technologies, including enhanced pump-and-treat methods (surfactants, pulsed pumping, and in-situ biological methods), physical barriers, and in-situ volatilization systems.

5.2 Limitations of Pump-and-Treat

Pump-and-treat has been found effective in achieving hydrodynamic control of contaminant plumes, and as a mechanism for recovering mobile free product. However, the technique is not effective for remediation of residual hydrocarbon and organic contamination (Hockman, 1991; Testa and Winegardner, 1991; Keeley, 1989; Mackay and Cherry, 1989; Mercer et al, 1990).

Point of Diminishing Returns Recognition of this point of diminishing returns for aquifer clean-up (particularly for hydrocarbons and other organic contaminants) is useful insofar as it may allow hydrogeologists and groundwater engineers to begin application of enhancements to pump-and-treat, such as pulsed pumping, chemical additions, in-situ bioremediation, and advanced source clean-up measures. A statistical technique for recognizing the onset of the asymptotic point has been developed by the American Petroleum Institute (API) Groundwater Technical Task Force (GWTTF), specifically for cases of hydrocarbon remediation. A computer-based statistical program distinguishes between the initial rapid clean-up phase and the later asymptotic phase, before the onset of the latter, providing lead-time for decision makers. Detailed discussion of the method is available in American Petroleum Institute (1991).

Remediation of Inorganic Contaminants and Acidic Groundwater. Pump-and-treat was recommended for application to contamination situations at Alberta sour gas plants involving dissolved inorganic contamination of groundwater. The specific situations considered involved inorganic salts such as chloride and sulphate. These were found to be the most common types of groundwater contamination at ASGP's (CPA, 1990).

In cases involving inorganic contamination, pump-and-treat is expected to be more successful in achieving plume control and remediation than for organics and LNAPL. Chloride, for instance, is a conservative ion, and will not be subject to the retardation effects of many organics. When concentrations of inorganics in groundwater are high, pump-and-treat can be expected to provide fairly rapid plume remediation. However, costs of treatment for inorganics are fairly high.

Most cases of inorganic groundwater contamination at Alberta sour gas plants involved concentrations of chlorides below 500 mg/L, and sulphate levels below 5000 mg/L (CPA, 1990). These concentrations are not especially high, and suggest that contaminant mass-removal efficiencies for pump-and-treat would be quite low. If these plumes are not associated with the presence of dissolved organics (process chemicals and BTEX), the expense of pump-and-treat for such problems should be carefully weighed next to the other alternatives of flushing and natural dissipation. Where active remediation is necessary, based on the results of a risk assessment, pump-and-treat should provide good results if properly designed, implemented and monitored.

5.3 Estimation of Clean-up Time

The time required for clean-up of a dissolved phase plume will vary according to the chemical properties of the contaminants, and the hydrogeological characteristics of the aquifer through which they are moving. The presence of contaminants of low solubility or with high sorption coefficients will lengthen remediation operations. As discussed above, if LNAPL subsurface sources are present, complete remediation of groundwtaer may not be possible.

Heterogeneities in the stratigraphy, such as clay lenses in a sand and gravel unit, will also slow down recovery. Diffusion of contaminants from lower hydraulic conductivity layers (which may contain strongly sorptive clay minerals) may contribute to the "tailing effect" often observed with pump-and-treat (Mercer et al, 1990). The hydraulic conductivity also controls the rate at which the water can be recovered. Pump-and-treat might not be applicable if the hydraulic conductivity is too small.

Non-Reactive Solutes. A simple method can be used to estimate time required for clean-up, based on the complete exchange of one pore volume of groundwater contaminated with a non-reactive solute from the complete volume of contaminated aquifer (Hall, 1988):

$$t = (A_c \,.\, b)\; n / Q$$

where:

A_c = Area of aquifer contaminated
b = thickness of contaminated aquifer
n = aquifer bulk porosity
Q = average pumping rate

Reactive Solutes. In reality, the volume of water pumped will greatly exceed this theoretical value. Even the most efficiently designed and operated pumping systems will capture clean groundwater from beyond the plume's boundaries. The effects of retardation, aquifer heterogeneity and the presence of subsurface sources of contamination will all tend to increase clean-up times. The effects of sorption can be estimated if the linear soil partition coefficient (ratio of mass concentration on solid phase to mass concentration in the aqueous phase) is known (Mercer et al, 1990):

$$w_r = w / R$$

where:

$$w = Ki / n_e$$

and:

$$R = 1 + [(K_{sp} \,.\, d_{b)} / n_e]$$

for:

w = average linear groundwater flow velocity (m/s);
w_r = retarded average linear groundwater velocity (m/s);

R = retardation factor
n_e = effective porosity
K = hydraulic conductivity (m/s)
i = hydraulic gradient
K_{sp}= soil partitioning coefficient
d_b = soil specific density

The effects of tailing on time to clean-up are shown in Figure I1.4.

LNAPL Condensate at Residual Saturation The following example illustrates the ability of pump-and-treat techniques to remediate a subsurface source of LNAPL condensate at residual saturation (contamination situation T1A), and the times required. A one cubic metre zone of glaciofluvial sand and gravel (effective porosity (n_e) = 0.2; hydraulic conductivity (K) = 10E-05 m/s; hydraulic gradient (i) = 0.01) is contaminated with LNAPL natural gas condensate at a residual saturation (S_{ro}) of 0.1. The condensate contains 15 weight percent water soluble BTEX components, and dissolves into groundwater at ambient temperatures (8 to 10 degrees C) at about 20 mg/L (based on observations at several condensate-contaminated sites in Alberta (Hardisty and Headley, 1991)).

Then:

mass to be dissolved,

$m_d = 1\ m^3 \cdot n_e \cdot S_{ro} \cdot (0.85) \cdot (0.15) \cdot (1000\ kg/m^3) = 2.55\ kg$

mass flux through area,

$F = 1\ m^2 \cdot (Ki / n_e) \cdot n_e \cdot (0.02\ kg/m^3) = 2E\text{-}09\ kg/s$
$= 0.06\ kg/yr$

time required to dissolve out all BTEX components,

t = 42.5 years

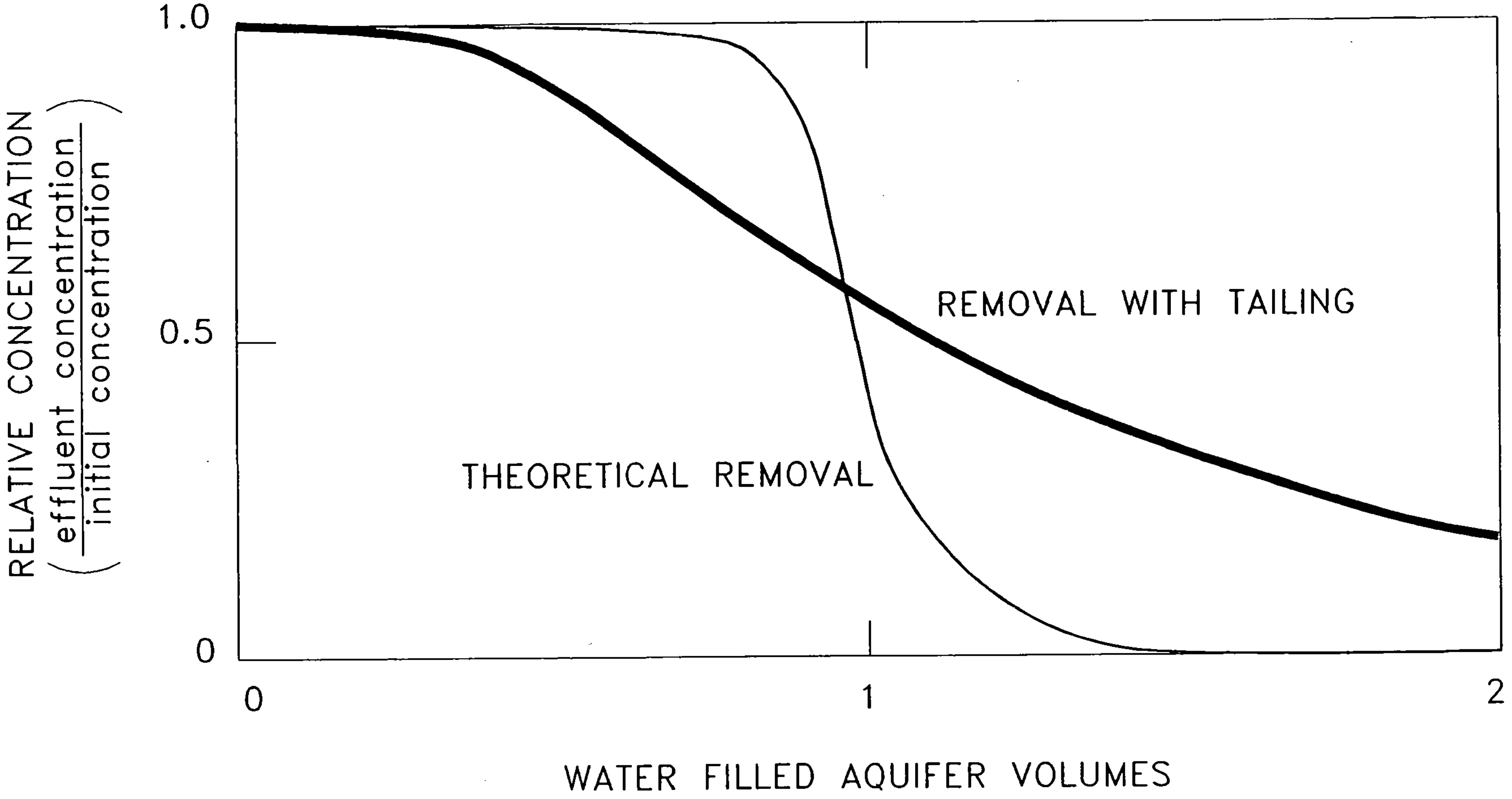


FIGURE I1.4
EFFECTS OF TAILING ON
PUMPING TIME (FROM KEELEY et. al, 1989)

This rudimentary calculation, which assumes complete flushing of the aquifer, demonstrates the profound impact which condensate trapped as residual saturation will have on pump-and-treat clean-up times. For practical purposes, pump-and-treat will not be effective for cleaning up LNAPL residual contamination.

6. Operation and Monitoring

6.1 Monitoring

Once the goals of the remedial action have been specified, the pump-and-treat system designed, installed and tested, a monitoring program must be designed to ensure goals are being met and monitor clean-up progress. In general, such a program should consist of water quality and water level monitoring at key locations in and around the plume. These data will help operators to adjust pumping and injection rates to meet changing conditions, and will allow assessment of the progress of the clean-up. Hydrochemical data from pumping and monitoring wells are used to anticipate the onset of asymptotic conditions, and characterize the plume's behaviour under pumping conditions. Monitoring can also point out problems such as the creation of stagnation zones, poor sweep efficiencies, and clogging of wells. Suitable modifications can then be made.

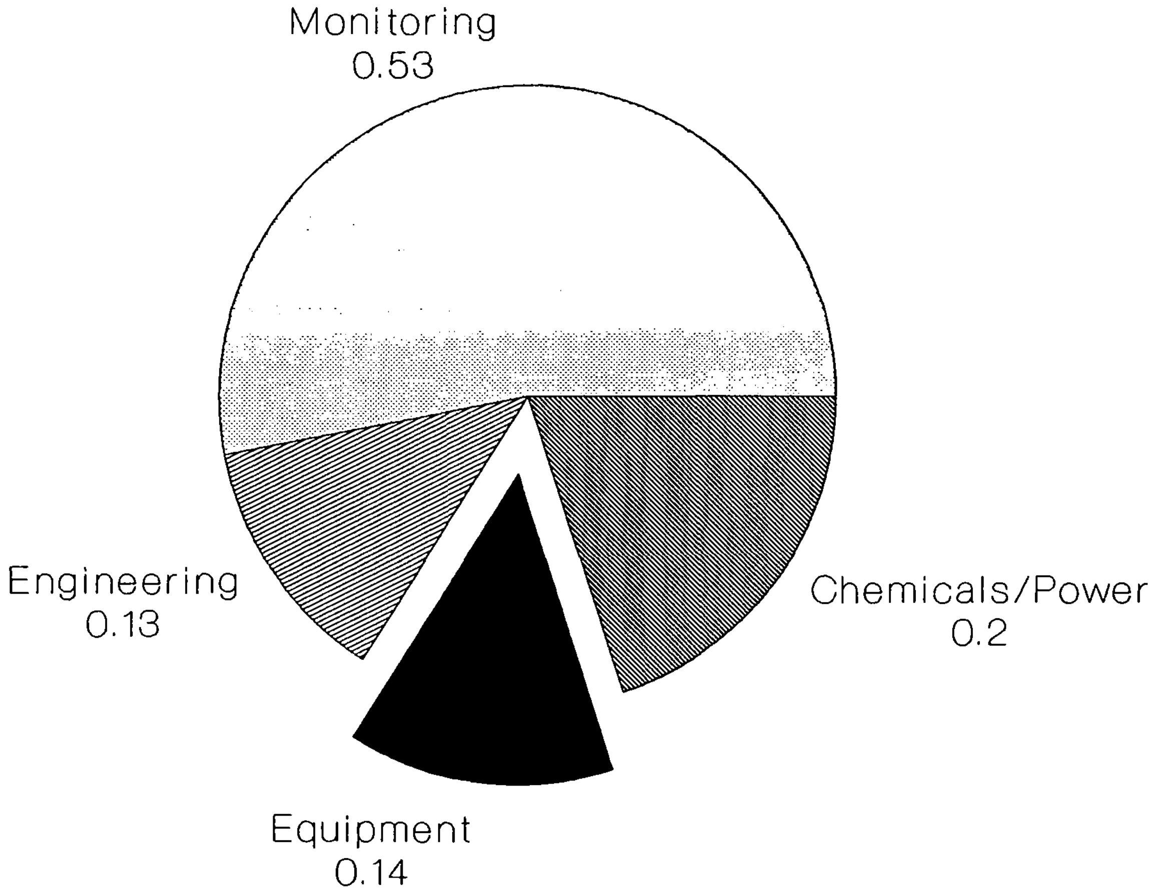
It is important to collect data prior to, during and after pumping. Monitoring should be performed on a regular basis. Case studies reveal that monitoring often represents the single largest component of total cost over a five year project (Figure I1.5). Mercer et al (1990) recommend that monitoring continue for several years after system termination.

6.2 System Modifications

Pumping changes the hydraulic regime in the aquifer significantly, and affects not only flow dynamics but hydrogeochemistry. The aquifer moves from equilibrium conditions to dynamic conditions. By its very nature, pump-and-treat is continually causing changes in the aquifer. For this reason, and because of the uncertainties associated with subsurface characterization (especially in the complex geological situation found in Alberta), modifications to the initial pump-and-treat design will usually be required (Mercer et al, 1990; Keeley, 1989).

FIGURE I1.5

2000 GAL DIESEL SPILL (Sullivan, 1991)



5 years, total cost $800,000

Modifications can result from a better understanding of the aquifer gained during system testing and operation, changes in produced water chemistry, seasonal fluctuations in groundwater levels and pumping rates, treatment facility constraints, or equipment problems. A good monitoring program will indicate which modifications are required. Mercer et al (1990) suggest:

> "Periodic review and modifications of the design, construction, maintenance, and operation of the pump-and-treat system will probably be necessary. The performance of the system should be evaluated annually, or more frequently, to determine if the goals and standards of the design criteria are being met. If not, adjustment or modification of the system may be necessary. Modifications may also be made as one part of the contaminant plume becomes clean or when portions are not showing the desired progress. Adjustments or modifications can include relocating or adding extraction wells or altering pumping rates."

Pulsed Pumping Once the asymptotic stage has been reached during pump-and-treat operations, continued flushing of the aquifer may become cost-ineffective. Large volumes of groundwater are being pumped and treated to remove a small mass of contaminant. Pulsed pumping has been recommended as a way of improving recovery efficiency and reducing operational costs (Keeley, 1989), and involves the intermittent operation of the pump-and-treat system. When the pumps are shut down, contaminants in low hydraulic conductivity zones are given time to diffuse out into the less contaminated higher hydraulic conductivity zones which have been swept previously. When pumps are turned on again later, higher contaminant concentrations are recovered. Figure I1.6 shows the reduction of residual contamination by pulsed pumping.

6.3 Termination

Termination of a pump-and-treat system should occur once the clean-up goals are met, or once optimum contaminant mass removal has been achieved, and it is of no practical use to continue operation (Mercer et al, 1990). The pump-and-treat system may also be converted or adapted to provide delivery and circulation of biological cultures, oxygen and nutrients for in-situ bioremedation, or surfactant solutions and binding agents.

If the goal of remediation at the site is containment of off-site migration of contaminants, and a subsurface source of contamination exists (such as residual condensate), termination may not be possible.

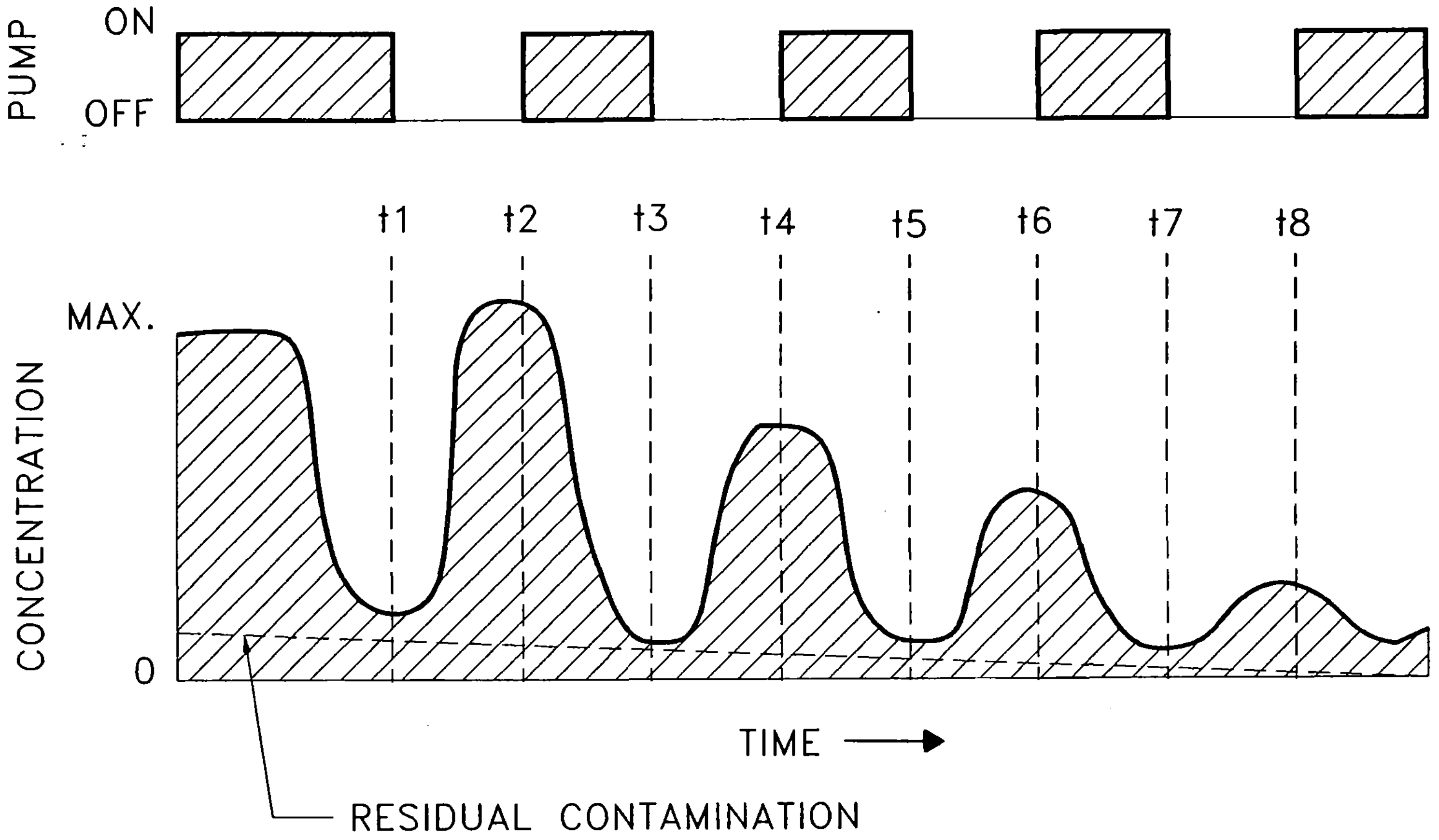


FIGURE I1.6
REDUCTION OF RESIDUAL CONTAMINANT MASS
BY PULSED PUMPING (FROM KEELY, 1989)

7. Costs

7.1 General Considerations

The level of effort applied during the characterization stage will have a direct impact on the efficiency of the pump-and-treat system designed. The clean-up time of a plume of known volume can be estimated roughly, however the real time required to clean-up the plume is likely to be much greater than this estimation because of the tailing effect. In remedial operations, as in most things, time means money. This reinforces the importance of proper system design and monitoring, and the need to tackle subsurface sources as soon as possible during a remediation program.

The efficiency of cleanups in fractured bedrock aquifers containing LNAPL is usually smaller than in granular aquifers since the distribution of LNAPL in the fractured media is much more complex. This fact will have a direct impact on the costs of remediation. In situations involving granular materials overlying and in hydraulic connection with fractured bedrock (XA), it is extremely important to prevent migration or smearing of LNAPL into the bedrock, if possible. If the groundwater surface usually lies in the granular materials, pumping and injection rates at the site should be carefully controlled and monitored to prevent drawdown into the bedrock.

The cost of a pump-and-treat system depends on the goals, size of the problem and hydrogeological conditions. The method of treatment has a very large influence on the total costs. EPA records of decision include cases ranging from US $750,000 in capital investment and US $100,000 annual O&M for an air stripping system to a capital investment of US $164,500,000 and annual O&M of US $12,539,000 for a reverse osmosis and granular activated carbon system.

7.2 Unit Costs for Pump-and-Treat Components at Alberta Sour Gas Plants

Table I1.2 shows typical capital and O&M costs for conventional recovery wells, large diameter recovery wells, and injection wells installed to a depth of 15 m. Costs are in 1991 Canadian dollars, and include design, field supervision and logging by a qualified hydrogeologist, materials, drilling costs, and testing. Costs of site preparation, tie-in, power and winterization are also provided. Costs were calculated based on current rates for contractors and suppliers in Alberta.

Table I1.2

Unit Costs For Pump-and Treat Components

Conventional Recovery Well

Design		$ 750.00
Drilling, materials, supervisor		$ 8,250.00
Testing and sampling, report		$ 1,500.00
Tie in and Winterization		$12,000.00
Pumps - water table depression		$ 8,000.00
	Total Capital Costs	$26,500.00
Annual O&M		
Maintenance, sampling, observation Power to pumps;		$ 4,000.00

Injection Wells

Design		$ 1,500.00
Drilling, materials, supervision		$10,500.00
Testing and sampling, report		$ 2,000.00
Tie in and winterization		$ 9,000.00
	Total Capital Costs	$23,000.00
Annual O&M		
Maintenance, monitoring, periodic flushing and de-fouling		$ 9,000.00

Large Diamater Recovery Well

Design		$ 750.00
Drilling, materials, supervision		$11,250.00
Testing, sampling, and report		$ 1,500.00
Tie in and winterization		$12,000.00
Pumps - water table depression		$ 8,000.00
	Total Caplital Costs	$33,500.00
Annual O&M		$ 8,000.00

7.3 Pump-and Treat Cost Estimate: Sour Gas Plant Model P-7

The main contamination situation at Plant P-7 involves LNAPL condensate in glaciofluvial sand and gravel and underlying fractured bedrock (situations T1A, R1A, XA). This case is an example of a relatively large LNAPL spill which has migrated some distance in the subsurface. Considerable vertical smearing of LNAPL is likely due to substantial seasonal water level fluctuations, creating a subsurface source of considerable potential.

Application of pump-and-treat at the site would be to control off-site migration of soluble and immiscible contaminants, and to begin recovery of mobile free condensate. To minimize water table fluctuations and achieve complete plume capture under these conditions, it is expected that a pump-and-treat system would require approximately 7 - 15 m deep recovery wells, pumping at an average rate of 10 igpm (45 L/min). Each well would be equipped with a water table depression pump and a product skimmer or scavenger. Treatment would include pre-treatment for iron, manganese and hardness (to prevent fouling of treatment equipment), followed by air-stripping to remove the bulk of dissolved BTEX. Off-gas treatment is not included in the cost-estimate. Treated water would be re-injected into the sand and gravels up-gradient of the plume through a system of ten gravity injection wells. All lines would require burying and winterization, and well heads and treatment equipment would be housed in heated shacks.

Table I1.3 shows a complete cost breakdown for the proposed pump-and-treat system. Costs do not include preliminary site characterization, hydrogeologic modelling and system design and optimization costs. Table I1.4 provides a summary of expected total costs after one, three and five years of operation and descriptions of expected clean-up progress, based on observations at similar sites in Alberta and from the literature. In this particular case it is clear that the presence of a continued source of subsurface contaminants (residual condensate) renders pump-and-treat ineffective and costly. When plume control has been achieved and a substantial portion of mobile LNAPL has been skimmed, complementary remediation technologies should be applied to such sites. As discussed in the technology selection section, soil vapour extraction used in conjunction with pump-and-treat is expected to yield good results. In-situ bioremediation should then be considered as a polishing step. In some special situations, physical barriers may also be employed to improve LNAPL recovery and contain plume migration.

7.4 Cost Estimate - Sour Gas Plant Model P-1

The main contamination situation at Sour Gas Plant Model P-1 involves dissolved inorganic and organic contaminants in till and fractured bedrock (situations T2BC/T1BC, R1BC). This case is a typical example of contamination from a leaking process water pond. A chloride plume (maximum concentration 300 mg/L) associated with low levels (<1 mg/L) of process chemicals and hydrocarbons (BTEX) has migrated about 500 m downgradient. In another part of the site, a sulphate plume extends downgradient from the sulphur block area. The relatively low (2000 mg/L) sulphate concentrations in this plume, and the naturally high concentrations of sulphate in groundwater in this area make active remediation unadvisable. For sake of argument, the results of risk assessment have shown that the chloride plume must be contained and if possible remediated.

As a first step in control of the chloride plume, the leaking pond has been decommissioned, removing the source and the driving head for the plume. A pump-and-treat system is the recommended approach to control plume migration and achieve contaminant clean-up. The levels of chloride are so low (around 300 mg/L) that reverse osmosis or distillation techniques are cost-prohibitive. The organics of concern are present at very low levels, and are to be treated by activated carbon filtration or AOP. To provide dilution of the sulphate plume, treated water from the chloride plume is to be mixed with clean groundwtaer from an on-site extraction well and reinjected into the sulphate plume area.

Table I1.5 shows a cost estimate for such a system, including cost of the on-site groundwater supply well. Costs of system design and preliminary site investigation are not included. A breakdown of the costs over one and three year periods, along with expected effects of the remediation are provided in Table I1.6. From a comparison with the previous example (Plant Model P-7), it is clear that pump-and-treat will be much more cost effective when applied to

Table I1.3

Pump-and Treat Cost Estimate - Model Plant P7

LNAPL Condensate Plume

Recovery wells required:	7
Injection wells required:	10

Average pumping rate, total = 70 ypm = (320 L/min)

Treatment system: pre-treatment for Iron; air-stripping

Component	Cost Category	Unit Cost	Number	Total
Recovery Wells	Capital	$15,000	7	105,000
	Pumps (dual)	$20,000	7	140,000
	Tie-in/ Winterization	$12,000	7	84,000
	Annual O&M	$ 4,000	7	28,000
Injection Wells	Capital	$15,000	10	150,000
	Tie-in/ Winterization	$ 9,000	10	90,000
	Annual O&M	$ 6,000	10	60,000
Annual Monitoring Costs	Engineering, laboratory, sampling, etc.	-	-	55,000
Treatment System For 70 ypm	Capital	$350,000	1	350,000
	Annual O&M	-	-	55,000

TABLE I1.4 - COST SUMMARY, PLANT P7 PUMP-AND-TREAT

	Capital Cost	O&M Cost	Total Cost	Effect
1 Year	919,000	198,000	1,117,000	- dissolved plume containment - reduction in plume concentration - some LNAPL recovered
3 Year	919,000	594,000	1,513,000	- plume dissolved levels decreasing - mobile LNAPL recovery slowing
5 Year	919,000	990,000	1,909,000	- asymptotic point reached - mobile LNAPL recovery complete

TABLE I1.5

Pump-and-Treat Cost Estimate - Model Plant P-1

Chloride Plume with Low Levels of Dissolved Organics

Recovery wells required:	2 @ 10 g
Injection wells required:	2
Groundwater Extraction well:	1

Treatment System: GAC filter, and dilution-mixing, reinjection

COMPONENT	COST CATEGORY	UNIT COST	NUMBER	TOTAL
Recovery Wells	Capital	$10,500	2	21,000
	Pump	$ 8,000	2	16,000
	Tie-in	$ 6,500	2	13,000
	Annual O&M	$ 2,500	-	2,500
Injection Wells	Capital	$15,000	2	30,000
	Tie-in	$ 9,000	2	18,000
	Annual O&M	$ 6,000	-	6,000
Groundwater Supply Well	Capital	$15,000	1	15,000
	Pump	$ 8,000	1	8,000
	Tie-in	$ 6,500	1	6,500
	Annual O&M	$ 2,500	1	2,500
Treatment System for 20 ypm	Capital	$90,000	1	90,000
	Annual O&M est.	$25,000	1	25,000

TABLE I1.6

COST SUMMARY - PLANT P1

PUMP-AND TREAT

TIME	CAPITAL COST	O&M COST	EFFECT
1 year	218,000	36,000	- plume migration controlled - reduction in plume concentration
3 year	218,000	108,000	- clean-up complete termination of P&T.

Model P-7), it is clear that pump-and-treat will be much more cost effective when applied to situations in which there are no major long-term subsurface sources. In cases involving relatively non-reactive solutes such as chlorides, plume capture and remediation can be relatively rapid, successful, and cost-effective.

8. Case Histories

8.1 Organic Contaminant Plumes in Granular Aquifers

Mackay and Cherry (1989) present a brief discussion of seven relatively well documented dissolved organic contaminant plumes from across North America. Contaminants range from BTEX to chlorinated solvents such as TCE and TCA. These case histories are summarized in Table I1.7. Plume characterization and treatment feasibility studies at each of the sites has cost in the millions of dollars to date. Ultimate clean-up costs for the plumes listed are estimated at tens of millions of dollars (Mackay and Cheery, 1989). For comparison, gas plant model P-7 has been included in the table.

These case histories highlight the enormous dilution of contaminants which takes place during spills of water-soluble organics. A few cubic metres of pure compound can contaminate millions of litres of groundwater. The longer the source of contamination remains active, the greater the size of the resulting plume, and the more expensive and lengthy the clean-up. According to Mackay and Cherry (1989) this shows clearly that "the primary challenge in groundwater clean-up is to remove the organic masses that serve, in effect, as subsurface sources and cause plumes to grow and persist, rather than simply to remove the mass of dissolved contaminants that defines the plume.

8.2 Selected Pump-and-Treat Applications Examples

Table I1.9 presents a summary of pump-and-treat applications at various sites in the USA. For each site, aquifer properties, types of contaminants present, remedial design, and effectiveness are discussed. No cost information was available for these cases.

8.3 LNAPL skimming - 400,000 L Gasoline Spill, Babylon, New York

In May of 1983, a gasoline leak was reported in an underground tank at a service station in

TABLE I1.7

Organic Contaminant Plumes in Sand-Gravel Aquifers.

(after Mackay and Cherry, 1989)

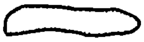
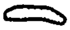
Site Location and Plume Map	Presumed Sources	Predominant Contaminats	Plume Volume (litres)	Contaminant Mass Dissolved in Plumes (as Equivalent NAPL volumes in litres
Ocean City, NJ 	chemical plant	TCE TCA	5,700,000,000	15,000
Mountain View, CA 	electronics plants	TCE TCA	6,000,000,000	9,800
Cape Cod, MA 	sewage infiltration beds	TCE Detergents	40,000,000,000	1,500
Traverse City, MI 	aviation fuel storage	Toluene Xylene Benzene	400,000,000	1,000
Gloucester, ON Canada 	special waste landfill	1,4, Dioxane Freon 113	102,000,000	190
San Jose, CA 	electronics plant	TCE Freon 113	5,000,000,000	130
Denver, CO 	trainyard, airport	TCE TCA	4,500,000,000	80
Gas Plant P-7 	gas plant	BTEX Natural Gas Condensate	500,000,000 est.	?

