COMMITTEE ON
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MODERN SOCIETY

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NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater

PHASE II
FINAL REPORT

APPENDIX IV — PROJECT SUMMARIES

Number 219

NORTH ATLANTIC TREATY ORGANIZATION

CONTENTS

Final Report
NATO/CCMS Pilot Study

Appendix IV — Project Summaries

Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater
(Phase II)

June 1998

NOTICE

This report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (USEPA). The document was funded by USEPA's Technology Innovation Office under the direction of Michael Kosakowski (Work Assignment Manager). Michael A. Smith of Berkhamsted, U.K., was the principal editor for the Pilot Study reports. The Final Report was edited and produced by Environmental Management Support, Inc., of Silver Spring, Maryland, under USEPA contract 68-W6-0014. Mention of trade names or specific applications does not imply endorsement or acceptance by USEPA.

PREFACE

The *Phase II Final Report* has been printed in two volumes. This volume contains Appendix IV — Project Summaries. The other volume (EPA 542-R-98-001a) contains Chapters 1-12 and Appendices I, II, III, and V.

The project summaries were prepared by a team comprising:

Paul Bardos	R3 Environmental Technologies Ltd, U.K.
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While the authors have made their best to provide accurate summaries, limited material was available for some of the projects. The summaries were edited and prepared for publication by Mike Smith and Environmental Management Support, Inc.

The starting point for preparation was a set of one-page summaries prepared for the U.K. Department of the Environment:

> Ian Martin and Paul Bardos. *Summary Report on the NATO/CCMS Pilot Study on Research, Development and Evaluation of Remedial Action Technologies for Contaminated Soil and Groundwater: Technical Status May 1996*, Centre for Research into the Built Environment, Nottingham Trent University, Nottingham, U.K., June 1996.

Table 1 is provided as a cross reference for the chapters in which the projects are discussed.

Table 1: Discussion of Projects by Chapters

Project	**Chapter**						
	4	**5**	**6**	**7**	**8**	**9**	**10**
1	✓						✓
2	✓						
3	✓						
4	✓						
5	*project withdrawn*						
6	✓		✓				
7				✓			
8			✓				
9	✓						✓
10		✓					✓
11			✓				
12	✓						
13				✓			✓
14		✓					
15	✓		✓				✓
16	✓						
17		✓					
18	✓						
19		✓		✓			✓
20				✓			
21				✓			
22						✓	
23	✓						
24		✓	✓				✓
25			✓				
26		✓	✓				✓
27		✓					✓
28			✓				
29					✓		
30		✓					
31		✓	✓				✓
32		✓					✓
33		✓					✓
34					✓		
35	✓		✓				

Project	**Chapter**						
	4	**5**	**6**	**7**	**8**	**9**	**10**
36		✓	✓				✓
37	✓						
38		✓					
39						✓	
40		✓					
41	✓						
42	✓						✓
43	✓		✓				
44		✓					
45	*replication of project 15*						
46	*project withdrawn*						
47	✓	✓					✓
48	*project withdrawn*						
49			✓				
50						✓	
51						✓	
52	*to be addressed in the Phase III report*						
53						✓	
54			✓				
55						✓	
56						✓	

Project No. 1

Trial of Air Sparging of a Petroleum-Contaminated Aquifer

Technical Contact:	Country:	Project Status:
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1. INTRODUCTION

Leaking pipework under a petrol station located in Adelaide, South Australia, led to contamination of the soil and groundwater with petroleum hydrocarbons (up to 2,100 mg/L), benzene (up to 1.5 mg/L), and xylene (up to 20 mg/L). Contamination occurred as dissolved, adsorbed, vapor, and minor free phases. The adsorbed phase occurred as a relatively thin and widespread zone above the water table at a depth of 7.5 m below ground surface. Based on initial investigations, it was believed that a remediation strategy involving soil vapor extraction with air sparging below the water table would be appropriate. Air sparging involves injection of air beneath the water table. As the air bubbles rise, volatilization of dissolved contaminants occurs from the groundwater into the vapor phase. Airflow carries the vapors to the soil surface. This vapor phase may then be extracted through soil vapor extraction wells. This project presents the results of air sparging and soil vapor extraction trials undertaken between September 1993 and April 1994 (no formal final report was provided for this project).

2. FIELD TRIALS

Three air sparging trials were conducted in total to determine the effectiveness of air sparging in combination with vapor extraction. In the first trial, the three vapor extraction wells were arranged in a triangle with an injection well at the center. Vacuum levels of 15-20 kPa resulted in an interpreted air permeability of 0.1×10^{-6} cm^2. Injecting air resulted in increased extraction of hydrocarbon vapor from the extraction wells.

In the second trial, vacuum extraction with and without air sparging was conducted. It was reported that the total concentrations of hydrocarbons and BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), as extracted by the vacuum wells, were substantially increased as much as a factor of 10 by the injection of air into the sparging well. Further, injection of air into one vapor extraction well while the other two wells were operating with vacuum also resulted in a much greater rate of hydrocarbon extraction than when the wells operated without any air injection. The system was estimated to be extracting between 1-3 kg of hydrocarbons per day.

A third trial, involving a longer operating time, was conducted to achieve a better indication of the effectiveness of air sparging and soil vapor extraction as a suitable combined remediation option. Detailed sampling of stack emissions and groundwater for hydrocarbons and oxygen was conducted throughout the remedial operation. Gaseous oxygen levels were used as an indication of microbial activity. The third trial highlighted that while air sparging substantially increased the amount of volatile hydrocarbons that can be removed by vapor extraction in the short term, the rate slowed dramatically within just a few days. It was considered by the authors that this reduction in extraction efficiency was due to the removal of hydrocarbons from the immediate vicinity of the borehole and through the more permeable soil layers being exhausted. The groundwater concentration of hydrocarbons in the sparging well was reduced to below detection levels during the sparging trial. Concentrations of BTEX at wells up to 3 m from the sparging well were also significantly reduced although petroleum hydrocarbon remained in the water. It was concluded that the zone of influence of air sparging in terms of positive remedial effects on groundwater chemistry appeared in this test to be restricted to a zone between 3 and 9 meters from the sparging well. Monitoring of the soil oxygen concentration during sparging indicated that levels of oxygen were increased from 10.5% to as much as 21% by sparging. The authors concluded that only a small percentage of this was being consumed by soil bacteria.

3. CONCLUSIONS

The study found that air sparging substantially increases the amount of volatile hydrocarbons that can be removed by vapor extraction from soil and groundwater. However, the zone of influence and rate of recovery of volatile compounds are site specific. The rate of extraction slowed dramatically after only a few days operation due to a combination of low site permeability and the creation of preferential flow pathways. Air sparging also produced mounding of the water table around the sparge well which may have resulted in the migration of the contaminants outside the influence of the extraction wells. Based on the results of the trials and given the interbedded sand and clay stratigraphy at the site clean-up to risk based standards were seen as difficult to achieve. The recommended remedial approach at the site therefore included extraction of groundwater at the source of the plume to reduce and contain the bulk of the contaminant mass, to employ soil vapor extraction with water table drawdown and *in situ* bioremediation rather than air sparging.

Project No. 2

Bioremediation of Petrochemicals Following a Major Fire

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1. INTRODUCTION

In August 1991, a major fire at the Coode Island petrochemical facility, near Melbourne, Australia, resulted in the widespread contamination of soil and groundwater with phenol, benzene, and acrylonitrile from damaged storage tanks. A site investigation in October 1991 found phenol concentrations as high as 24,000 mg/kg in near-surface soils and 700 mg/L in the groundwater. The concentrations of volatile organic compounds (VOCs) found in soils and groundwater included up to 200 mg/L of methyl ethyl ketone (MEK), 100 mg/L acrylonitrile, and 50 mg/L benzene. In addition, considerable quantities of contaminated stormwater and water used to fight the original fire were stored on-site.

The biodegradation of phenol has been well documented, and while it is possible to degrade phenolic compounds, the inherent biotoxicity of the chemical is believed to significantly inhibit its practical remediation. This Pilot Study project reported on the development of an *in situ* bioremediation approach to remediate and manage the site.

2. LABORATORY AND FIELD TRIALS

A preliminary characterization of the contaminated sandy clay soil showed that it was very low in available nitrogen and phosphorus and had a low microbial population especially phenol degraders. Bench-scale studies using 8 kg soil samples showed that significant phenol toxicity to soil micro-organisms occurred at concentrations above 4000 mg/kg. Results of a simple slurry bioreactor showed that rapid phenol degradation was possible with the addition of a microbial inoculant and nutrient source. It was concluded by the authors that such a system would be impractical for treating the whole site. Therefore a model system was constructed that was comprised of a percolation column (containing 1 kg of soil) and a 1-L continuously-stirred tank bioreactor. This process was designed to take advantage of the water solubility of phenol by transferring the contaminant into an aqueous solution that could be treated in a conventional bioreactor. Results showed that soil phenol concentrations in the soil column could be reduced by up to 90% in 14 days with up to 50% of the phenol degraded *in situ*. The flushing-biotreatment system was further investigated at field-scale.

A field study using 100 tonnes of soil from selected hot-spots (containing up to 2,000 mg/kg phenol) was initiated in March 1992. The principal objectives of the study were to determine the effectiveness of the treatment system at field-scale; to determine the fate of contaminants; and to identify significant factors likely to limit treatment effectiveness. After four months of operation, the microbial population of the soil was found to have increased from an initial 10^5 microbes per gram to more than 10^7 microbes per gram, which included up to 50% phenol degraders. Phenol concentrations declined steadily to a mean value of 120 mg/kg after 45 weeks. A mass balance analysis showed that nearly 85% of the phenol had been degraded *in situ* with only 10% flushed from the soil to the bioreactor. This result had not been expected since the dissolved oxygen concentration of the irrigation water had been relatively low. Mixing of the soil pile had occurred twice during the trial and results showed that degradation rates were significantly increased after each mixing. The authors speculated that this may be due to the introduction of air into the soil and the creation of new macropores and fresh soil surfaces for microbial colonization.

3. FULL-SCALE IMPLEMENTATION

The program of remediation for this site, developed in the aftermath of the fire, included disposal of contaminated fire-, storm- and groundwaters to local treatment works for aerobic lagoon biotreatment; UV-peroxidation of firewater and stormwater; and soil vapor extraction and sparging of VOCs; and *in situ* bioremediation of phenol-contaminated soil using a soil flushing process. Hot spots were excavated and treated in a pond on site as a slurry. The Pilot Study report only reviewed the soil bioremediation efforts.

Full-scale implementation of *in situ* bioremediation was integrated with treatment of the large volume of ground-, storm- and firewater stored on site. A damaged storage tank (60 m^3) was refurbished to serve as a bioreactor to treat the large volume of phenol-contaminated water generated by soil flushing on the site. Recovered process water was treated in this bioreactor and used in turn as irrigation water for further soil flushing.

Treatment of 1,600 m^2 of soil by soil flushing commenced in early May 1993 with addition of gypsum and 10 kg controlled release nutrients, plowing to 0.5 m to break up compacted surface soil, followed by regular irrigation with treated water. Gypsum was found to reduce the ped size of the massive clayey soil structure and therefore to increase treatment accessibility. Phenol was expected either to be mobilized from the vadose zone into groundwater and recovered for treatment above ground, or biodegraded *in situ* with the utilization of whatever electron acceptors were available.

Phenol concentrations decreased rapidly in the top 0.6 m of soil after treatment commenced. Monitoring of soil microbiology during November 1993 showed high concentrations of phenol degraders (up to $5x10^7$ per gram) were being maintained. Two months after *in situ* treatment began, phenol concentrations in the groundwater rose to 1,000 mg/L, and then gradually declined to about 1 mg/L during early 1994. It is claimed that recent results show that phenol hot spots (to a depth of 2.5 m) have smaller microbial populations than in other treatment areas. This supports the findings of the treatability study, which predicted the biotoxicity of phenol towards the site microbiology.

Remediation of the remaining 3,000 m^2 commenced in September 1993.

4. CONCLUSIONS

It was concluded that the *in situ* flushing-bioremediation process has substantially reduced the total soil contamination burden at the site and as a consequence greatly reduced the potential migration of contamination off-site. No economic data were reported to the Pilot Study, nor was final disposition of the site remediation effort. However, attainment of <1 mg/L of phenol in the groundwater throughout 1994 met the remediation criterion for this medium.

Project No. 3

Bioclogging of Aquifers for Containment and Remediation of Organic Contaminants

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1. INTRODUCTION

Recent studies have suggested a correlation between increased microbial biomass density in aquifer materials and reduced saturated hydraulic conductivity of aquifers. This process may be termed “bioclogging.” In the field, aquifer clogging during *in situ* bioremediation has been recognized as a potential operational nuisance during treatment. Bioclogging is believed to result from several different processes such as the production of low-solubility gaseous end products, the excretion of extra-cellular polysaccharide, and the increase in bacterial cell numbers.

The aim of this Pilot Study project was to investigate the potential benefits of bioclogging to provide a temporary partial subsurface containment of contaminated areas, and to act as a site for enhanced biodegradation of organic contaminants. The field site chosen for bioclogging tests is located at Largs North on the eastern side of LeFevre Peninsula near Adelaide, Australia. Gasoline contamination detected in 1987 resulted from a fractured pipeline. Contamination at the site consisted of petroleum hydrocarbons in soil and groundwater. The hydrocarbons (diesel fuel and gasoline) may both have come from the fractured pipeline. Dissolved BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) existed to a maximum of 2.5 meters below the water table.

The intention was to investigate both the benefits of containment and biodegradation through laboratory and field studies of an aquifer contaminated with BTEX. An important aspect was identification of indigenous strains of polysaccharide-producing bacteria at the field site and determination of the optimal conditions (nutrient and carbon source requirements) for polysaccharide production. A final step was to be determination of how these identified conditions can be recreated under field conditions.

The interim report presented the results of the laboratory studies and preliminary characterization of the field site up until February 1996. Field studies focused on collecting geotechnical, geochemical, and hydrogeological site data. No bioclogging in the field had yet been attempted. No additional information on the progress of the study had been provided by the time this summary was prepared in November 1997.

This work was funded by South Australian Department of Environment and Natural Resources Office of the Environment Protection Authority, BP Australia Ltd., Minenco and CRA.

2. LABORATORY STUDIES

The objectives of the preliminary laboratory studies were:

1) to establish whether polysaccharide-producing bacteria were present at the field site;

2) to determine the hydrogeochemical conditions required for polysaccharide production; and

3) to determine the carbon and nutrient requirements for optimal polysaccharide production by indigenous bacteria.

Other researchers had reported that:

1) Bacteria produce polysaccharides in the presence of excess sources of carbon and energy, and a deficit of nutrients; and

2) The conversion of a carbon source to extra-cellular polysaccharides often requires a nitrogen source.

Initial laboratory studies investigated the optimal C:N ratio (using glucose and ammonium additives) for polysaccharide-production for a known bacterium *Xanthomonas campestris* in liquid culture. No significant interaction between glucose and ammonium additives was observed. Glucose concentration alone had the most significant effect on polysaccharide and biomass production.

Subsequent bench-scale studies examined the effect of aerobic and anaerobic (with nitrate as the electron acceptor) conditions on polysaccharide-production by indigenous bacteria collected from the field site. Substantial differences were observed in polysaccharide production in soil slurry cultures using aquifer material from different depths. For the aquifer material from 4.0-5.0 m below ground, aerobic cultures with atmospheric oxygen produced the highest polysaccharide concentrations. Tests of the oxidation of aquifer materials by hydrogen peroxide (as a potential mode of oxygen delivery) suggested that high concentrations of the reagent and dissolved oxygen were unlikely to persist in the aquifer due to matrix reactions (*e.g.*, oxidation of the aquifer material). Overall, samples with hydrogen peroxide did not attain high polysaccharide concentrations and in the long term, performed only marginally better than control samples. In both aerobic and anaerobic cultures, there was an observed loss of polysaccharides after their concentrations had reached a maximum. The study recommended that further investigation of these loss mechanisms was warranted since overcoming them could greatly enhance the potential for bioclogging. Polysaccharide production under anaerobic conditions for the aquifer material from 1.8 - 2.8 m below ground was much greater than for the material from 4.0 - 5.0 m under both aerobic and anaerobic conditions. The study suggested that a further investigation of polysaccharide production with aquifer material depth would be useful to identify the matrix and ecological properties which affect polysaccharide production.

The effect of polysaccharide production on hydraulic conductivity was investigated using a test column of 0.5 m length by 0.08 m diameter, packed with dry aquifer material (from depth of 1.8 - 2.8 m) to a bulk density of 1.6 Mg/m^3. The test leachate (containing growth medium, glucose, and sodium nitrate) was passed through the column at a constant volume flux density of 0.11 m^3/day. Results showed that polysaccharide production can lead to a significant (at least one order of magnitude) reduction in column hydraulic conductivity. The study also suggested that after initial delivery of amendments (e.g., nutrients) the reduction in hydraulic conductivity appeared to be long-lived. The most rapid change in K_{sat} occurred in the first 18 hours of the experiment, with further slow reductions after 50 hours.

3. GROUNDWATER MODELING

Groundwater modeling activities were aimed at helping identify the critical hydrological parameters in the Largs North aquifer system; developing models and data sets to describe how the unperturbed aquifer behaves; and designing and optimizing the system for delivering the bioclogging amendment solution.

A two-dimensional plan model investigated pumping strategies for delivering the amendment solution to promote bioclogging. The model considered two pumping wells, one for injecting the amendment solution and one for extracting groundwater. For the computer simulation, the two wells were set 10 meters apart, and the pumping and injection rates were equal. Desired pumping rates should be large enough to push water 10 meters through the aquifer in no more than 5 days, the time during which clogging occurs. Results from this modeling showed that pumping over the 10 meter distance would not significantly disturb the existing BTEX plumes at the site. Unfortunately, the time taken to deliver the amendments over this distance was longer than 5 days. Uncertainty in the K_{sat} value used in the model leads to uncertainties in the predicted time to deliver the bioclogging amendment. Obtaining better estimates in the field for K_{sat} will improve on the model's ability to provide acceptable pumping strategies.

4. FIELD TRIAL

The objectives in bioclogging at the field site were to produce a pilot-scale barrier of reduced hydraulic conductivity 10 m long by at least 2 m wide and extending to 4 m below the water table. The goals were to stimulate this barrier by a once-off addition of the appropriate amendment solution and be able to determine the effect on hydraulic conductivity. Challenges in designing a cost-effective system to deliver amendments include: efficiently targeting the specified volume of the aquifer; delivering the amendments before clogging takes place; overcoming effects of injecting a dense fluid into the aquifer; and minimizing disturbance to existing contamination.

A 3-dimensional, density-coupled groundwater flow and transport simulation package was used to design the amendment emplacement strategy and to assess techniques for measuring changes in hydraulic conductivity. Results of modeling showed a linear, balanced injection/extraction scheme with five wells would deliver the amendment solution to the desired volume of the aquifer most efficiently. A total pumping rate of 50 m^3/day would ensure delivery between wells after 1-2 days, after which a short reversal of the scheme will give a near rectangular distribution of amendment. Density-coupled simulations showed that it may be impossible to limit the amendment solution to the top half of the aquifer given the density of the amendment solution. Relatively large dispersivities were used to maintain stability in the simulations, which may lead to underestimations of the effect of density-driven flows. On the other hand, anisotropy and stratification within the aquifer may limit density-driven vertical migration.

An amendment solution containing a glucose carbon source, NO_3^- electron acceptor, and NH_4^+ as a nitrogen source was successfully added at the field site. Although the injection was designed to deliver the amendment to a maximum of 4 m below the water table, there was evidence that the greater density caused the amendment to move to the bottom of the aquifer. This was in accord with model predictions. Microorganisms within the aquifer were stimulated by the addition of the amendment. The most obvious manifestation was gas evolution within the aquifer for a period of several days. Cores taken from the site also showed increases in the amount of polysaccharides in the aquifer and groundwater samples showed utilization of the glucose carbon source. Pump tests specially designed to evaluate the change in hydraulic conductivity in that part of the aquifer targeted by the amendment showed a reduction by an order of magnitude. However, this reduction did not persist, and the reduction in hydraulic conductivity was only about a factor three a month after the addition of the amendment. Evaluation of results from the field trial are continuing.

5. REFERENCE

Johnston, Colin D., et al., *Studies of bioclogging for containment and remediation of organic contaminants*, Centre for Groundwater Studies, CSIRO Land and Water, Perth, Western Australia, November 1997.

Project No. 4

Remediation of Methyl Ethyl Ketone Contaminated Soil and Groundwater

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1. INTRODUCTION

Significant soil and groundwater contamination has occurred on the site of an operational oil terminal in Melbourne, Australia. The petroleum storage center has operated as a distribution center for approximately 65 years with subsurface contamination resulting from minor "operational spills" and specific instances of pipeline and storage tank leaks. This Pilot Study project reports on the development and implementation of the site remedial strategy, which incorporates *in situ* recovery of free product and contaminant vapors. Full-scale remediation started in mid 1994 and was still in progress in February 1996 when the Interim Report was prepared. No additional information was available in November 1997.

2. THE SITE

The site geology consists of a thin layer of clay and reworked soil (up to 3 m deep) overlying basaltic lava flows to a depth of 30 m. The basalt is an extremely heterogenous host aquifer (water table at depth of 12 m) comprising discontinuous very low to moderately permeable layers with occasional interconnecting joints and fractures. Extensive hydraulic testing at the site indicated a range of two orders of magnitude in local permeability. Contamination resulted in development of three free product contaminant plumes covering an area of over 7 ha. These plumes included a lubrication oil plume up to 2 m thick, a methyl ethyl ketone (MEK) plume with concentrations over 10,000 mg/L, and a mixed plume containing BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), petrol, turpentine, and kerosene.