TABLE I1.8

SELECTED PUMP-AND-TREAT APPLICATIONS

(after Mercer et al, 1990)

Site Name & State	GW Region	Aquifer Properties	Major Contaminants	NAPL	Remediation Design	Treatment	Monitoring Capabilities	Effectiveness/ Limitations
Des Moines, IA	Glaciated Central Region	Highly permeable, unconfined sand and gravel aquifer. Laterally extensive SS,SH, and LS bedrock aquifers below	TCE and byproducts: trans-1,2-DCE, VC. Max. conc. TCE = 8,967 ppb	No	7 recovery wells, total pumpage =1300 gpm.	Air stripper	60 wells & piez. monthly WQ from 36 wells for 34 VOCs plus WLs.	o Effective zone of capture developed within 6 months o Lack of fine grained seds. in aquifer favors extraction o Significant decline in concentrations. o Vadose zone contamination may cause lengthy remediation
Site A, FL	Southeast Costal Plain	Biscayne aquifer, sole source. Highly permeable sand and limestone, flat water table.	Mostly limited to upper portion of aquifer. Benzene, CB, 1-4-dichlorobenzene trans -1,2-DCE, VC	No	1 recovery well, total pumpage = 30-50 gpm, screened 15 to 25 ft bls.	Air stripper, discharge to city sewer system	14 wells sampled 6 times over 6 months	o Chemical concentrations in most monitor wells have been reduced significantly. o Overoptimistically designed 25 to 60 day cleanup not obtained, but appear to be making good progress
Fairchild Semiconductor Corp, CA	Alluvial Basin	300-400 ft of Quaternary alluvium. Multiaquifer system. Aquifers A-D are sand and gravel, separated by silt and silty clay.	Xylene, Acetone, TCE, IPA, Freon-113, Max conc. in aquifer A: Acetone = 99,000,000 ppb, Xylene = 76,000,000 ppb. Chemicals have migrated laterally and vertically.	Concen. exceed solubility	Included soil removal, slurry wall construction, aquifer flushing, in-situ soil aeration, and pump and treat. 36 recovery wells phased in. Total pumpage started at 1,260 gpm from 1 well, peaked at 9,200 gpm, and has since been reduced to 2,100 gpm.	Air stripping or hauled offsite. Discharge to Canoas Creek via San Jose storm sewer system. GAC used if needed.	40 recovery wells sampled biweekly. 84 monitor wells sampled sporadically.	o in operation for 7 yrs. o Hydraulically successful. o Chemical concentrations reduced 3 orders of magnitude in upper 3 aquifers. o 90,000 pounds of solvents removed.

TABLE 11.8
SELECTED PUMP-AND-TREAT APPLICATIONS
(after Mercer et al, 1990)

Site Name & State	GW Region	Aquifer Properties	Major Contaminants	NAPL	Remediation Design	Treatment	Monitoring Capabilities	Effectiveness/ Limitations
Verona Well Field, MI	Glaciated Central Region	Glacial outwash (sand, gravel and some clay locally) overlying a fractured, permeable sandstone aquifer.	1,1-DCA, 1,2-DCA, 1,1,1-TCA,1,2-DCE, 1,1-DCE, TCE, PCE. Totals VOCs> 100,000 ppb.	Yes, LNAPL p to 6 in. thick mostly tourene based.	3-phase approach. To protect wellfield, 5 existing production wells pumped "at minimum. Onsite, 9 water-table recovery wells, total pumpage = 400 gpm. 23 PVC wells for vapor extraction.	Carbon pretreatment (if nec) and air stripping (vapor-phase carbon adsorption, if needed). Discharge to Battle Cr. Rv.	Water qualtiy from 5 extraction wells.	o Effectively blocked migration. o Residual LNAPL slows cleanup. o Vapor extraction has accelerated cleanup.
General Mills, Inc., MN	Glaciated Central Region	Glacial drift aquifer underlain by till and several bedrock (SH, SS,LS) aquifer.	TCE, PCE, TCA, BTX and organic degradation byproducts.	No effort to detect	5 recovery wells in water-table aquifer, total pumpage = 370 pgm. 1 recovery well in deep aquifer at 20-30 gpm.	3 wells: air stripping then discharge to storm sewer. 3 wells: discharge directly to storm sewer.	Not clear.	o Significant concentration declined in 1988 but drought year. o Hydraulic gradients (particularly vertical) not satisfactorily controlled; part of plume is being missed. o It is unlikely cleanup goals will be achieved: shallow <270 ppb TCE, deep <27 ppb TCE.
Amphenol Corp., NY	Glaciated Central Region	200 ft. alluvial sequence. Sand and gravel with some silt and clay. Relatively permeable, heterogeneous.	VOCs, mostly TCE and chloroform. Max. VOC concentration in well = 329 ppb.	No	2 recovery wells: shallow zone - 57 gpm, deep zone - 150 gpm	Air stripping, discharge to Susquehanna River	Sampled 12-17 wells quarterly.	o Groundwater divide successfully developed between plume and production wells. o VOC concentrations have been reduced during 1 1/2 years operation and flucutate much less. o Seasonal recharge and river fluctuations strongly influence flow patterns and may temporarily modify desired capture zones. o Remediations status is on schedule, anticipate 5-10 years remediation

North Babylon, New York. An estimated 100,000 gal had been lost. Observation wells installed in the service station property revealed that floating free product was present 11 to 12 ft below the ground surface.

In some places the gasoline plume was found to be as much as 18 in thick. Forty-four observation wells were installed to develop groundwater contour and to determine the direction of groundwater flow. Once the plume was located, surface-mounted product recovery pumps were sent down some of the 4-in observation wells to initiate the cleanup process while an automated system was being devised. In the first week, 750 gal of gasoline was recovered.

To contain the migration of the plume and increase product recovery rates, three 26-in wells were installed. The wells were placed 100 to 200 ft apart in a line parallel to the water gradient. In the upgradient well, which was nearest to the center of the gasoline plume, a 15-hp submersible water table depression pump was deployed. The pump extracted water from below the water table surface at a rate of 300 gal/min. As gasoline accumulated in the well, it was removed with surface-mounted product recovery pumps. The system began operating on July 3, 1983, and within five months 27,000 gal of gasoline had been recovered. Gasoline that had migrated beyond the influence of the upgradient well was recovered in the first downgradient well. The second downgradient well has yet to recover any gasoline. To date (November 1986), 28,500 gal of gasoline has been recovered.

The water being extracted from the wells contains dissolved hydrocarbons, and it therefore requires further treatment with air stripping towers. Air strippers are able to remove from 90 to 95 percent of the dissolved constituents. Once air stripping is complete, the treated water is being discharged to a natural water course, and the recovered gasoline is being re-refined and sold. The total cost of recovery, including the three wells, three dual pump systems, labour, engineering, and O&M costs to date has been nearly $225,000 ($337,500 if air and water testing and indoor vapour monitoring costs are included). This translates to $7.89 ($11.89) per gallon of gasoline recovered.

8.4 USEPA ROD - Verona Well Field, Michigan

In 1981, contamination by volatile organic compounds (VOC's) was detected in a well field belonging to the city of Battle Creek, Michigan. The source of the contamination was identified as a solvent company. As a control measure, a pump-and-treat system consisting of interceptor wells and air-stripping was installed to prevent further movement of the plume. The second phase of operations was directed at source control, and included installation of a groundwater extraction well system at the plant site to remove contaminants from groundwater. Vapour extraction wells were added later to enhance volatilization of VOC's from the unsaturated zone. Total estimated cost for the remedial alternative is expected to be US $1,660,000, with O&M costs of US $90,000 for the first two years and US $46,000 for each year thereafter. Remedial operations have been in progress for approximately ten years.

9. Requirements for Further Research

Pump-and-treat, despite its limitations, continues to be an invaluable tool in groundwater remediation. In almost all cases of groundwater contamination, some form of pump-and-treat will be used. Indeed, pump-and-treat is recommended as part of the remedial strategy for almost all groundwater contamination situations at Alberta sour gas plants. In many cases, a pump-and-treat system will act as one part of an overall remediation system.

Recognizing its importance, and limitations, a number of recent studies and initiatives have identified pump-and-treat as a topic for renewed study and research. This is due in no small part to the fact that many other remedial techniques, particularly the new in-situ technologies such as bioremediation and surfactant flushing, are dependent on pump-and-treat for their application, and hence share many of the same limitations as pump-and-treat. The USEPA SCAMP (Subsurface Clean-up and Mobilization Processes) Initiative is presently funding efforts to study and improve the efficacy of pump-and-treat remedial actions. They have identified the most common and serious problems related to pump-and-treat efficiency. These are (Schmelling, 1991):

- aquifer heterogeneity;
- interactions of contaminants with the geologic matrix, particularly as a result of sorptive phenomena;
- the presence of separate phase immiscible fluids in the plume.

Notably, the limitations are all due to subsurface phenomena. Once the contaminants have been removed from the ground, effective treatments are available. Hence, renewed focus towards understanding sub-surface processes are required. At Alberta sour gas plant sites, the complexity of hydrogeologic conditions, and the presence of a wide variety of troublesome contaminants, makes this type of research important. From this perspective, pump-and-treat must still be considered as an "experimental/innovative" technology when applied to organic plume clean-up (Feenstra, 1991).

During 1991 and 1992, the SCAMP initiative will be funding research into the following areas (Schmelling, 1991):

- surfactants (30% of effort);
- mixed solvents (10%);
- complex hydrogeology (20%);
- physical model demonstration/evaluation (20%);
- site characterization (20%).

This breakdown reinforces the need for study into characterization of hydrogeological conditions at Alberta sites, and studies of the behaviour of complex systems during remediation. Virtually no serious research has been conducted in these areas at Alberta sites.

Mercer and Cohen (1990), in their comprehensive review of immiscible fluids in the subsurface, also identify areas in which future research should be focused. All of these areas of research also apply directly to Alberta sour gas plants:

- development and demonstration of improved methods to measure in-situ saturations of NAPL;
- measurement of relative permeability functions;
- because of the importance of residual saturation as a continuing source for vapour transport and/or chemical transport, an improved understanding of in-situ volatilization and dissolution is needed;
- although much of the data required for NAPL simulation are unavailable, model improvements can be made. This would require an improved understanding of mass-transfer mechanisms;
- as with any contamination problem, the ability to define spatial variability, including fracturing, is important to understanding NAPL migration and recovery.

- improved manuals that provide documentation and guidance on procedures and priorities for investigating NAPL contaminated sites are needed by NAPL site investigators;
- many NAPL remediation technologies are largely untested; field-scale demonstrations are required to determine which technologies work effectively and under what conditions. These studies require careful control to evaluate actual mass recovered and left in-situ.

In addition, the following areas have been identified by this study for future research in connection with pump-and-treat (and other remediation technologies):

- The categorization, classification, and study subsurface behaviour of sour gas plant process chemicals. In particular, studies of their prevalence, biodegradability, physical and chemical properties, behaviour in groundwater, and treatability are required. Very little information on process chemicals is presently available.

- Study of the chemical and physical properties of natural gas condensates as they apply to subsurface remediation. Almost no information pertaining to the behaviour of condensate as a subsurface contaminant is available, including the proportions of water soluble and insoluble compounds, biodegradability, and behaviour in fractured media;

- Site characterization methods for LNAPL spills in fractured bedrock aquifers, and study of smearing and residual saturation of condensate in fractured rock, and its implications for remediation and site closure;

- Further investigation into the extent of low pH problems at ASGP's, and the detailed characterization of the factors controlling its genesis and occurrence.

I.1.2 AIR STRIPPING AND GAC POLISHING

1. Introduction

Aeration of water to remove volatile compounds is a commonly used technique in the water treatment field: carbon dioxide, hydrogen sulphide and ammonia have been treated this way for many years. Since the mid-1970's the use of aeration for the removal of volatile synthetic organic compounds (VOC) has become practical and popular. Aeration relies on the exposure of the contaminated water to be treated to a fresh air supply. As the air and water mix, the volatile compounds in the water are driven out of solution and into the vapour state. Maximizing air\water contact is the key to any aeration system. There are many ways to achieve this goal, but packed tower aeration is by far the most commonly applied for the removal of VOC's from water (Sullivan and Lenzo, 1989).

Due to the generally hydrophobic nature of VOC's and their tendency to partition into other phases, they can be removed from groundwater by aeration or adsorption, or a combination of these. As a general rule, aeration is most effective with low-molecular weight, highly volatile compounds, while adsorption works best with high-molecular weight substances with low solubility (Willey and Williams, 1986). Air stripping is an aeration-based technology which has been designated by the U.S. EPA as the best available technology for removal of all regulated VOC's (Lenzo, 1988).

A list of the maximum contaminant levels for regulated VOC's has been compiled by the Federal Register (1987). The following are all treatable by air stripping.

Compound	Maximum Allowable Concentration (ppb)
Benzene	5
Carbon Tetrachloride	5
1,2-Dichloroethane	5
1,1-Dichloroethane	7
1,1,1-Trichloroethane	200
p-dichlorobenzene	75
Trichloroethene	5
Vinyl Chloride	5

Many other organic compounds have been listed for future regulation which are amenable to air stripping. These include methane, propane, ethylbenzene, and xylene (Sullivan and Lenzo, 1989).

Air stripping is a widely used and established technology, and is recommended for treatment of groundwtaer contaminated by BTEX and other VOC's. If required, final polishing can be accomplished effectively by granular activated carbon filtration systems.

2. Air-Stripping: Packed Towers

There are several types of air strippers. The type most widely used is a packed tower. The major components of a packed tower consist of a tower shell, tower internals, packing, and air delivery systems (Figure I1.7). The tower shell is usually cylindrical. This is for strength, ease of fabrication, and to avoid any corners that might induce channelling of the air or water.

The typical packed tower air stripper is a countercurrent design, where water flow is in the opposite direction to air flow. Contaminated water is introduced to the top of the tower by nozzles or distribution trays. Water flows by gravity around and through a packing material in the tower, which is designed to spread out the water into thin films to maximize surface area, thus improving mass transfer of the contaminant from water. A blower forces air upward through the packing where it picks up the volatile chemicals and is exhausted through the top of the tower. Water collects and leaves the stripper through a sump at the bottom of the tower (McFarland, 1989).

2.1 Packing Tower Components

Materials of construction include aluminum, stainless steel, coated carbon steel, and fibreglass. Fibreglass and aluminum are the least expensive, with coated carbon steel and aluminum costing slightly more (Nyer and Montgomery, 1989).

The tower internals serve to ensure that the mass transfer process takes place under optimal conditions and at the most economical cost. Starting at the top of the top, the first component that requires attention is the air exhaust ports. These ports are typically located around the circumference of the tower, and are sized to permit the air to escape with a minimum pressure drop. If the tower is for potable water, the outlets should be screened with 24-mesh screen to prevent contamination by windborne material entering the tower.

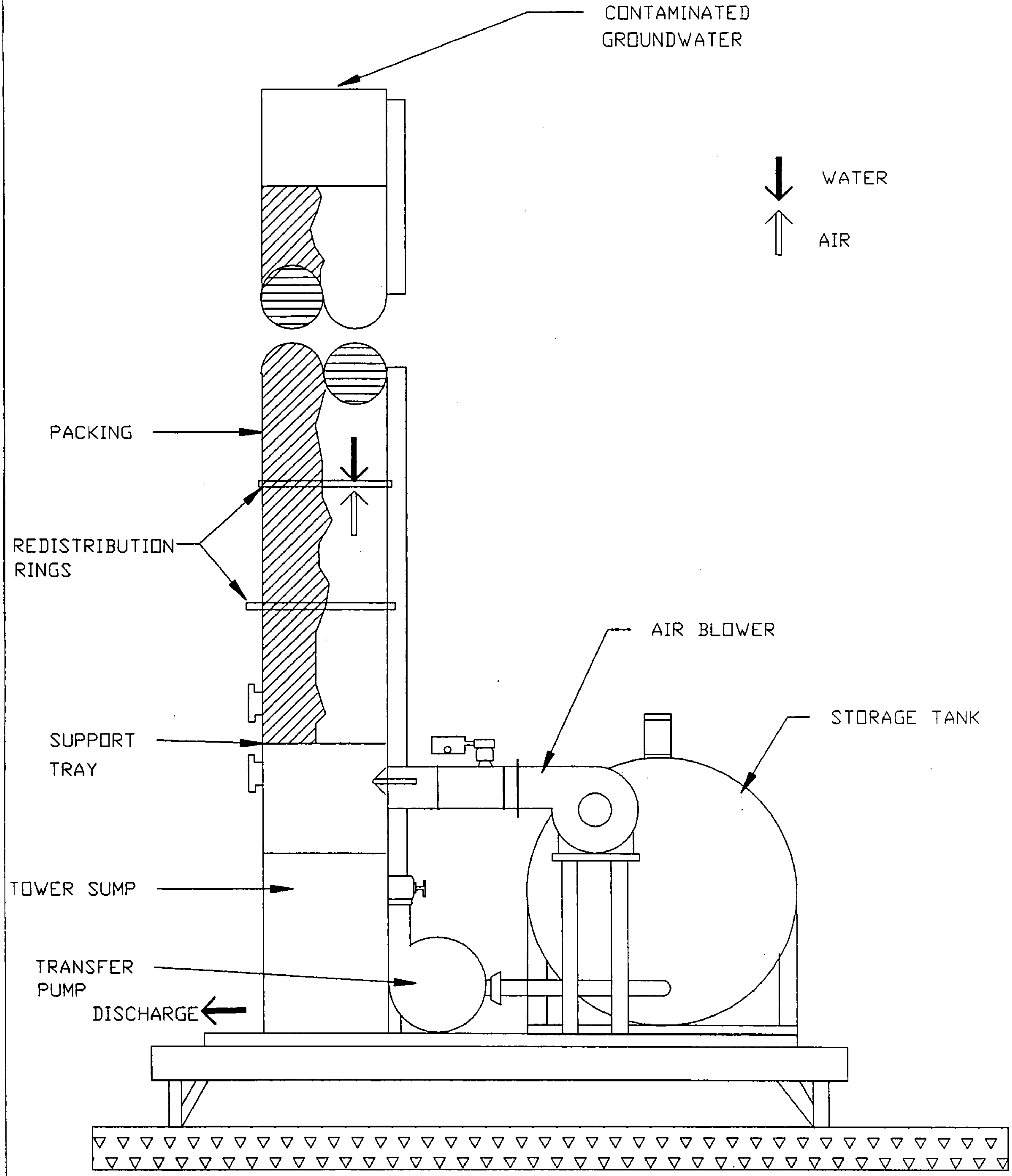


FIGURE I1.7
AIR STRIPPING TOWER

Continuing downward, the next component encountered is the demister, placed in the tower to prevent the discharge of large quantities of water entrained in the airstream. This is accomplished by forcing the airstream through a series of bends to impinge the water droplets on the surface of the demister. When the droplets grow to a large enough size, they fall back into the tower.

Water is introduced into the tower by means of a distributor, which ensures that the water is evenly distributed across the surface of the packing, while allowing for smooth, unimpeded airflow upward to the top of the tower. The distributors fall into four general categories: distributor trays, trough-and-weir arrangements, header-lateral piping, and spray nozzles (Nyer and Montgomery, 1989).

Below the distributor lies the packing, which is held up by a packing support plate. This plate must be structurally capable of supporting not only the weight of the packing, but also the weight of any water present in the packed bed. At the same time, the plate must have enough open area to minimize flooding, a condition that results when the water flows downward through a tower and is significantly impeded by the gas flow.

The design of the base of the tower will vary with system configuration; an integral clearwell (storage basin) may be supplied as part of the tower, or the water may flow by gravity to a recharge trench or recharge wells or a stream or sewer.

The single most important component selection is the tower packing. The ideal tower packing will provide a large surface area for the air and water to interact, and it will also create turbulence in the water stream to constantly expose fresh water surfaces to the air (Nyer and Montgomery, 1989). Packed towers typically have void volumes in excess of 90 percent which minimizes air pressure drop through the column (Willey and Williams, 1986).

The final component of an air stripping system is the air delivery system. Usually a forced draft blower is provided at the base of the tower or housed nearby in a building if noise control is a design constraint.

Air stripping in packed towers is a continuous process which is readily adapted to automation. Level sensors and switches can be installed to start and stop pumps, activate alarms and start and stop the blower.

2.2 Design Considerations

The effectiveness of air stripping is dependent on the kinetic theory of gases which states that molecules of dissolved gases can readily move between the gas and liquid phase. Since the groundwater contains volatile contaminants (BTEX) in excess of equilibrium levels the contaminants will move from the liquid phase to the gas phase until equilibrium is reached.

Two (2) major factors are used to determine the removal efficiencies for the BTEX components by air stripping. First, the ratio of a component's concentration in the gaseous phase to the concentration in the aqueous phase at equilibrium (measured by Henry's Constant), and second, the rate at which equilibrium is obtained. The Henry's Law Constant, which is a measure of the equilibrium distribution between air and dilute solutions, is used as an indicator of stripability.

Generally, compounds with higher vapour pressure and lower solubility in water are more efficiently air stripped. The BTEX compounds dissolved in the groundwater have relatively large Henry's Law Constants and are thus readily air stripped from the groundwater.

The straight-line equilibrium relationship commonly known as Henry's Law is shown as equation 1:

(1) $P_a = H_a X_a$ at equilibrium, where:

P_a = Partial pressure of component 'A' in the gas phase
H_a = Henry's constant
X_a = Mole fraction of component 'A' in the liquid phase

Alternatively, this equation can be written as:

$Vp = HS$ where:

Vp = Vapour pressure
H = Henry's Constant
S = Solubility in water

It is also important to know the temperature of the influent groundwater since Henry's constant increases with increasing temperature. For treatment at a gas plant, stripability could be optimized by increasing the groundwater temperature by using waste heat from the plant.

Most commercially available air stripping units can be built up in a modular fashion with a series of units. The effectiveness of an air stripper is dependent on a number of factors including the tower dimensions, packing material and shape, influent air parameters and air to water ratio (Piteau, 1990).

Equation 1 can be used to calculate the number of transfer units in the column for each compound that was quantified in the influent. The height of a transfer unit is calculated by dividing the packed height by the number of transfer units, as shown by:

(2) $H = Z/N$ where:

H = Height of an overall liquid phase transfer unit (m)
Z = Packed height (m)
N = Number of transfer units

Mass transfer coefficients can be determined from the relationship:

(3) $K_{la} = L/H$ where:

K_{la} = Overall liquid phase mass transfer coefficient (sec -1)
L = Superficial liquid velocity (m/sec)

Based on the significantly lower Henry's Law Constant for xylene for example, its relatively low vapour pressure, and its high initial concentration, this compound was used to determine the height for the air stripping tower. The influent flow rate is used to size the tower diameter. An air flowrate/water flowrate ratio and the water flowrate/tower cross-sectional area ratio are incorporated to ensure the required removal efficiencies. The maximum flow capacity could be increased by adding height and packing to the tower and increasing the transfer pump and blower output capacities (Dworkin and Cawley, 1988).

The key factors that affect the removal rates of BTEX and thus the design of the air stripping tower are:

1. Physical and chemical characteristics of the contaminants, particularly volatility as measured by Henry's Constant.
2. Water and air temperatures.
3. Air-to-water ratio.
4. Contact time.
5. Available area for mass transfer.

The first two (2) factors are determined by the characteristics of the BTEX components to be removed from the groundwater. The remaining factors are dependent on the treatment facility operating conditions, and are designed prior to pilot testing (Willey and Williams, 1986).

The air stripper design should be based on the highest anticipated intake flow rate, highest contaminant concentrations, lowest air temperature and lowest effluent limits expected over the duration of the pilot test. A safety factor should be considered when sizing the tower, packing size and depth and the blower output. A "rule of thumb" says that a liquid loading rate of 20 gpm per square foot of cross sectional area is acceptable. A second "rule of thumb" is that the ratio of the packing size to the diameter of the tower should be at least 1 to 6 (Nyer, 1988).

For engineering design purposes, it is very important to be able to determine the anticipated BTEX removal efficiency of an air stripping system. Equation 4 can be rearranged to give an expression useful for predicting the percent removal for a given column height and specified set of operating conditions. The final form of this expression is:

$$(4) \qquad E = \frac{100\,R\,(1 - e^{Q})}{(1 - Re^{Q})}$$

where: $Q = \dfrac{Z_t\,(K_{la})(R-1)}{RL}$

and E = the removal efficiency on a percent basis.
Z_t = total column packed height (m);
G = gas loading (m^3 of gas/m^2/min);
L = liquid loading (m^3 of liquid/m^2/min);
K_{la} = overall mass transfer coefficient (min^{-1});
R = stripping factor (the operating G/L ratio divided by the minimum G/L ratio required for 100% removal in an ideal column)

After the tower size and blower output design are completed, other critical features must be specified for the final tower design. For example, the tower column was designed with internal stainless steel rings to redistribute drippage. The tower packing material is selected to re-direct the water to the centre of the column and optimize removal efficiencies.

The tower and associated skid should incorporate easily accessible valves and unions to allow quick isolation and removal of the air stripper. The air stripping equipment should be skid mounted to simplify installation and removal of the system.

The tower sump can be designed for easy access cleaning and removal of any precipitates or sediments that may accumulate. This design feature also allows for periodic acid washing or hydrogen peroxide cleaning of the packing and tower, if necessary (McFarland, 1989).

For winter climates, heat tracing can be installed on the tower sump and storage tank to prevent freezing at temperatures as low as -40 degrees C. This feature also eliminates the potential freezing problems in the tower itself which, as a result of the high air-to-water ratio, tends to overcool the droplets in the tower packing.

A summary of the basic factors which must be considered in any design are summarized in the following table (Sullivan and Lenzo, 1989).

	Design Factors
Water Flow Rate	- Determines tower cross-sectional area
Treatment Efficiency	- Determines packed bed depth
Compounds Treated	- Determines air to water ratio
Other Factors	- Aesthetics, Inorganic Water Quality, Water Temperature

2.3 Problems Inherent with Packed Towers

Certain inorganic water quality parameters pose an operation and maintenance concern in aeration systems, especially packed towers. Of particular note are the effects of dissolved iron and manganese, suspended solids, high microbial populations, and hardness.

During the aeration process, oxygen is introduced into the water leading to the oxidation of dissolved metals such as iron and manganese. In most situations the pH of the water is such that manganese deposition is not a problem. However, the transformation of ferrous iron to ferric iron is a real and often destructive problem in air stripping operations. The oxidized iron deposits on the packing material and in time causes a build up that will bridge and clog the packed bed, leading to a decline in system efficiency. The degree to which iron deposition affect system performance is directly related to the level of dissolved iron in the water and other water quality characteristics such as pH and dissolved solids. Iron deposition can be controlled through the application of pretreatment technologies such as filtration and chemical removal (Sullivan and Lenzo, 1989). Alternatively, there are two other types of aeration treatment exist which, if applicable, would be much more cost effective than pre-treatment. The two types are cooling towers and diffused aeration tanks, and will be discussed later in the report.

The presence of high populations of microbial bacteria can lead to a biological build up within the packed bed. This problem occurs since the packing material and highly oxygenated water offer an excellent environment for microbial growth. As with oxidized iron a biological build up can lead to a deterioration of system performance. This problem is controlled through the use of chlorine solutions generally added prior to the air stripper on an intermittent or continuous feed basis. Periodic dosing of the column with a hydrogen peroxide solution has also been effective.

Calcium hardness is another operation/maintenance consideration. In the air stripping processes the potential for destabilization of the water is increased as a result of the removal of dissolved carbon dioxide from the water. The removal of carbon dioxide can lead to calcium carbonate deposition within the packed tower and in any post treatment distribution system. If the destabilization is sufficient and occurs over a long enough period of time the packing will become clogged with calcium carbonate. The problem can be controlled by minimizing the air to water ratio as much as possible - thus minimizing the stripping effect on carbon dioxide - or through the use of pretreatment. Pretreatment can take the form of softening systems or chemical sequestering agents (Sullivan and Lenzo, 1989).

2.4 Packed Tower Costs

Figure I1.8 presents capital cost charts for various system components (tower, holdup tank, water pumps and blowers). These charts provide a quick reference for costing equipment based on anticipated flow rate, surface area requirements, and air-flow rates.

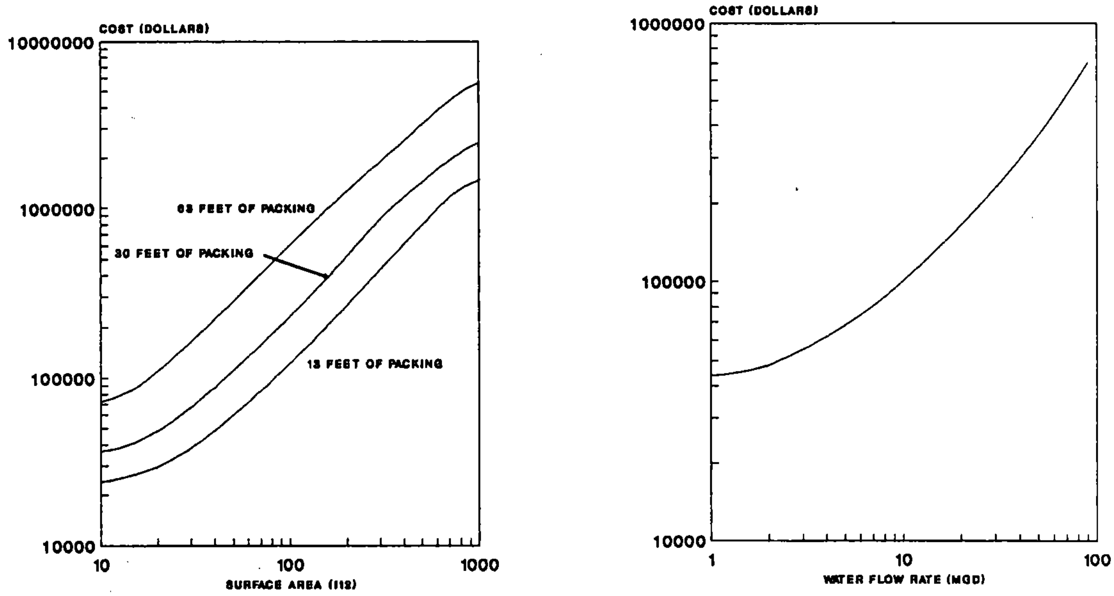
3. Alternative Air-Stripper Designs

The packed tower design is probably the most efficient method of contacting air and water in order to achieve high percent removal of volatile compounds. However, there are two other designs which could be more cost effective when the conditions are favourable. Cooling towers are appropriate for

FIGURE I1.8
COST FUNCTIONS FOR AIR-STRIPPERS
(FORM USEPA, 1988)

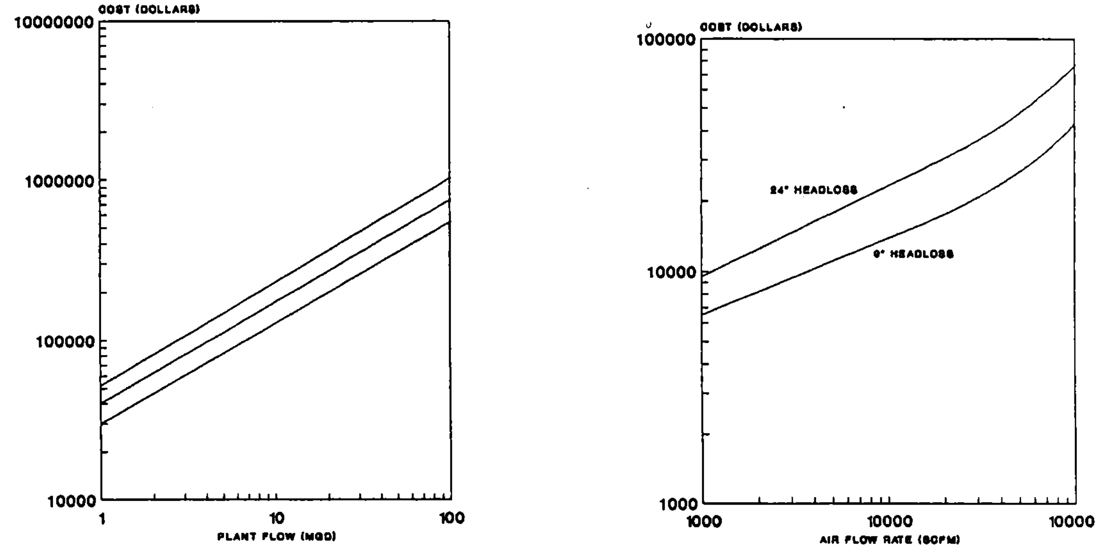
CAPITAL COSTS FOR PACKED TOWER (BASED ON SIZE)

CAPITAL COSTS FOR CLEARWELL



CAPITAL COSTS FOR WATER PUMP

CAPITAL COSTS FOR AIR BLOWER (BASED ON PRESSURE DROP)



high flow rates greater than 1000 gpm. Diffuse aeration tanks are suitable for very low flow rates (less than 40 gpm). As the flow rates encountered at sour gas plants ranges from approximately 50 to 200 gpm, these technologies are not applicable to gas plant remediation. However, these technologies can be useful in other remediation applications, such as leaking underground storage tanks or petroleum spills.