3. REMEDIATION SYSTEM DESIGN AND COMMISSIONING

The initial remedial strategy consisted of a combination of pump-and-treat for free phase product, and soil vapor extraction for volatile and adsorbed contamination. Since contaminant distribution can be distinguished as three separate plumes, the remediation plan addressed separate recovery and treatment systems for each of them. Over 50 boreholes were sunk on site with specially designed "top loading" pumps to recover floating free product. These modified displacement pumps use compressed air to pump the recovered fluid to the surface. Injection of "clean" water around each plume was used to force free product towards the recovery wells. The pumping operations for all three recovery schemes were controlled by a computer using a Programmable Logic Controller which enabled constant monitoring and control of each borehole (*e.g.*, turning pumps on/off and varying pumping rates). The project managers had concluded that due to the size of the project, standard air control systems for each borehole would be impractical. Fifteen vapor extraction boreholes were nominated for the site and were integrated with the boreholes constructed for free product recovery. An advantage of this approach is that vapor recovery takes place almost simultaneously with the creation of unsaturated ground from de-watering. The vacuum generated at each well in the range of 10-20 kPa.

Recovered vapor, free product and groundwater were treated at the surface in a "treatment compound" comprising the following stages or processes:

1) Oil water separation via three oil water separators;

2) Groundwater treatment via an heated air stripper (operating at 20-60°C). MEK recovery ranges from 40-90%, which is lower than anticipated from its volatility (MEK partitions strongly into water);

3) Transfer to a treated wastewater storage tank that is drained or pumped to a municipal sewer (consent concentration of 300 mg/L MEK); and

4) A thermal destruction system (using a methane gas carrier to ensure full product combustion) to treat all hydrocarbon waste streams from the air stripper as well as the vacuum manifold system. When operated at 760°C and a retention time of 0.5 seconds, the system ensured total destruction of hydrocarbons. Emissions met the 10 mg hydrocarbon/Nm^3 objective.

At the air stripper, influent groundwater contained an average of 3,000 mg/L MEK, but this value sometimes peaked at 5,000 mg/L. In contrast, the stripped water often contained MEK at well below the discharge criterion of 300 mg/L. Off-gases leaving the stripper had an average MEK concentration of 1,500 mg/Nm^3. However, water leaving the air stripper contained around 10 ppm benzene. This residual benzene would normally be removed by an air stripper. The solubility of benzene in MEK, another contaminant in the extracted groundwater, may explain why higher than expected levels of benzene remain in air-stripped groundwater.

1,2 dichloroethene was found in both recovered liquid hydrocarbon and in stack emissions. Concentrations in the stack gases were well below the threshold limit value (TLV).

4. FULL-SCALE REMEDIATION

Full-scale remediation began in August 1994 with the initial remediation phase characterized by the recovery of a large volume of free product with an associated high concentration of dissolved contamination. Remediation was on-going through February 1996 with average rate of groundwater recovery in the order of 50,000 L/day. By the end of 1995, over 25 million liters of groundwater had been recovered and treated including 0.5% free product. Total recovered hydrocarbons could be categorized as free phase product (113,000 L), dissolved phase (61,000 L), and vapor phase (70,000 L).

Since operation commenced, the rate of hydrocarbon recovery declined significantly over time. *In situ* bioremediation was being considered in 1996 to treat the residual contamination within the basalt aquifer after pumping operations were completed.

Project No. 5

In Situ/On-Site Bioremediation of Industrial Soil Contaminated with Organic Pollutants: Elimination of Soil Toxicity with DARAMEND®

Technical Contact:	**Country:** Austria	**Project Status:** Project withdrawn

Project No. 6

In Situ/On-Site Bioremediation of Industrial Soils Contaminated with Organic Pollutants: Elimination of Soil Toxicity with DARAMEND®

Technical Contact:	Country:	Project Status:	
Dr. Alan G. Seech GRACE Bioremediation Technologies 3451 Erindale Station Road P.O. Box 3060, Station A Mississauga, Ontario L5A 3T5 tel: (905) 272-7427 fax: (905) 272-7472 E-mail: gracebio@fox.nstn.ca	Canada	Accepted by study Interim Reports Final Report	1992 1993 -1995 1996

1. BACKGROUND

The key to consistent achievement of effective bioremediation is understanding the complex relationships that exist among the soil matrix, contaminants, and the microorganisms degrading the contaminants. A fundamental point often neglected in soil remediation is that all the biological processes take place in water held against gravity within soil pores. Water-holding capacities of contaminated and uncontaminated soil from the same sites are often dramatically different—hydrocarbon contamination often coats part or all of a soil agglomerate with oil, thereby rendering the soil hydrophobic. The hydrocarbons close the soil pores and coat nutrient-providing soil organic matter, limiting the supply of nutrients, oxygen, and biologically available water. As a result, even in soil containing microorganisms with an enzymatic capacity to degrade the target compound, the rate of bioremediation may be too slow to be useful. DARAMEND® bioremediation was developed to overcome these limitations naturally and cost-effectively.

The DARAMEND® process was demonstrated in an *ex situ* application on dredgings from Hamilton Harbour (see also Project 10), and *in situ* at a fuel-contaminated military site in the far north at Alert, Northwest Territories. The U.S. Environmental Protection Agency audited a full-scale demonstration at the Domtar Wood Preserving facility in Trenton, Ontario, under the auspices of the Superfund Innovative Technology Evaluation (SITE) program. At the Domtar site, initial chlorophenol concentrations of up to 276 mg/kg and total polynuclear aromatic hydrocarbons (PAHs) from 577 to 2068 mg/kg were encountered. Both *in situ* and *ex situ* applications of the technology were demonstrated at Domtar.

2. TECHNICAL CONCEPT

DARAMEND® bioremediation is based upon careful microbial husbandry, creating optimal conditions for the destruction of organic pollutants by indigenous microorganisms. Organic amendments are homogeneously incorporated into the contaminated soil to supply biologically available water, nitrogen, phosphorous, micronutrients, and oxygen to support biodegradation of the pollutants. Concurrently, the amendments reduce the acute toxicity of the soil's aqueous phase by transiently adsorbing pollutants, and providing surfaces for microbial adhesion and development of biofilms. The composition of DARAMEND® organic amendments is soil-specific and based upon the results of a thorough physical and chemical characterization (*e.g.*, texture, moisture retention, C:N ratio, nutrient profile, and identity and concentrations of target compound) and treatability studies of the soil or waste to be treated.

3. PROCESS DESCRIPTION

The DARAMEND® process is suitable for *ex situ* or *in situ* remediation of soils, and can also be used to treat sediments *ex situ* following dewatering. Key features include:

- Addition of proprietary solid-phase organic amendments with soil-specific particle size, nutrient profile, and nutrient release kinetics;
- Incorporation of amendments and aeration of soil using specialized tillage equipment; and

- Strict control of soil moisture content.

Soil amendments are introduced at 1-5% by weight using conventional agricultural equipment (tractor, tiller, *etc.*), followed by regular tilling and irrigation. For *ex situ* application, the soil or sediment to be treated is transported to the treatment area and homogenized by tilling with a power take-off driven rotary tiller. Homogenization is necessary both to distribute the organic amendments uniformly and to minimize the small regions of very high contaminant concentration, which may especially inhibit biological detoxification. *In situ*, roto-tilling equipment is used for homogenization. Soils and sediments can be treated as deeply as effective tillage can be achieved.

During the remediation process, soil moisture content is maintained within a narrow range by drip irrigation. Excess moisture can limit diffusion of oxygen through the soil matrix to microbially active microsites where biodegradation occurs. Conversely, if soil moisture falls below the optimum range, biodegradation can be inhibited by an inadequate supply of biologically available water. Optimal soil moisture contents are determined during the treatability studies.

Soil undergoing treatment is tilled approximately once every two weeks. Soil moisture is monitored gravimetrically in the 0-200 mm zone and in the 200+ mm zone. The shallower depth is where most of the moisture flux occurs due to microbial utilization, evaporation, and gravitative flow. Deeper samples indicate accumulation of excess water. The two moisture samples together are used to determine irrigation requirements.

4. RESULTS

Data indicate that DARAMEND® bioremediation provides a significant improvement in bioremediation rates, as compared to standard bioremediation practice (*i.e.*, inorganic nutrients, irrigation, and tillage). Conversion of added ^{14}C-labeled phenanthrene to $^{14}CO_2$ verifies that DARAMEND® bioremediation promotes complete biodegradation of the target compound. Impressive removals and toxicity reductions were achieved. In addition, soils previously thought to be so highly contaminated that bioremediation was impossible, were successfully treated.

Hamilton Harbour sediments were treated for 46 days, which resulted in an 84% reduction in total PAH, from 1,146 mg/kg to 187 mg/kg. Sediments which had been pretreated with $CaNO_3$ showed a 72% reduction. A control plot (tillage only) showed a 40% reduction. Recalcitrant PAHs were effectively treated with DARAMEND®. Benzo(a)anthracene reduction was 60%, 58%, and 30%, respectively, for non-pretreated, pretreated, and control sediment.

At the Alert site, the most northern permanently-inhabited settlement in the world, the pilot *in situ* plots were covered by temporary greenhouses to control soil moisture content and to increase soil temperatures through solar heating. Three DARAMEND® formulations were tested, and after 10 days, 89%, 62%, and 75% reductions in total petroleum hydrocarbons (TPH) were observed. No TPH reduction was observed in the control plot.

After 254 days in the *ex situ* demonstration at the Domtar site, PAHs were shown to be reduced 94%, from 1,710 mg/kg to 98 mg/kg; chlorophenols 96%, from 352 mg/kg to 13.6 mg/kg; and TPH by 87%. The control area showed a reduction of 41% in PAHs, but no reduction in either chlorinated phenols or TPH. Toxicity, as measured by earthworm mortality and seed germination, was eliminated or greatly reduced only in the treated soil.

Grace Bioremediation Technologies has provided a composite results table (see Table 1) based on numerous treatability studies and demonstrations.

5. COSTS

Detailed economic analysis can be found in the SITE report (3), based upon the experience of the Domtar demonstration. The cost estimates assume a contamination scenario similar to the Domtar case, and neglect extremes of geology, geography, and climate. Estimates also do not include the cost of treatability studies.

The unit cost of using DARAMEND® technology was estimated to be U.S.\$92/m^3 (\$70/yd^3) for *in situ* application and \$140/m^3 (\$108/yd^3) for the *ex situ* case. This estimate includes the cost of disposal of residual oversized particles screened out during pretreatment and deemed to be hazardous. Without this cost, unit costs decreased to \$46/m^3 (\$35/yd^3) for *in situ* application and \$96/m^3 (\$73/yd^3) for *ex situ* application. Either way, *in situ* application is more

Table 1: Initial and intermediate concentrations of a variety of contaminants in soil and/or sediment treated using DARAMEND® technology.

Parameter	Initial Conc.[1] (mg/kg)	Final Conc.[1,2] (mg/kg)	Destruction Efficiency (%)	Treatment Time (days)
Hydrocarbons				
PAHs	16,886	1,546	91	241
PAHs	2,029	100	95	211
PAHs	1,442	36	98	240
Heavy Oil	100,367	4,260	96	293
Heavy Oil	42,033	1,875	95	343
Hydraulic Oil	35,000	5,400	85	204
Fuel Oil	41,000	2,700	93	225
TPH	8,700	35	>99	182
Phthalates				
Total Phthalates	4,350	26	99	130
DOP[3]	2,700	19	99	130
DNOP[4]	1,640	7.1	>99	130
Nitroaromatics				
TNT	7,200	19	>99	125
Pesticides/Herbicides				
Metolachlor™	139	4.0	97	187
Total CPs	180	1.5	99	109
PCP	11	1.5	86	61
PCP	155	0.8	99	109
PCP	702	4.0	>99	345
Total OCPs	249	87	65	13
Total OCPs	2,125	404	81	147
Total OCPs	354	164	54	28
p,p-DDT	66	1.1	98	13
p,p-DDT	684	1.9	>99	147
p,p-DDT	124	14	89	28
Dieldrin™	128	38	70	147
Toxaphene™	1,050	244	77	147
Toxaphene™	40	1.9	97	142

1. Rounded to the nearest 0.1 for concentrations >0 and <10
   1 for concentrations >10 and <1,000
   10 for concentrations >1,000
2. These values do not necessarily represent final residual levels; however, they provide an indication of remediation rates.
3. bis(2-ethylhexyl)phthalate
4. di-n-octylphthalate

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economical, although *ex situ* treatment is more robust to higher toxicity or contaminant levels. The Domtar demonstration produced no leachate, so effluent treatment or disposal was not a cost factor.

Higher *ex situ* cost was due to increased materials required to construct the pad, sand buffer, and greenhouse and to the additional labor required to build the initial *ex situ* plot and to clear treated soils and spread fresh soils for the batchwise operation.

6. SAFETY

The DARAMEND® process poses no inherent dangers to workers or the community. Hazardous material safety procedures appropriate to the target contaminants apply, as well as appropriate safety precautions for the machinery used.

7. CONCLUSIONS

DARAMEND® is an effective treatment technology for remediating soil or sediment highly contaminated with a variety of organic materials. Total contamination and toxicity can be reduced to target levels in a reasonable amount of time, and the treated soil regains a high degree of usefulness as fill or topsoil.

8. REFERENCES

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Project No. 7

Demonstration of Thermal Gas-phase Reduction Process

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1. INTRODUCTION

The ECO-LOGIC thermo-chemical process employs hydrogen to chemically reduce organic compounds to mineral components at temperatures of about 900°C. Soils are treated with the aid of a novel thermal desorber involving use of a molten metal bath. A technology demonstration at the Middleground Landfill in Bay City, Michigan, USA was conducted in 1992 under the U.S. Environmental Protection Agency's (USEPA) Superfund Innovative Technology Evaluation (SITE) Program with partial funding from the Canadian and Ontario Governments(1,2). The wastes processed were oily-PCB contaminated water, high-strength PCB oils, and PCB-contaminated soil.

2. BACKGROUND

The Middleground Landfill accepted municipal wastes for approximately 40 years. A 1991 investigation indicated elevated levels in groundwater of trichloroethene, polychlorinated biphenyls (PCBs), 1,2-dichloroethene, methylene chloride, toluene and ethylbenzene. The groundwater also contained lesser concentrations of benzidine, benzene, vinyl chloride, chlorobenzene, polycyclic aromatic hydrocarbons (PAHs), lindane, dieldrin, chlordane, and DDT metabolites.

3. TECHNICAL CONCEPT

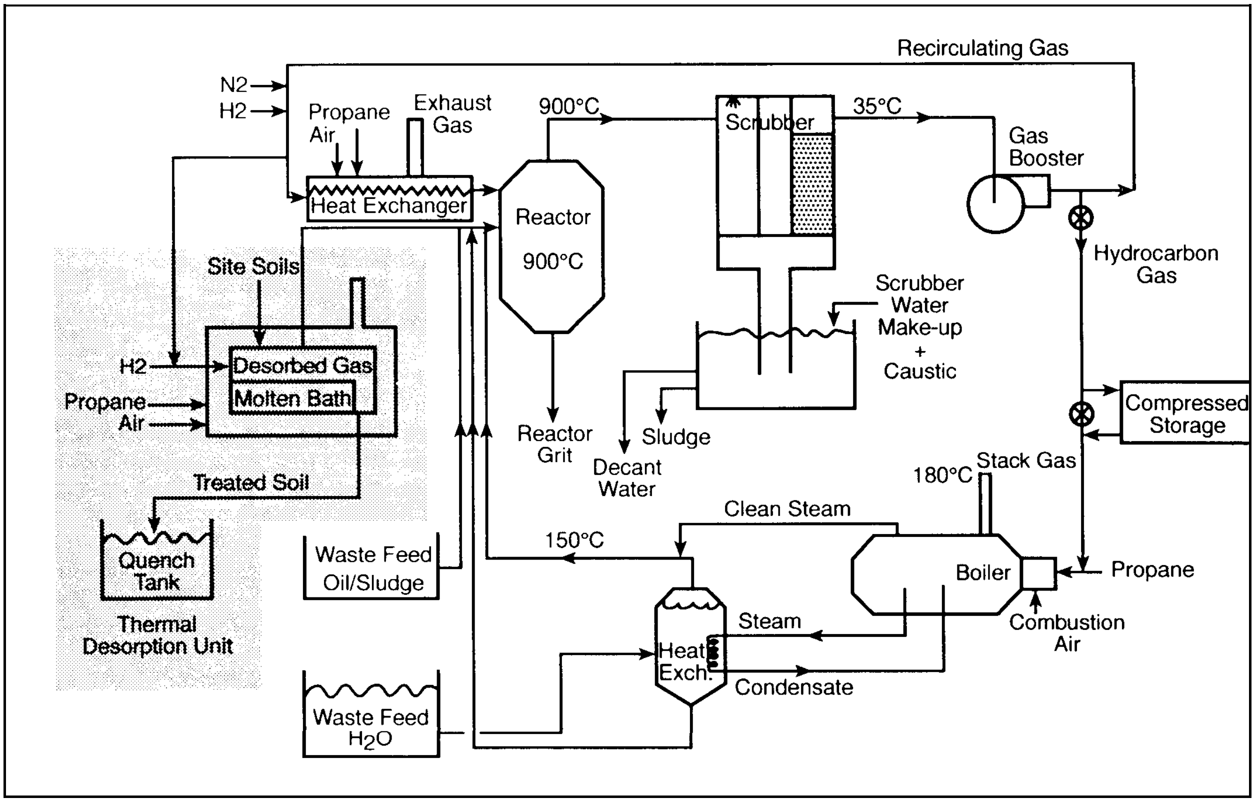
The ECO-LOGIC thermo-chemical process employs hydrogen to chemically reduce organic compounds to mineral components at temperatures of 850°C or above at near ambient pressure. Chlorinated hydrocarbons, such as PCBs and polychlorinated dibenzo-p-dioxins, are converted to methane and hydrogen chloride, while non-chlorinated organic compounds, such as PAHs, are reduced to methane and ethene. (Incomplete reduction and combustion in the system may result in benzene formation; as noted below residual benzene was a problem in the demonstration project). Ethene formed by contaminant breakdown may undergo additional conversion to methane. Methane reacts with water vapor to form hydrogen and carbon monoxide. The hydrogen chloride is scrubbed out in a caustic soda scrubber downstream of the processor. The reformed process gas can then be recirculated in the system or used as fuel in various stages of the process. The absence of free oxygen in the reactor inhibits dioxin (PCCD) and furan (PCDF) formation. The process employs automatic monitoring to maintain optimum operating conditions.

The reactor feed is dependent upon the soil or waste being treated. Aqueous streams, such as groundwater, are preheated in a vaporizer using steam from a boiler and fired by propane and/or process gas, before injection. When soils or sediments are to be processed, they are first pretreated in a linked thermal desorption unit (TDU). In this novel unit, the soil or sediment is floated on a bath of molten tin. Volatilized contaminants are sent to the reactor through a separate port. Contaminated solids, such as transformer parts, can be handled in sequencing batch vaporizer chambers. The process is shown schematically in Figure 1.

4. THE DEMONSTRATION REACTOR

The demonstration-scale reactor (Figure 2) was 2 m in diameter and 3 m tall, mounted on a 15 m drop-deck trailer. The trailer carried a scrubber system, a recirculation gas system, and an electrical control, center. A second trailer held a propane boiler, a waste preheating vessel, and a waste storage tank. ECOLOGIC designed the process to treat

Figure 1: Reactor and Thermal Desorption Unit Schematic Diagram



3.6 tonnes/day[a] of waste oil, 9.1 tonnes/day of wastewater, and 22.7 tonnes/day of soil, depending on the nature of the contaminants, their degree of chlorination, and their water content.

For the demonstration, a heat exchanger evaporated contaminated aqueous feedstock to form steam and a concentrated liquor. Atomizing nozzles sprayed the heated liquor with associated particulates into the reactor. The PCB-rich oil was injected directly into the reactor through a separate set of atomizing nozzles. Compressed hydrogen-rich recirculation gas passed through a gas-fired heat exchanger and entered the top of the reactor tangentially. The tangential entry swirled the fluids to provide effective mixing. As indicated in Figure 2, the swirling mixture traveled downwards in the annulus formed by the reactor wall and the central ceramic-coated steel tube, past electrically heated silicon carbide elements. These elements heated the mixture to 900°C. At the bottom of the reactor, the mixture entered the central tube and flowed upwards to the reactor outlet. The reduction reactions occurred as the gases traveled from the reactor inlets to the scrubber inlet.

Heavy particulates dropped out of the gas stream and collected at the base of the reactor in a grit box. The gas leaving the reactor was scrubbed using a caustic alkaline wet scrubber (pH 9), which removes steam, particulates, and gases such as hydrogen chloride. Ninety-five percent of the exhaust gases (reheated to 500°C) were recycled, with an additional 5% being used as a supplementary fuel for the propane-fired boiler. The boiler produced steam used in the heat exchanger and burned the reformed gas. The exhaust from this boiler was the only source of air emissions from the process.