3.1 Cooling Towers

For high flow rate remedial designs (>1000 gpm), cooling towers may be more cost-effective and easier to operate and maintain than packed towers. The standard cooling tower is similar in design to the packed tower, except that air flow is induced using a fan at the top of the tower. The rest of the components are very similar to an air stripper.

One of the main differences between a cooling tower and a packed tower is that cooling towers use different packing media. The packing is structured, and is placed in the unit as large bricks of media. When using a cooling tower for volatile organics removal, the air to water contact can be optimized by removing the commonly used film sheets, and spraying the water into the tower.

Consider the case in which 1000 gpm of ground water containing 25 ppb trichloroethane requires treatment to reduce the TCE to less than 5 ppb, approximately 80 percent removal. A packing tower system for this application would cost approximately US $50,000 to US $60,000. Instead, a cooling tower was installed at a cost of US $20,000.

3.2 Diffused Aeration Tanks

Packed tower air strippers are frequently specified for the removal of volatile organic compounds from streams containing high concentrations of inorganics. In a low flow scenario, the use of diffused aeration tanks could prove to be a cost effective alternative.

For example, a case involved 5 gpm of groundwater requiring treatment to reduce 1 ppm of TCE to less than 5 ppb. The ground water also contained 25 ppm of iron. The cost of the packing tower was budgeted at US $8,000. Due to the high iron content of the ground water, the packing required replacement every two months. The total packing replacement cost per year is approximately US $5,000.

A diffused aeration unit could also be used to reduce the TCE concentrations and would not present the fouling problems typical to packed towers. Diffused aeration tanks are simple units consisting of a tank, a small bubble air diffuser, and a blower. This is a straightforward design. The water enters the tank, and is put into contact with air from a diffuser placed at the bottom of the tank. The volatiles transfer from the water to the bubbles and are removed from the system.

High air-to-water ratios must be maintained to meet the required treatment efficiency of 99.5 percent. A 5 gpm diffuser unit with a 2 to 3 hp blower and a tank sized for a 30 minute retention time (300 gallon) would cost approximately US $5,000. The capital cost of this system is lower than the cost for the packed tower. The operating costs are significantly lower even though more power is required for the diffused aeration system. The difference in electrical costs between operating the packed tower and the diffuser unit is approximately US $1,000 per year. Even at higher flow rates, the media replacement costs will be more expensive than the difference in power requirements (Nyer and Montgomery, 1989).

4. Granular Activated Carbon (GAC) Filtration

The use of the carbon adsorption process following air stripping is an effective method of reducing hydrocarbon concentrations to low levels, while reducing the frequency of adsorbent regeneration. The bulk of organic contaminants would be removed by air stripping. Any remaining low levels of contaminants could then be treated by GAC. This use of GAC is often termed 'polishing' in the literature.

Activated carbon as an effective and reliable means of removing low-solubility organics (Nyer, 1985). GAC is described as being suitable for treating a wide range of organics over a broad concentration range, and is not extremely sensitive to changes in concentrations or flow rate. However, the system is quite sensitive to suspended solids and oil and grease concentrations.

Carbon adsorption capacities can be theoretically estimated using single solute isotherm data for each BTEX compound (Nyer, 1985). For a typical 150 L/minute flow rate, a minimum of 1.2 cubic metres of carbon would be needed to maintain a minimum 20-minute contact time. These estimates ignore the potential competitive effects of the multicomponent mixture but can provide a close approximation.

To increase the contact time, and as a safety factor, the actual amount of carbon used can be increased. Increased flow capacities can be achieved by increasing the cross-sectional area of the carbon unit and the amount of carbon in the unit.

From the isotherm data, the rate of carbon use can be estimated. For a system designed to treat 150 L/min of water contaminated with 0.1 mg/L total BTEX, approximately 1 to 6 kg/day of carbon would be consumed. Carbon adsorption is effective, but is relatively expensive, and produces potentially large volumes of spent carbon which require disposal or regeneration (both of which are costly). For these reasons, GAC is recommended only as a polishing step, and only where surface release of groundwater is the only disposal option. Treatment by air-stripping can remove 99.9% of dissolved BTEX contaminants, if properly designed. If possible, reinjection of this water is preferred to GAC treatment. In some cases, however, there will be no other option than to treat for surface release.

5. Case Histories

Case 1 - Leaking Underground Storage Tank

Approximately 110 gallons of unleaded gasoline were released at a gasoline station. Short term remediation included contaminated soil removal and use of sorbent materials to remove free product from storm water in an adjacent drainage ditch.

Long term remediation included installation of a gravel-packed interception ditch with an integral recovery well. A submersible pump was installed to pump contaminated water to an air stripper which discharged to a reinjection trench, packed with gravel.

The air stripper treated 10 gpm of petroleum-contaminated groundwater with initial total BTX levels of approximately 8 ppm. The air stripper removed over 99.9 percent of the VOC's from the groundwater in each pass, resulting in reductions of BTX to undetectable levels, even in cold winter months. With this recovery system and air striping, total groundwater BTX levels in the aquifer were reduced to fewer than 40 ppb in an 8 month period. After the groundwater was cleaned up to acceptable levels, the air stripper was removed for future re-use at another location (McFarland, 1989).

Case 2 - Petroleum Terminal Contamination

Groundwater contamination of uncertain origin was discovered under a large petroleum terminal by monitoring wells. Two recovery wells were subsequently installed and equipped with submersible pumps. Low soil permeabilities in the area limited the maximum pumping rate to 1 gpm per well, although this was sufficient to create an acceptable zone of depression and prevent off-site migration of the contamination. Contaminated groundwater from the recovery wells was pumped to an air stripper, located on the terminal property.

Groundwater from the two recovery wells had an average total BTX level of up to 15,000 ppb, which was reduced by air stripping to fewer than 1 ppb, representing efficiencies of over 99.9 percent. During the cold winter months, removal efficiencies dropped slightly but effluent quality was acceptable with fewer than 30 ppb total BTX discharged.

Effluent from the air stripper was routed to an oil/water separator, which collects runoff from the terminal loading rack area. Surface discharge of oil/water separator had been a problem in the past due to high BTX levels resulting from gasoline contamination of loading rack runoff. The air stripper was designed with sufficient capacity to allow continuous recycling of the oil/water separator effluent through the air stripper to remove volatile organic compounds. Using a recycle rate of 15 gpm resulted in a reduction of BTX in the oil/water separator effluent from 380 ppb to 40 ppb. This shows that air stripping can be an effective removal technique for cleanup of wash water and contaminated stormwater, as well as contaminated groundwater (McFarland, 1989).

Case 3 - Sour Gas Plant Groundwater Treatment for BTEX from Condensate

The presence of groundwater contamination by free phase natural gas condensate was discovered at a gas plant in Alberta. The contamination originated from the process area and extended downgradient towards a muskeg. A pump and treat approach was designed involving separate phase skimming from recovery wells, treatment of groundwater with dissolved phase contamination, and reinjection of water. This operation produced significant volumes of groundwater requiring treatment and disposal.

The maximum flow rate to the treatment facility was 100 L/min (22 igpm). The groundwater contained elevated levels of iron, manganese and calcium. The elevated levels of these inorganics indicated that they were likely to form precipitates on the treatment system piping and equipment. The elevated levels of these inorganic materials would also lead to their precipitation in the carbon bed and thus adversely affect the adsorption capability of the carbon system. These factors, along with the difficulties the precipitates would cause in the injection wells, indicated that the iron, manganese and calcium would need to be removed from the groundwater prior to the removal treatment for organics.

A target removal efficiency of greater than 90% was used for the BTEX components. The target cleanup concentrations for the inorganics were less than 0.3 mg/L for iron and less than 0.05 mg/L for manganese. The calcium concentration was to be below levels at which calcium carbonate would precipitate.

Air stripping was chosen over granular activated carbon (GAC) adsorption as the primary treatment method for the removal of organics at this site. Preliminary calculations indicated that higher removal efficiencies could be achieved with air stripping at much lower operating costs than those projected for GAC from isotherms.

The system design included the following sequence of treatments:

1. Chemical precipitation and filtration of iron and manganese;
2. Ion exchange softening for calcium removal;
3. Air stripping to remove most of the dissolved BTEX components;
4. Granular activated carbon adsorption for the reduction of hydrocarbon concentrations to trace levels.

Capital Costs

The approximate capital costs for each of the treatment system components were as follows:

1. Filtration Units	$ 20,000.00
2. Ion Exchange Softeners	$ 15,000.00
3. Air Stripper and Skid	$ 53,000.00
4. Carbon Adsorption Unit (GAC)	$ 10,000.00
Subtotal	**$ 98,000.00**

The other capital costs associated with the pilot phase treatment study were approximately as follows:

1. Building and concrete pad	$ 50,000.00
2. Lighting	$ 3,000.00
3. Pneumatic System	$ 17,000.00
4. Plumbing	$ 12,000.00
5. Pumps, valves & level controls	$ 10,000.00
6. Electrical	$ 55,000.00
Subtotal	**$ 147,000.00**

The analytical costs for the pilot phase study were approximately $ 12,000 and the professional costs were about $ 25,000. Total capital costs for the treatment system were approximately $282,000.

Operational Expenses

The operational expenses included potassium permanganate for oxidizing the iron and manganese, salt required for regeneration of the ion exchange softeners, electricity and carbon. Based on the influent BTEX concentrations to the carbon adsorption unit and a flow rate of 100 L/ minute the 1.6 cubic metres of carbon would have to be regenerated once or twice per year. The cost of carbon replacement would be approximately $6,000 annually and disposal of the used carbon would be about $6,000 per year. Carbon regeneration to remove such volatile hydrocarbons as BTEX could probably be accomplished using waste steam from the gas plant. Long term use of carbon adsorption without regeneration capabilities would lead to extremely high carbon disposal and replacement costs. The operating costs of a regeneration process are difficult to estimate at this time. However, it is anticipated that regeneration would be both capital and operating cost intensive. The most significant operating cost component was makeup carbon to replace that lost to generation of fine particles or combustion in the regeneration process.

Significant operational costs for pretreatment includediron and manganese removal and softening. The operational costs associated with the filtration system are primarily for replacement of the potassium permanganate used as an oxidizing reagent. The cost for potassium permanganate, based on a 100 L/minute flow rate, are expected to be about $ 7,000 per year. The cost of potassium permanganate may fluctuate considerably over the life of a remediation project. The cost of sodium for regeneration of the softening units was expected to be about $ 4,000 per year based on the same flow rate and maximum calcium concentrations.

The estimated power costs, based on the horsepower of the blower motor and transfer pumps, as well as the lighting, were approximately $ 18,000/yr. The cost of electricity for heating the treatment facility could not be estimated during the pilot phase as electrical heaters were not installed. The estimated cost to operate two (2) 50,000 kilojoule heaters and keep the treatment facility at about 10 °C was $ 6,000 per year.

The only operational costs associated with the air stripping tower were expected to be replacement of the packing material and cleaning of the tower. The cost of these two operations may vary, but were expected to be between $ 2,000 and $ 5,000 per year. It was estimated that air stripping prior to carbon adsorption would reduce the operating costs of the GAC system by about 80%.

The annual operating costs for the treatment facility, based on the flow and groundwater chemistry of the pilot phase, were expected to be as follows:

1. Filtration Units	$ 6,000 - 7,000
2. Ion Exchange Softeners	$ 3,000 - 4,000
3. Air Stripping Tower	$ 2,000 - 5,000
4. Carbon Adsorption Unit	$ 6,000 - 12,000
5. Electricity	$ 18,000 - 24,000
Subtotal	**$ 35,000 - 52,000**

The operation cost listed did not include the costs of chemical analyses, operator or maintenance time, or the costs of equipment replacement.

I.2 GROUNDWATER REMEDIATION - NEW AND INNOVATIVE TECHNOLOGIES

I.2.1 IN-SITU VOLATILIZATION AND VENTILATION

1. Introduction

The subsurface volatilization and ventilation system (SVVS) has been designed for the simultaneous remediation of saturated and unsaturated zones contaminated with volatile organics. As such, it is ideal for cases involving condensate LNAPL which has been smeared vertically across the aquifer as a result of large water-table fluctuations and possibly dewatering operations attempted as part of abortive remedial strategies. Both these situations have been documented at ASGP's and have resulted in high residual LNAPL concentrations at some sites. The SVVS system uses air-sparging to provide a new way to remediate hydrocarbon-contaminated soils and groundwater.

There are comparatively few references to the technique in the literature. References to both vacuum extraction and air-sparging (or in-situ air-stripping) abound, however. Both of the aforementioned remedial technologies are in widespread use at various sites throughout North America and Europe. The methodologies and equipment for their implementation are widely available and well-tested. On this basis, the SVVS technique shows promise for demonstration and testing at Alberta Sour Gas Plants and other petroleum contaminated sites.

2. Description

2.1 General

The SVVS system consists of nested well pairs or patterns of air-injection wells completed below the groundwater surface and vacuum extraction wells completed in the unsaturated zone (Figure I2.1 shows a schematic of an SVVS pair). The vacuum extraction wells are designed in the conventional manner, and fitted with vacuum pumps which create a negative pressure and remove vapours from unsaturated zone pore space. The air-sparging wells are hooked-up to an air-compressor which delivers air under positive pressure into the aquifer.

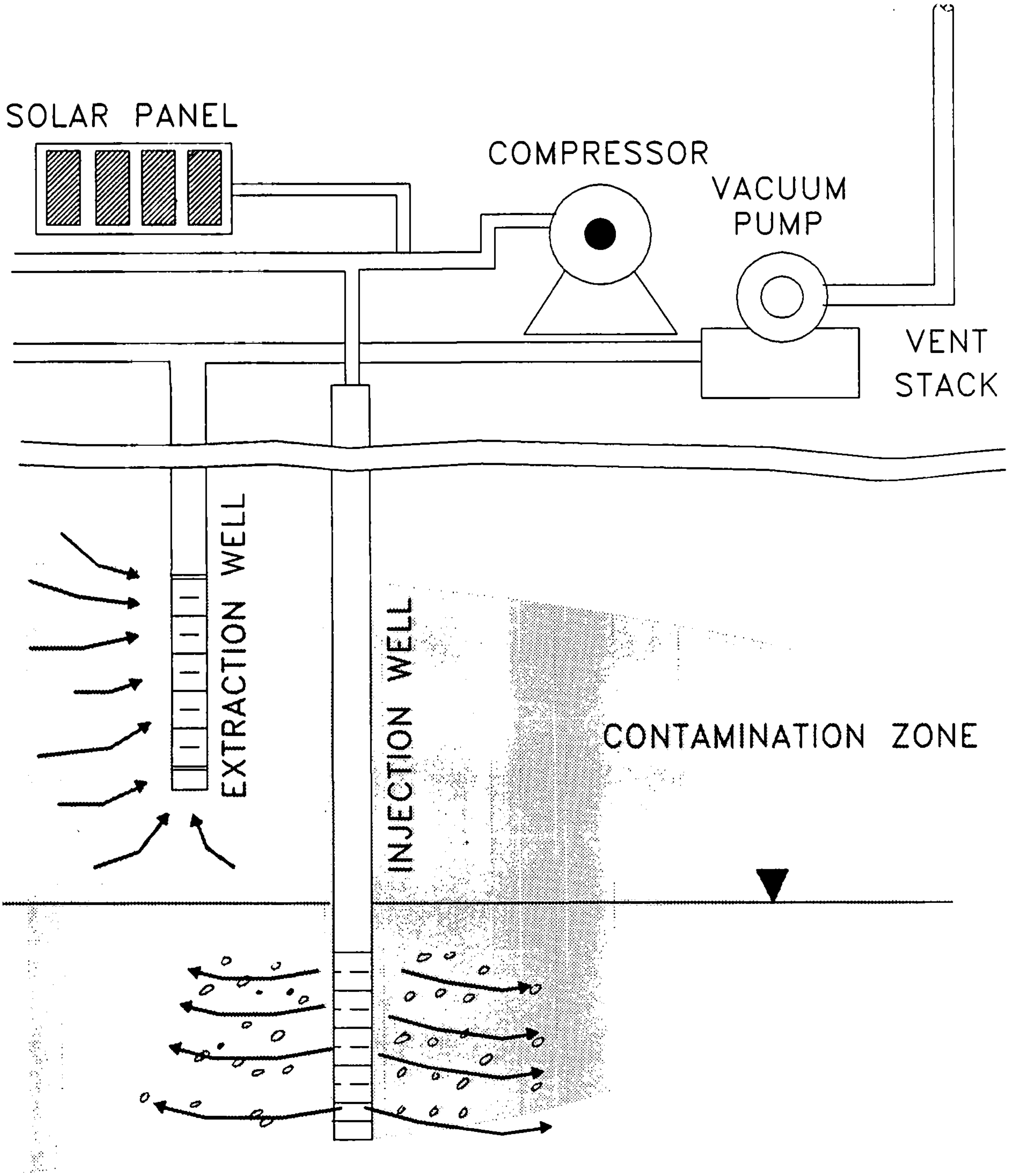


TABLE 12.1
SVVS SCHEMATIC

As air bubbles out into the aquifer, volatile organics are stripped out into the vapour phase, and carried to the water table, where they are released into the unsaturated zone. Vacuum extraction wells then remove the vapour-phase VOC's to surface for collection and treatment.

The method essentially combines the effects of vacuum-extraction and air sparging to address the problem of residual hydrocarbon contamination. In addition, natural biodegradation of condensate is enhanced through delivery of additional oxygen to both the saturated and unsaturated zones. Air-sparging has been shown to be an efficient and cost-effective method for delivering molecular oxygen to groundwater for in-situ bioremediation (see in-situ bioremediation section of this report). Moreover, the increased oxygen levels available to micro-organisms in the unsaturated zone during vacuum extraction has been well documented (Mendoza, 1990). The term "bioventing" is often used to describe this process (BATELLE CONFERENCE REFS).

The coordinated application of these techniques, therefore, holds significant promise for the remediation of condensate LNAPL in soils and groundwater at ASGP's.

2.2 Theory

As discussed in the section of behaviour of condensate LNAPL in the subsurface, the potential for trapping of residual saturation is high, especially in complex geological media, such as have been identified at many ASGP's (CPA, 1990). Once trapped as residual saturation, condensate liquids are essentially rendered immobile, and are no longer available for recovery through pumping-skimming operations. Other remedial technologies must then be applied.

Condensate essentially consist of lighter hydrocarbon fractions (C_5 - C_{12}) predominate) including aromatic compounds. These compounds generally have high vapour pressures and Henry's constants, and thus are readily volatilized from liquid to vapour phase, or 'stripped' from aqueous to vapour phase. It is possible that a significant proportion of light condensate can be mobilized into the vapour phase (Mendoza, 1990).

The application of vapour extraction techniques has been recommended in this report as a remedial strategy for condensate contamination of the unsaturated zone. However, the remediation of condensate trapped as residual LNAPL is granular or fractured media is a more complicated problem.

3. Vapour Extraction

Forced ventilation and vacuum extraction of VOC- contaminated vapours from the subsurface are discussed in detail in this report (soil vapour extraction section, Appendix I (Mendoza 1980)). This technique is one of the recommended "established" remedial technologies for ASGP's. The technique is most suited to sites with relatively permeable geological materials contaminated by light condensates or other volatile organic compounds.

The three main factors contributing to the performance of SVE systems are chemical composition of organics, vapour flow rates through affected areas, and flow paths relative to contaminated areas (Johnson, 1990)

4. Air-Sparging

Air-sparging is a method by which air is delivered to the aquifer via injection wells. Compressed air is forced through the well screen and into the saturated zone. The technique has been widely applied as a way of delivering oxygen to the subsurface to enhance in-situ biodegradation.

As air bubbles into the aquifer, it will begin to move up towards the groundwater surface, moving through pores and fractures in the rock. If residual condensate LNAPL has been trapped below the current groundwater surface it may be contacted by the migrating air-bubbles. Upon contact, some volatilization of the condensate into the air will occur, based on the contact-time between LNAPL and air, the chemical nature of the condensate, and the ambient temperature.

This will be a non-equilibrium process in most cases, as air bubbles will move relatively quickly to the groundwater surface, where they emerge and release VOC's into the unsaturated zone. During migration through the saturated zone, some additional partitioning between the vapour and aqueous phases may also occur, depending on the concentrations of dissolved hydrocarbons in the aquifer, concentration of hydrocarbons in the vapour phase inside individual air bubbles, and aquifer temperature. For this reason, control of groundwater flow in the contaminated area should be maintained, as air-sparging may cause local increases in dissolved phase (BTEX) groundwater contamination. A complete discussion of phase-partitioning relationships is provided in the report section on condensate.

5. Biodegradation

A complete discussion of in-situ bioremediation for organic-contaminated groundwater is found in this report (in-situ bioremediation section, this appendix).

Many naturally occurring bacteria present in the substrate at most sites (including ASGP sites tested) are capable of degrading hydrocarbons and other organics (Forrester, 1990b). Biodegradation is influenced by many factors, including the presence of appropriate organisms, contaminant types, concentrations of nutrients, nature and heterogeneity of the aquifer. Biodegradation is in many cases an oxygen limited process (Forrester, 1990a).

In most natural near-surface aquifers in Alberta, dissolved oxygen levels are quite low (< 1 mg/L). Effective in-situ bioremediation of hydrocarbon contaminated sites in Alberta will as a rule require addition of molecular oxygen. Air-sparging has been described as one of the more effective oxygen delivery systems in terms of mass oxygen delivered per unit cost (Huling and Bledsoe, 1991).

Air sparging as part of an SVVS system should increase levels of dissolved oxygen in the aquifer to about 8-12 mg/L, depending on groundwater temperature and system operation (Huling and Bledsoe, 1991). Evidence has shown that oxidation of hydrocarbons in the subsurface may proceed effectively at these levels (Hinchee and Downey, 1987).

In addition, vacuum extraction coupled with active or passive air injection will increase the flow of uncontaminated oxygenated air through the contaminated areas of the unsaturated zone. Significant mass-flow rates can be achieved by vacuum air-injection systems. Increased oxygen availability can thus increase natural biodegradation of condensate in the unsaturated zone. This process is known as "bioventing" (Huling and Bledsoe, 1991).

The enhancement of biodegradation rates in both saturated and unsaturated zones is an added feature of the SVVS system. Monitoring of contaminant removal may be complicated by the number of mechanisms acting simultaneously in contaminants.

6. Applicability

The SVVS technique may be applicable to cases at ASGP's involving contamination of the subsurface (soils and groundwater) by condensate, petroleum product spills, or the highly volatile organic compounds in particular situations in which LNAPL has been smeared over significant of distances across the section. (Water table fluctuations as great as 10 m have been recorded at ASGP's, (Piteau Engineering Ltd. 1990c)). Smearing due to water table fluctuations (natural and induced) may trap significant volumes of LNAPL as residual contamination in both saturated and unsaturated zones (Mercer and Cohen 1991).

In cases involving complex and heterogenous geology, the problems associated with removing residual LNAPL, especially in the saturated zone, may be considerable. Where residual LNAPL smearing below the water table is not extensive, pump-and-treat techniques can be used to depress the groundwater surface and expose LNAPL for vacuum extraction. One of the more common contamination situations identified at ASGP's was condensate (LNAPL and dissolved phase) in mixed aquifers consisting of glaciofluvial sand and gravel overlying and in hydraulic connection with underlying fractured bedrock. Under these conditions, condensate LNAPL may become trapped in the fractured bedrock to significant depths (5-13 m below natural groundwater surface) (CPA, 1990). SVVS systems show particular promise to such situations, where other conventional technologies are not readily applicable.

At sites where initial plume control and recovery of mobile LNAPL have been accomplished by pump-and-treat, removal of residual source contamination is the next obvious step. The application of SVVS is especially attractive if in-situ bioremediation is to be considered as a polishing step. Oxygen delivery is provided by SVVS, which also encourages volatilization of LNAPL and may also release additional contaminant mass into the aquifer as dissolved phase, where it is available for biodegradation.

7. Design and Operational Considerations

The effective operation of the SVVS-type system will be dependent on the following factors (Ardito and Billings, 1990).

- placement of sparging, vacuum-extraction and air-introduction wells;
- proper design, construction and installation of wells;
- subsurface characteristics, aquifer heterogeneity, hydraulic conductivity of media;
- physical and chemical properties of contaminant;
- proper operation and monitoring of the system.

7.1 Design

System design should attempt to discretize the contaminated areas. Each section should then operate independently, consisting of a sparging well and vacuum extraction well(s) (Ardito and Billings, 1990). Use of sparging/vacuum well patterns and the possibilities of more efficient system operation should be investigated through numerical models.

Well spacing should optimize coverage of the contaminated area. Such considerations are site-specific, and will depend on local geologic conditions. Placing sparging wells too far apart, for example, may result in significant volumes of contaminated aquifer remaining unremediated. Conversely, well placement which is too-dense is cost-inefficient. Additional wells mean increased capital, operation and maintenance costs, for no additional remedial benefit. A thorough understanding of site hydrogeology will allow optimization of well placement through the use of mathematical modelling techniques.

Efficient vertical coverage of the contaminated section is also important. Vertical spacings of vapour extraction wells are critical to system optimization (Ardito and Billings, 1990). In many cases, contamination is concentrated near and about the capillary fringe. As such, maximum effectiveness of vapour-extraction system is obtained by screening wells as close to the water table as possible, while preventing groundwater from entering screens. In cases involving LNAPL contamination, water level control is desirable to prevent additional smearing (Testa and Ulinegardner, 1991), and dampen seasonal water level fluctuations. Vertical spacing of air-sparging wells should also be carefully chosen to maximize aquifer volume affected.

7.2 Pressure Considerations:

During operation of SVVS systems, positive (sparging) and negative (vacuum) pressures must be carefully balanced (Ardito and Billings, 1990). Air-sparging systems must be designed to maximize the number of air-bubbles produced. Greater bubbling will result in better 'sweep' of air through the aquifer, and increase the surface area available for reaction (volatilization of contaminants and dissolution of oxygen) (Bird et at, 1960). Excessive air-injection pressures can limit oxygen dissolution, and reduce volatilization rates by preventing bubble formation.

Vacuum pressures must also be carefully regulated to optimize system operation. Excessive vacuum pressures can induce up-welling of the groundwater table, drawing groundwater into extraction wells. To enhance biological processes, air flow rates in the unsaturated zone must be maintained at appropriate levels. Excessive flow rates may inhibit biodegradation (Ardito and Billings, 1990).

7.3 Temperature

Volatilization of organics from the dissolved or liquid phase into the vapour phase is partly a function of temperature. Biological metabolism of organics also proceeds more effectively at higher temperatures (Forrester, 1990). Typical groundwater temperature in near-surface aquifer in Alberta vary between 4 and 10 °C. Increasing subsurface temperature is one way of enhancing both volatilization/vaporization and biodegradation.

Injection of heated air into the saturated zone (through the sparging wells) and into the unsaturated zone should significantly improve rates of condensate volatilization, and increase metabolic activity of hydrocarbon-degrading microorganisms. Waste heat available at many gas plants could be harnessed for this purpose.

7.4 Limitations

As with all in-situ processes, the considerable effects of medium heterogeneity may be a limiting factor to remedial effectiveness. The ability of air-sparging techniques to volatilize contaminants and reach all parts of the aquifer will be affected by the presence of high-permeability zones or fracture sets. Similarly, air-flow in the unsaturated zone will tend to move through zones of highest permeability, a large extent by-passing surrounding low-permeability layers or lenses (where significant contamination may remain unaffected). The possible influences of site heterogeneity must be carefully evaluated before deciding on, designing and implementing remedial methods of this sort. Sparging and vacuum extraction wells should be completed to copy with (and take advantage of) heterogeneity and anisotropy in the subsurface.

Heavier molecular weight hydrocarbons present in some natural gas condensates (C15 and higher) may not be readily volatilized or biodegraded. In general, however these compounds represent a relatively small mass-fraction of most Alberta condensates, and are largely water-insoluble (see Section 4.0 of this report). As such, relatively environmental significance is limited. For practical purposes, if the bulk of lighter condensate fractions, (including the water-soluble and environmentally significant aromatic fractions (BTEX) can be eliminated, site clean-up has been successful. Residual immobile heavy condensate fractions in subsurface pore space are of lesser practical environmental significance.

8. Case Histories - New Mexico, USA

Ardita and Billings (1990) present a series of case-histories from several sites in the Alberquerque Basin in New Mexico. In all cases, shallow water table aquifers consisting of interbedded sands, silt and clay (recent alluvial deposits) were contaminated by gasoline from leaking underground storage tanks. Unit thicknesses vary between 25 and 40 meters, and overlie basin fill deposits of Miocene-Pliocene age. Groundwater flow directions in the area are strongly influenced by municipal water supply wells. Depths to groundwater at sites described are between 2 and 5 metres.

8.1 Isleta site

The SVVS method was first applied by the City of Alberquerque Environmental Health Department (Underground Storage Tank Department) at the Isleta site in 1989, after three years of pump-and-treat operations. The site was contaminated with 40,000 US gallons of leaded gasoline.

Pump-and-treat operations were severely hampered by the presence of high concentrations of dissolved iron and manganese in groundwater. Iron bacteria were also present at the site. Biological and chemical precipitate formation caused frequent clogging of injection and pumping wells. At one point wells were being acidized every two weeks to maintain flow rates.

Modelling of contaminant migration under non-pumping conditions indicated that significant plume migration would not occur if the pump-and-treat system were turned off. Based on this information, a SVVS system was chosen for implementation. (Figure I2.1 shows the extent of the contaminated plume and locations of SVVS well nests installed.

Operation of the SVVS system began in the winter of 1988. Figures I2.2 and I2.3 show the reductions in BTEX concentrations and increases in dissolved oxygen in groundwater over the first year of operation. In the first six months of operation, BTEX levels in groundwater were reduced one order of magnitude. Based in these data, the authors concluded that the system had been successful, and was worthy of continued operation.

The authors estimate a savings of US $9000/month over the pump-and-treat system, for an approximate 90% savings in cost per percent of Benzene reduction. Installation (capital) costs were similar for pump-and-treat and SVVS systems of this site. Figure I2.4 shows a comparison of remedial technologies tried at the site over a six-year period.

No mention was made of problems associated with bacterial and iron-manganese fouling of sparging wells. It is logical to assume that given conditions described by the authors precipitation of iron and manganese and proliferation of iron bacteria around sparging sites would be a problem.

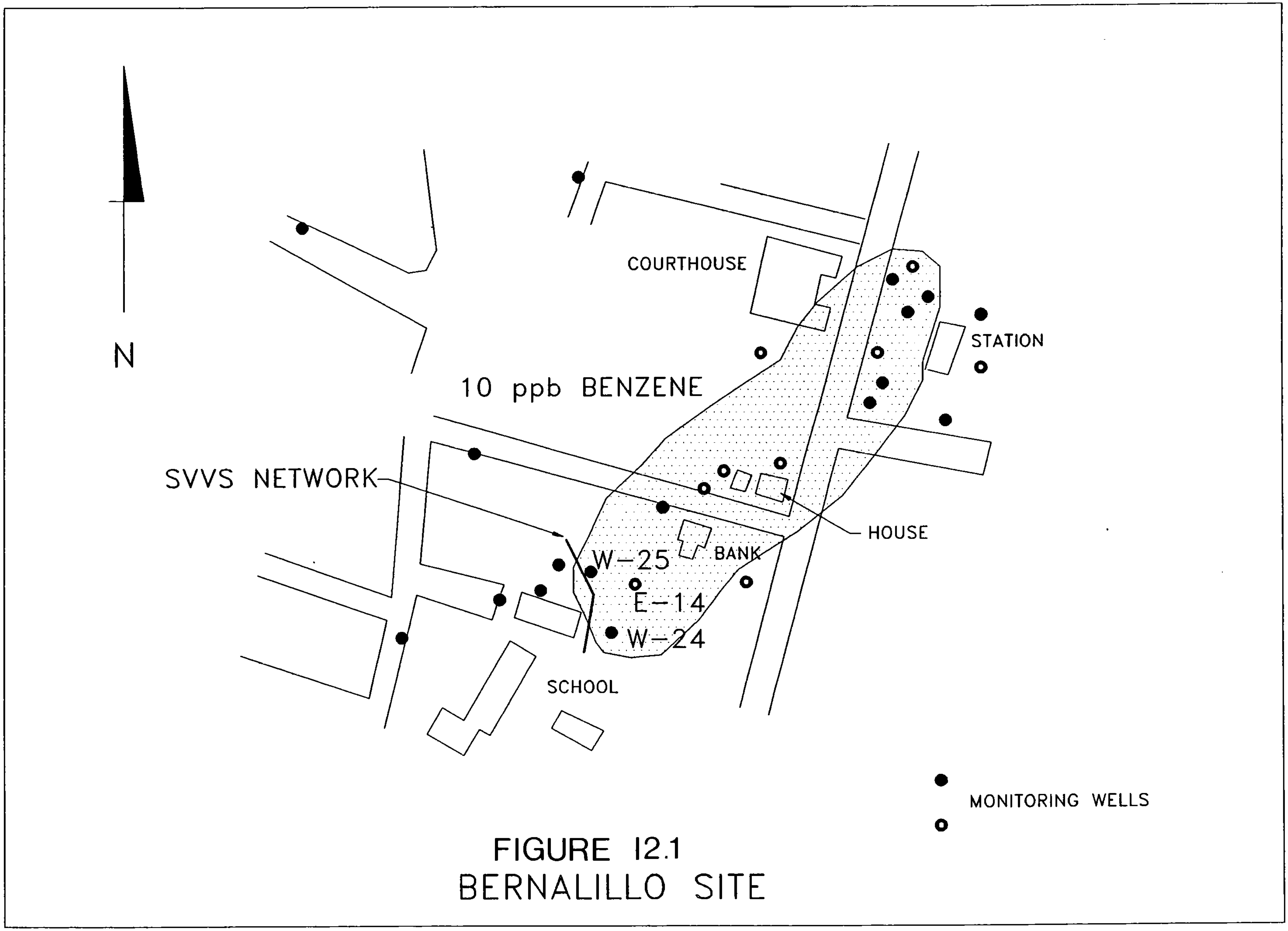


FIGURE 12.1
BERNALILLO SITE

FIGURE I2.2
BTEX CONCENTRATIONS OVER 1st YEAR OF OPERATION - ISLETA SITE

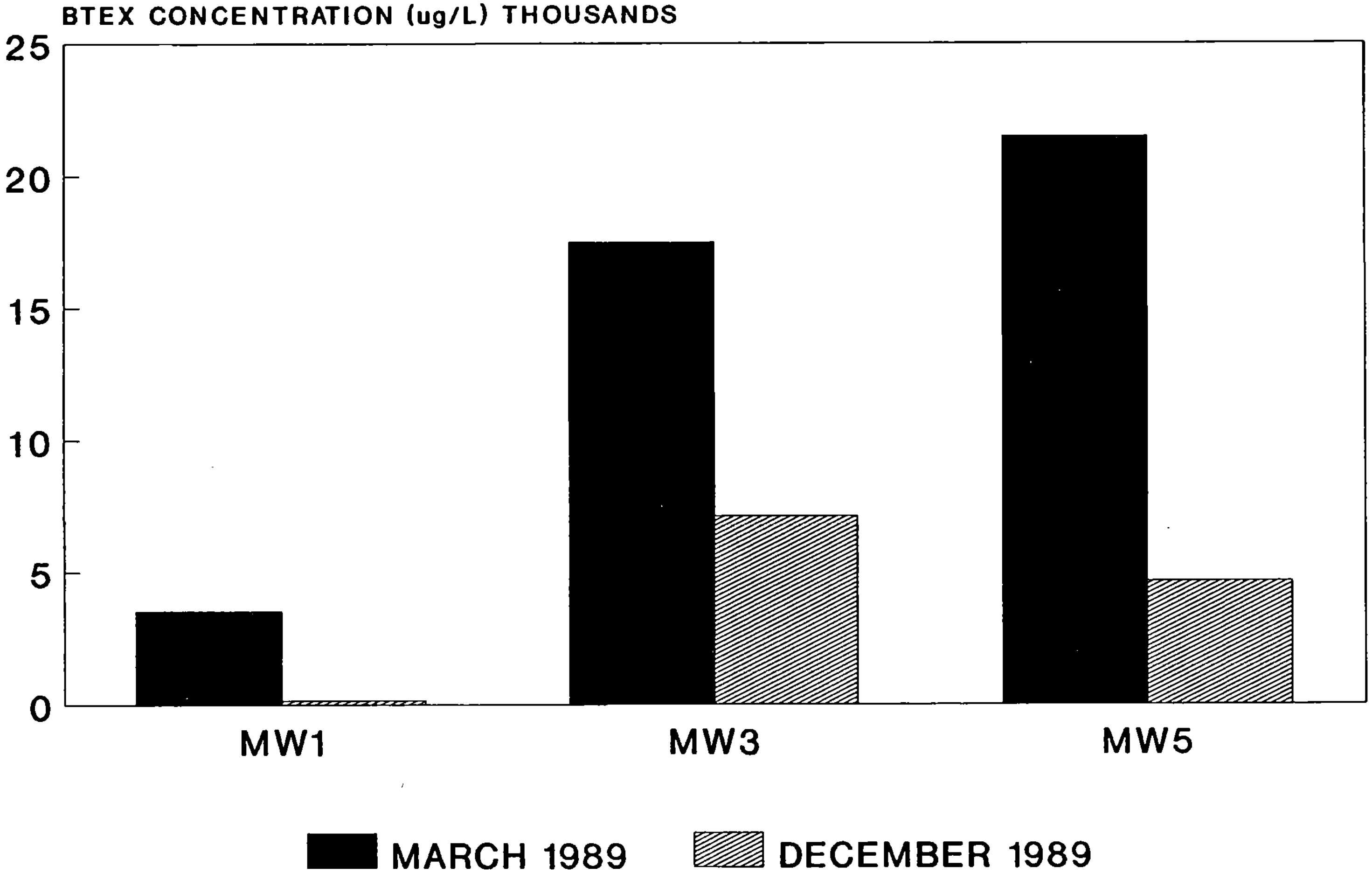


FIGURE 12.3
DISSOLVED OXYGEN CONCENTRATION BEFORE AND AFTER SVVS - ISLETA SITE

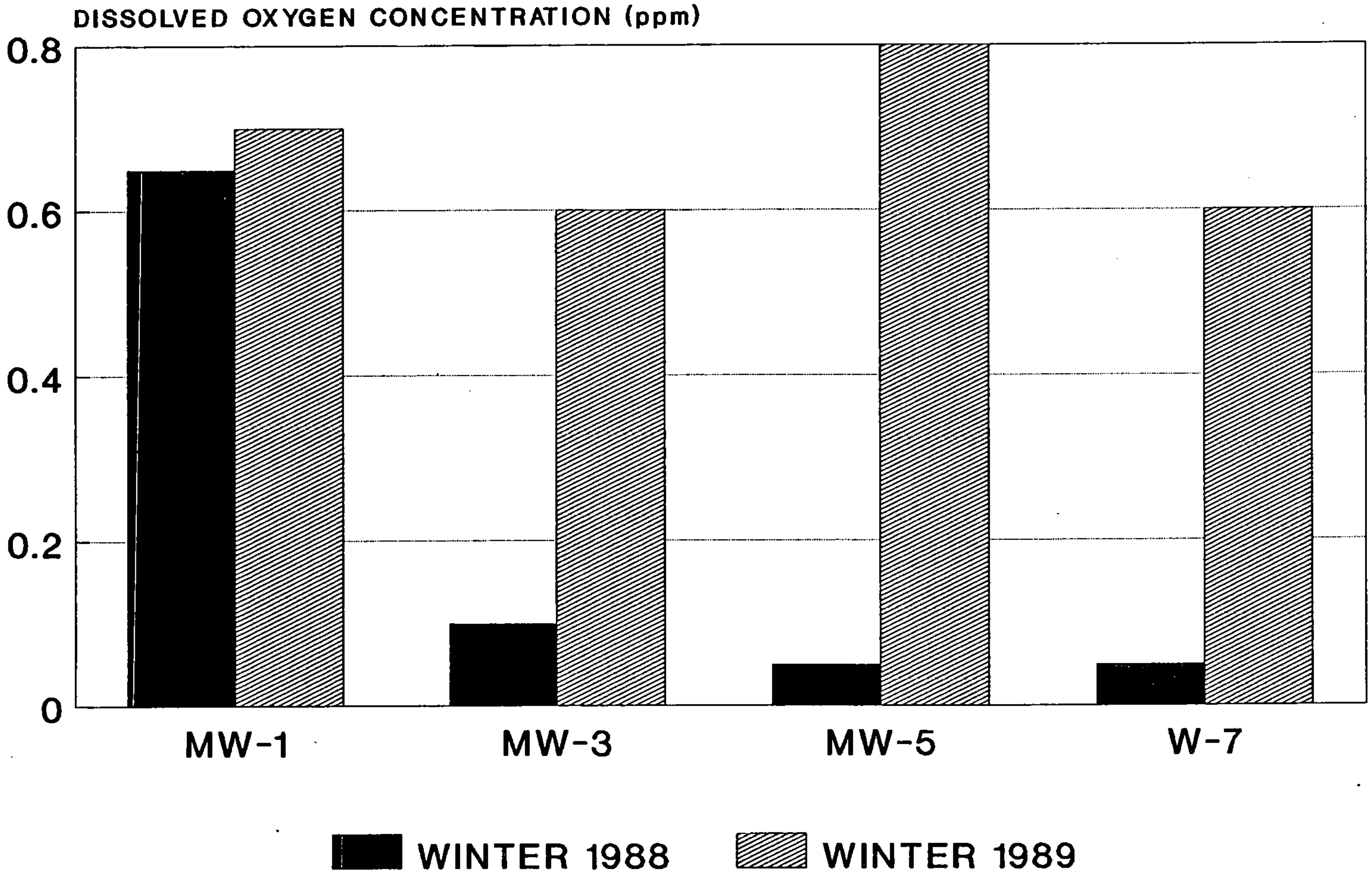
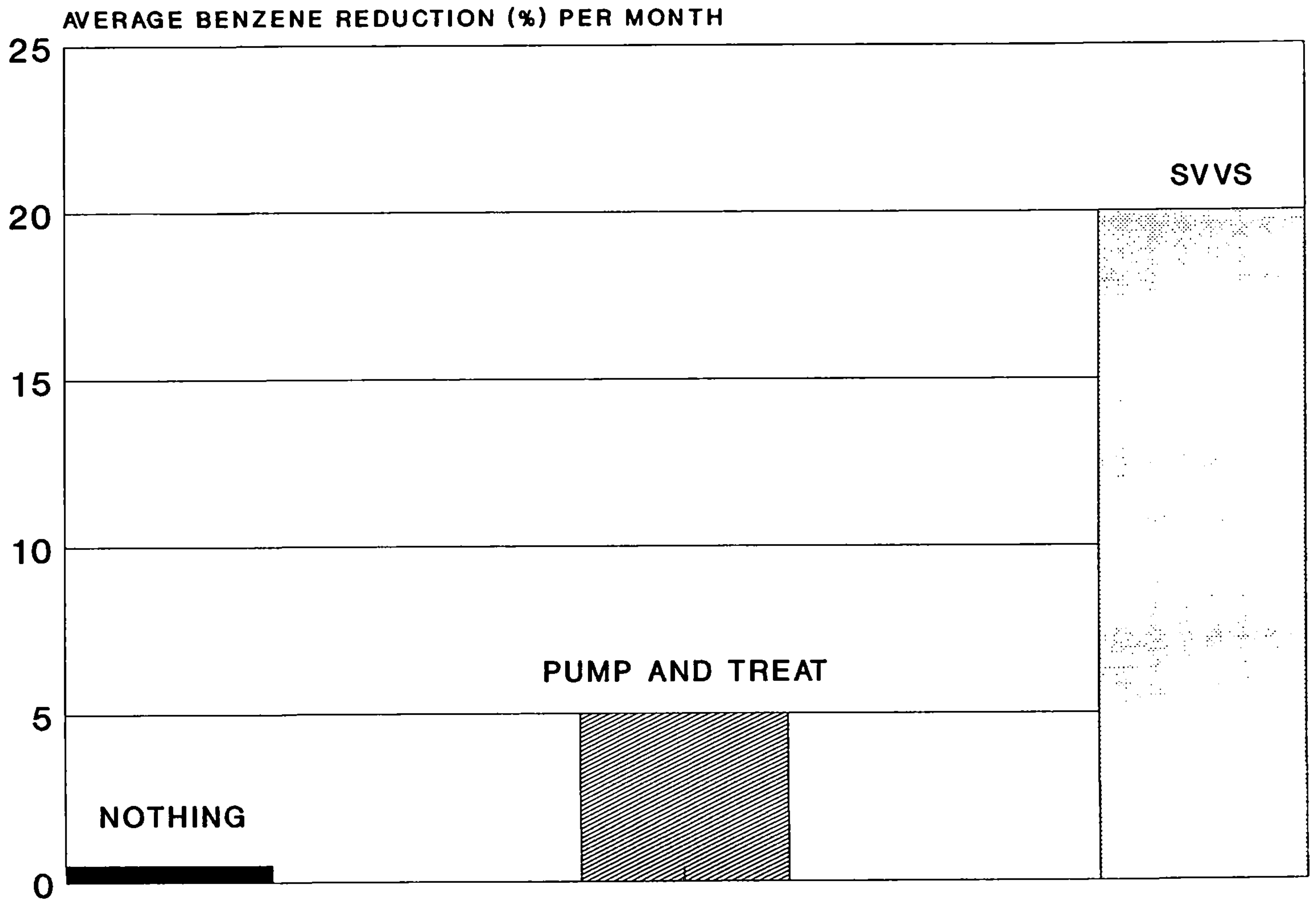


FIGURE I2.4
COMPARISON OF REMEDIATION TECHNOLOGIES
(ISLETA SITE)



8.2 Bernalillo Site

In 1988, 13,0000 US gallons of gasoline were released into the subsurface at a private residence. The resultant dissolved phase plume contained elevated levels of BTEX and methyl tertiary butyl ether (MTBE). In this case, SVVS was implemented as a barrier to further downgradient migration of contaminants (Figure I2.5). Again, significant reduction in BTEX concentrations were recorded over the first year of operations.

No discussion on which of the mechanisms involved in SVVS (volatilization vs biodegradation) were responsible for clean-up was provided. No cost information for this case was available.

8.3 Arsenal site

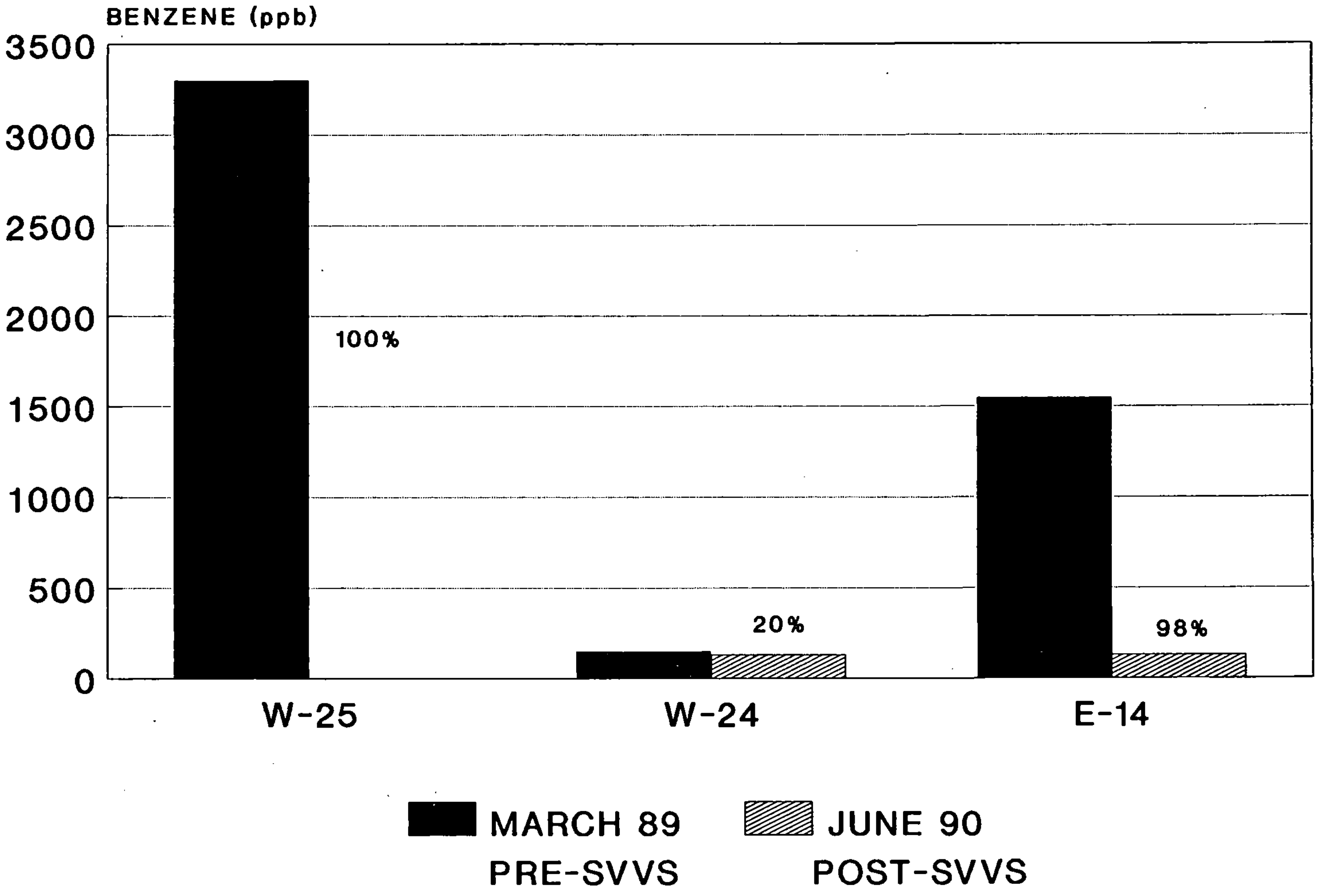
A leaking underground storage tank released an estimated 4000 US gal of unleaded gasoline into the groundwater. Hydrogeologic investigation revealed the presence of free product on the groundwater surface and a dissolved phase plume. The free product plume covered an area of some 7200 m^2, and attained apparent thicknesses of up to 35 cm. Benzene concentrations in groundwater beneath the free product plume ranged from 23,000 to 43,000 mg/L.

Free product skimming began in spring of 1989, and the SVVS system was implemented in November of 1989. After about 15 months of skimming operation, 210 US gallons of gasoline had been removed, and no free product was observed in monitoring wells. BTEX concentrations in groundwater were reduced to 730 to 63000 mg/L. No cost information was provided.

8.4 Discussion

Available case histories stress the effectiveness of SVVS in remediating dissolved phase contamination (mostly BTEX) in granular media. In cases where free mobile product was present, skimming was implemented first. Results seem to indicate that the method is successful under the conditions described, but not determination of which remedial mechanisms are operative/responsible can be made. Case histories seem to indicate that O&M costs for the method compare favourably to pump-and-treat, while capital costs appear to be similar. However, mass of contaminant removed per unit cost seems to much higher for SVVS than pump-and-treat the examples discussed.

FIGURE I2.5
BENZENE CONCENTRATION BEFORE AND AFTER SVVS - BERNALILLO SITE



Air-sparging systems may cause precipitation of inorganic compounds due to addition of oxygen. This can clog well screens and the surrounding aquifer material. Iron bacteria and buildup of biomass around injection wells may also cause clogging of aquifer pores, resulting in decreases in intrinsic permeability of as much as 100% (Schaffner et al, 1990). This problem should be seriously considered when designing and costing any SVVS system.

As a demonstration technology at Alberta sour gas plants, the SVVS technique holds much promise. Coupled with in-situ bioremediation, and taking advantage of available waste heat from plant operations, SVVS may be applicable to contamination situations involving bulk residual LNAPL condensate and associated dissolved phase BTEX contamination. Where residual LNAPL saturation in the saturated zone is a concern, this system is a promising alternative.

For application as a demonstration technology at ASGP's, the following need to be investigated and documented:

- Qualification of which processes are responsible for contaminant removal, and to what degree;

- Assessment of the effects of the process on residual LNAPL contamination in the saturated zone;

- Investigation of possible enhanced dissolution of BTEX into groundwater by mobilization from trapped residual LNAPL into vapour phase and back into dissolved phase.

- Seriousness of potential aquifer and screen clogging at air-sparging sites, and nature of processes involved (bacterial, chemical precipitation, etc.)

- general effectiveness and applicability of the technique in granular and fractured media.

- design and optimization considerations and methodologies.

- quantification of effectiveness of air-sparging systems in increasing levels of dissolved oxygen in groundwater.

- effects of air-sparging/SVVS on microbial activity in both saturated and unsaturated zones.

- Rigorous analysis of air-flow rates to sparging wells, and effects of varying injection pressures;

- Analysis of costs involved in design, installation, operation and maintenance of an SVVS system at ASGP, including costs of winterization and exploration of waste heat from plant operations.

8.5 Costs

The following provides a cost breakdown for design, installation operation of an SVVS system, based on implementation of the system as gas plant model 3 (Strachan) developed for this study.

Costs are for typical Alberta conditions, using local drilling contractors, consultants and materials (as possible) quoted in 1991 dollars (Canadian $). Off-gas treatment is not included.

Unit Costs

Capital

o	air-sparging well, 6" with 3 m stainless steel water well screen; total depth 10-15m Design, materials, professional supervision rig time, development and testing	$20,000.00
o	Air compressor system, housing, hookup winterizing	$10,500.00
o	Electrical natural, hookups	$ 2,500.00

o 50 mm Vacuum extraction well, PVC construction, pump, hookup, surface facilities, winterizing	$ 7,500.00
	$41,500.00

Annual O & M

o Power costs to compressors/pumps	$ 2,000.00
o Routine maintenance (mechanical electrical)	$ 3,500.00
o Well cleaning/acidizing (2/year)	$ 4,500.00
	$10,000.00

ASGP - Site Example

For plant model 3 an SVVS system designed to remediate the majority of the most contaminated areas would require between 10 and 30 SVVS well pairs. This number, as discussed would depend on site characteristics and the results of the optimization exercise. Installation and operation of an SVVS system consisting of 10 sparging-vacuum well nests would cost in the order of $715,000.00 over a three year period (costs are not discounted).

I.2.2 IN-SITU BIOREMEDIATION

1. Introduction

Many techniques for controlling and remediating groundwater contamination have been developed over the last decade. Remedial methods have in many cases stressed removal of contaminated groundwater by pumping, followed by appropriate treatment at surface. This method is commonly known as "pump-and-treat". More recently, *in-situ* methods have been receiving greater attention, either as complements to other remediation technologies, or as "stand alone" solutions. These are techniques which work within the contaminated aquifer itself. One of the more promising *in-situ* remediation techniques is the introduction or enhancement of microbial populations capable of degrading organic compounds, or *in-situ* bioremediation.

Recent research into bioremediation has focused primarily on three groups of organic chemicals: chlorinated solvents (such as TCE, TCA, etc.), polyaromatic hydrocarbons, and lower molecular weight hydrocarbons (Forrester, 1991). In the past few years, many laboratory studies of biological degradation processes have been conducted, and numerous pilot and field scale trials of the technique have been completed. The results of this research have highlighted both the promise and the limitations of the method.

In situ bioremediation essentially involves the use of specific microorganisms to break down contaminants present in the subsurface. Under normal subsurface conditions, biodegradation rates of hydrocarbon-based compounds are generally quite slow (Forrester, 1991). If conditions suitable for rapid growth of the microbial populations are provided, substantial degradation of the contaminant may occur. Appropriate microbes may exist naturally in the subsurface, or may be introduced from specially formulated cultures (inoculum). Hydrocarbon degrading bacteria, for example, are ubiquitous in the subsurface. More than 200 soil microbial species capable of degrading hydrocarbons have been identified (Savage et al., 1985). Bacteria capable of degrading natural gas condensate have been identified in samples of the substrate collected from a gas plant in Alberta (Forrester, 1990a). Several commercial bacterial formulations designed to treat specific contaminants are also available. The success of an in-situ bioremediation program will depend on three main conditions being satisfied: appropriate organisms must be present; conditions suitable for the microorganisms must be provided and maintained; and the organisms must be brought into contact with the contaminants. If all three of these things occur, field trials have shown that in-situ bioremediation can be a cost-effective way of achieving clean-up of contaminated sites. Therein lies the promise and the limitation of the method. Due to the complex hydrogeological conditions present at the vast majority of sites, one or more of these conditions often cannot be fulfilled, or can only be partially met.

2. Biodegradation

2.1 Biological Processes

Bioremediation involves the metabolic breakdown of contaminants as a food and energy source for microbial populations. Biodegradation of organics in the subsurface may occur either aerobically (requiring oxygen) or anaerobically (in the absence of molecular oxygen). For hydrocarbon compounds, aerobic degradation has shown to be the most effective. Most research into in-situ bioremediation has been directed towards aerobic processes. Recent investigations of anaerobic bioremediation of gasoline using nitrate as an electron acceptor have not been promising (Barbaro et al, 1991). Anaerobic processes, however, have shown promise for degradation of specific contaminants, and are the subject of continuing research. Aerobic biodegradation processes are recommended for condensate bioremediation at ASGP's (Forrestry, 1991a).

Many chemicals have been shown to be biodegradable in the subsurface, including petroleum products such as crude oil, gasoline, and diesel fuel, solvents such as acetone, methanol and trichloroethylene (TCE), and aromatic hydrocarbons such as benzene, toluene and xylenes (BTX) (Lee et al, 1991).

2.2 Factors Affecting Biodegradation

The rate of microbial degradation of contaminants will depend on the following factors:

Contaminant Type and Concentration

The chemical structure of target compounds will determine in part how effectively they can be biodegraded. In general, the more complex organic compounds are less easily degraded. For hydrocarbons, the saturated straight chain aliphatic compounds are most readily metabolized. Simple mono-aromatic hydrocarbons are more easily degraded than the more complex aromatics and asphaltenes. Light hydrocarbon fuels such as gasoline can be almost completely biodegraded. Many contaminants can be toxic to microbes if present at high concentrations. This may occur when free product is present. Specific chlorinated aliphatics have been shown to be toxic to certain aerobic bacteria (Arvin and Broholm, 1991).

Presence of Oxygen

The presence of molecular oxygen is often the limiting factor for aerobic biodegradation of hydrocarbons. Levels of dissolved oxygen in natural near-surface groundwater in Alberta are typically low (below 1 mg/L). To achieve significant rates of contaminant degradation, oxygen concentrations in the target aquifer must be increased substantially. Methods which have been used to deliver oxygen to the system include air sparging, ozone enrichment, hydrogen peroxide injection, and introduction of colloidal gas apherons (Major, 1991). Figure I2.6 shows basic diagrams of hydrogen peroxide injection and air-sparging systems.

Each of these methods has advantages and disadvantages. Hydrogen peroxide has been found to be a quick and efficient way of producing substantial increases (up to several hundred mg/L) in molecular oxygen levels in groundwater (Huling and Bledsoe, 1991). The technology involved and the hydrogen peroxide itself are expensive, however. Air sparging involves bubbling of air into the aquifer. This system is considerably less expensive to install and operate than a peroxide system, but typically delivers oxygen less efficiently to the aquifer. Sparging systems can however be plagued by bacterial buildup (biofouling) at injection sites.

Temperature

In general, microbial activity decreases at lower temperatures. Many successful field trials of in-situ bioremediation have been conducted at sites in the southern United States, where groundwater temperatures of 20 °C or higher are common. However, groundwater temperatures in near-surface aquifers in Alberta typically range from 4 to 10 °C. Microbial populations cultured at surface at 20 °C and then injected, or developed for Californian conditions, may experience significant difficulties at these lower temperatures. The problem of lower *in-situ* activity levels can be overcome by selecting and acclimating organisms to lower temperatures (Forrester, 1990; Staps, 1990).

Researchers at the Borden aquifer in southern Ontario have measured significant hydrocarbon degradation at low water temperatures (ca. 10° C) (D. Major, pers. comm.) For inoculated

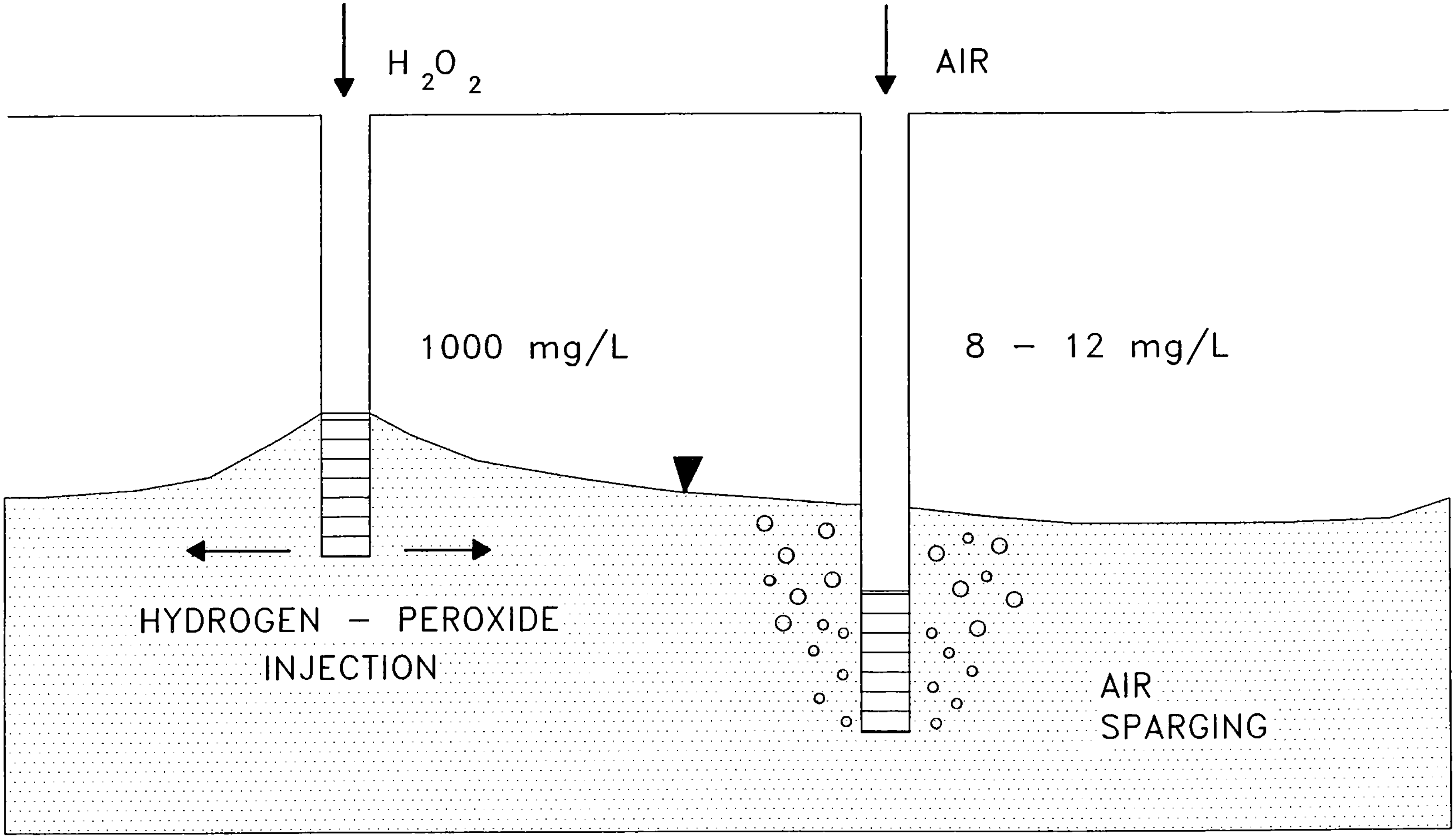


FIGURE 12.6
OXYGEN DELIVERY SYSTEMS

bacteria, similarly high activity levels may be achieved provided the microorganisms are cultured at the appropriate temperature prior to injection. If the microorganisms have been cultured at 25-30° C (normal temperature for a running bioreactor) then the resulting population will have practically zero activity at typical ASGP site temperatures. However, if a population is isolated and grown in the 10-15° C range, substantial activity will be retained at ambient aquifer/soil temperatures. It is essential to select a microbial population suited to the in-situ temperature. This is one of the main reasons why introduced bacteria fail to significantly increase the biodegradation rate.