5. THERMAL DESORPTION UNIT (TDU)

The TDU desorbs organics at 500-600°C into a hydrogen-rich carrier gas from soil supported on a molten tin bath. Hydrogen and tin are used because they do not react. Tin offers favorable properties such as high density, low vapor pressure, high surface tension (which means it does not “wet” the soil and enter into pores), high thermal

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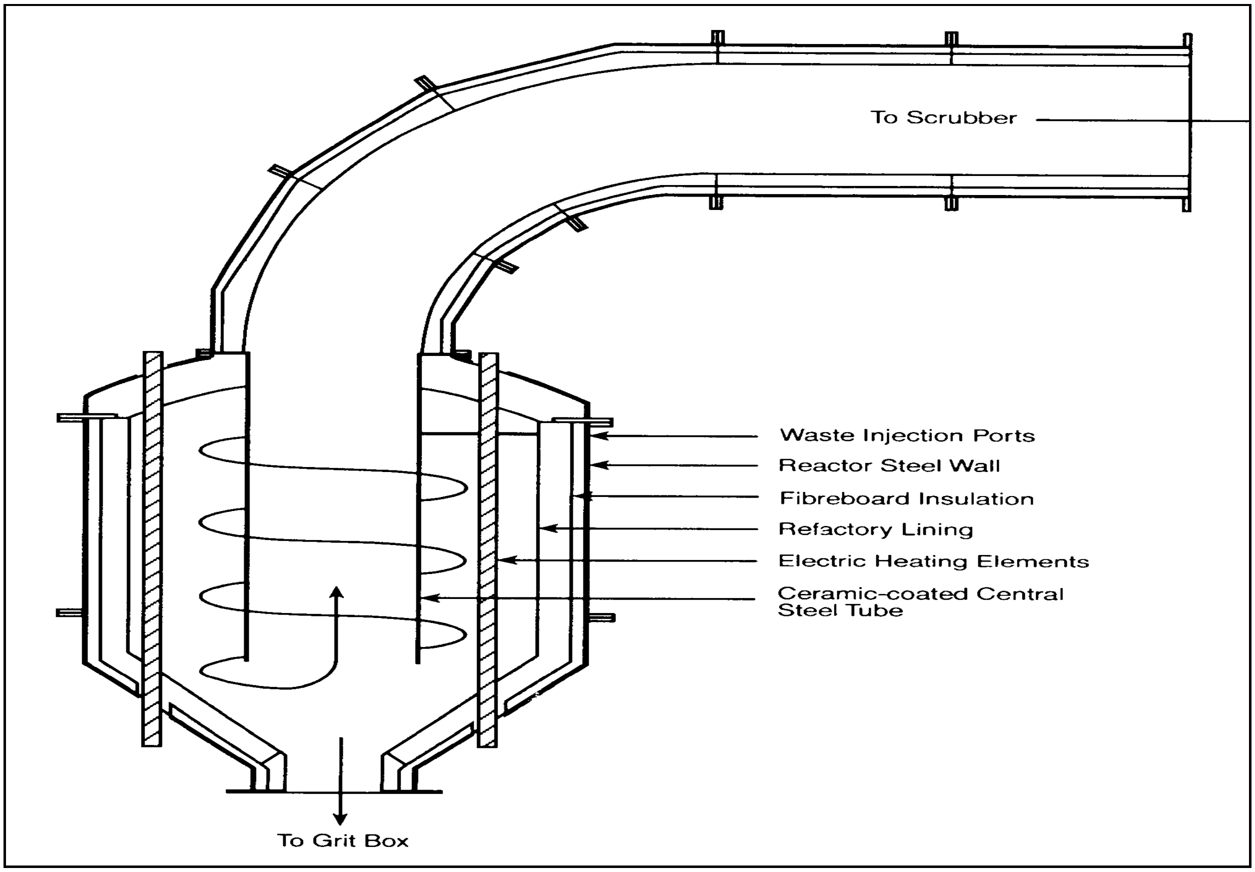
[a] *The SITE reports uses U.S. units (e.g., 1 ton = 2,000 lbs). These have been converted to metric units on the basis that 1 lb = 0.45359 kg. 1,000 kg = 1 (metric) tonne. Thus, 1 U.S. ton = 0.907 tonne. 1 U.S. gallon = 3.785 liters (1000 liters = 1 m^3).*

Figure 2: The ECO-LOGIC Reactor



conductivity, and good solvent properties for heavy metals such as lead, cadmium, and arsenic.

Some of each volatile metal present in the soil passes to the reactor; some dissolves in the molten tin bath, and the remainder stays in the soil. Non-volatile metals remain in the treated soil. Quench water cools the soil before disposal.

During the demonstration, a hopper with a screw feed dropped waste soil onto the tin bath. The screw feeder provided a gas seal between the hydrogen and the outside air. Once inside the TDU, the soil floated on the molten tin. A paddle wheel removed treated soil from the end of the tin bath and fed it to the quench tank.

6. MATERIALS PROCESSED

At the Middleground Landfill site, the wastes processed were oily-PCB contaminated water, high-strength PCB oils, and PCB-contaminated soil extracted directly from the landfill. The tests on the two liquids provided information on reactor performance. The tests on the soil provided information on the functioning of the complementary thermal desorption unit.

A liquid pool of waste within the landfill provided feedstock for the tests. Perchloroethene (PCE) was added to the feedstocks to serve as a tracer to determine DEs[b]. The reactor program treated approximately 2.6 tonnes of wastewater contaminated with 3,757 mg/L PCBs and 3,209 mg/L PCE at a rate of 1.73 kg/min, and 0.2 tonnes of waste oil containing 25.4% PCBs and 6,203 mg/kg PCE was treated at a rate of 0.385 kg/min. Additional feedstock contaminants included fluoranthene, naphthalene, phenanthrene, other PAHs, chlorobenzene, chlorophenol, methyl chloride, tetrachloroethene, toluene, and various metals.

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[b] *DE is a measure of the system's ability to achieve destruction of organic compounds as measured around the system and all output streams.* $DE(\%) = \{(1-Mass_{output})/Mass_{input}\}*100$

Two runs were carried out with the TDU on PCB-contaminated soil. The two runs treated 1 tonne of soil contaminated with 627 mg/kg PCB and 14,693 mg/kg hexachlorobenzene (HCB).

7. RESULTS

The runs employing liquid feeds confirmed the feasibility of the gas-phase reduction process for treating PCBs and other chlorinated organic compounds, producing a fuel gas from contaminated liquids, and providing environmentally acceptable air emissions. In general, the reactor system effectively destroyed PCBs, reducing them to lighter hydrocarbons.

Theoretically, the overall effectiveness of the destruction process could depend on the functioning of both the reactor system's gas phase reduction process (which produced the reformed gas), and the propane/reformed gas-fired boiler. Destruction and removal efficiencies (DREs)[c] for PCBs in the scrubbed reformed gas were essentially equal to the DREs at the boiler stack. This shows that combustion of the reformed gas in the boiler is not required to complete PCB destruction.

Stack emissions generally met stringent regulatory standards. However, average benzene concentrations in the stack gas (corrected to 7% oxygen) and scrubber liquor required close monitoring. Benzene emissions of 73-113 micrograms per dry standard cubic meter (µg/dscm) exceeded the regulatory limit. The scrubber liquor required either disposal as a RCRA waste or recycling through the system for additional treatment.

Demonstrated DREs for PCBs ranged from 99.9999 to 99.99999%. The demonstrated DE for PCE was 99.99%. There was no net formation of PCDD or PCDF.

The TDU did not operate to specification. The most important finding was inefficient desorption from soil during one of the runs. The DE for HCB ranged from 72.13 to 99.99%.

8. AIR EMISSIONS

The USEPA evaluated emissions of criteria air pollutants and HCl, as well as compliance with the Michigan Department of Natural Resources (MDNR) permit. During the tests, continuous emission monitors (CEMs) measured the concentrations of the criteria air pollutants at the stack: nitrogen oxides (NO_x), sulfur dioxide (SO_2), total hydrocarbons (THC), and carbon monoxide (CO). Each of these pollutant concentrations was well under the level established in the permit.

The demonstration boiler operated between high and low fire, depending on the system's steam requirements. The test analysis showed out-of-range spike concentrations of THC and CO (indicators of combustion efficiency) during low-fire operation, most notably during treatment of the wastewater when cycling between high- and low-fire conditions.

HCl emissions were well below the MDNR permitted level of 4 lbs/hr (1.81 kg/hr), or 99% removal). Average stack concentrations ranged from 0.66 mg/dscsm at 109 mg/hr to 0.81 mg/dscm at 198 mg/hr. Removal efficiencies reached 99.98%.

9. PROCESS RESIDUALS

Process residuals included reactor grit, scrubber sludge, scrubber decant, scrubber liquor, compressed tank condensate and stack gas—and when the TDU was used—treated soil. The SITE reports contain information on the production rates of these residuals and their composition. The reactor grit contained PCBs, PAHS, and a number of other organic compounds. However, ECO LOGIC intends to recirculate the grit through the reactor in a full-scale plant. Scrubber residuals also contained metals and a variety of organic compounds, but again recycling through the plant should be possible.

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[c] *DREs compare the mass flow rate of selected feedstock compounds, in this case PCBs, to their mass flow rate in the boiler stack gas.* $DRE(\%) = \{(1-Mass_{stack})/Mass_{input})\}*100$

10. COSTS

The 12 cost categories established for the SITE Program[d] formed the basis for the cost analysis for the treatment of liquid wastes. Costs were estimated for the reactor system, processing an average 2.2 kg/min, as operated at the Middleground Landfill site. For this estimate, it was assumed that 378 m^3 (100,000 U.S. gallons) of wastewater and 114 m^3 (30,000 U.S. gallons) of waste oil were stockpiled for treatment. Based on the economic analysis, the estimated cost in 1994 U.S. dollars for treating liquid wastes similar to those at the Bay City site ranged from U.S.$2,205/tonne (60% utilization factor) to U.S.$1,840 (80% utilization factor). The most important element affecting cost is labor (52%), followed by site preparation (15%), supplies (12%), and start up/mobilization (12%).

Site preparation costs for the demonstration were U.S.$127,400. Capital costs (for the reactor and immediately associated equipment, but excluding the TDU) for a commercial operation are estimated to be U.S.$585,000. The costs of treating contaminated soils were estimated at U.S.$695/tonne (at a 60% utilization factor) and U.S.$550/tonne (80% utilization factor). Important elements of these costs are fuel (67%), equipment (11%), and labor (9%).

11. SAFETY

The principal safety considerations concern the physical hazards common on construction and remediation sites, chemical use, equipment integrity, and process control. The chemical hazards arise from the use of propane, liquified nitrogen/oxygen, hydrogen, industrial chemicals, and hazardous feed materials. In addition, the process generates methane. Standardized industrial procedures provide adequate guidance for storing, transporting, and handling these materials.

There should be no undue concern associated with hydrogen usage in the process. Well-established and proven procedures are available for safe hydrogen storage and use. Hydrogen is no more dangerous than gasoline or methane, but it must be handled with regard to its unique properties. Verification of system integrity is essential for process safety. Hydrogen is more difficult to contain because of its small molecular size. Therefore, interfaces of equipment, instruments, and piping must be leak-free. To provide additional safeguards, the process is operated at a slight positive pressure to prevent oxygen ingress; internal oxygen concentrations are monitored; and gas feeds (propane and hydrogen) are maintained at low pressure to minimize the likelihood of pipeline breaks. The plant is fitted with an automatic safety system, which initiates plant shutdown in the event of a hazardous situation.