Availability of Nutrients

Aerobic bacteria also require the inorganic nutrients nitrogen and phosphorous during metabolism of hydrocarbon. In many cases, small levels of these nutrients must be added to the system to maintain acceptable activity levels. Either food or agricultural grade products may be used. Nutrients can be delivered via injection wells or infiltration galleries.

pH of Groundwater

Most hydrocarbon degrading bacteria are pH sensitive, and seem to prefer neutral conditions (6.0 to 8.0). Most natural Alberta groundwaters have pH levels at or near neutral. However, some forms of industrial contamination may create acidic or basic groundwater conditions. The production of large quantities of elemental sulphur at sour gas plants in Alberta, for instance, has resulted in several cases of acidic groundwater (CPA, 1990). Under such conditions, buffering would be required before proceeding with *in-situ* bioremediation.

Contact Between Organism and Contaminant

One of the most fundamental factors affecting rates of biodegradation is physical contact between organism and contaminant. In the laboratory, or in bioreactors at surface, this is readily achieved. In the subsurface, however, and especially in heterogeneous aquifers, contact may be elusive.

3. Hydrogeological Considerations

Implementation of a successful *in-situ* bioremediation project requires a sound understanding of the hydrogeology of the site. Our ability to understand and control the hydraulic behaviour of the aquifer will to a large degree determine how effectively we can control biological activity within it. To be able to successfully deliver appropriate levels of oxygen and nutrients to the organisms, hydrogeologists must be able to control and direct flow towards the contaminated zone.

3.1 Aquifer Control

At present, one of the most common groundwater remediation techniques employed is pump-and-treat. Contaminated groundwater is withdrawn from a number of pumping wells and treated at the surface to remove contaminants. This technique is often adapted during implementation of *in-situ* bioremediation. Treated water is dosed with oxygen, nutrients and possibly bacterial cultures, and reinjected into the contaminated aquifer. This provides a closed-loop system, effectively controlling the plume.

Treated groundwater may be re-introduced into the aquifer through infiltration galleries, injection wells, or irrigation. These systems must be carefully designed and monitored to reduce clogging from biofilm accumulations and precipitation of inorganic compounds as a result of nutrient addition and oxygenation of groundwater. Intrinsic permeability in gravel packs and aquifer pores has been found to decrease as much as 100 % due to biofouling during *in-situ* remediation (Schaffner et al, 1990). Pump-and-treat is discussed in detail in another section of this appendix.

3.2 The Role of Heterogeneity

Geologic heterogeneity occurs on all scales, and may be described as a fractal process. Apparently uniform sand bodies may contain layers of more uniformly sorted grains or higher clay content. Sandstones may grade laterally into siltstone and shale. Fracturing has been observed at the microscopic and continental scales. Examples of heterogeneous aquifers include till and glaciofluvial deposits, interbedded sand and clay, and fractured clastic bedrock - all extremely common in Alberta.

Heterogeneity in aquifers will affect the directions, patterns and rates of groundwater flow. Groundwater will flow preferentially through zones of higher hydraulic conductivity such as sand lenses or fracture zones. Although saturated, groundwater will move much more slowly through finer grained layers or lenses, or matrix in a fractured bedrock. In many cases, however, such lower hydraulic conductivity materials may also be contaminated. During pumping, contaminants in zones of high hydraulic conductivity will be removed quickly. Subsequent pumping will continue to flush these same zones, however. Contaminants trapped in less permeable layers, or in the matrix pores of a fractured bedrock system, will be released into the surrounding more permeable zones only slowly. This can be described as a diffusion-limited process. Similarly, oxygen and nutrients delivered to the aquifer will tend to move along these same high permeability pathways. Often this results in the bypassing of significant zones of contaminated aquifer.

Major (1991) identified the eight most common problems encountered during *in-situ* bioremediation. Of these, five are directly related to the physical properties of the aquifer (including heterogeneity) and the ability to control aquifer behaviour:

- clogging of screens and infiltration galleries with fines and microbial growth;
- maintenance of stable oxygen concentrations over time and throughout the contaminated zone;
- fluctuations in the water table causing a release in bound contaminants;
- clay units which act as sinks for hydrocarbons and thus become long-term sources;
- fuel residuals in the vadose zone occluded in pores making them inaccessible to passing water and hence nutrients and oxygen.

The effects of heterogeneity on our ability to deliver essential elements to the microbes, and on the microbes' ability to make contact with the contaminants are major limitations of the *in-situ* bioremediation method. From this perspective, detailed characterization of site hydrogeology is essential for deciding if *in-situ* bioremediation is applicable, what the chances of success are, and how it should best be implemented.

4. Implementation

Successful implementation of an *in-situ* biological remediation program should involve the following:

- detailed site investigation;
- initial contaminant plume control and clean-up. If separate phase product is present, it should be removed as far as possible;
- biodegradation laboratory feasibility study, and study of enhancement effectiveness;

- pilot phase operation and monitoring;
- system design, installation and testing;
- operation and monitoring.

4.1 Site Investigation

Detailed site investigation should include:

- identification of important geologic features controlling groundwater distribution and movement at the site;
- horizontal and vertical mapping of all important hydrogeologic units;
- assessment of the hydrogeologic regime at the site (groundwater flow directions, vertical and horizontal gradients);
- characterization of the hydraulic and physical properties (transmissivity, storativity, hydraulic conductivity, effective porosity) of the various aquifers;
- delineation of the contaminant plume and assessment of the types, concentrations and distribution of contaminants;
- estimates of volumes and mass of contaminants involved;
- assessment of potential impacts and risk associated with the groundwater contamination.

The information collected will allow a detailed assessment of which remedial techniques will be appropriate to the particular site. In general, if bulk hydraulic conductivities are above 10^{-6} m/s, bioremediation may be suitable. However, the potential limitations caused by aquifer heterogeneity should be considered.

4.2 Contaminant Control

Once the site has been fully investigated, remedial operation can begin. At sites where LNAPL condensate is present on the groundwater surface, product recovery should be initiated before bioremediation. This can be done using dual pump recovery systems. Usually, the initial stages of such a program will involve the application of some form of hydraulic control of contaminant migration, through pumping wells or trenches. Contaminated groundwater removed can be treated using a variety of techniques including air-stripping, granular activated carbon, surface bioreactors, and advanced oxidation.

4.3 Laboratory Study

As investigative and remedial operations are underway, initial laboratory experiments can be conducted. Such experiments should ideally be performed under conditions as close to those found in the aquifer as possible. The presence and activity levels of microbes capable of degrading the target contaminant should be determined. For these tests, samples of soil, groundwater, and contaminants should be collected during drilling and sampling programs. Minimum nutrient requirements should be established, and isolation and culturing of native bacteria attempted (Forrester, 1990).

4.4 Pilot Phase

If conditions are deemed appropriate for *in-situ* bioremediation, the process can be tested at a pilot scale before moving into full-scale implementation. The advantage of a pilot test is that delivery mechanisms and field equipment can be tested and modified on a small scale, at relatively low cost, before commitment of substantial resources. A pilot test stage is especially helpful at large sites, but is often dispensed with for smaller projects.

4.5 System Design

Once the results of the pilot test have been evaluated, the full scale project can be designed. Design elements will include a system to circulate groundwater through the aquifer, water treatment and disposal systems, equipment for introducing oxygen and nutrients into the aquifer, and monitoring points. Surface bioreactors would also be required if bioaugmentation were selected.

4.6 Operation and Monitoring

Once installed on-site, the system should be operated under careful scrutiny, at least for the first few months of operation. A good monitoring program is an essential component of any *in-situ* remedial system. In general, groundwater from recovery wells and specified piezometers should be monitored for general water quality indicator parameters, concentrations of target contaminants or indicators, and microbial population levels. Changes in the relative concentrations of these key parameters will provide information on system performance and effectiveness, and signals that inputs need to be varied. A sudden decline in the numbers of microbes, for instance, could indicate that hydrogen peroxide concentrations are too high in injection water, and peroxide toxicity is killing off organisms.

Careful operation of hydrogen peroxide systems is crucial. H_2O_2 is expensive, corrosive, and requires special handling and equipment such as stainless steel tanks. In addition, at high concentrations, hydrogen peroxide can be toxic to microbes. Careless handling or monitoring of this type of system could lead to problems, delays, and cost overruns.

4.7 Bioaugmentation: Pros and Cons of Adding Microbes

The question of whether to simply stimulate *in-situ* bacteria with oxygen and nutrients (biostimulation) or to also add organisms cultured at the surface (bioaugmentation) has been hotly debated. In most current applications of bioremediation of hydrocarbon-contaminated sites, no inoculum was added (David Major, pers. comm, 1990; Ronald Lewis, pers. comm.,1990). For the vast majority of the components in natural gas condensate, there likely exist microorganisms *in-situ* capable of degradation. Usually, however, these microorganisms are initially insufficient in number and activity to rapidly degrade the large quantities of hydrocarbon (and perhaps sulphur compounds) present in condensate.

The potential advantages and disadvantages of adding microbes are:

Advantages:

1) Quicker start-up: biostimulation may be a slow process (particularly in cold climates), requiring months before *in situ* bacteria reach sufficient numbers for substantial degradation. Bioaugmentation serves to rapidly increase subsurface populations.

2) Degradation of recalcitrant compounds: while most components of gas condensate are expected to be easily degraded, some "recalcitrant" compounds may exist. During lab tests these compounds can be isolated and bacteria specially cultured for maximum degradation.

3) Protection against predators: As bacterial populations increase, so too may predators such as protozoa. Since bioaugmentation permits the rapid replenishment of aquifer populations, it is less affected by periodic increases in predator populations.

4) Nitrate injection: if nitrate is added in lieu of oxygen, the de-nitrifying bacteria MUST be present in the sub-surface. These bacteria may not be present *in situ*, and therefore may require inoculation.

Disadvantages:

1) Adsorption to soil particles: Staps (1990) states that most of the injected microbes are rapidly adsorbed to soil particles, and are therefore not capable of travelling sufficient distances from their injection sites. This problem will be exacerbated in low permeability soils, particularly with high clay or organic matter content. The problem of soil adsorption was frequently mentioned by site managers contacted for this study.

2) Cost: the injection of microbes adds a small supplementary cost to the total project cost.

The most compelling argument against inoculation is that hydrocarbon degrading organisms are generally present *in-situ*. Thus, it is recommended that the addition of bacteria be tried only if early attempts at stimulation with oxygen and nutrients fails to substantially increase microbial populations.

4.8 Costs

The cost of *in-situ* bioremediation projects varies widely, as it depends both on site specifics (amount and type of contamination, site hydrogeology, etc.) and on the choice of technology to be used (biostimulation vs. bioaugmentation; hydrogen peroxide, air sparging or nitrate, etc.) In addition, very few companies are willing to share information on project costs.

Staps (1990) evaluated 23 bioremediation projects in the United States the Netherlands, and (West) Germany. The projects were divided into two groups, based primarily on the amount of contaminated soil and groundwater (Table I2.2).

The choice of oxygen source may have a large impact on overall project costs, particularly if hydrogen peroxide is chosen. Staps (1990) noted that in some extreme cases, 90% of project costs have been for hydrogen peroxide. A cost breakdown of various oxygen sources for a specific site was prepared by Brown (1989) and is presented in Table I2.3).

As can be seen in Table I2.3, soil venting may be a very cost-effective means of promoting bioremediation. In most cases, however, an additional oxygen source will be required. The choice of hydrogen peroxide or air sparging will depend on the site specifics: the degree of contamination, location of contaminant, and hydrogeological and microbiological factors.

Table I: Costs of bioremediation (Staps, 1990)

Description	Contaminated Surface Area (m^2)	Contaminated Groundwater Volume (m^3)	Costs (US$)
Service Stations	400 - 1,000	1,000 - 5,000	62,000 - 750,000
Refinery/Industrial Sites	20,000 - 75,000	30,000 - 400,000	330,000 - 16,000,000

Given the experimental nature of this technology, the lack of detailed cost information is not surprising. Pilot studies should be performed as a means to determine the costs and effectiveness of bioremediation at gas plant sites.

Table II Cost/performance comparison for various oxygen systems: high degree of contamination

System	Capital Cost	Operation Cost ($/month)	Maintenance ($/month)	kg/day oxygen	% Site treated	Utilization Efficiency	Time of treatment (days)	$/kg oxygen used
Air Sparging	35,000	800	1200	3	41	70	858	57
Water Injection	77,000	1200	1000	4	75	50	1580	62
Venting System	88,500	1500	1000	1810	60	5	132	8
Peroxide System	60,000	10,000	1500	86	100	15	330	41
Nitrate System	120,000	6500	1000	96	100	12.5	335	49

5. Industry Experience

5.1 Case History: Horseheads, N.Y.

Knispel Construction Site, Horseheads N.Y., U.S.A.

This clean-up involved a ~1000 U.S. gal. petroleum spill in a sand aquifer from an underground storage tank located 400 ft. up-gradient from a village water supply well. Initially, a pump-and-treat system was installed and operated over a two year period, substantially reducing measured BTX concentrations. Benzene, toluene, and xylene concentrations varied from near-zero to 20-40 ppb. These levels exceed the New York State drinking water standards.

To further reduce BTX levels, bioremediation was commenced. Oxygen was supplied by hydrogen peroxide introduced into a trenching system 100-150 ft upgradient of the contaminated area. A proprietary nutrient formula was also injected. Prior to bioremediation, higher BTX levels coincided with higher water table levels, presumably the result of flushing of contaminants adsorbed to soil particles. Within six months, dissolved BTX concentrations were non-detectable in groundwater samples. Subsequent sampling has confirmed these results. The total cost of the bioremediation component of the project was estimated at US$ 200,000-250,000.

5.2 Case History: Ultramar Canada Ltd.

Brown et al. (1989) describe the use of bioremediation at an Ultramar Canada Inc. service station contaminated by petroleum leakage from underground storage tanks (USTs), pumps and lines. The site consisted generally of an engineered fill overburden overlying fractured limestone bedrock. The fill consisted of gravelly sand with variable silt and clay content increasing with depth. The fill varied in depth from seven to ten feet across the site. A commercial building, downgradient of the spill, was also contaminated. The basement was cut into limestone bedrock and some clayey soils, and underlain with 1 foot of crushed stone.

The authors distinguish among three contaminated areas. Area A was lightly contaminated, with most contamination in the fill material. Area B, located near the underground storage tanks, was highly contaminated in both the fill and the bedrock. Area C was contaminated primarily in the fill underlying the basement.

The initial attempt at *in-situ* bioremediation involved the simple addition of aerated water (presumably by air sparging). This resulted in only a small increase in the *in situ* bacterial population. Population growth was further stimulated through the addition of nutrients (nitrogen and phosphorous). Finally, hydrogen peroxide was added, resulting in "an order of magnitude increase in bacteria relative to background levels."

Area A, the lightly contaminated fill, responded rapidly to bioremediation. Hydrocarbon levels were reduced 95% in five months, after which the injection was ceased. Contamination levels were unchanged six months later.

Area B, the highly contaminated zone near the UST, did not respond as well. While dissolved levels were reduced by 40-50% in the first few months, there was subsequently little change. The authors postulate that:

> "The difference in response in (*sic*) related to the distribution of subsurface hydrocarbons in the aquifer. This initial rapid response represents a treatment of adsorbed petroleum in the more permeable fill. The slower, subsequent and more variable response represents treatment of contamination in the bedrock. Part of the variability in the results is dependent on whether the water table is in the fill or bedrock. When the water level falls into the bedrock (at approximately /.0 to /.5 feet depth), the dissolved levels increase. This is because groundwater flow through the bedrock is much slower than in the fill and therefore dilution of the dissolved plume is not as great."

The authors also note that the low water temperatures in Canada were not a crucial factor to the outcome of this bioremediation project:

> "The effect of the Canadian climate, in this case, did not preclude the effectiveness of the technique. The key to successful application is to ensure Transport of nutrients and oxygen into the affected area."

5.3 Earth Associates Case Histories

Yaniga (1982) related a case involving a gasoline leak which contaminated fractured shale and siltstone aquifer overlain by a silty loam. Altogether, 12 domestic water supplies were affected by the spill, with hydrocarbon concentrations in the water ranging from <10 ppb to >15,000 ppb. Initial treatment attempts included air stripping and air sparging. However, it was noted that dissolved oxygen concentrations remained below 1 mg/L within the plume for 6 weeks after the treatment was begun. After 20 months of treatment, hydrocarbon concentrations had been reduced 50-75% across the site, although significant levels of contaminants remained in some locations. The following year, very little improvement was noted and this was attributed to an inadequate oxygen supply. A trial experiment was then initiated, in which batch additions of 100 ppm hydrogen peroxide solutions were added to the aquifer through the injection wells. Two benefits of this treatment process were: (1) oxygen concentrations increased within the aquifer, which in turn resulted in increased biological activity, and (2) the peroxide solution helped to control biofouling of the injection well screens. With the hydrogen peroxide treatment, hydrocarbon concentrations were reduced below detectable levels in 8 of the 12 wells originally affected, and to between 200 and 1200 ppb in the 4 remaining wells.

Study #2

Westray et al (1985) describe another study in which leaking tanks located near a laboratory facility contaminated a sand and sandy clay fill with benzene, xylenes, toluene, ethylbenzene and various C_4-C_{12} aliphatic compounds. It was estimated that, after the liquid phase recovery program, 1100 to 3400 L of product remained in the ground. Cost analyses for treatment indicated that *in-situ* biorestoration would be considerably less expensive to perform than carbon adsorption with pump-and-treat ($270,000 vs $850,000). The nutrient stream consisted of ammonium chloride, sodium phosphates and hydrogen peroxide. Within 44 days of commencing the treatment, an estimated 570 to 1500 L of product had been degraded.

5.4 Gasoline spill at Ambler Pennsylvania

In July 1971 there was a spill of approximately 300,000 litres of high octane gasoline from a break in a Sun Pipe Line Company pipe line. The gasoline seeped into an underground aquifer and contaminated the Whitemarsh Township municipal water supply. Approximately 50% of the gasoline was recovered by pumping and consultants estimated that it would take many years to remove the remaining 50%. Thus alternative methods for remediation were pursued.

Gasoline biodegradation was found to be occurring in the recovered groundwater. Thus it was decided to see if this could be encouraged in the aquifer to remove the remaining gasoline.

A laboratory experiment showed that the numbers of gasoline degraders could be increased 1000 fold by the addition of supplemental nitrogen and phosphorous salts. Small scale field test were also conducted which confirmed the laboratory results.

A large scale bioremediation programme was initiated. A nutrient amendment consisting of ammonium sulphate and di- and mono-potassium phosphates was injected into the aquifer as a 30% concentrate. Oxygen was supplied to the aquifer by sparging air into the wells using paint sprayer-type compressors.

Success of the programme was noted when bacterial levels in the aquifer increased by four orders of magnitude and gasoline could not be detected in the monitoring wells after 10 months of treatment.

5.5 In situ bioremediation combined with other technologies.

A gasoline clean up was conducted in which air stripping was used to reduce the level of contaminants of withdrawn groundwater and to supply oxygen before the water was recirculated to the aquifer via an infiltration gallery. Before recirculation, ammonium chloride, sodium mono- and di-phosphates, ferrous sulphate and manganese sulphate were added in slug batches to the water. In addition, oxygen was supplied by sparging air into the wells.

Dissolved oxygen in the aquifer increased from a range of 0-5 to 5-10 ppm; hydrocarbon degrading bacteria increased from 10^2-10^3 to 10^3-10^4 cells per ml with air stripping and sparging and then increased to 10^6 cells per ml with nutrient addition.

5.6 Use of hydrogen peroxide

Hydrogen peroxide was used as an additional oxygen supply involving the gasoline contamination of a relatively impermeable soil (groundwater movement 0.6 - 0.9 m/year). Approximately 50-60% of the free product was recovered by pumping methods. However, concentrations of hydrocarbon in the range of 3,700 - 7,200 ppm remained in the soil. After 2 months of treatment with hydrogen peroxide and inorganic nutrients the level of adsorbed hydrocarbon had been reduced to 2300 - 2,900 ppm.

In a second bioremediation program to clean up gasoline contamination from an underground storage tank the level of hydrocarbon was reduced by 50-85% in a 20 month period with addition of nutrients and air sparging only. Continued treatment for another 11 months did not reduce the hydrocarbon levels any further so to increase the level of dissolved oxygen 100 ppm hydrogen peroxide solution was introduced into the aquifer. As a result the dissolved oxygen in a pumping well 12.2 m from the injection well increased from 0.5 to 8 ppm within 24 hours with a concomitant increase in microbial activity. After a short time period the level of dissolved hydrocarbon had been reduced from 15 to 2.5 ppm. Continued treatment resulted in removal of hydrocarbon from 8 to 12 wells and levels of 200-12,00 ppb in the other four wells.

In addition to supplying oxygen to the aquifer the hydrogen peroxide controlled the growth of the biofilm which had formed on the screens on the injection wells.

5.7 Bioremediation of Soil and Water Contaminated with Jet Fuel

In 1984, 75,000 - 100,000 litres of JP-4 fuel contaminated over 3,000 m^3 of soil and shallow groundwater at Kelly Air Force Base in Texas. Several remediation technologies were tried at this site including bioremediation.

In the bioremediation test, three delivery systems were used to test their relative effectiveness. These included two shallow injection wells, a shallow infiltration gallery and a spray irrigation system. Results showed that there was rapid breakdown of the hydrogen peroxide in the unsaturated zone and thus less oxygen was delivered into the aquifer than was calculated. After 18 months of hydrogen peroxide and nutrient addition soluble aromatic concentrations in the groundwater had been reduced from 8 ppm to 200 ppb.

However, there was very little reduction of hydrocarbons in the unsaturated zone especially in the spray irrigation area. It was concluded that the high residual hydrocarbon levels were due to the fact that the fuel may have been trapped in micro pores in the soil particles. However, a recent paper has shown that tightly bound toluene can be degraded in soils. Thus it is more likely that the poor degradation in the unsaturated zone was due to low levels of hydrocarbon degrading bacteria in this zone or to the fact that there was not good contact between oxygen, nutrients, bacteria and hydrocarbon in this zone due to the experimental design.

5.8 Observations

In many ways, *in-situ* bioremediation of contaminated groundwater must still be considered as an emerging remedial technology, for which additional research is required. There have been very few documented cases of successful application of the method in Alberta, at sites typical of Alberta conditions (heterogeneous geology, cold temperatures). Field scale demonstrations of the technique under these types of conditions are required in Alberta.

The role of aquifer heterogeneity cannot be underestimated as a factor in determining the effectiveness of the method. From this perspective, biorestoration shares some of the limitations of pump-and-treat. Remedial effectiveness is partially a function of the hydraulic conductivity of the medium. Long-term sources of contamination as a result of diffusion limited releases from low permeability lenses, layers or matrix, can be a problem.

Supply of oxygen to the aquifer is an important factor in the process. Experience has shown that hydrogen peroxide systems can deliver high concentrations of molecular oxygen quickly and effectively. However, their operation and maintenance is expensive. Air sparging, while less effective in-terms of oxygen concentrations achieved, is much simpler. Capital and O&M costs for sparging systems are significantly lower. Overall, sparging may deliver more cost-effective performance.

In many cases, bioremediation may be implemented as a polishing step after bulk free phase and dissolved phase contamination has been removed by pump-and-treat. Under these circumstances, the additional costs associated with bioremediation may be quite small. Delivery and circulation systems are already in place, and sparging may be accomplished using existing wells on site. However, costs have been found to vary considerably, depending on the nature of the site and systems used.

Nine months of in situ bioremediation combined with a vapour elimination programme succeeded in removing free product and mitigated the vapour problems at two restaurants. Biodegradation of the gasoline was enhanced by circulating well-aerated groundwater amended with inorganic nutrients. After 7 months of treatment, the concentration of gasoline in the soil ranged from 100-500 ppm and the average concentration of dissolved organic carbon in the groundwater was 20 ppm. After an additional 3 months of treatment, the dissolved organic carbon levels in the groundwater had decreased to <5 ppm.

6. Innovative Technologies for Improving In-situ Bioremediation

6.1 Combination of Biotreatment with Other Forms of Treatment

Soil Venting

Soil venting is a physical method which is used frequently to remove low boiling hydrocarbons from the soil. Soil venting can be used in conjunction with bioremediation since it is a very good method to supply air to subsurface soil or water. In fact, bioremediation may be occurring in a number of situations where soil venting was being used without the operator's knowledge.

Pump and Treat

Contaminated water can be pumped from an underground aquifer, air stripped then passed into a bioreactor where nutrients and oxygen are added. This will result in a decrease in soluble hydrocarbon, an increase in the oxygen saturation and an increase in the numbers of native microorganisms. The treated water is then injected back into the aquifer and will substantially increase the rate of biodegradation in the aquifer.

Radio Frequency Heating of the Subsurface Matrix

A recent report has shown that the subsurface soil can be heated to a temperature of 150° C in as little as 8 days by the application of RF radiation. The rationale for this was to evaporate volatile chemicals out of the subsurface soil. However, if less radiation was used it may be possible to raise the temperature of the soil and water by only 10-20°C which would greatly enhance the biodegradation rate.

The economics of such technology should be explored.

6.2 Novel Technologies

Horizontal Wells

The use of horizontal drilling techniques in the Oil Industry is becoming quite common today. This is technology which has potential to be used in bioremediation processes. Horizontal wells should be more effective for introducing nutrients and oxygen into the aquifer since they will allow for much greater contact with the soil and water.

New Techniques for Introducing Air into the Aquifer

A review of the literature pertaining to the injection of air into underground oil reservoirs to support in situ combustion should be made. Some of the advances made in this area recently may be applicable to in situ bioremediation.

Use of Surfactants and Mobility Control Agents

The addition of surfactants is commonly used to increase the rate of biodegradation of hydrocarbons in soils and on beaches. The effectiveness of using them in aquifers should be studied. If large numbers of hydrocarbon degrading bacteria are added to the aquifer this will introduce large quantities of biosurfactants since these bacteria always produce them when they are grown on hydrocarbons.

The use of mobility control agents such as xanthan gum or polyacrylamide will give better sweep efficiency in the aquifer and will thus maximize contact between the hydrocarbon degrading bacteria, the oxygen and nutrients in the water and the hydrocarbon material.

6.3 Genetic Engineering

Classical Adaption

The use of classical adaption methods for manipulating the properties of hydrocarbon degrading microorganisms is a very useful tool. Bacteria can be made resistant to heavy metals and to high salt concentrations by this method. In addition, temperature profiles of the organisms can be altered so that a population isolated from elsewhere can be adapted to site specific conditions.

In addition, classical mutation techniques can be used to create depressed mutants which allow for an overproduction of degradative enzymes.

Recombinant DNA Technology

The use of recombinant DNA technology has been over-emphasized in bioremediation applications. The technology offers numberable marvellous manipulations in the test tube but most do not offer any significant advantage to cultures isolated by much less controversial techniques. In fact, most rDNA strains would appear to be most inappropriate for use in soils or groundwaters since the host for most genetic transfers is E. coli, a human intestinal bacterium which would be quickly eliminated from any soil or natural water. In addition, it is potentially pathogenic and thus should not be used indiscriminantly.

There may be potential for use of rDNA once more genetic mapping has been carried out on native soil and groundwater bacteria and a more suitable host has been identified. Until then, traditional manipulation approach must suffice.

The Use of Bio-Barriers

One of the problems associated with any form of clean up is the migration of product off the site once the clean up has been initiated. Bio-barriers can be used to prevent the movement of contaminants. A trench is dug to a depth greater than the water table and is filled with porous fill. A nutrient solution and large inoculum of hydrocarbon degraders is mixed with the fill. Air is sparged in at the bottom and the trench becomes a highly active biodegrading curtain which will degrade any hydrocarbons which flow through it. In many ways it can be thought of as a vertical trickling filter.

7. Summary

In-situ bioremediation is potentially an attractive remediation option for contaminated groundwater at many sites. Successful application of the technique requires good cooperation between microbiologists and hydrogeologists. Advantages include good clean-up levels under the right conditions, on-site treatment of the problem, and generally low additional costs. In general, some form of enhancement of biodegradation through the addition of oxygen and/or nutrients is required.

Limitations of the method include problems associated with aquifer heterogeneity, and the practical challenges associated with oxygen and nutrient delivery. The presence of LNAPL in the aquifer further complicates matters, requiring free product removal, and providing a potential long-term source of dissolved contaminants. At present, little work on *in-situ* bioremediation of groundwater has been done in Alberta. Additional research and field-scale testing of the technique at complex sites and under Alberta conditions are required.

I.2.3 ADVANCED OXIDATION PROCESSES

1. Introduction

Advanced oxidation processes (AOP) are groundwater treatment techniques which may provide a technically effective, economical alternative to the more commonly used methods of treatment. This process is considered as a second generation remediation technology, it leaves no waste residue requiring further treatment or disposal. The principle of AOP, their applicability to treat groundwater contaminated by condensate and the different techniques available will be presented and discussed in this section.

2. Theory

AOP are techniques using oxidation to breakdown the organic compounds present in contaminated groundwater. The most effective way to oxidize organic compounds is by using chemical reactants with a high oxidizing potential. The oxidizing agent chosen must not create a new contamination problem. The options to meet this requirement are to use the additions of non-polluting oxidizing agents such as hydrogen peroxide (H_2O_2) and ozone (O_3) and the in-situ generation of reactive species, primarely the hydroxyl radical (OH). Several different variations of the technique exist, the main difference between each one being the way to generate the short-lived oxidation radicals. The simplest way to obtain highly reactive OH radical is by direct photochemical cleavage of hydrogen peroxide. It is also frequently obtained from the photolysis of ozone and in some cases from heterogeneous photocatalytic decomposition of water using a titanium dioxide (TiO_2) semi-conductor. The most commonly commercially applied processes involve the use of various combinations of ultraviolet light (UV), ozone, and hydrogen peroxide. The methods have been developed to stages ranging between laboratory experiments to a full-scale commercial product.

3. Applicability

AOP applications have been most successful in the treatment of groundwater with less than 100 ppm of chlorinated solvents, aliphatic aromatic hydrocarbons such as benzene, chlorinated phenolic compounds, pesticides and metal/cyanide complexes. Inorganic chemistry of the groundwater to treat is to be considered. Carbonate and bicarbonate ions can slow the oxidation of organic compounds by reacting preferentially with the hydroxyl radicals. Solids can be generated in the effluent from the oxidization of inorganic compounds such as ferrous and manganous, sulphite, nitrite and ammonium ions (Gosset and Harries, 1990). Depending on the method, the initiation, promotion and bicarbonate scavenging might be negatively affected by the pH of the influent.

A complete oxidation reaction leads to environmentally friendly end-products, CO_2, H_2O and salts. In the case of an incomplete oxidation, the resulting products usually exhibit an enhanced biodegradability (Carey, 1990). Care should be taken to identify intermediate reaction products.

4. Emerging Technologies

4.1 High Energy Electron Beam Irradiation

This technique is being developed at the Electron Beam Research Facility, Virginia Key, U.S.A.. The high-energy of a 1.5 MeV electron beam created in an horizontal accelerator is used to irradiate groundwater and remove organic contaminants at low concentrations. The installation can treat a flow of up to 460 L/min (100 IGPM). Cooper et al., (1990) report removal efficiencies between 85 and 99%, a decrease in benzene concentration from 90 to < 10 ppb, and from 150 to < 10 ppb in the case of toluene. The facility was built at a cost of $1.7 million.

4.2 Semiconductor-catalysed Photooxidation (SCPO)

The most commonly used SCPO method consists in the photolysis of TiO_2 (anatase crystalline form) with near UV light (300-400 nm). A prototype called Nulite, a division of Nutech Energy Systems Inc., is in the product development stage. Skala and al, 1988, report effective degradation of organic compounds in a model solution containing 2.5 ppm of each of the following compounds: benzene, toluene, chlorobenzene, trichloroethylene, 1,1-dichloroethylene, diethylether, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane and chloroform. The technique is currently in a research stage and appears to have potential as a commercial technology (Ekabi et al, 1990).

4.3 Ozone/Ultraviolet Light (O_3/UV)

Oxidation by ozone (ozonation) and by UV light can be combined to increase the effectiveness of the oxidation process. The two methods can be combined in one step or divided in an initial ozonation step followed by UV irradiation for the production of hydroxyl radicals from the dissolved ozone, as patented by WEDECO (Leitzke and Whitby, 1990). This later process was tested in the lab and in two full scale field tests, one with contaminated groundwater and one with landfill leachate. The contaminated groundwater was treated at a flowrate of 167 L/min (37 IGPM). Its initial concentration of 500 ppb of chlorinated hydrocarbons was reduced to < 8 ppb. The operation and maintenance (O&M) costs of this system was \$0.075/m^3 of water. The capital costs, including installation and start-up was \$52,000 and supplies and maintenance \$3,400/year.