13. CONCLUSIONS

The SITE Program concluded that the ECO LOGIC Process efficiently treated liquid wastes containing oily PCBs and other organic compounds, and water containing PCBs, other organic compounds, and metals. Stack emissions met stringent regulatory levels. The scrubber effluent (the principal residual stream) concentrated metals and some organics (benzene, PCBs, and PAHs), indicating that additional treatment (*e.g.*, recycling through the process) might be required prior to disposal. However, throughput reliability was only 20-55% of design and system availability—a reliability of 24% indicates that system reliability needs improvement. A number of technical problems were encountered during the operation of the plant and are recorded in the SITE program report. The boiler should be operated at firing rates and air/fuel ratios that prevent the spikes of THC and CO observed during the trial.

The reactor system is best suited for processing liquids and TDU off-gases and water vapor. The waste's organic content limits the demonstration-scale system's feed rate because of the reformed gas generation. Currently, ECO LOGIC plans to improve throughput by storing excess reformed gas after compressing it. Future users should consider the implications, logistics, and costs of this approach.

The TDU did not perform to design specifications. The USEPA categorized the TDU test data as a system proof-of-concept, rather than as a comprehensive evaluation of a fully-developed unit. The TDU only achieved acceptable desorption efficiencies at the expense of throughput. In addition, ECO LOGIC experienced material handling problems with the TDU feed. The combination of feed problems and inadequate organics desorption showed a need

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[d] *Site preparation, permitting and regulatory, capital equipment, mobilization and start-up, operations labor, supplies, utilities, effluents, residuals, analytical, repair and maintenance, demobilization.*

for further development. Nevertheless, the demonstration did show that the TDU can desorb PCBs, and that satisfactory treatment in the reactor system was possible.

Cold-weather operations may inhibit efficient destruction because of the incremental amount of energy required to heat the reactor. In addition, feedstock liquids would require melting prior to treatment, and liquid residuals could freeze in the unheated storage tanks. Winterization (including heat tracing) is necessary to provide adequate feedstock and to ensure uninterrupted processing.

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2. U.S. Environmental Protection Agency, *Eco Logic International Gas-Phase Chemical Reduction Process -The Thermal Desorption Unit: Applications Analysis Report*, Washington, DC, 1994, EPA/540/AR-94/504.

Project No. 8

Biodegradation/Bioventing of Oil Contaminated Soils

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1. INTRODUCTION

Biogénie, Inc., under the auspices of the DESRT technology demonstration program, has developed a biopile-based approach to soil treatment. This is an *ex situ* bioremediation technique whereby soil is heaped in contained areas, (*e.g.*, on an asphalt pad with drainage collection) and supplied with oxygen, moisture, and nutrients via an integrated irrigation and air blower system to enhance natural degradation processes. Biopiles are reportedly suitable for a wide range of organic compounds and can incorporate addition of surfactants, co-substrates, or acclimated bacteria, when needed. This Pilot Study project reviewed the bench-, pilot-, and full-scale development of this technology including reports on specific aspects of process development—such as the exhaust air treatment system (Oxford meeting, 1994).

2. THE FIELD TRIALS

Under the DESRT program, two full-scale trials were conducted at sites selected for their contrasting contamination and soil characteristics. The first trial was conducted at Boucherville, near Montreal. Boucherville was a former electrical distribution station with a heavy clay soil contaminated by up to 14,000 mg/kg of mineral oil and grease. The second site, located in Jonquiere, north of Quebec City, was contaminated by up to 54,000 mg/kg mineral oil and grease, which resulted from spills of locomotive fuel oil. The interim results of these two studies included bench-scale treatability studies (optimizing aeration, tilling, type and amount of soil amendments, and nutrient additions) and field tests (Quebec City meeting, 1993).

The field tests used 500 m^3 of contaminated soil from each site which was transported offsite to prepared treatment facilities. At the Boucherville site, remediation was continued during the winter by installing a 15-kW heater to the pile during November. After 34 weeks of treatment, 72% of the hydrocarbons present were degraded (final concentration 3,800 mg/kg) despite over half the test period taking place during the winter. At the Jonquiere site, after 28 weeks of treatment, up to 68% of the hydrocarbons present had been treated (final concentration 17,100 mg/kg). This trial did not continue over the winter.

It was concluded that biopiles were effective for soils with high levels of contamination and for difficult soil types such as heavy clay. However, the Jonquiere soil did not meet criteria for industrial soil, and neither cleaned soil met the criteria for residential redevelopment. The bench-scale treatability studies showed a degradation efficiency of about 80-90% after 20 weeks which was not reproduced by the field tests.

Application costs predicted from these studies were around 90 Canadian dollars[a] (Cdn$90) per m^3 for the whole treatment.

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[a] *It is assumed that costs were reported in Canadian dollars, rather than U.S. dollars.*

3. TREATMENT OF EMISSIONS

The Biogénie, Inc. approach reportedly uses an innovative filtration system for treating off-gases (containing several hundred parts per billion volatile organic compounds (VOCs) from the exhaust of the air blower system. Whereas traditional technologies include carbon adsorption, thermal or catalytic oxidation, and wet scrubbing, the *Biogénie Inc.* process uses a biofilter. The biofilter technology was field tested at a petrol station near Quebec City where soil and groundwater had been contaminated with petrol leaks from an underground storage tank. A combination of *in situ* bioventing and air sparging was used to clean the site with the biofilter employed to treat the off-gases produced.

The biofilter technology consists of an air/water separator followed by a trickling filter and a biofilter in series. The separator was used to eliminate excess water in the inlet gas. A mixed culture of microbial hydrocarbon degraders (sustained on VOCs) was housed in a trickling filter, which was supported by nutrients added to irrigating water. Contaminated air was bubbled through the filter countercurrent to the irrigation water. After the trickling filter, contaminated air and water were passed through a biofilter consisting of a column filled with composting materials. Contaminants were sorbed to the filter medium and degraded by indigenous microbes (from site soil) and transported microbes (from trickle filter). No nutrient supplementation was needed since the compost provided sufficient levels. During the demonstration, the system operated under winter conditions with results after 127 days showing a removal of 90% of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) with a filter residence time of less than 2 minutes.

4. OTHER STUDIES

By February 1996, a further 17 field studies were conducted using the biopile and biofilter technologies. In total, over 390,000 tonnes[b] of contaminated soil have been treated, with average removal efficiencies of 75% for mineral oils, 99% for BTEX, 95% for pentachlorophenols, and 90% for total PAHs (>99% for naphthalene).

5. COSTS

Remedial costs were suggested to vary according to soil quantity and site location but, in general were reported to be between Cdn$45-90 per ton for soil quantities up to 5,000 tons, and between Cdn$15-30 per ton for soil quantities greater than 25,000 tons.

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[b] *The reports do not make it clear whether the term “tons" refers to metric ton(nes), short (U.S.) tons (2,000 lbs), or imperial tons (2,240 lbs).*

Project No. 9

Field Demonstration of an *In Situ* Process for Soil Remediation Using Well Points

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1. INTRODUCTION

An *in situ* remediation process combining soil flushing using surfactants and bioremediation is being field demonstrated at an aliphatic- and hydrocarbon-contaminated site. This demonstration is sponsored by Serrener/Varisco Consortium, the National Research Council of Canada, Environment Canada, and the Ministry of Environment of Québec.

2. TECHNICAL CONCEPT

The process is based on a wellpoint system developed by VARISCO SPA for the control of the water table in construction projects. The treatment process consists of a recirculation system with injection and extraction wells. A surfactant/co-surfactant solution is injected into the wellpoints to immobilize the contaminants. The extracted contaminated washings are sent to an effluent treatment plant. The remaining hydrocarbon residual located in the subsurface is biodegraded by injecting nutrients and air or hydrogen peroxide into the wellpoints.
The project scope includes: laboratory-scale selection of surfactants; *in situ* soil washing tests using the selected surfactant; *in situ* biodegradation testing of residual hydrocarbons and the contaminated washing solution; and subsequent monitoring to verify contaminant removal.

Over 50 types of surfactants and co-surfactants were tested to establish the pairings and concentrations required to extract over 95% of the hydrocarbons from the contaminated soil. Tests on the toxicity of the surfactants on the microbial populations and effects on degradation are being conducted.

BTEX (benzene, toluene, ethylbenzene, and xylenes) and aliphatic hydrocarbon degraders have been identified. Degradation of the aliphatic hydrocarbons present in the soil appears to be inhibited, perhaps by the presence of heavy metals, and will be studied further.

Project No. 10

Integrated Treatment Technology for the Recovery of Inorganic and Organic Contaminants from Soil

Technical Contact:	Country:	Project Status:
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1. INTRODUCTION

Two sites in Canada exceeded guidelines for industrial reuse due to soil concentrations of heavy metals and polycyclic aromatic hydrocarbons (PAHs). The Ataratiri site covers 32 hectares in Toronto and was contaminated with PAHs and heavy metals such as lead, copper, and zinc. It was estimated that a minimum of 500,000 tonnes of soil on the site did not meet the commercial/industrial usage criteria. At the Longue Pointe site in Montreal, approximately 155,000 tonnes of soil was contaminated with lead smelter fly ash and by lead battery recycling. In places, site soils had a high clay content or very high lead content. Bulk soil samples (up to 35 tonnes) representative of distinct areas of both sites were collected for pilot scale evaluation of the treatment technology. The technology was also evaluated at the bench scale on sediments collected from Hamilton Harbour in Ontario. These sediments were enriched in organic and metal contaminants and had a total organic carbon load exceeding 10%. Some of the metals (*e.g.*, Cd, Cr, Fe, Mn, Ni, Pb, and Zn) exceeded the “severe effect level” based on Ontario’s sediment quality guidelines.

Demonstration and evaluation of the technology was sponsored by the Ontario Ministry of Environment and Energy, Environment Canada through its Development and Demonstration of Site Remediation Technologies (DESRT) program and the Contaminated Sediment Treatment Technologies Program, and National Defence Canada.

2. THE PROCESS

The evaluated remediation technology incorporated physical-chemical treatments to recover both metal and organic contaminants. Pretreatment included the screening of large site debris, such as bricks, and a wet scrubbing to break down softer agglomerates such as clay clods. The slurried soil was then classified by particle size, density, or magnetic susceptibility to produce contaminant concentrates which were reported to be recycled offsite, and a “clean” fraction, which required further treatment through the organic and metal washing processes.

Organic contaminants were washed from the soil using a solvent extraction process. The organic-depleted soil slurry was subsequently treated in a hydrometallurgical circuit where fine metal contamination was selectively leached from solution and recovered using metal selective adsorbents. It was suggested that the filter cake produced by this process was suited to off-site metal recycling. The depleted soil slurry was then washed, dewatered, and recombined with the other soil products.

3. RESULTS

3.1 Ataratiri

The pretreatment of the Ataratiri soils produced metal-contaminated concentrates containing up to 55% by weight of iron for potential recycling. Overall, the “clean” soil fractions, which represented up to 95% of the original soil weight, appeared to comply with residential criteria for some contaminants, and industrial criteria for others, such as certain PAHs. For example, benzo(b)fluoranthene in the soil was reduced from 14 mg/kg to 4 mg/kg after treatment, but this value still exceeded residential guideline values. Reduction in metal concentrations ranged from 4,026 mg/kg to 360 mg/kg for zinc, while copper levels (100 mg/kg) were unaffected by treatment.

A report highlighted the different outcomes of Ataratiri soils treated by coarse metal recovery and organic recovery only, and with the added hydrometallurgical recovery step. After treatments to recover coarse metal and organic contaminants, two soils that originally exceeded industrial guidelines for various heavy metals and PAHs resulted in 95% of the original material that were within industrial guidelines for certain PAHs. Other soils that had the additional hydrometallurgical recovery step produced 86% of the material as clean soil suitable for reuse for residential purposes.

3.2 Longue Pointe Soils

At Longue Pointe, treatment tests on the soils revealed that most of the lead contamination occurred in fine soil particles and could be recovered by the hydrometallurgical extraction and Vitrokele™ adsorption. After this treatment, soil contained as little as 7% of its initial lead content, and this residual concentration met the regulatory limits of either 1000 mg/kg for industrial use or 500 mg/kg for residential use.

It was reported that the Longue Pointe site is now undergoing full-scale remediation. Overall, 115,000 tonnes of lead-contaminated soil were to be treated through the plant at a rate of 600 tonnes per day. Excavation of the soil from the Longue Pointe site was to be secured in a temporary on-site holding cell by late autumn 1994 with treatment scheduled to begin by summer 1995.

3.3 Hamilton Harbour Sediments

Bench-scale tests with a 20-kg test sample collected from Hamilton Harbour included flotation, magnetic separation, and gravity separation techniques. When compared to the original feed, clean tailings contained only 4.1% of the total oil and grease, 4.9% of the PAHs, less than 2% of the lead, and 11% of the zinc. In contrast, metals like Cd, Ni, and Fe were reduced but remained between 24% and 30% of the original load. The recovered organic product contained 27% of the total mass and captured 62% and 74% of the original oil and grease and PAHs, respectively. It was also enriched in Pb, Zn, Cd, Ni, and Fe at 81%, 60%, 54%, and 32%, respectively, of the original content.

4. COSTS

It was indicated that for Ataratiri and Longue Pointe, treatment produced a soil which was of a suitable quality for recycling. An estimate of the remediation cost of the Ataratiri site, involving a total of 500,000 tonnes of soil, was presented as U.S.$75 per tonne.

Based on bench-scale tests, the treatment process for Hamilton Harbour sediments would consist of screening, magnetic separation, concentration of organics by flotation, and a hydrometallurgical extraction if required to remove residual Zn, Cu, Ni, and Pb from feeds to the leach circuit. For this treatment, the contractor estimated costs of U.S.$60-75 per tonne assuming at least 20,000 tonnes require treatment.

5. RESIDUALS

Residuals consist of inorganic concentrates for disposal or recovery of metals, organic concentrates, waste water from sizing and classifying material during treatment, as well as treated material for use as fill on-shore or off-shore.

Project No. 11

On-site Biodegradation of PAHs in Soil at a Former Gasworks Site

Technical Contact:	**Country:**	**Project Status:**
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This project reports on the experimental studies at the Frederiksberg Gasworks site located in the middle of Copenhagen, Denmark. The gasworks operated from 1895 to 1964 for the production of coal gas which gave rise to several wastes, such as naptha, benzol, ammonia, cyanide, sulfides, and sulfates. Investigation of the site in connection with the demolition of the site buildings identified a large area of soil contaminated with polycyclic aromatic hydrocarbons (PAHs). Analysis of the site soil indicated that concentrations of individual PAHs were in the range 0.8-23 mg/kg, and the average total PAH concentration was 400 mg/kg.

The objective of the project was to define the most suitable method for the biological treatment of the tar compounds in the soil. Laboratory tests were used to determine the population of tar degrading micro-organisms present within the site soil. Identified degraders were subsequently evaluated for their interaction with temperature, humidity, nutrients, and composting materials such as bark and wood chips. The effect of adding proprietary detergents to the system was also evaluated.

Among the more important conclusions of the study, was that the condition of the soil at the time of sampling and analysis (*e.g.*, consistency and soil moisture content) may affect the measured PAH concentrations.

1. INTRODUCTION

The pilot project at Frederiksberg gasworks site was one of six pilot projects on the remediation of municipal gasworks sites financed by the Danish government and the municipalities involved. The pilot project involved three phases, including both bench-scale and field tests:

- Phase 1: The population of microorganisms and the population of tar-degrading microorganisms in the soil from the site was investigated. In addition, 10 detergents were assessed for their ability to mobilize PAHs and make them accessible to biodegradation.

- Phase 2: Microcosm tests were conducted to monitor the degradation of PAHs under different test conditions over a period of 325 days. Column tests were conducted over a period of 126 days. Subsequently, the degradation of PAHs was examined in a slurry test in which soil samples from the microcosm test were suspended in distilled water and put on a shaking table in the dark for 69 days.

- Phase 3: The degradation of PAHs was monitored for 496 days in 10 windrows: five in the open air on the former gas tank foundation and five in the former covered tar basin. The affect of the following test conditions on PAH degradation was examined: addition of wood chips, addition of compost, addition of detergents, aeration by windrow turning, continuous aeration, windrow location (inside vs. outside).

2. BENCH-SCALE TESTS

2.1 Assessment of Microbial Populations

In Phase 1, the number of natural PAH-degrading bacteria was measured by adding ^{14}C-marked PAH compounds to soil samples and determining the quantity of radiolabeled carbon dioxide that was released. Results showed that a population of 10^7 bacteria per gram of soil were present on the site and that they showed potential for degrading phenanthrene, anthracene, and pyrene.

2.2 Examination of the Microbial Degradation over a Period of 325 Days

During the Phase 2 bench-scale tests (microcosm tests), the degradation and removal of PAHs from site soil by three treatments (radiation, temperature, and detergent) was monitored over a period of 325 days. The soil was thoroughly homogenized and particles greater than 4 mm were removed prior to the test.

PAH degradation was insignificant during the first four months (120 days), but after four months, the concentration of the PAHs examined (phenanthrene, anthracene, fluoranthene, pyrene, and benzo[a]pyrene) decreased significantly. The number of phenanthrene-degrading bacteria decreased in the initial period, but generally increased during the last 198 days of the test. The total number of cultivable bacteria did not show similar fluctuations. The PAH degrading bacteria were, therefore, probably affected by the initial test conditions, but adapted during the first four months. The reason for this temporary inhibition is believed primarily to be the high pH of in the soil after addition of nutrient salts.

During the first 127 days of the test, the concentrations of PAHs were generally lower in the samples treated by detergents than in the corresponding radiated samples and background samples. The detergent mix applied probably had an initial effect on the degradation of PAH that diminished and disappeared in time, probably due to total or partial microbial conversion of the detergent. The addition of detergent to the soil did not enhance the growth of the phenanthrene-degrading bacteria.

An increased incubation temperature of 25°C compared with 15°C did not generally affect the removal of PAHs.

During the last 198 days of the test period, 66%, 74%, 66%, 64%, and 71% of phenanthrene, anthracene, fluoranthene, pyrene, and benzo(a)pyrene, respectively, was removed *independently* of the treatment given (Table 1).

Table 1: Percentage of PAHs removed in the microcosm test from day 127 to day 325 (198 days) calculated using estimated regression equations

PAH	mg PAH/kg soil DM		%PAH removed	$t_{1/2}$
	day 127[1]	day 325		
Phenanthrene	9.8	3.4	65.7	128
Anthracene	6.2	1.6	73.5	103
Fluoranthene	17.4	5.9	66.4	126
Pyrene	12.8	4.6	64.3	133
Benzo(a)pyrene	6.6	1.9	71.2	110

[1] No degradation or removal of PAHs occurred from day 0 to day 127. Note: t½=half-life

2.3 Examination of the Microbial Degradation in Slurry Tests over a Period of 69 Days

Soil samples from the microcosm test were suspended in distilled water and put on a shaking table at 100 rpm. The samples were shaken in the dark for 69 days (slurry test) with the temperature maintained at 22°C. The PAH content of the soil and water phases were analyzed and it was concluded that:

- Incubation of the suspended soil generally did not lead to any reduction of PAHs. Exceptions were anthracene and fluoranthene, the concentrations of which tended to decrease after the 69-day test.

- There was no difference in degradation rates between the different treatments (radiation, temperature, and detergent) of the test soil.

- The content of benzo(a)pyrene tended to increase.

The reason for the lack of reduction and degradation of PAHs may be the age of the soil contamination (*i.e.*, a very strong bond of the PAHs to the soil particles and possibly to tar residues) and the low initial concentrations of PAHs. The benzo(a)pyrene content significantly increased at the conclusion of the test. This may have been due to either analytical variation or to mobilization of benzo(a)pyrene during the test. If the latter is the case, both mobilization of PAHs and partial mineralization of the mobilized PAHs may have occurred at the same time.

3. FIELD TESTS

Field tests were initiated at Frederiksberg gasworks site in June 1994 and were concluded in October 1995 (a total of 496 days). The soil used in the field tests was excavated in and around the former tar basin in 1990. During this time, the soil was processed to remove wood, bricks, concrete, and heavily tar-contaminated soil and then stored in two windrows at the gasworks site.

The test soil was a sandy soil with a total PAH concentration of around 400 mg/kg. Prior to placing the soil into the test windrows, the soil was mixed and homogenized, and particles larger than 80 mm were removed. The soil was then split into five piles, and water, nutrient salts in the form of NPK fertilizer, wood chips, compost, and detergent solution were added. Then the soil was placed in 10 windrows of which five were located in the open on the former gas tank foundation (windrows 1G-5G) and five were located in the covered former tar basin (windrows 1B-5B).

Table 2 shows the treatment given to each test windrow and the treatment carried out in the test period. Table 3 shows the results of chemical analyses and measurements carried out on the test soil.

Table 2. Treatment of each test windrow

Windrow	Soil Volume (m^3)	Aeration Method[2]	Treatment at Initiation of Test	Treatment During the Test
1G (control)	33	-	-	Addition, as required, of: - NPK fertilizer - calcium nitrate - water
1B (control)	21	-	-	
2G	19	Turning	+ 11 m^3 wood chips	
2B	19	Aeration	+ 11 m^3 wood chips	
3G	20	Turning	+ 10 m^3 compost	
3B	20	Aeration	+ 10 m^3 compost	
4G	32	Turning	+ detergent solution[3]	
4B	32	Turning	+ detergent solution[3]	
5G	33	Turning	-	
5B	36	Turning	-	

4. RESULTS OF THE FIELD TEST

4.1 Initial Processing of Results: Correlation Analysis

A correlation analysis of the results of all 946 samples analyzed was carried out to determine whether the results for total PAHs correlated with the individual PAHs in the samples. From the results of the correlation analysis, it generally appears that there is *poor* correlation between total PAH and individual PAH concentrations. In further processing of the results, only the individual PAH results were used.