5. State-of-the-art Methods

5.1 ULTROX

The ULTROX process uses a combination of UV light and the oxidizing agents, ozone and hydrogen peroxide. This process has been applied at industrial, Department of Defense and Superfund sites to treat water containing different organic compounds, including BTX, over the past four years. A stepwise approach is taken to the implementation of the process at a site. First, a treatability study is realized in the lab to test the feasibility. Then, a pilot treatment plant is operated on site to develop the final treatment design and operating costs. This step usually takes about two weeks and if results are satisfactory, the system is installed as a permanent on-site treatment centre.

Zeff and Barich (1990) describe several applications of the ULTROX process on wastewaters and contaminated groundwater. The case most similar to the situation of our interest, involves the treatment of groundwater containing 7 to 10 ppm of trichloroethylene, perchloroethylene, toluene and trichloethane to storm sewer standards at a rate of 946 L/min (208 IGPM). This treatment involved a capital investment of \$300,000 to \$350,000 and O&M cost of \$0.3 to \$0.37/m^3 (Zeff and Barich, 1990). Costs depend on the type and concentration of organic compounds to treat and the discharge standards. The type (H_2O_2 or O_3) and quantity of oxidant and number of UV lamps is adjusted according to these parameters. ULTROX has developed systems costing from \$45,000 to \$440,000 (uninstalled).

There were concerns that bubbling of O_3 used in the process was stripping the volatile compounds resistant to oxidation. Tests were conducted to verify the extent of VOC stripping from the bubbling of ozone. Stripping of compounds difficult to oxidize presented a problem. However, the stripped compounds were removed in the nickel-based catalyst used to convert reactor off-gas ozone to oxygen (Lewis et al., 1990).

5.2 RAYOX

The RAYOX process uses a combination of ultraviolet light and ozone or hydrogen peroxide. The process makes use of a broad based light source that can be calibrated to emit light at the appropriate wavelength for the absorbency of the compounds. The lamps accelerate the remediation by promoting the photolysis of the initial contaminants and the intermediate by-products. By optimizing the system design, a treatment rate as much as three times higher compared to oxidation alone can be obtained. This process is also implemented stepwise. A pilot scale is first completed with a 80 to 210 L batch sample or at a flow of 20 to 200 L/min (4.4 to 44 IGPM), depending on the desired application.

A system was installed to treat groundwater contaminated by NDMA at the Uniroyal site, Elmira, Ontario. NDMA is the product of nitrosation of dimethylamine (DMA) with nitrite (NO_2). The system treated 22775 L/min (500 IGPM) and reduced NDMA concentration from 3 ppb to 3 ppt, which represents an efficiency of more than 99.9% (CH2M Hill and Solar Chem Environmental Systems, 1990). The contaminated groundwater also contained chlorobenzene, nitrobenzene, 2-chlorophenol and benzene although no removal efficiencies were available for these compounds. In this case, high iron concentration (up to 200 ppm) were found to cause extreme fouling and coating of the UV lamps. A pretreatment for iron and trace heavy metals was required (Gosset and Harries, 1990). At a different site, an on-site trial of the system has succeeded in reducing the concentration of total petroleum hydrocarbon from 10 ppm to 10 ppb and the BTEX from more than 10 ppm to < 10 ppb (Cater et al, 1990). No costs were available for these treatments.

5.3 Perox-pure

This process also uses ultraviolet light and hydrogen peroxide as an oxidizing agent. It has been applied to over 100 cases over the past 5 years. The process uses high intensity lamps that reduce costs and decrease the problems related to high concentrations of organic compounds and interference with inorganic ions. Costs reported for this treatment range between \$0.13/m^3 for groundwater with low organic contaminants loads (< 1 ppm) and

\$31.7/m^3 for wastewaters (Froelich, 1990). With low concentrations, treatment rates of up to 1514 L/min (333 IGPM) can be handled. Bernardin (1989) mentions that in an application, the system cost one-third that of GAC.

5.4 Cav-Ox

The Cav-Ox Process (COP) combines the use of induced cavitation, UV, and when required, hydrogen peroxide. The technique allows the initiation and continuation of auto oxidation reactions after the removal of the ultraviolet stimulus. Cavitation is the point at which the vapour pressure of a liquid is greater than the surrounding pressure. The developers of this process, The Watergroup, suggest that the imploding bubbles created during cavitation promotes the oxidation process. Concentrations of benzene up to 700 ppm can be effectively reduced. Performance data of the system include reduction of gasoline concentrations from 20 ppm to below detection limits, and benzene from 280 ppm to below detection limits. Treatment costs for the benzene example at a rate of 94 L/min (21 IGPM) are a capital investment of \$38,000 and O&M of \$9,254 (or a treatment cost of \$0.19/m^3) and are compared to capital costs of \$135,000 and O&M costs of \$108,050 (or \$2.2/m^3) for UV/H_2O_2 system of competitors (treatment costs based on 50 years of operation). The developers of this process claim that their system is a third less costly than the other AOP technologies.

6. Discussion

All technologies presented have shown very promising results for treatment of organic compounds. State-of-the-art technologies, however, have over the emerging technologies the advantage of much extended testing. The state-of-the-art technologies reviewed were all applicable to the treatment of the organic compounds expected in the groundwater at sites contaminated by condensate. Most of these systems can be design for batch process or continuous operation or a combination of the two modes. The destruction efficiency of these systems depends on the residence time (or flowrate) and can be adjusted according to the clean-up level of effort. It is reasonable to expect 99% destruction of organic compounds with a full-scale AOP treatment system (Gosset and Harries, 1990). One of the greatest advantages of AOP over other treatment methods is that they remove contaminants without transferring them to wastes requiring disposal or recycling (like GAC), and without emission in the atmosphere (like air stripping).

Some inorganic parameters of the influent might negatively affect the efficiency of AOP. Very turbid waters decrease the efficiency of the UV lamps, some ions act as OH scavengers and might form undesirable precipitates, the pH and alkalinity also affects the process. Most of these problems can be solved by adding a pretreatment step. According to Peyton (1990), O_3/UV and O_3/H_2O_2 systems are superior over H_2O_2/UV systems for the treatment of high concentrations of organic compounds. The order of preference of the methods in the case of high alkalinity is O_3/UV, O_3/H_2O_2, then H_2O_2/UV. In the case of low pH conditions, the O_3/H_2O_2 method seems the most affected and less favourable while H_2O_2/UV seems the least affected.

Costs of AOP system are very site specific. They depend on one hand on the chemistry of the water to treat and the efficiency requirements, and on the other hand on the design of the system (type and quantity of oxidants, type and number of lamps, electricity). For systems using UV and either ozone or hydrogen peroxide, the higher costs related to using ozone lower the cost of UV while hydrogen peroxide is less expensive but requires more expenses in UV. Implementation and maintenance of a system using hydrogen peroxide are easier than with ozone (Peyton, 1990).

All the state-of-the-art technologies presented above could be recommended on the base of their successful results and costs generally lower than that of traditional treatment methods. In the context of contamination by condensate, systems using hydrogen peroxide might be preferable over ozone systems for several reasons. Ozone systems seem more sensitive to low pH conditions (Peyton, 1990), which are likely to be encountered. Hydrogen peroxide is less expensive and easier to handle. The potential stripping of VOC associated with ozone bubbling can then be avoided. Both Perox-pure and Cav-Ox UV/H_2O_2 based systems that appeared efficient and economical. The Cav-Ox process seems very efficient since it often does not require the use of oxidants. The degree of monitoring required and availability of a trained operator are also elements to consider in the selection of a system.

I.2.4 FREEZE CRYSTALLIZATION TECHNIQUES

1. Introduction

Freeze crystallization is a process which separates solutions into their components by freezing. This enables, for example, the removal of inorganic contaminants or mixed organic, inorganic, and heavy metal contamination from groundwater. The technology is uncommon in groundwater applications, and current technologies are relatively expensive for the contaminant concentrations typically found at natural gas processing plants. However, modifications to the technology may be possible which would take advantage of Alberta's cold winter climate, rendering the process more viable.

2. Theory

The freeze separation process is based on the difference in concentrations between solid and liquid phases in equilibrium (Figure I2.7). As a solution (say, sulphates dissolved in otherwise "pure" groundwater) at point A is cooled, there will be some temperature at which a solid crystalline phase (pure sulphate) appears in the liquid phase (point B). Usually only a single, pure component will crystallize. Initially, a small amount of solid crystal (sulphate) will form. This results in a lower concentration of sulphate in the liquid phase. The temperature of the solution must be progressively lowered to crystallize more sulphate, resulting in still lower concentrations of sulphate. The composition of the solution moves from point B to C to (ideally) D, at which point all the sulphate will have crystallized. By removing sulphate crystals, the groundwater may be purified.

Naturally, all practical problems involve a number of components: in groundwater, the contamination might involve sulphates, chlorides, and trace organic and inorganic in addition to pure water. This results in a much more complex equilibrium relationship (diagram), but does not change the principles outlined above. Unlike some of the other technologies presented, freeze crystallization can be used with a mix of organic and inorganic contaminants.

3. Components of Freeze Crystallization System

The "Freeze Technologies Corporation" system consists of the following components, depicted in Figure I2.8 (Freeze Technologies Co., 1990):

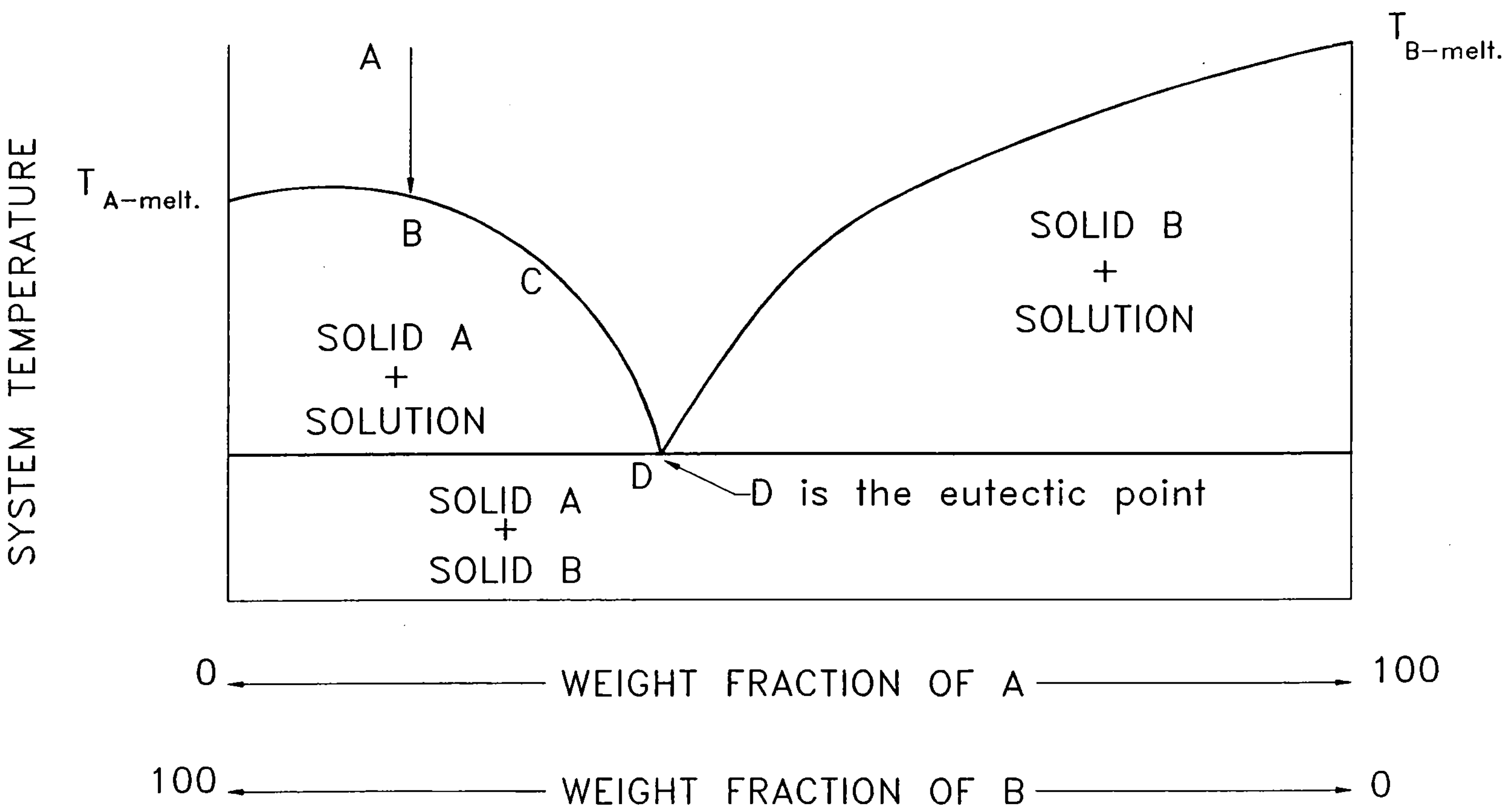


FIGURE 12.7
SIMPLE BINARY SOLID–LIQUID EQUILIBRIUM DIAGRAM

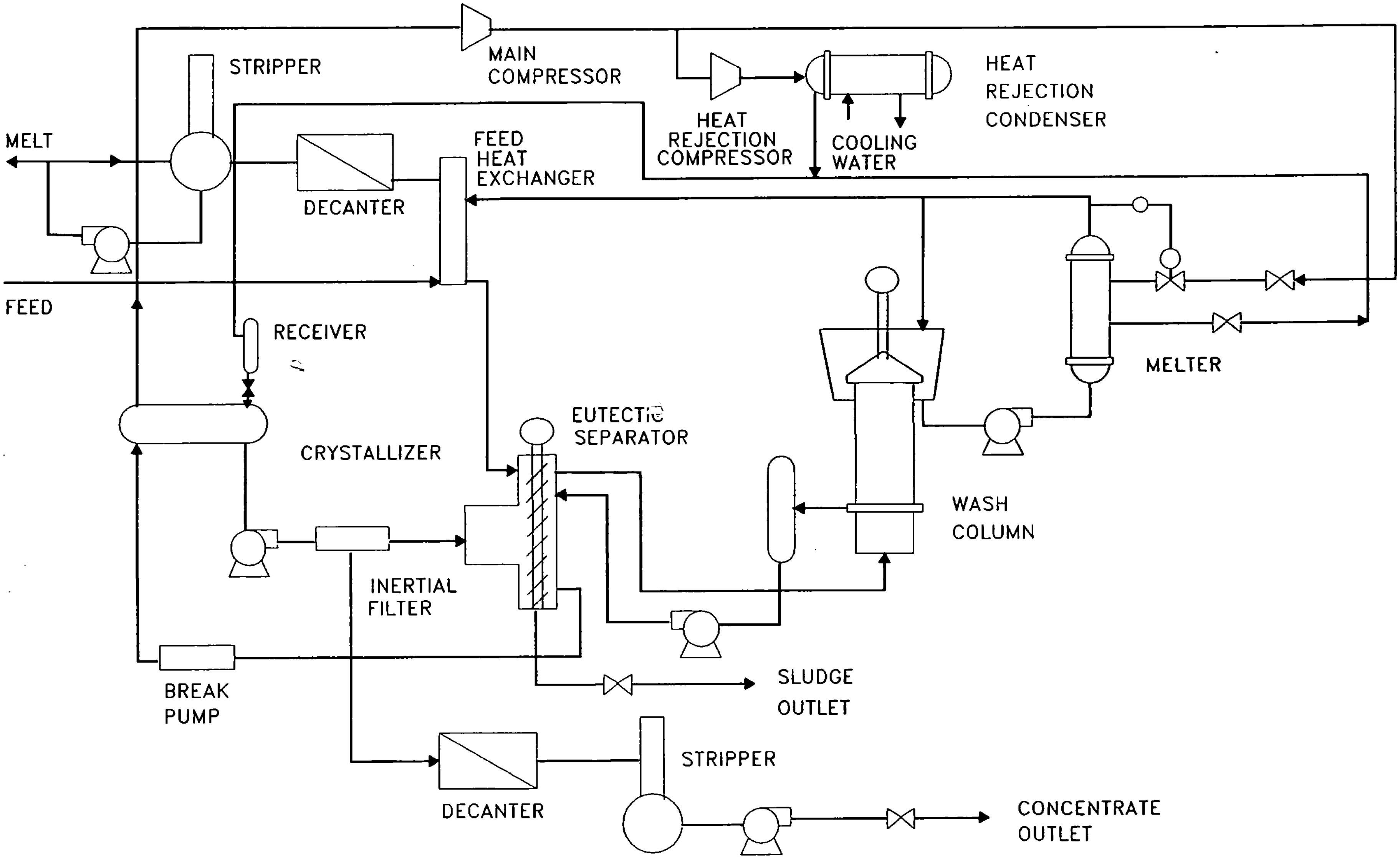


FIGURE 12.8
FREEZE PROCESS FLOW SCHEMATIC

1. Crystallizer - Heat is removed to lower the temperature of the material to the freezing temperature of the solution (usually crystallizing the solvent first).

2. Eutectic separator - Segregates the crystals of solvent and solute into different streams, so that each can be recovered in pure forms.

3. Crystal Separator/Washer- Removes the crystals from the mother liquor in which they are slurried, and washes adhering brine to very low levels so that the recovered crystals have high purity.

4. Heat-pump refrigeration cycle - removes refrigerant vapour from the crystallizer, and compresses it so that it will condense and give up its heat to melt the purified crystals.

5. Heat exchangers - recovers heat from the cold effluent streams, improving the efficiency of the process.

6. Decanters & Strippers - Required in some processes to remove volatile materials and/or refrigerant from the effluent streams before discharge.

7. Utilities, Controls, Electrical Switch Gear, Pumps and Piping - Required to implement the freeze process in a continuous closed system.

4. Implementation and Costs

Freeze crystallization is currently an expensive process, best suited to concentrated waste streams. Freeze Technologies Corporation (1990) suggests that the process is economically viable in the following situations:

i) Heavy metal concentrations in the waste stream of 0.1-1% (1,000-10,000 mg/L)
ii) Dissolved organic concentrations of 3-7% (30,000-70,000 mg/L)
iii) Mixed organic and heavy metals at 0.5-1.5% (5,000-15,000 mg/L)

The limited information available suggests that most applications invole contaminant concentrations from 1-5% (10,000-50,000 mg/L). At most gas plant sites where inorganic contamination has been identified as significant, concentrations generally range from 0.1-0.5% (1000-5000 mg/L) and occasionally as high as 1.2%, well below the current economic limits of the technology. To be cost effective, this technology would require adaptations to treat lower-concentration wastes. Alternatively, steps could be taken to concentrate the influent stream. This might involve routing pumped groundwater through evaporation ponds prior to freeze crystallization. A further cost savings might be possible through modifications to the process. Alberta's ample supply of cold winter weather might be put to good use through savings in electricity for cooling and in undersizing of cooling equipment.

4.1 Effectiveness

Freeze Technologies Corporation state that their "DirCon" freeze crystallization process results in effluent with the following characteristics:

i) Water: 90% of influent, >99.99% pure
ii) Waste: 10% of influent, contains 99.99% of contaminants in influent

Costs for flow rates of 5-40 USgpm (10-151 L/min) are presented in Table 12.4, below.

5. Summary

Freeze crystallization is an emerging technology for treatment of inorganic contamination at gas processing plant sites. Currently, the costs of this technology are high, but it may be possible to reduce costs by modifying the current process to take advantage of the cold Alberta winters. It is recommended that further consultations be made with experts in the field of freeze crystallization to determine if modifications can be made to render this technology economically attractive.

Costs of Freeze Crystallization (Freeze Technologies Co., 1990)

Cost Component	Costs for Varying Plant Sizes (US$/USgal)		
	5 USgpm	10 USgpm	40 USgpm
Amortization, 5 year SLD	0.080	0.050	0.015
Labour	0.040	0.020	0.005
Electricity	0.008	0.008	0.006
Supplies, Chem., etc.	0.010	0.008	0.005
Maintenance	0.007	0.005	0.004
Total Costs ($/gal)	0.145	0.090	0.035
Total Costs ($/yr)	381,060	473,040	735,840

Note: All units in U.S. dollars and U.S. gallons

I.3 SOILS REMEDIATION TECHNIQUES

I.3.1 SOIL VAPOUR EXTRACTION

1. Introduction

Soil vapour extraction, or vacuum extraction, has been selected as recommended technology for situations involving contamination of the un-saturated zone by condensate. In many cases, application of the technique will be in conjunction with a pump-and-treat system. Pumping of groundwater would be used in these circumstances to depress the groundwater surface and expose more of the residual contamination for vacuum extraction. In addition, pump-and-treat would be used to skim free mobile product.

Factors controlling the applicability and effectiveness of vacuum extraction systems include the physical properties of the medium, the chemical characteristics of the contaminant and the method of implementation. These aspects are discussed in the next sections. Several possible methods for enhancing recovery are also discussed. In addition, a brief guide to implementation and design of vacuum extraction systems is presented, along with a discussion of relevant case histories.

2. Physical Properties

The primary physical properties that control the movement of gas in the unsaturated zone are the permeability and the moisture content of the porous medium. The moisture content and fraction of organic carbon also have implications for phase partitioning and migration rates. Heterogeneities and their distribution also play an important role in controlling where gases flow in the subsurface. In this section we also briefly consider processes at the capillary fringe.

2.1 Gas Flow

To be effective, a vacuum extraction system must transmit sufficient quantities of air to the subsurface to remove large amounts of contaminant mass. Thus, high permeabilities are favourable to significant mass removal.

The permeability of a porous medium, and its distribution, control the flow path of air and the rates of air transmission to the surface. In fact, the permeability of interest is the effective gas permeability which depends strongly on the moisture content: as the moisture content is increased, the pore space available for the movement of gas decreases and the effective permeability decreases. Thus, the effective permeability does not equal the intrinsic permeability of the porous medium. In the literature this distinction is generally not made. Most 'permeabilites' are reported as hydraulic conductivities (ie., permeabilities modified to reflect the flow of water through the medium under water-saturated conditions). This is convenient from a hydrogeologist's point of view, but obscures the fact that the conductivity to air may be more limited due to the presence of soil moisture in the pores. For vacuum extraction, the greatest flow of air will be realized when the soil moisture contents are at, or below, field capacity. To be consistent with the literature, hydraulic conductivities will generally be presented in this report, with the understanding that the moisture content may severely alter the effective conductivity to gases in the unsaturated zone.

If the unsaturated zone has lithologic units with wide ranges of permeability, channelling of air flow may result. In this case, most of the air travels through the most permeable layers. The more permeable layers are thus cleaned up after a short period of time, while the less permeable layers remain contaminated. Mass is lost from the tighter layers only by diffusion to the high flow layers - generally a slow process. This is one reason for removal efficiencies to drop dramatically shortly after initiation of the vacuum extraction process.

Good cleanup results are claimed in the literature for porous media with hydraulic conductivities ranging down to 10^{-8} cm/s (eg. Stinson, 1989). Such a material corresponds to a relatively tight clay (for unconsolidated deposits). The authors' view is that except for sites in dry climates, claims for cleanup at such low conductivities must be viewed with some scepticism and alternative technologies should be explored. Scepticism is warranted because these materials, besides having low intrinsic permeabilities (ie., $10^{-17}m^2$), also tend to have relatively high moisture contents, and therefore low air contents (eg., Stinson (1989) reported 15%). This combination should lead to very limited air flow through these deposits, especially if surrounded by more permeable units that can preferentially transmit air. Thus, removal of contaminants from these tight zones will occur primarily by diffusion.

The above being said, two points should be kept in mind: if the deposits are fractured, sufficient air may be transmitted to remove significant quantities of contamination; and, the flow of air at such low permeabilities does not follow Darcy's law due to the Klinkenberg effect (slip along the pore walls leading to non-zero velocities) which results in flow rates in excess of those predicted by traditional analyses. Also, if the climate is very dry, blocking of the pore space by soil moisture might not be an issue. More research is required on the applicability of vacuum extraction in materials with low permeabilites.

As a result of the low conductivity of these units, the radius of influence of wells tends to be very small (eg., 1 m reported by Agrelot et al. (1985)) requiring many closely spaced wells. Also, the vacuum required commonly approaches 1 atmosphere which severely limits the potential for vapourization since the maximum possible extraction concentration is limited to the absolute air pressure.

In view of the above discussion, until well documented research or field tests show otherwise, it may be prudent to expect significant recoveries using vacuum extraction only when the geological materials which have bulk hydraulic conductivities in excess of about 10^{-6} cm/s. This should not, however, preclude its use where there are small lenses of lower permeability. Such a limitation might exclude a great many sites where substantial cleanup is possible despite the lower permeability lenses.

2.2 Gas Transport

High advective rates of transport do not necessarily guarantee large removal rates. As vapour migrate in the subsurface they partition to the aqueous and solid phases. Thus, their migration is retarded relative to the bulk flow of the gas-phase. Assuming equilibrium, a retardation factor that is analogous to that used in aqueous transport may be calculated for vapour transport (Baehr, 1987):

$$R = 1 + (M_w/M_a)(1/H) + (d/M_a)K_D/H) \qquad (1)$$

where M_w is the volumetric water (moisture) content, M_a is the volumetric air content, d is the soil bulk density, H is the Henry's constant, and K_D is the aqueous-solid partitioning coefficient (distribution coefficient). The middle term on the right accounts for dissolution while the last term accounts for sorption. This equation shows that as the soil moisture content is increased (and the soil air content correspondingly decreases) the retardation factor will increase. It should be noted, however, that such equilibrium partitioning may not apply at high advective gas velocities (Johnson et al., 1987).

Equation (1) does not account for partitioning directly from the gas-phase to the solids. Research on this partitioning is currently in its infancy, however, preliminary results show that this type of sorption can be dramatic (Chiou and Shoup, 1985). Generally a monolayer of water molecules is thought to be sufficient to limit this sorption process. Thus, it is desirable to have a low moisture content but not allow the soil profile to dry out. Field capacity is therefore a desirable moisture content to maintain (as for maximizing the effective gas permeability).

In areas with dry atmospheric air, it may be beneficial to humidify air input into the unsaturated zone by the vacuum extraction system. This would generally require a ground surface cover and gas input (passive or active) wells. These sorption processes may have detrimental consequences for remedial techniques that inject hot dry air into the unsaturated zone.

In the absence of advective movement of the gas-phase, diffusion is the primary vapour transport mechanism. Relative to aqueous diffusion, vapour diffusion is rapid; however, relative to force advection, vapour diffusion is slow. As discussed above, transport by diffusion primarily comes into play in low permeability zones where the zone is bypassed by the moving gas-phase.

2.3 Capillary Fringe

The behaviour of contaminants at the capillary fringe is of great importance when considering LNAPL remediation. Since the watertable and capillary fringe form the base of the unsaturated zone, a large mass of contaminants can accumulate in this region: free product will pool, and possibly migrate along this boundary. In addition, if the watertable fluctuates the pure product contaminant will form residual, due to capillary trapping, throughout the capillary fringe and possibly below the watertable.

Due to surface area considerations mentioned above free product is usually best removed by skimming or bailing, rather than completely by vacuum extraction. Drawdown of the water table by pumping is usually required to achieve this goal efficiently. Drawing down the watertable has the added advantage of leaving behind residual contamination and possibly exposing product that previously had been trapped below the watertable. This residual can then be efficiently removed by vacuum extraction. Such control of the water table elevation is usually necessary for another reason. As vacuum is applied to the unsaturated zone, the air pressure is decreased. This decrease in air pressure causes an increase in watertable elevation. Without drawdown of the watertable by pumping, additional contaminants will be incorporated into the groundwater flow system (Johnson et al., 1989).

3. Chemical Properties

The chemical properties of compounds also control their propensity for removal by vacuum extraction. Vapour source concentrations are determined by either vapour pressures and liquid molar fraction or Henry's constants. Henry's constants also affect migration rates along with distribution coefficients. Vapour pressures and Henry's constants are both strongly affected by temperature. Whether or not equilibrium is achieved under vacuum extraction is another question that needs to be addressed. Finally, all of these aspects combined help to delineate the applicability of vacuum extraction to certain compounds.

3.1 Source Concentration

For the pure phase the equilibrium vapour concentration for a particular constituent is determined by its vapour pressure multiplied by its mole fraction in the liquid phase (Raoult's Law). In most cases, equilibrium appears to be an appropriate assumption for vapourization, even under force advection (McClellan and Gillham, 1990); however, equilibrium concentrations may not be observed due to dilution by cleaner air in heterogeneous systems (Benson et al., 1989). With free product, much of the air withdrawn from the subsurface is not in direct contact with the pure phase; thus, mixing with saturated air results in lower observed concentrations. For residual, similar effects are observed since the residual may be heterogeneously distributed throughout the pore space.

For contaminants that are a mixture of compounds the source concentrations will change over time due to fractionation of the source liquid phase. The most volatile components will be preferentially lost to the gas phase because of their higher vapour concentrations. Loss of these compounds leads to an increase in the mole fractions of the remaining compounds and corresponding increases in their vapour concentrations and thus losses to the gas-phase. Thus, progressively less volatile constituents will be removed from the liquid product. For a given class of compounds, this generally means that the lightest compounds are removed first and the heaviest compounds are removed last (if at all, to any significant degree).

The equilibrium vapour concentration for dissolved contaminant is determined by the compound's Henry's constant which describes the equilibrium ratio of gas concentrations to water concentration. Under force advection, it appears that equilibrium is rarely achieved

(Johnson et al, 1987). This is likely due to slow desorption kinetics as contaminants move from the solids to the aqueous phase. For trichloroethylene, McClelland and Gillham (1990) observed concentrations over an order of magnitude less than equilibrium.

3.2 Retardation

The concept of retardation of vapour phase transport was introduced earlier. Equation (1) shows that retardation depends on two chemical properties of the compound: the Henry's constant and the distribution coefficient. The Henry's constant is introduced in the previous section. The distribution coefficient is generally taken to be the same as for aqueous solutions. For organic compounds, the distribution coefficient is often directly related to the fraction of organic content in the soil (f_{oc}) with the proportionality constant being the organic carbon partitioning coefficient (K_{oc}). Thus, retardation is increased in soils with higher fractions of organic carbon.

The process of source fractionation described above leads to a concentration of heavy organic constituents in the subsurface. It has been postulated that these compounds can act as a sink for other compounds migrating in the vapour phase and so the retardation factor in increased. The validity of this hypothesis has yet to be confirmed.

3.3 Temperature

Temperature has a significant effect on two important chemical properties: the vapour pressure and the Henry's constant. As temperature decreased, the values for both of these properties decreases dramatically. For common chlorinated solvents, a decrease in both these properties (Mendoza and Frind, 1990). Similar decreases would be expected for other organic compounds. Since most textbook values are reported for 20°C, adjustments must be made for applications at lower temperatures. Other compound properties such as diffusion coefficients and viscosities are only slightly affected by temperature variations.

An important consequence of this temperature dependence is that, relative to higher temperatures, lower subsurface temperatures lead to decreased removal efficiencies due to lower vapour concentrations. In addition, retardation of vapour migration will be increased at lower temperatures.

Surface temperatures in Alberta may be as low as -45°C during the winter and groundwater temperatures are typically between 2 and 10°C. Temperatures in the near surface region of the unsaturate zone can therefore be expected to vary significantly throughout the year and be less than 0°C for much of the winter months. These cold temperatures have severe consequences for the vapourization of organics in the unsaturated zone. As discussed above, vapour pressures decrease dramatically with decreases in ambient temperature. Although not a linear relationship, a decrease of almost 40% may be expected for each 10°C decrease in temperature. So, for much of the year temperature effects will result in a decrease of removal efficiency of a vacuum extraction system.

Note that the analysis of Johnson et al, (1990) above assumed a temperature of 20°C. For decreased temperatures, compounds with even lower boiling points than 150°C may not be significantly removed by vacuum extraction.

3.4 Compound Applicability

Reports in the literature provide some guidelines on the suitability of vacuum extraction for different compounds. Based on information from a vendor, Stinson (1989) suggests a lower limit for (dimensionless) Henry's constant of about 0.001. Hutzler et al. (1989) suggest a lower limit of 0.01.

Johnson et al. (1990) suggest that the removal rates of less than 1 kg/day will generally be unacceptable. In order to achieve such a rate, they state that the total source vapour concentration should exceed 0.0001 atmospheres (for an air extraction rate of 1800 l/min). For gasoline compounds at 20°C, this corresponds to compounds having boiling temperatures greater than bout 150°C. These limits are primarily based on economics (Johnson, 1990). If surface treatment requirements are minimal, and therefore costs are greatly diminished, it may be possible to continue vacuum extraction with even lower recovery rates.

That there is a limit to the concentrations that can be removed by vacuum extraction appears to be a concept that is gaining recognition (eg. Johnson et al., 1990; CH2M HILL, 1990). Even for light compounds that have favourable vapour pressures, as the source mass is depleted the vapour concentrations will reach a level where vacuum extraction is no longer feasible. At this point some other technology must be used or the site must be termed 'remediated'.

Condensate shares many properties, and indeed many compounds, with gasoline. Both are lighter than water and both are comprised of hydrocarbons (although gasoline tends to have a wider range of complex hydrocarbons). However, the heaviest compound commonly found in gasoline is dodecane, while more than 40% (on a mole basis) of the compounds in condensate are heavier than this. For similar compounds, molecular weight is a useful parameter since, in general, boiling points increase with increasing molecular weight, and both vapour pressures and Henry's constants decrease with increasing boiling point (Eastcott et al, 1988). Thus, we expect that it will be much more difficult to vapourize and completely remove condensate from the unsaturated zone than gasoline. Section 4 of this report provides a complete discussion of natural gas condensates.

Johnson et al. (1990) claim that a boiling point of less than about 150°C is necessary for a compound to be readily extractable by vacuum extraction. This corresponds to alkane hydrocarbons lighter than nonane (Eastcott et al, 1988). Two-thirds of the compounds in condensate have boiling points that exceed 150°C. Also, from the regression analysis of Eastcott et al. (1988), alkanes with more than 12 carbon atoms will have Henry's constants less than 0.001. Thus, many of the compounds in condensate may not be readily removed by vacuum extraction. However, if surface treatment requirements are low, as they might well be at a sour gas plant, even somewhat heavier compounds may be economically removed by long-term operation of a vacuum extraction system.

From this cursory analysis based on boiling points and carbon numbers, it is clear that, even if other conditions at a site favour vacuum extraction, some additional remedial method may be required, or the heavier ends of the condensate may be left in the subsurface. It should be noted that the most undesirable compounds (benzene, toluene, xylene, and related compounds) generally have relatively low boiling points and should be almost completely removable.

4. Implementation

The method of implementation of a vacuum extraction system can have consequences for its operation and efficiency. Johnson et al. (1990) outline a general procedure for evaluating the utility of using vacuum extraction at a site. In general a pilot study is advisable to check the assumptions that go into a preliminary analyses.

The radius of influence for an extraction well will determine how many wells are required. Thus, it is desirable to have as large a radius of influence as possible. In the literature, in materials with conductivities greater than about 10^{-6} cm/s, radii of influence of between 10 and 30 m are commonly reported. In fine-grained soils the radius of influence may drop to as little as 1 m. The depth to the watertable also affects the drawdown radius. Depths in excess of 6 or 7 m are usually recommended for efficient recovery.

The radius of influence for a well may be increased by use of a cover on the ground surface. Such a cover could be specifically placed (eg. plastic or asphalt), or might be an existing parking lot, building, etc. A cover increases the radius of influence by requiring that air enter the unsaturated zone around the edges of the cover. In this way, short-circuiting of air from the surface directly to the well screen is prevented. If an existing cover is extensive it may be necessary to install input ventilation wells to supply air to the system. An added advantage of a cover is that infiltration is prevented and so the moisture profile may be controlled. Placement of well screens below less permeable layers may have the same effect as constructing a ground surface cover.

For efficiency, wells should be placed within the contaminated area and screened across the contaminated zone. This maximizes the volume of air passed through the contaminated soil and reduces dilution effects. In conjunction with the above, wells should be screened as close to the watertable as possible (while still remaining in the zone of field capacity moisture content). This draws air deep into the unsaturated zone so that it passes through as much soil as possible (Wilson et al., 1988). Deep placement of screens will also help to increase the radius of influence of extraction wells.

To minimize the effects of channelling through higher permeability zones, it may be advisable to screen extraction wells in a contaminated zone that has a slightly lower permeability than the surrounding material. This might result in the lower permeability zone being cleaned along with the higher permeability zone since air will still be easily transported through this zone). This is a speculative technique that has not yet been documented in the literature.

Water vapour and liquids are commonly associated with vacuum extraction. To prevent freezing problems in the winter plumbing at or near the ground surface needs to be well insulated and possible heated. Sinson (1989) reports successful operation during the winter months in New England.

5. Surface Treatment

Once vapours are extracted and transported to the ground surface, they must be disposed of in some manner. The method of disposal is generally controlled by the type of compound, the concentration and local regulatory practices. Common options for disposal include, but are not limited to, flaring or burning, scrubbing with activated charcoal, and air stripping or atmospheric dispersion.

6. Costs

Costs for typical vacuum extraction operations are relatively low when compared to such methods as excavation. Materials tend to be fairly common-place,with the basic materials commonly including PVC pipe, commercial air blowers and tanks for liquid trapping and separation. Surface treatment and disposal may add more complications and may significantly increase costs (eg. scrubbing). Energy costs are typically quite low. Costs quoted in the literature range from US $10 to US $150 per ton of contaminated soil (Stinson, 1989). The lower of these costs correspond to minimal surface treatment costs.

Table I3.1 shows typical unit costs for installation of a conventional vacuum extraction system at a site in Alberta. Costs are based on quotes obtained from local suppliers of PVC and other equipment.

TABLE I3.1

VAPOUR EXTRACTION SYSTEMS
UNIT COSTS FOR ALBERTA SOUR GAS PLANTS

Equipment:		
Indirect -	Depreciable (Contingency)	$ 1.00
Indirect -	Nondepreciable (Option Processing and Training)	$ 0.50
Operating and Maintenance:		
A.	Variable	
	Power ($0.10/KWH)	$ 0.50
	Activated Carbon (off-gas treatment)	$14.00
	Waste Disposal	$ 9.00
B.	Semivariable	
	Labour	$ 2.10
	Living	$ 1.05
	Maintenance	$ 0.35
	Analysis:	
	Pretest and Postest - soil	$19.00
	Wellhead and Stock Gas Dining Operation	$ 1.70
C.	Mobilization/Demobilization	
	Site Preparation	$ 3.05
	Transportation/Setup	$ 1.00
	Start-up	$ 0.50
	Decommissioning	$ 0.50
D.	Fixed	
	Depreciation	$ 0.70
	TOTAL/m^3	**$54.25**

7. Vacuum Extraction Design

7.1 Introduction

This section outlines the necessary steps to be taken for the design and implementation of such a remedial program. The data that must be collected during the site investigation stage, and the different methods of doing so, are detailed. Sources of compound property data, along with correlation and estimation equations for some of the major constituents of condensate, are also discussed. The basic equipment necessary for a vacuum extraction operation are briefly mentioned; however, because of the wide range of equipment available, no specific equipment is recommended. These sections are followed by a discussion on different methods for designing a vacuum extraction system and for evaluating its effectiveness. A pilot test is strongly encouraged before full-scale implementation of the remedial program.

7.2 Site Investigation

A thorough site investigation is the obvious prerequisite for designing a remediation scheme. In particular, the type and distribution of the contaminant must be determined, the geologic setting and its physical properties must be evaluated, and any constraints on the siting of equipment must be delimited. These aspects are discussed in the sections below.

Contamination Evaluation

A complete understanding of the contamination scenario is necessary to properly design the vacuum extraction scheme and to determine the amount of mass to be removed. The lateral and vertical extent of contamination, the compounds involved and their concentrations must be thoroughly evaluated. In addition, if possible, the mode of contamination (e.g., residual, free product or dissolved phase) should be determined. This will assist in correctly placing extraction wells, choosing appropriate surface treatment technologies, estimating the probable success of the remedial scheme and assessing the results of the remedial operation.

Contamination by organic compounds in the unsaturated zone is commonly delineated using soil cores and vapour samples which are analyzed using GC or GC/MS techniques to determine the composition and the amount of contaminant present. Vapour samples generally only demonstrate the lateral and vertical extent of contamination, but may also indicate whether pure product is present or not if high concentrations are encountered. By using phase partitioning calculations in the analysis, core data may give more information concerning the mode of contamination. Recovery of free product from the waterable results in a clear indication of the composition of the liquid contaminant present at the site.

Geology

The distribution of different geologic units at a site may have serious implications for the success of a vacuum extraction remedial scheme. Of primary importance are the physical properties of each different geologic unit. In addition, heterogeneities within a particular unit may affect the air-flow distribution and thus contaminant extraction efficiency. The geologic character of the site can be evaluated through the use of standard techniques, such as soil coring and geologic mapping, in conjunction with determining physical properties.

Physical Properties

The most important physical properties that must be determined for each different geologic layer or lithologic unit are porosity, soil moisture content, soil organic carbon content and effective gas-phase permeability.

Both the porosity (n) and the soil moisture content (M) are determined from cores using standard laboratory techniques. The moisture content, which may vary widely within a lithologic unit, strongly influences effective permeabilities, effective diffusion coefficients and migration retardation factors.

The distribution coefficient, which describes the partitioning of a specific compound between the aqueous and solid phases, and so affects retardation factors, is commonly correlated to the fraction of organic carbon (f_{oc}) in the soil.

This is discussed below. Organic carbon contents are easily determined from cores by standard laboratory methods.

For vacuum extraction operations, the large-scale effective gas permeability (k^*) is a critical property that controls the rate of air flow, while the small-scale permeability distribution controls the air flow path. Unfortunately, representative permeability values are often difficult to determine. This is largely because intrinsic permeabilities may vary by many orders-of-magnitude and because effective permeabilities depend strongly on soil moisture content.

Intrinsic permeabilities (k) may be estimated by determining sample (aqueous) hydraulic conductivities from grain-size analyses (eg., Hazen or Kozeny-Carmen relations) or from permeameter tests (eg., constant or falling head tests) performed in the laboratory. Freeze and Cherry (1979) outline analyses by these methods. The intrinsic permeability is then obtained directly from the definition of hydraulic conductivity:

$$K=k\frac{d_w g}{U_w} \qquad (1)$$

where U_w is water viscosity, d_w is water density and g is the gravitational constant.

Large-scale, average effective permeabilities may also be determined by performing the equivalent of a pump test, using air, in the unsaturated zone.

Since it is commonly both the large-scale effective gas permeability and the small-scale permeability distribution that are of interest for vacuum extraction systems, it is recommended that pumping tests be performed in conjunction with grain-size analyses or permeameter tests.

Site Conditions

During a site investigation, the location of all structures and services should be noted since their location places constraints on the placement of extraction wells and other equipment necessary for vacuum extraction operations.

7.3 Compound Properties

To adequately describe the behaviour of contaminants in the unsaturated zone, a number of properties of the target compounds must be known. Important properties include the gas viscosity, free-air diffusion coefficient, vapour pressure, Henry's constant, distribution coefficient (or organic-carbon partitioning coefficient) and aqueous solubility.

Table I3.2: Correlation expressions for compound properties [Eastcott et al., 1988]

property	n-alkanes	aromatics
vapour concentration	$\log c = 4.35 - 0.57N$	$\log Co = 4.35 - 0.57N$
aqueous solubility	$\log S = 2.45 - 0.57N$	$\log S = 1.88 - 0.24N$
Henry's constant	$\log H = 1.90$	$\log H = 2.47 - 0.33N$

N is the compound's carbon number. All data are for 25°C.

Saturated vapour concentrations and aqueous solubilities are in mol/m^3.

Henry's constants are dimensionless.

Values for these compound properties can often be found in the literature; however, in some cases, it may be necessary to estimate values using correlation or regression equations, or to perform laboratory experiments to obtain reliable values. Sources of information include: chemical engineering handbooks (eg., Gree (1984), Dean (1985), Weast (1987)); texts on estimation methods (eg., Lyman et al. (1982)); or, journal articles (eg., Mackay and Shiu (1981), Eastcott et al. (1988)).

Correlation or regression equations for a particular class of compounds typically depend on the molecular weight, boiling point or carbon number of the compound of interest. Correlation equations for several properties of n-alkane and aromatic compounds were determined by Eastcott et al. (1988) and are presented in Table I3.2.

Gas Viscosity

The viscosity (u) of the extracted gas is one of the factors controlling its mobility in the unsaturated zone. If values for the viscosity of the compound of interest cannot be found in the literature, the method of corresponding states may be used to estimate the gas viscosity. Gas viscosity is a weak function of temperature.

Free-air Diffusion Coefficients

Diffusion coefficients (D_a) usually control the migration of vapours in the absence of induced pressure gradients. They are used in calculations of passive vapour migration and in determining the rate at which vapours will diffuse from finer-grained lenses. Gaseous diffusion coefficients may be obtained from the literature, or estimated from Grahame's Law or the method of Fuller and others (see Appendix B). Free-air diffusion coefficients are commonly several orders of magnitude greater than aqueous diffusion coefficients and are a weak function of temperature.

Vapour Pressure

The vapour pressure(P_v) controls the vapour concentration in zones containing pure product. The vapour pressure of a compound may be found using the Antoine equation. Either the Antoine equation or the Clausius-Clapeyron equation may be used to determine the temperature dependence of vapour pressure for a specific compound (see Appendix B). For n-alkane and aromatic, correlations for saturated vapour concentrations, which are directly related to vapour pressure through the ideal gas law, are presented in Table I3.2.

Henry's Constant

The Henry's constant (H) describes the equilibrium partitioning of a compound between the gaseous and aqueous phases. Thus, it influences the retardation factor for gaseous transport and the soil vapour concentration in the presence of dissolved contaminants. Since the Henry's constant is closely related to the vapour pressure and the aqueous solubility generally varies little with temperature, its temperature dependence will be similar to that of the vapour pressure. Table I3.2 presents correlations for n-alkane and aromatic compounds. Note that the Henry's constant does not vary significantly (ie., more than about an order-of-magnitude) for n-alkane. Care must be taken to determine the units being used for quoted values of Henry's constants: values are commonly either dimensionless or expressed in units of atm.mol/m^3.

Distribution Coefficients

The retardation of a compound in both the unsaturated and saturated zones is strongly affected by its distribution coefficient (Kd). Since the distribution coefficient is a function of the soil as well as the compound, it is common to approximate the distribution coefficient for hydrophobic organic compounds with the relation:

$$K_D = K_{oc} f_{oc} \tag{2}$$

where K_{oc} is the compound's organic-carbon partitioning coefficient. K_{oc} values may be estimated using the same methods used for the saturated groundwater zone. If necessary, distribution coefficients for specific compounds in specific soils can be measured in the laboratory using batch tests.

Table I3.3: Summary of equipment for vacuum extraction operations.

Required	Optional
extraction well pipes and headers blower or vacuum pump flow controllers and valves monitoring wells pressure transducers/vacuum gauges air flow meters gas chromatography	liquid-air separator contaminant removal system ground surface cap air inlet wells input air humidification heating insulation

Aqueous Solubilities

Aqueous solubilities (S) are useful for assessing a compound's potential for causing saturated zone contamination. Such an analysis is especially appropriate when drinking water standards are included. Correlations are included in Table I3.2. Solubilities may be estimated by dividing the compound's vapour pressure by its Henry's constant (expressed in appropriate units).

7.4 Equipment Evaluation

The equipment needed to perform a vacuum extraction operation is summarized in Table I3.3. Monitoring equipment is listed as being 'required' because a quantitative evaluation of the remedial program is necessary to assess system performance.

During the early stages of the design program, potential suppliers should be contacted for information on the availability and costs of different materials and equipment that might be needed for constructing the extraction system. This will allow for a full evaluation of the different technical and economic options in later stages of the design process. Information of special importance includes detailed specifications and capabilities for blowers or pumps (eg., flow rates, pressure drawdowns, efficiencies, etc.) and monitoring equipment (eg., range, sensitivity). Capital, operating, and maintenance costs may all be important components in the final economic analysis.

7.5 System Design

After all site and compound information has been collected, the final system must be designed under appropriate technical and economic constraints. Although this design phase can incorporate both empirical approximations and numerical modelling, some form of modelling is usually preferred due to its low cost, its potential for better estimates, its flexibility and its utility in analyzing field results. However, due to uncertainties in both the input parameters and the modelling process, modelling should be viewed as giving only rough estimates of expected performance, and the analysis should be re-evaluated in light of actual performance in the field.

The overall objective of the system design phase is to determine the optimum remedial scheme by analyzing air-phase mobility and contaminant transport mechanisms subject to different design constraints. The primary design variables that can be investigated to meet this objective include lateral and vertical well point locations, gas extraction rates (Q_a) (or pressure drawdowns (P)), lateral extent of ground surface covers, and degree of watertable drawdown.

By using numerical models for the flow of air in the unsaturated zone, the likely effects of varying these design variables can be investigated. In this way, the radius of influence of a well, and thus the required well spacing, can be determined for different design scenarios. Also, the distribution of air flowlines can be assessed with respect to the known location of contaminants. Groundwater flow simulations can be combined with these air flow analyses to determine the optimum withdrawal rates (Q_w) for groundwater wells. Finally, with a thorough understanding of the many limitations involved, vapour transport models might be used to estimate effluent concentrations expected during different stages of the extraction program.

Preliminary Calculations

Some preliminary calculations need to be made to estimate the relative transport potential of the contaminants by different processes and for use as input into different approximation equations and models. In general, if the liquid product is a complex mixture of constituents, calculations are only performed for a few selected compounds that represent molecular weight groupings of different structural classes of compounds.

Effective Gas Viscosity:

The overall viscosity of the effluent gas is commonly calculated using a weighted average of all of its constituents (including soil gas). In many situations, however, the effluent concentrations are relatively low and the effective gas viscosity is dominated by that of the soil gas. Thus, air flow estimates may not be in great error if the viscosity of clean air is used. Although generally not critical, the viscosity of air at the correct subsurface temperature should be used.

Effective Diffusion Coefficients:

The effective diffusion coefficient is described by:

$$D_a^* = T D_a \qquad (3)$$

where T is the tortuosity.

The tortuosity is an empirical factor that accounts for the tortuous pathways that molecules must travel in a porous medium. Although several models have been proposed for T, the most common approximation is that of Millington and Quirk [1961]:

$$T = \frac{n_a^{7/3}}{n^2} \qquad (4)$$

where n_a is the air-filled porosity. Note that the tortuosity, and therefore the effective diffusion coefficient, is strongly dependent on the soil moisture content. This relation appears to be valid up to water saturations of about 70%. At higher saturations a continuous, connected air phase ceases to exist and aqueous diffusion begins to play a greater role in the diffusion process.

Retardation Factors:

The retardation factor for vapour transport is described by:

$$R_a = 1 + \frac{n_w \;\; 1}{n_a \;\; H} + \frac{d \;\; K_D}{n_a \;\; H} \qquad (5)$$

where d is the porous medium bulk density. The magnitude of this factor indicates a constituent's rate of migration, under equilibrium conditions, relative to a compound that does not partition appreciably from the vapour phase.

Similarly, the retardation factor for the saturated groundwater zone is described by:

$$R_w = 1 + \frac{d \;\; K_D}{n} \qquad (6)$$

This term may be used as an indicator of the potential for a contaminant to migrate once it enters the groundwater zone.

Source Concentrations:

In the presence of pure product, under equilibrium partitioning conditions, the saturated vapour concentration for constituent i adjacent to a liquid product source is described by Raoult's Law:

$$C_{oi} = \frac{X_i \; P_{vL}}{RT} \qquad (7)$$

where X_i is the constituent's mole fraction in the liquid phase. The source concentration is expressed in mol/m^3 by using the universal gas constant (R) and the temperature (T). This concentration is easily converted to mass units by multiplying by the compound's molecular weight (M).

The total source concentration is determined by summing the individual source concentrations of all the liquid product constituents. However, it must be remembered that the source concentration will change over time as the pure product becomes 'weathered' (ie., as the more volatile components are removed and the liquid source becomes enriched in the less volatile compounds). In addition, this source concentration does not account for dilution effects arising from channelling of air flow through clean sections of porous media.

Effective Permeabilities:

If permeabilities are obtained using a field pump test, effective permeabilities (k^*) are obtained directly. However, variations due to temporal changes in moisture content during vacuum extraction operations will not be accounted for. If intrinsic permeabilities were obtained during the site investigation, a correction factor must be determined to account for the strong dependence of effective permeability, where the relative permeability has a value between 0.0 and 1.0. Estimates may be made by comparing measured effective permeabilities with measured intrinsic permeabilities in the same unit. Models for calculating relative permeabilities include those of Brooks and Corey (1964) and van Genuchten (1980); however, their application is outside the scope of this report.

Empirical Estimation

Johnson et al. (1990) present a number of empirical relations for estimating gas flow rates and effluent concentrations. Volumetric gas flow rates per unit height of well screen may be estimated by the relation:

$$Q'_a = \frac{k}{U_a} P_w \frac{[1 - (P_{atm}/P_w^{2}]}{\ln(r_w/r_i)} \qquad (8)$$

where r_w is the radius of the well, r_i is the radius of influence, P_w is the pressure at the well and P_{atm} is atmospheric pressure.

Although this relation may provide a first approximation to the flow solution, it has a number of drawbacks and rigorous numerical model simulations may be more useful. This relation includes a term for the radius of influence, which depends on factors such as the permeability of the porous medium, the extent of the ground surface cover, and the placement and geometry of the well screen. Thus, the radius of influence is not known a priori. They correctly point out that the solution for the extraction rate is not extremely sensitive to this parameter, however, the radius of influence does have a significant impact on well spacing and needs to be determined.

Effluent concentration estimation relations are presented for the ideal case discussed above, for scenarios involving liquid sources distributed asymmetrically about the extraction well, for flow above a zone of free product and for flow past a lower permeability lens that contains saturated vapours. Changes in vapour concentration with time are neglected and equilibrium is assumed. Again these expressions may provide useful first approximations to mass removal rates; however, they will likely always overstate the rate of removal. Although numerical transport modelling might give slightly better information, in light of the limitations on modelling, the best estimates of effluent concentration and mass removal rates will be obtained from field tests.

Transport During Extraction:
At present the simulation of transport during extraction is not very accurate. The main reasons for this are that channelling around finer-grained lenses is not readily accounted for and that kinetic effects appear to play a major role in partitioning between the aqueous and gaseous phases. Kinetic partitioning presents a serious problem because the parameters necessary for its description have not yet been quantified with any certainty. Thus, models that assume equilibrium partitioning will almost always overestimate removal rates. In addition, the multi-component nature of the pure product makes the source concentration behaviour very complex over time.

Watertable Drawdown:
Most vacuum extraction operations are accompanied by some form of watertable control to counter-act upwelling of the watertable and to expose contamination residing below the watertable. Analysis of watertable drawdown is performed in the usual way, except that the effects of decreased air pressure in the vicinity of the vacuum extraction well need to be accounted for. Superposition of the deviation in air pressure from atmospheric along the watertable on to the solution for watertable drawdown under ambient pressure conditions will give a good estimate of the net watertable drawdown that will be achieved.

8. Pilot Project Implementation

A small-scale pilot project must be performed in order to evaluate the applicability of the equipment and the chosen design. By altering design variables in the field, the chosen design may be further improved and the optimum system operating conditions maybe obtained.

The pilot project normally consists of a single extraction well placed in an area of significant contamination. Extraction rates and pressure drawdowns are altered and the response of the system is monitored. Under some circumstances the ground surface cover might also be modified. Monitoring should include measurement of subsurface pressure distributions (and so the radius of influence), effluent concentrations and subsurface concentrations. After an extended period of operation, a thorough site investigation should be undertaken to delineate changes in contaminant distribution. The field results of the pilot test should be compared to any numerical model simulations and, if necessary, additional simulations should be performed that incorporate information gained from the pilot test. After extended operation, mass removal rates may be extrapolated, with caution, into the future. This should only be done with the understanding that large decreases in removal rates are anticipated and that the effluent composition will change over time.

9. Full-scale Implementation

Following a successful pilot test, the vacuum extraction operation should be gradually expanded. Additional wells should be placed on an incremental basis to avoid unnecessary installations. Continual monitoring of results should be altered as deemed necessary for the most efficient removal of contaminants. When most of the residual has been removed, it might be prudent to investigate the benefits of pulsed operation in order to recover the greatest amount of dissolved contamination possible at the least cost.

10. Case Study Summaries

There are many case studies in the literature. Very few studies are documented in enough rigorous detail to fully evaluate the method or the results. Typically results are only given for pilot studies and time-to-cleanup is extrapolated from this data. Only a few selected case studies, along with some experimental studies, are reviewed here. The GASRep report by CH2M HILL (1990) contains a large number of summaries; duplication has been avoided where possible.

10.1 San Juan, Puerto Rico

Reference:

Agrelot, J.C., J.J. Malot and M.J. Visser, 1985. Vaccum: Defense system for groundwater contamination. NWWA Fifth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, Columbus, OH, May 21-24, pp. 485-493.

Overview:

Field application of vacuum extraction immediately following a massive carbon tetrachloride spill. Deep unsaturated zone comprised of clayey silt and karstic limestone. Very large mass of spilled contaminant recovered from low permeability material.

Observations:

15,000 gallons carbon tetrachloride released near San Juan, Puerto Rico. Karst aquifer at 300 feet. Field observation showed much of contaminant trapped in unsaturated zone. Unsaturated zone consists of thick silt-sand-clay layer over-lying limestone. "Permeability" of soils between 10^{-5} and 10^{-7} cm/sec.

Pilot test for vacuum extraction emplaced almost immediately. Extraction wells located in most contaminated zone between 20 m and 55 m depth. Initial drawdown of about 1 atmosphere with minimal air flow. Steady-state pressure distribution after 3 months with over 0.5 atmosphere drawdown at the well screen. Maximum radius of influence measured was about 3 metres.

Flow rates steadily increased until steady-state. Maximum recovery of about 100 kg/day. Effluent concentrations dropped over time. More than 70% of mass recovered in 30 months.

Conclusions:

Vacuum extraction successful for removal of volatile organics from low permeability unsaturated zone.

Comments:

Radius of influence very limited. Many wells necessary to treat contamination over a large area.

Possibility that fractures play a part in transport of air through the formation. Only bulk conductivity given. Probably little effect of moisture content in a relatively dry climate such as this.

10.2 Laboratory Experiments

Reference:

Benson, W.B., G.J. Farquhar, and E.A. McBean, 1989. Experiments with removal of volatile contaminants from soil from forced air venting. Proceedings, Environment Ontario 1989 Environmental Research Technology Transfer Conference, Toronto.

Overview:

Laboratory experiments in columns and boxes to evaluate equilibrium assumptions and effects of source emplacement heterogeneities during vacuum extraction. Numerical modelling of results.

Observations:

Experiments performed in moist Ottawa sand.

Different sized plugs of residual contamination placed in columns.

If source occupied full cross-sectional area, close to equilibrium concentrations observed for heptane, hexane and trichloroethylene. Equilibrium also observed if hexane mixed at less than residual saturation.

If source occupied only a portion of the column cross-sectional area, concentration is constant but less than saturation. Concentration not dependent on air flow rate.

Similar results for hexane placed in a box and vented.

Numerical model simulations show similar behaviour if boundary layer theory is used to describe transport into areas with no residual contamination.

Conclusions:

Equilibrium assumption is valid if air passes through zone of residual contamination. Less than equilibrium concentrations observed if part of zone is uncontaminated.

If geometry of contamination zone known, reasonable predictions may be made using boundary layer theory. However, geometry is likely to be unknown in true field situations.

10.3 Controlled Field-tests

Reference:

McClellan, R.D. and R.W. Gillham. 1990. Vapour extraction of trichloroethylene under controlled field conditions. Presented at, IAH Conference on Subsurface Contamination by Immiscible Liquids, April, Calgary.

Overview:

One-dimensional vacuum extraction of uniformly distributed residual TCE in a steel box driven into natural sands. Equilibrium concentrations when residual present; non-equilibrium when only dissolved contamination present.

Observations:

When residual present, effluent concentration at saturation for ambient subsurface conditions. Residence times as low as 5 minutes. Constant concentration for variable flow rates.

After residual removed, effluent concentrations over an order of magnitude less than saturation. Concentrations decreased when flow rate increased. Soil concentrations increased after blower turned off.

Long tail of low concentration after residual removed.

After 22,650 pore volumes effluent concentration of 0.9 ppmv. Soil gas concentration increased an order of magnitude in 19 hours after shutdown.

Removal efficiencies decreased by 20 times once residual removed. Continue to drop as dissolved phase concentrations decreased.

Conclusions:

Equilibrium between gas-phase and residual appears to occur.

Gas-phase and dissolved-phase not in equilibrium during advective flow of gases. Gas concentrations over an order of magnitude less than equilibrium.

Removal efficiencies greatly decreased in the absence of residual. With no residual, low flow rate and pulsed operation appears to be most efficient.

Comments:

Good confirmation of applicability of equilibrium assumptions.

Likely overstated removal efficiencies since residual was uniformly distributed throughout box. In "real-world", such uniform distributions do not occur and channelling will lead to lower observed concentrations.

10.4 Grovelands, Massachusetts Site

Reference:

Stinson, M.K., 1989. EPA SITE demonstration of the Terra Vac in situ vacuum extraction process in Groveland, Massachusetts. Journal of the Air and Waste Management Association, 39(8), pp. 1054-1062.

Overview:

Application of vacuum extraction technology, under the supervision of the EPA, to a site with chlorinated solvents present as free product. Extensive monitoring over eight weeks showed significant mass removal. Total cleanup predicted within 250 days.

Observations:

Site underlain by a layered sequence of fine- to medium-grained sands and coarse-grained sand and gravel separated by a 1 m thick clay layer. Water table at 8 m.

Extensive contamination by chlorinated solvents (primarily TCE).

Four extraction wells emplaced - each with riser pipes to screens in the upper and lower permeable sections. One extraction well plugged with silt during test. Four soil gas monitoring wells.

Plumbing insulated and heat traced to prevent freezing (performed in winter). Soil gas and bulk soil samples taken before, during and after.

Soil vacuum extracted for eight weeks. TCE concentrations drastically reduced (by 95%). Estimated 600 kg removed.

Large reduction in soil concentrations in clay near one extraction well. Same well that had highest pre-test concentrations. Only well where clay was contaminated prior to test.

Steady (exponential) decline in effluent concentration over time.

Soil concentrations calculated from effluent gas using Henry's law do not agree with measured soil concentrations (measured values generally one to two orders of magnitude too high).

Utility requirements low. Total costs between $10 and $150 per ton of remediated soil. Off-gas treatment drastically increased costs.

Conclusions:

Vacuum extraction is a viable technology that can fully remediate soils contaminated with volatile organic compounds. 250 days estimated for full cleanup. Process works for wide range of permeabilities, including clays.

Good correlation between recovery rates and time.
Reliable system.
Economical process.

Comments:

No mention of whether a ground surface cover was present or not.

Full details of geologic properties are not reported.

It seems quite possible that the clay that was contaminated, and cleaned up was fractured. This would account for both the contamination and cleanup.

Concentrations may have been drastically reduced; however, they were still in the ppmv range.

How long after stopping the extraction system were soil gas samples taken?

Was it long enough for equilibrium to be achieved?

Calculated soil concentrations would be expected to be low if only Henry's law used in calculation. Also need to consider sorption and possibility of free product being present.

The basis for claiming total cleanup is questionable. It assumes that rate of decline in removal rates remains constant. The test needs to be actually performed for 250 days to determine that the site can be totally cleaned in 250 days.

11. Summary

Vacuum extraction promises to be a useful in-situ technology for the remediation of unsaturated zone soils at ASGP's. It has the advantages of being relatively low cost and unobtrusive. It is ideally suited for the recovery of residual organic contaminants; its usefulness for remediating floating free-product and dissolved contamination may be a bit more limited due to low surface-to-volume ratios or due to kinetic mass transfer limitations.

Disadvantages include the likelihood that it is not suited to the remediation of organics in very low permeability environments. Non-equilibrium phase transfer effects may also prove to be a problem in achieving adequate remediation of dissolved and sorbed contaminants.

Despite its many advantages, and few disadvantages, vacuum extraction does appear to have limits. In most cases, the technology cannot fully remediate a site due to the very low source (and therefore effluent) concentrations that result after prolonged operation. This is especially true after most of the pure product has been removed and only dissolved/sorbed contamination remains. Alternative methods may need to be used to remove the remaining contamination. Also, the method is not efficient for the removal of semi-volatile contaminants since they do not significantly partition to the gas-phase. Since volatility is affected by temperature, subsurface temperatures may have a significant effect on mass removal and the efficiency of vacuum extraction systems.

I.3.2 IN-SITU SOIL WASHING

1. Introduction

Soil washing can be used to remove a variety of contaminants from the soil matrix by flushing with a washing fluid. The method can be applied either in-situ or ex-situ to remove organic (condensate and process chemicals), metals or inorganic compounds from soil. This section describes the in-situ procedure under typical ASGP conditions.

2. Description

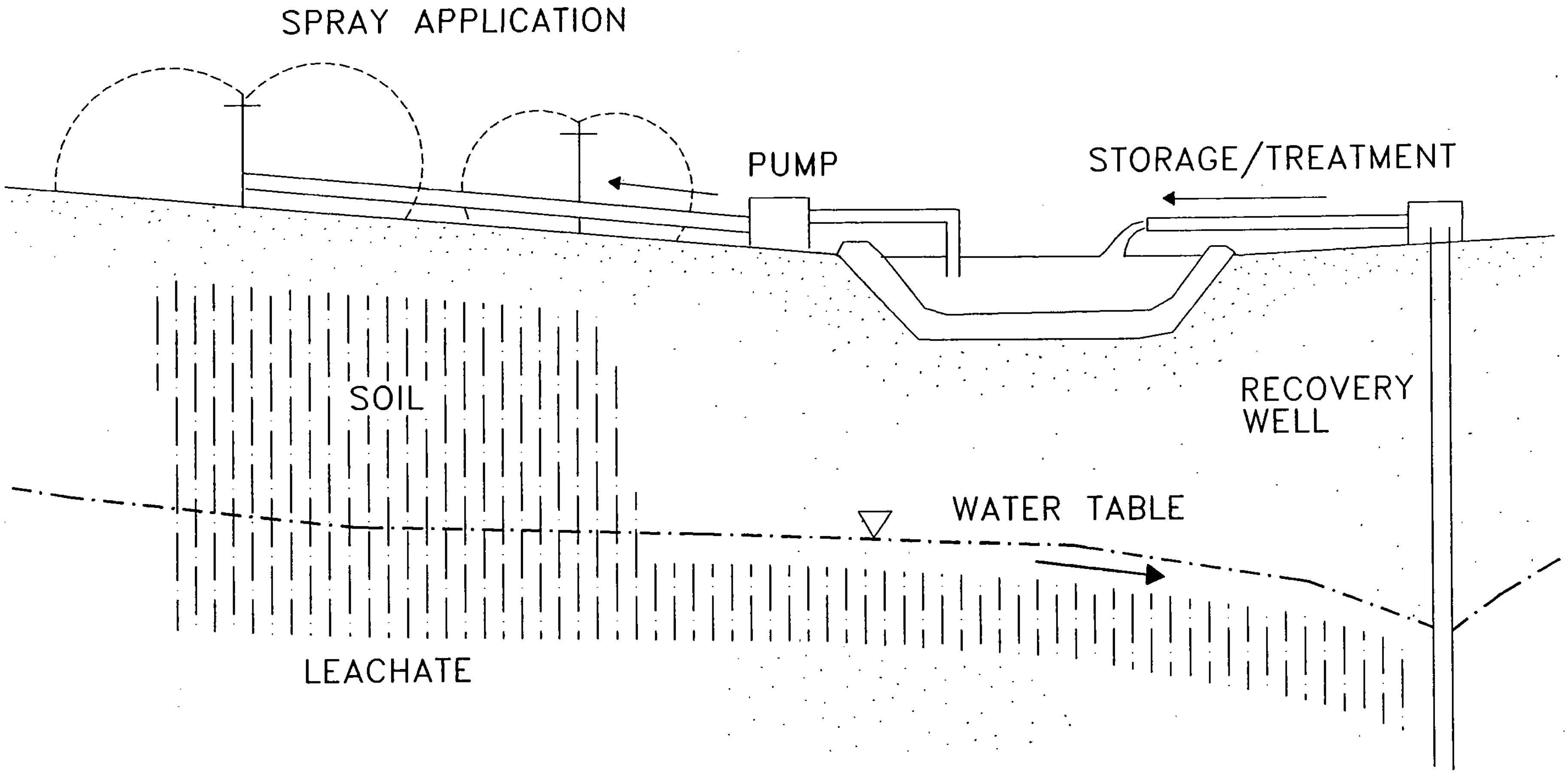
The in-situ application of soil washing involves passing a washing fluid through the soil to actively leach out target contaminants. The chemical properties of the washing fluid are chosen based on the types of contaminants present. Water is often chosen to leach out water-soluble organic and inorganic species. The washing fluid is applied to the surface by means of a spray-irrigation system, or possibly through specially built infiltration systems (designed to allow year-round operation). Leachate is then collected via a system of pumping wells designed to capture all leached contaminants, or via an existing pump-and-treat system. Figure I3.1 shows a typical in-situ soil washing system design.

3. Use of Additives

Additives may be used to enhance the effectiveness of flushing water. Additives may include detergents (which reduce interfacial tension of organic) and biodegradable surfactant for organic treatment, acids to mobilize metals, or alkalis such as NaOH and Na_4SiO_4. In some cases, soil washing can be accomplished using organic solvents such as methanol, hexane or triethylamine (TEA). For in-situ applications, however, solvents are not recommended and are not applicable to most ASGP contamination situations.

4. Costs

Little cost information was available for in-situ application of soil washing. However, assuming a pump-and-treat system had already been installed which was capable of collecting all leachate produced, additional costs would be associated only with the irrigation system and flushing fluid



(SOURCE: EPA, 1984a)

FIGURE 13.1
SCHEMATIC OF A SOIL WASHING
AND LEACHATE RECYCLING SYSTEM

preparations. If contaminants other than those presently being treated by the pump-and-treat system were to be used, additional treatment systems may also have to be mobilized. Based on these considerations, estimates of cost are extremely site specific.

5. Case Histories/References

Several case histories of ex-situ soil washing are presented in USEPA (1988). Richard and Trost (1986) evaluated a soil washing system for removal of gasoline components, diesels kerosene, tetrachloroethylene, and creosote coal tars. The system used biodegradable surfactant and alkalis to liberate organic from a clay, silt and sand soil. Soils were excavated and slurred with the washing fluid. Slurred soils were separated using froth-flotation systems, and cleaned soils returned to the site. The authors reported achieving the following removal efficiencies:

Toluene:	99.4%
Gasoline:	99.5%
Diesel:	99.7%
kerosene:	96.1%

The process is highly dependent on the make-up of the soil being treated. Higher clay and natural organic content resulted in lower removal efficiencies.

Additional case histories are reported in the Superfund Records of Decision (ROD) Summaries. These include use of surfactant at a chemical site to remove PCB's, chlorophenols and crude oil components from loamy soils (USEPA ROD, 1989). No cost or efficiency information was provided. In Amersfoot, Netherlands detergents and NaOH additives were used with water to clean soil contaminated with heavy metals, aromatic, solvents and hydrocarbons. The system components consisted of soil sorting/preparation equipment, a hydrolyser to remove low density organic material, hydrocyclones to remove fines, on a belt press dewatering system. No data on treatment efficiencies were provided. Capital costs for the system were $3 million. A similar system in the Netherlands used front-floation to remove contaminants from the slurry mixture, and used complete recycling of process water. Capital costs were estimated at $3 million also.

I.3.3 REMEDIATION OF SULPHUR-CONTAMINATED SOILS

1. Procedures

As outlined in the Technology Overview section of this report, there are two principal forms of elemental sulphur contamination around sour gas plants; (1) sulphur dusting as a result of operational sulphur handling facilities, and (2) sulphur contamination in soils that have been formerly overlain by sulphur blocks. Soils contaminated by sulphur dusting do not generally contain more than 1% elemental sulphur, while elemental sulphur concentrations in soils left after basepad recovery is complete can be as high as 15%.

Concentrations of sulphur in waste soils generated from the sulphur recovery process and in areas around the blocks can be even higher. These highly contaminated soils are often excavated and disposed of in landfills. The use of landfills for the disposal of this material is currently being questioned and alternative disposal options should be researched.

The remediation technology for sulphur-dusted soils is fairly well developed and has been practised for at least fifteen years. Based on annual soil monitoring programs around sour gas processing facilities in Alberta, which are required by Alberta Environment, liming recommendations are drawn up to neutralize the acidity generated by the oxidation of the elemental sulphur. Because the degree of contamination is usually low (<1%), calcium carbonate application methods are fairly well defined. The major issue in liming sulphur dusted soils is making sure that the limestone reaches the area that requires treatment.

Contaminated soils associated with sulphur blocks present a very different type of remediation problem. A number of potential alternatives are available to treat sulphur-contaminated waste soil which can contain levels of elemental sulphur ranging from 5 to 80%. At levels below 10% elemental sulphur, the contaminated areas can usually be remediated on-site. At levels above 80%, sulphur can be removed from the soil and sold as product. It is for levels of sulphur between 10% and 80% that alternatives need to be found.

One alternative to landfilling the contaminated material is to continue to treat the sulphur contaminated soils in situ, with limestone, using the 3.2:1 ratio. In the case of soils which are not severely contaminated (less than 5% sulphur), this may be the most efficient and viable technique despite the problems outlined in Section 4.3.1. Different approaches should be considered, however, for soils that have higher levels of contamination.

An in situ alternative for higher levels of elemental sulphur would be to actively encourage and maximize sulphur oxidation by the microorganisms present in the soil, by maintaining optimal soil conditions for their existence. This would involve the application of limestone and possibly nutrients. Surface and drainage water interceptors would be required to capture the acidic leachate produced from the site. This approach differs from the technology currently being practised, as it would attempt to maximize sulphur oxidation rather than trying to maintain a neutral soil pH. This technique has not yet been tried, but deserves consideration.

If the basepad area is not suitable for this type of process, (i.e., if the area has a high water table) then the contaminated material could potentially be excavated, crushed, and placed in a "bioreactor". This would permit sulphur oxidation to take place under a controlled environment. After the oxidation process is completed, the "clean" soil could be replaced onto the basepad site. This process would be applicable for soils containing a wide range of sulphur contamination.

A third alternative involves re-use of the sulphur within the agricultural industry. In Alberta, large agricultural areas could potentially benefit from sulphur additions. It has been estimated that 1.2 million hectares of improved cropland in central and northern Alberta are low in sulphur for cereal and grass production, while 2.5 million hectares in these areas may be sulphur deficient for oilseed and legume production. There exists a willingness within the farming community to take advantage of sulphur contaminated waste soil as a sulphur source. Agricultural demand for the material as a fertilizer would make landspreading an attractive method of recycling this waste.

Elemental sulphur has been shown to be an effective source of plant available sulphur (Janzen et al., 1987). This is especially true of finely divided elemental sulphur, which can begin to supply crop requirements within a year after application if it is well mixed with the soil. An additional benefit of this material is that it represents a residual source of crop-available sulphate. Larger pieces of sulphur would oxidize over subsequent seasons, thus providing a longer term source of crop available sulphur.

The effects of sulphur addition, and eventual oxidation, on soil pH will be dependent on the amount of sulphur added and the buffering capacity of the soil. As an indication of the amount of material required for a given change in pH, consider a one hectare furrow slice, 15 cm deep, in a medium-fine textured Chernozem soil. As a general guideline, 0.5 to 1 tonne/hectare of elemental sulphur will lower soil pH by 0.5 to 1 unit. Assuming that the sulphur contaminated soil contains 20% elemental sulphur, 5 tonnes of material would lower the pH by 0.5 to 1 unit. Higher loading rates could be achieved with the addition of limestone to control excess acidity generated by the oxidation of larger amounts of elemental sulphur. Care must be taken in determining rates of limestone application as high quantities of limestone can cause various physical and chemical soil problems.

A potential drawback to landspreading this waste is the addition of the subsoil fractions that are included in this material. Addition of subsoil fractions to topsoil may be detrimental to the soil texture and structure of some soils, depending on the application rates. Given the relatively low application rates of the waste material, addition of sub-soil fractions may be a limiting factor only in very fine textured soils and the material may be a valuable amendment in coarse textured soils.

Another potential agricultural use of sulphur contaminated soil would be as a pH amendment. In Alberta, although alkalinity is not a widespread problem, small pockets of alkaline soils exist. The benefits of lowering soil pH closer to neutrality are numerous. They include: (1) increased availability of most plant nutrients; (2) improved nitrogen and phosphorus cycling; and, (3) reduced soil conductivity (Sonntag and Leggett, in prep.).

Sulphur contaminated soil has the potential to be used as a less expensive method of lowering soil pH, compared to the addition of pure elemental sulphur. Bole(1986) indicated that acidification with elemental sulphur may improve certain soil characteristics in irrigated, calcareous Solonetzic soils. Interest in obtaining sulphur contaminated soil has also been expressed by some specialty crop producers in western Canada. It is thought that the waste could provide a cost-effective means of adjusting soil pH for acid-loving crops, such as blueberries.

One last alternative currently being investigated is the potential use of cement kiln dust in lieu of limestone as a neutralizing agent on sulphur contaminated soil. Cement kiln dust is a by-product of the cement manufacturing process and is currently landfilled. It may prove to be an acceptable and less costly amendment than limestone.

In the past five to ten years, a wide range of sulphur concentrations have been left in the soil, but the current provincial guidelines state that no more than 4% elemental sulphur can be left in soils (H. Regier, 1991, pers. comm.). Although this criteria will improve the reclamation success on former basepad sites, it also means that material containing more than 4% and less than 80% has been and continues to be trucked to landfills. Efforts in the development of alternative treatment technologies should be directed towards soils that are contaminated with these levels of sulphur.

2. Costs

Costs associated with reclaiming soils in situ, by the application of limestone in a 3.2:1 ratio, depend on a number of factors such as the level of sulphur left in the soil, site accessibility and size, and year of treatment. Based on three case histories, Leggett and England (1990) estimated that reclamation costs ranged from $3000 to $7000/hectare during the first year of the program. Costs fell to approximately $2000 to $3000/hectare by the third year.

The other alternatives presented are only conceptual at this point and, as such, there is no available cost data. Experimental field trials would have to be run for these alternatives to determine their feasibility.

A primary cost associated with attempting to maximize the oxidation of sulphur would be the installation of surface water and leachate collection systems. This cost would depend on the size and geographical characteristics of the site. In addition to this initial expenditure, it is estimated that annual reclamation costs would be approximately $25,000/year or $7500/hectare, based on a 3.4 hectare site. These costs would likely drop after the first two to three years of treatment. If a pilot "bioreactor" was to be designed and tested, costs would be significantly higher and would likely have to include the cost of a means of reducing the sulphur particle size, such as crushing.

A principal cost of using sulphur contaminated waste as an amendment in the agricultural industry would be the adaptation and maintenance of a crusher and/or grinder and a shaker/screener machine to ensure that a reasonably consistent product could be produced. This equipment could be developed cooperatively and moved from site to site. It is estimated that a pilot system could be developed to produce 500 tonnes of product, with an average sulphur particle size of 5 mm, for $85,000 to $100,000. The other major costs associated with this alternative would be the time spent producing the product, trucking charges associated with hauling it to the appropriate area, and the cost of spreading the product. It is estimated that, for every 0.5 tonnes of elemental sulphur spread above the initial application rate of 0.5 to 1 tonne of elemental sulphur, it would cost approximately $100/hectare to apply the appropriate amount of limestone.

Cement kiln dust would likely be available at a very low purchase price. Therefore, if it was proven useful in the neutralization of sulphur contaminated soil, the principal cost associated with its use would likely be transportation to the site and application.

3. Clean-up Efficiency

Clean-up efficiency of most of the alternatives described is difficult to measure. Unlike clean-up strategies for other contaminants, the reclamation of soil contaminated with sulphur does not usually involve the removal of the sulphur from the soil. The process which will result in the least amount of sulphur remaining in the soil in the shortest time frame would be the maximization of the elemental sulphur oxidation rates. The use of a "bioreactor" for small batches of soil, if feasible, would likely result in the most complete removal of elemental sulphur from contaminated soil.

4. Case Histories

There are a number of ongoing projects in Alberta involving the reclamation of soil that has been formerly overlain by a sulphur basepad and block. Leggett and England (1990) have documented three case histories. Some general observations from those sites have been noted. The first of these is that elemental sulphur levels across a site are highly variable. Although the average levels for a site are low, the range of values can be quite wide. Without sampling on a very small scale grid, it is difficult to accurately determine elemental sulphur levels. Because of the variability in sulphur levels, repeated liming and seeding operations are required to treat areas that continue to not support growth.

Secondly, some site preparation is generally required as part of the reclamation program. This includes landscaping in order to improve site drainage and rock-picking. It is important that acidic materials not be buried during landscaping. It is most efficient to leave the sulphur contaminated soil on the surface where limestone can be easily mixed with it. Thirdly, the areas that are re-acidifying and not supporting plant growth generally exist around the perimeter of where the sulphur block was located and where piles of sulphur contaminated material, remelt pits or equipment were located during basepad recovery operations.

Finally, the methods used for seeding and the types of seeds used are crucial to the success of the program. Finally, as the reclamation programs progress, a shift in focus has evolved. Once the initial site assessments are made and limestone has been applied a sufficient number of times, there is a shift from managing soil pH levels to the long term development and maintenance of adequate soil structure needed for agricultural production.

5. Design and Implementation Criteria

Application of limestone using the 3.2:1 ratio is fairly well understood for soils which have elemental sulphur concentrations below 5%, although there are still problems noted with this type of approach in the 4 to 5% elemental sulphur range. Refinements to the process would include the use of a limestone source that has minimal levels of magnesium carbonate and more precision in the control of application rates.

The principal factor that needs to be considered in the maximization of oxidation rates is whether this type of approach is operationally feasible. A well controlled, field based feasibility study will be required to determine the potential merits of this approach. Results of this study will yield the criteria that need to be taken into account in the design and implementation of a system that will encourage maximum elemental sulphur oxidation rates.

A major design criteria for the re-use of waste soils contaminated with elemental sulphur will be the development of machinery and procedures that can be used to produce a reasonably consistent product which can be used by the agricultural industry. Field trials will also be required to assess the effects of a variety of product application rates on crop production and levels of elemental sulphur and sulphate-sulphur in soils.

The feasibility of using cement kiln dust as an alternative neutralizing agent will depend on its chemical composition. Field trials will be required to determine its effectiveness compared to limestone.

6. Discussion

Soils contaminated with elemental sulphur have been reclaimed in Alberta for the last fifteen years. The technology involved in applying limestone to soils that contain less than 5% elemental sulphur is relatively well understood. Currently, soils that contain more than 5% and less than 80% are often landfilled. The costs and potential environmental concerns associated with placing sulphur contaminated material in landfills, coupled with the decreased numbers of landfills that will accept this type of waste, has prompted concern for how to effectively handle the waste.

In 1990, there were approximately 800,000 tonnes of contaminated sulphur associated with operational sulphur facilities (Sonntag and Leggett, in prep.). Remediation of soils contaminated with elemental sulphur will be ongoing in Alberta for many years. The timely development of environmentally sound, innovative technologies will ensure the safe disposal of this material without incurring ongoing liabilities for materials placed in landfills.

I.3.4 SOILS BIOTREATMENT

1. General Requirements

The successful bioremediation of soils and groundwater requires: 1) adequate oxygen level, 2) modest amounts of mineral nutrients, (eg. nitrogen and phosphorus), 3) pH reasonably near neutrality and 4) intimate contact between the organisms (indigenous and/or inoculated) and the contaminant.

1.1 Oxygen

Most of the organisms that have demonstrated significant capabilities in the degradation of organic contaminants are aerobic organisms, thus the strong requirement for oxygen. The oxygen is most often supplied by the atmosphere, however when treatment goes on in atmospheric oxygen limited situations, oxygen may be supplied indirectly through the addition of hydrogen peroxide (H_2O_2) which will decompose into oxygen (O_2) and water (H_2O). A limited number of organisms, some of which have proven degradation activity, can use other electron acceptors as an alternative to oxygen and therefore can continue to metabolize contaminants in the absence of free oxygen if given nitrate (NO_3) or sulphate (SO_4).

1.2 Mineral Nutrients

Microbes require certain mineral nutrients in order to use the organic contaminants as food and energy sources. If these mineral nutrients are lacking in the soil or groundwater to be remediated, they must be supplemented to allow biodegradation to take place. Remembering from the previous paragraph that some microbes can substitute NO_3 or SO_4 for atmospheric oxygen, it is useful to add some nitrogen, if required, in the NO_3 form.

1.3 pH

Bacterial metabolism of organic contaminants is most effective in the 6.5 to 7.5 pH range. Contaminated soils or groundwater which will be biologically remediated can be adjusted to this range if it is feasible. When fungi are used in the remediation process, a lower pH material may be desirable, however many fungi have the capability to produce a desirable microenvironment pH in the immediate vicinity of their vegetative stage, regardless of the overall pH of the surrounding soil. In most remediation cases, pH does not play an important role, because more often than not the pH range is adequate for biological activity.

1.4 Contaminant/Microbe Contact

Perhaps the most difficult of the biotreatment requirements to meet is getting the microbes in contact with the contaminant (especially in the case of soil bioremediation). Much of the preliminary metabolism of bacteria and fungi involves secretion of enzymes into their immediate environment in order to breakdown complex molecules into more manageable sizes which may be transported into the cells for continued metabolism. Secreted enzymes have a limited zone of influence, therefore it is crucial that the contaminant be close enough to the microbial cell to be effectively impacted by degradation enzymes or imported into the cells directly if possible. This contact is usually the limiting factor in in situ bioremediations because of poor soil permeability, particularly when inoculated organisms are utilized. In the case of groundwater remediation, the flow levels through the above ground treatment system must be adjusted to insure that the microbes see enough nutrients (contaminants) to maintain the growth of a significant and healthy population.

The decision whether or not to use inoculated organisms to enhance biodegradation activities is often hotly debated. Many naturally occurring (biogenic) complex organics have been degraded successfully by indigenous microbial populations for years, however more recent xenobiotic (man made) organics have had less time to prompt the evolution of highly efficient degradation pathways in the microbial population as a whole. Although environmental researchers continue to find evidence that naturally occurring microbes are often able to degrade some xenobiotics, the presupposition that organisms with such capabilities will be universally present in most environments is questionable.

The fundamental approach to biodegradation requires providing optimal conditions for microbial metabolisms to take place. These conditions will enhance any indigenous microbes which may possess the desirable degradative capabilities, however those same conditions will enhance the activity of introduced microbes known to possess these same desirable capabilities. Economic considerations notwithstanding, it makes good sense to add capable organisms, however this may add another degree of complexity to the remediation process depending upon the site configuration. When only indigenous microbes are being stimulated, only soluble chemicals must traverse the soil matrix to get to the ensconced microbes already present, however when external microbes are added, particulate cells, albeit of small size, must traverse the soil matrix and those travels can be affected by a myriad of factors.

2. Solid-Phase Biotreatment

Solid-phase biotreatment relies on principles established by agriculture to biocycle vegetation left over from crop stands. The conditions for biodegradation are enhanced by regular tilling of the soil and by the addition of nutrients and water. One type of solid-phase biotreatment that has been used for years by the oil industry to treat oily sludge and other refinery wastes is land farming. Another "dry" solid-phase treatment technology just now under development is the dry mix treatment. A brief description of each technique will follow.

2.1 Dry Mix Treatment

A treatment technology is emerging which attempts to increase the speed of solid-phase biotreatment. The treatment is containerized, which gives better control of emissions and leachate, but may limit throughput. The dry mix technique is depicted in Figure I3.2. The actual treatment apparatus looks very similar to a concrete truck mixing body with a central axis through the center of the chamber. Soil is loaded into the mixing chamber and water, nutrients and inoculum are added from a sprayer at the core of the axis support. The addition of liquid is monitored carefully to maintain moist but not sloppy conditions, therefore this does not qualify as slurry treatment.

The advantages of such a treatment system are many. Aeration is adequate, and usually free (atmospheric), although further oxygen can be added. Mixing is thorough, which in turn enhances all of the important parameters for successful biotreatment. Since the treatment is optimized, the time frame for treatment may be shortened dramatically.

Conversely, the disadvantages are many. The cost for equipment purchase of lease may be significant, although it may not be much more than most land farm site preparations. The soil may need to be derocked to reduce equipment wear. The actual remediation time will be limited by the size and number of treatment chambers (usually <100 tons).

Although the dry mix treatment technique is not widespread at this time, the advantages appear to outweigh the disadvantages, furthermore the cost should not be much above a well managed landfarm operation.

2.2 Slurry-Phase Biotreatment

In slurry-phase biotreatment, contaminated soils are treated as an aqueous slurry in either an in-ground slurry cell or mobile bioreactors. The early development of slurry technology as a treatment method was described as liquid/solids treatment and was usually done in the excavation site from which the contaminants were removed. A general overview of slurry-phase biotreatment is depicted in Figure I3.3. Because slurry technology utilized propellers or blowers to keep the soil in suspension to optimize biological activity, rocks and other debris must be removed. After derocking the soil is placed into the slurry reactor. The excavated pits that are converted into slurry reactors require preparation similar to land farm sites. The bottom is usually compacted and an HDPE liner with heat welded seams is used to line the pit. The pit is filled with water to which nutrients and inoculum have been added. The soil is loaded into the slurry pit in batch amounts. When a batch is finished, the slurry is pumped to a device designed to separate the soil from the water. The recovered water can be returned to the slurry pit as makeup water, which is helpful since it already contains some "veteran" microbes which have become acclimated to the surroundings, including the contaminant. The final disposition of the soil depends of the degree of "clean" and local regulations.

A variation of the slurry pit technology is in use along the gulf coast of the United States where it is used to remediate contaminated sediments from the bottom of oil well production pits. Blowers are used to dislodge the bottom sediment in the ponds, and aerators keep the slurry in suspension while nutrients and inoculum hasten the degradation of the oily sludge. After the slurry meets acceptable limits, the slurry is treated with a coagulate to drop out the solids. The water is pumped off to an appropriate destination and the pond sides are pushed in to bury the treated sludge.

Mobile bioreactors have all but replaced the slurry pit technique. Aeration and mixing are usually better, air emission control is more manageable, and sophisticated plumbing allows easier transport of the slurried soil. Once treatment is complete, the slurry is dewatered as described above and the water is returned as makeup water, treated further by wastewater techniques or discharged to the environment. The slurry bioreactors operate very efficiently and can reduce biodegradation times considerably.

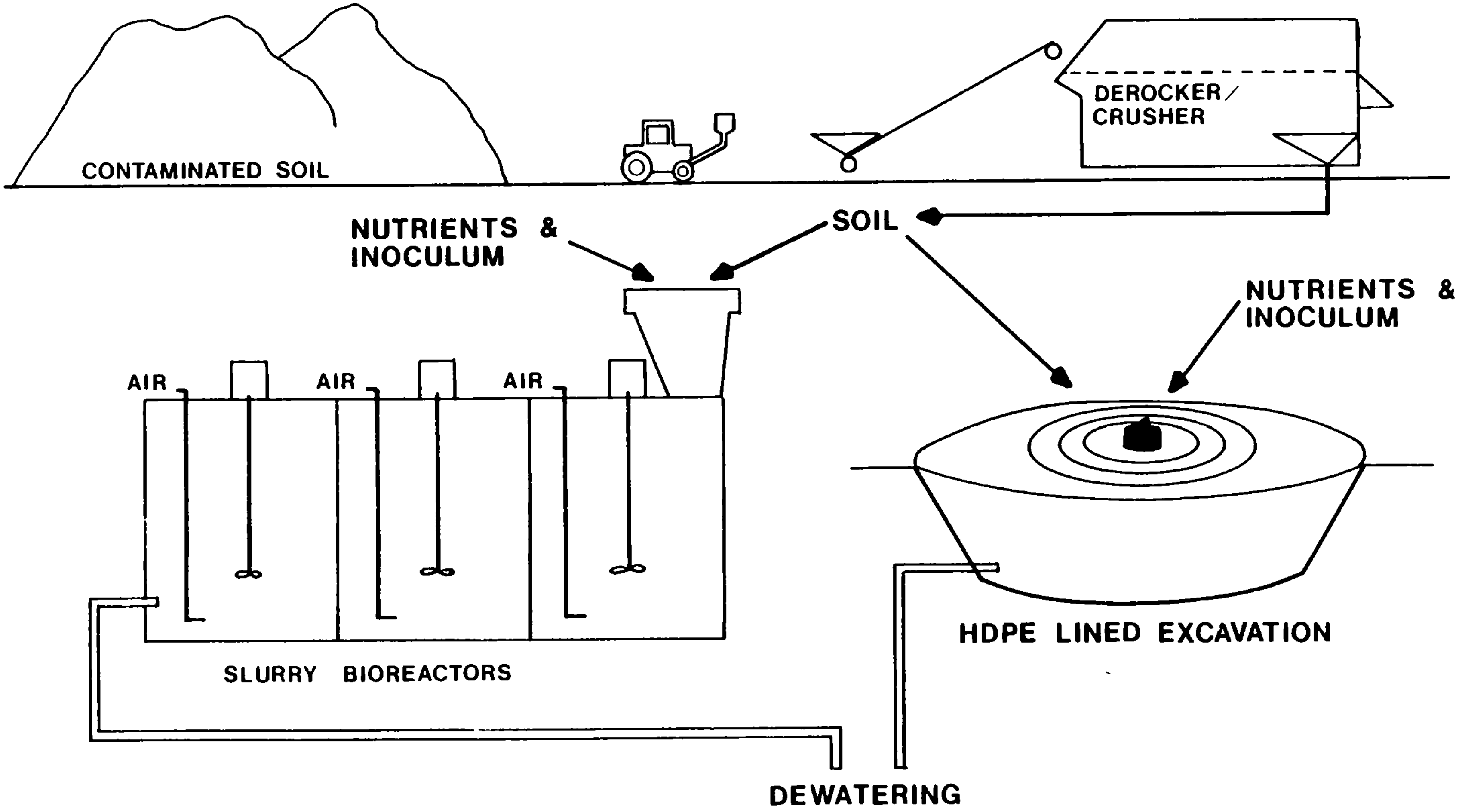


FIGURE 13.3
SLURRY-PHASE BIOTREATMENT
AFTER FARLEY, 1990

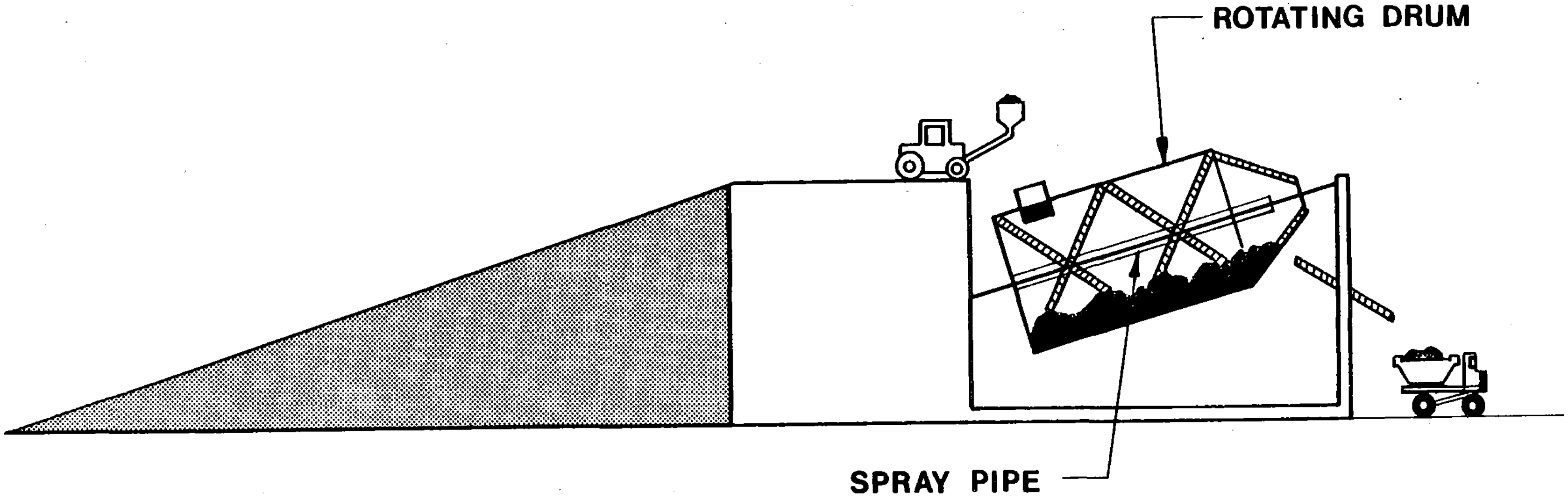


FIGURE 13.2
SOLID-PHASE
DRY MIX TREATMENT
AFTER FARLEY, 1990