Table 3. Time for sampling of chemical analyses and measurements

Chemical analyses and measurements on samples[1]	**Time in days**[2]											
	0	55	103	134	173	289	320	372	406	441	468	496
Tar (PAH)[3]	+	+	+	+	+	+	+	+	+	+	+	+
Tar (PAH)[3]	-	-	Samples frozen and after the conclusion of the test freeze-dried and analyzed for their content of tar									
Ignition loss	+	+	+	+	+	+	+	+	+	+	+	+
Dry substance	+	+	+	+	+	+	+	+	+	+	+	+
pH	+	+	+	+	+	+	+	+	+	+	+	+
Inorganic material[4]	+	-	-	+	-	-	+	-	+	+	+	-
Microbiology[5]	-	-	-	-	-	+	-	+	-	+	-	+
Measurements on site	**Time**											
Humidity	Measurements carried out continuously throughout the test period											
Oxygen (O_2), carbon dioxide (CO_2) and methane (CH_4)	Measurements carried out on the dates mentioned in the table and every day during short periods of the test period											

[1] If not otherwise indicated, all windrows were subjected to analyses and measurements.

[2] Time 0 is 94.05.20 and time 488 is 95.10.02

[3] 12 PAH single substances by GC/MS/SIM, and total PAH by GC/FID

[4] Total carbon, total nitrogen, total phosphorous, total potassium, nitrate number, potassium number, and phosphorous number

[5] Determination of the population of total cultivable bacteria and phenanthrene decomposers by plate count and determination of PAH degradation potential for phenanthrene and pyrene decomposers (the latter was conducted on day 441 and only in windrows 1G-5G).

4.2 PAH Content in Ordinary Samples and in Freeze-dried Samples

Soil samples from sampling rounds t_2 through t_{11} were collected from each windrow and frozen for analysis the conclusion of the test. At this time, all of the frozen samples were freeze-dried and analyzed for PAHs. The purpose of freezing and freeze-drying samples from each round for concurrent analysis was:

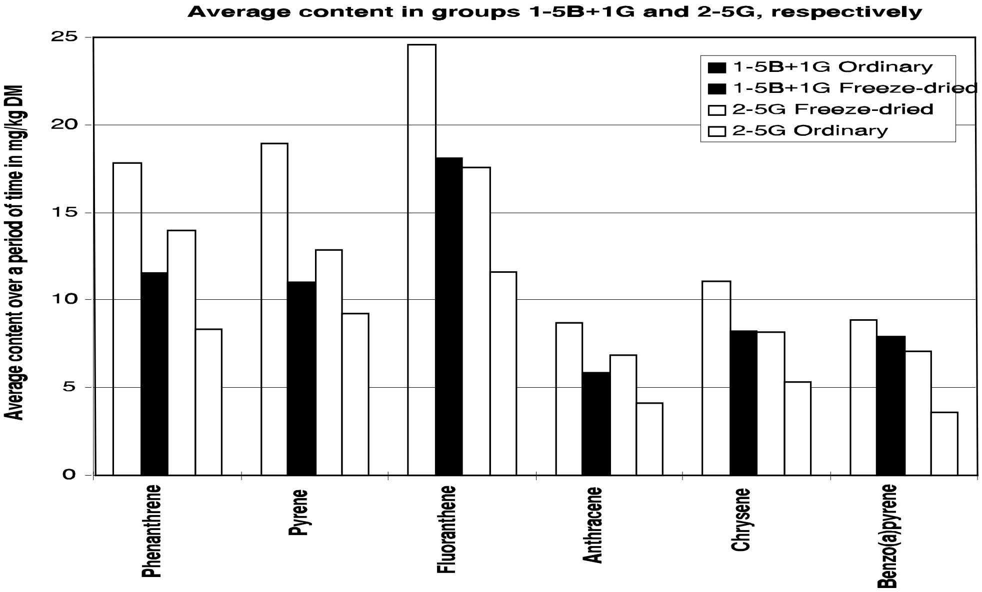
- to examine whether when the samples were analyzed might have affected their results. This may be indicated by the results from analysis rounds t_0-t_{11}. Hence, results from the same sampling round, in general, tended to be similar in that when a high concentration was measured in one sample, high contents were typically measured in the other samples.

- to assess whether the water content (the soil consistency) of the samples affect their results. (Very different soil consistencies were observed between the windrows located inside and outside).

Generally, the effect on the PAH content of ordinary samples (samples analyzed immediately after sampling rounds t_0-t_{11}) and those samples that were frozen and freeze-dried for analysis at the conclusion of the test), respectively, is considered significant ($\alpha = 5\%$). The freeze-dried samples from the windrows located inside (1B-5B) had an average PAH content that was about 70% of the PAH content of ordinary samples. The ordinary samples from the windrows located outside (2G-5G), on the other hand, had an average PAH content that was about 60% of the PAH content of the freeze-dried samples. The exception was samples taken from windrow 1G where the freeze-dried samples had a PAH content of around 70% of the content found in the ordinary samples.

Comparison of the results for ordinary and freeze-dried samples showed that there was a significant difference between the PAH content of ordinary samples from windrows 1B-5B and 1G and the PAH content of windrows 2G-5G. In contrast, the content of PAHs in frozen and freeze-dried samples was almost identical (Figure 1).

Figure 1. Average content of PAHs in group 1-5B and 1G and group 2-5G, respectively



The only general difference between the ordinary and the frozen freeze-dried samples was that the water content in the freeze-dried samples was markedly lower than in the ordinary samples. The water content could possibly have a negative or a positive impact on the efficiency of the extraction of PAHs from the samples; however, a clear-cut connection was not established between the water content of the samples and the PAH concentrations in the ordinary and freeze-dried samples.

It was not immediately possible to explain the difference in PAH content of the ordinary samples measured in test windrows 1B-5B & 1G and test windrows 2G-5G. As mentioned previously, the ordinary samples from windrows 2G-5G generally had a lower dry matter content than the ordinary samples from 1B-5B and 1G. A marked difference in the soil consistency of the above two groups of samples was also registered during sampling and by the analysis laboratory. Thus, the samples from test windrows 2G-5G had a muddier consistency than the samples from test windrows 1B-5B (located inside) and windrow 1G (located outside, but not turned during the test period).

In summary, it was concluded that freezing and freeze-drying of samples created similar soil conditions (including soil consistency and water content). This, in turn, resulted in similar PAH contents among test groups. In contrast, the difference in soil conditions of ordinary samples affected their PAH content. Thus, it was concluded that the soil consistency and water content affect PAH content.

4.3 Change in PAH Content over a Period of Time

The reduction in concentration of the six PAHs analyzed during the test, under the test conditions applied, was examined regression analyses. Soil samples were collected from both the inside and outside test windrows. Soil samples were collected during each of the 12 sampling rounds (t_0-t_{11}) over a period of 496 days. In the regression analyses, the most probable linear reduction in the PAH content of the samples with time was estimated. It was also examined whether the slope of the decay curve could be assumed to differ from 0, which would then indicate a significant (α = 5%) reduction in the PAH content of the samples over the test period.

4.3.1 Effect of different treatments

During the test period of 496 days, a significant reduction in the PAH content in test windrows 1B, 1G, 4B, 4G, and 5B was registered. From the results, it appears that there was no significant difference in the half-lives (t½) of these windrows. Hence, the addition of detergent solution did not lead to an increased removal of PAHs, as compared with the removal of PAHs in test windrows 1B and 1G (see Table 4).

In none of the windrows with a significant reduction of the PAH content, could the effect be unambiguously attributed to the treatment the windrows received. Neither addition of wood chips nor compost had any positive impact on the removal of PAHs over time. On the other hand, the results achieved for test windrows 1G and 1B could be interpreted to mean that addition of wood chips and compost inhibited the removal of PAHs.

Table 4. Reduction of PAHs in test windrows located inside (1B-5B) and test windrows located outside (1G-5G) during the test period of 496 days.

	Phenanthrene		**Anthracene**		**Chrysene**		**Fluoranthene**		**Pyrene**		**Benzo(a)pyrene**	
	Effect	$t_{1/2}$	Effect	$t_{1/2}$	Effect	$t_{1/2}$	Effect	$t_{1/2}$	Effect	$t_{1/2}$	Effect	$t_{1/2}$
1B	Effect	573	None		Effect	610	Effect	720	Effect	634	Effect	565
2B	None		None		None		None		None		None	
3B	Effect	491	None		None		None		None		None	
4B	Effect	608	None		Effect	626	Effect	742	Effect	701	Effect	578
5B	None		None		None		None		None		None	
1G	Effect	751	None		Effect	636	Effect	760	Effect	807	Effect	717
2G	Effect	583	None		None		None		None		None	
3G	Effect	466	None		None		None		None		None	
4G	None		None		Effect	412	Effect	623	Effect	576	Effect	415
5G	Effect	602	Effect	809	Effect	575	Effect	600	Effect	565	Effect	474

$t_{1/2}$ = half-life, in days, following t_0
Effect= indicates significant decrease of substance content over time
None= indicates no significant decrease of substance content over time

In general, no significant removal anthracene was observed in any of the test windrows. This may be due to the fact that the content of anthracene, as compared with the content of other PAHs, was generally low. Hence, the anthracene may not have been accessible to microbial degradation, or the removal of anthracene might have been overshadowed by the relatively great standard deviations of the results.

4.3.2 Effect of location of test windrows: inside/outside

No difference was found in the development of PAH content between test windrows located inside and test windrows located outside. An exception was test windrow 5G in which PAHs were significantly reduced, whereas there was no significant reduction in windrow 5B. The reason for the difference in the results from windrow 5B (located inside) and windrow 5G is not readily explainable. No difference in the development of PAH content between windrows aerated by turning (2G, 3G) and windrows aerated continuously (2B, 3B) was found.

From the results of the ordinary samples, it appears that within the test period a relatively great difference in the PAH content was observed during period t_4-t_8, when the content in test windrows 2G-5G was lower than in test windrows 1B-5B and 1G. The fact that no mineralization of the PAHs occurred in windrows 2G-5G during this period appears from the results from time period t_9-t_{11}, in which the PAH content is generally larger than the content of PAHs in period t_4-t_8.

A lower PAH content was observed in windrows 2G-5G than in 1G, but these windrows were all located outside so the difference in the results cannot be explained their location. The consistency of the soil differed greatly for the two groups of windrows in the period t_4-t_8. Hence, the soil in windrows 2G-5G had an almost muddy consistency. Windrow 1G, which was not turned, did not have this muddy consistency. It should be noted that this great difference in soil consistency was not clearly reflected by data on dry matter content.

The manner in which the difference in soil consistency affected the accessibility of the PAHs was not conclusively determined. However, possible reasons for the low content of PAHs in windrows 2G-5G during t_4-t_8 include:

- The PAHs were leached to the bottom of the windrow. This scenario is not very likely because soil samples were taken for analysis while turning the windrows; therefore, soil was taken from the entire soil profile.

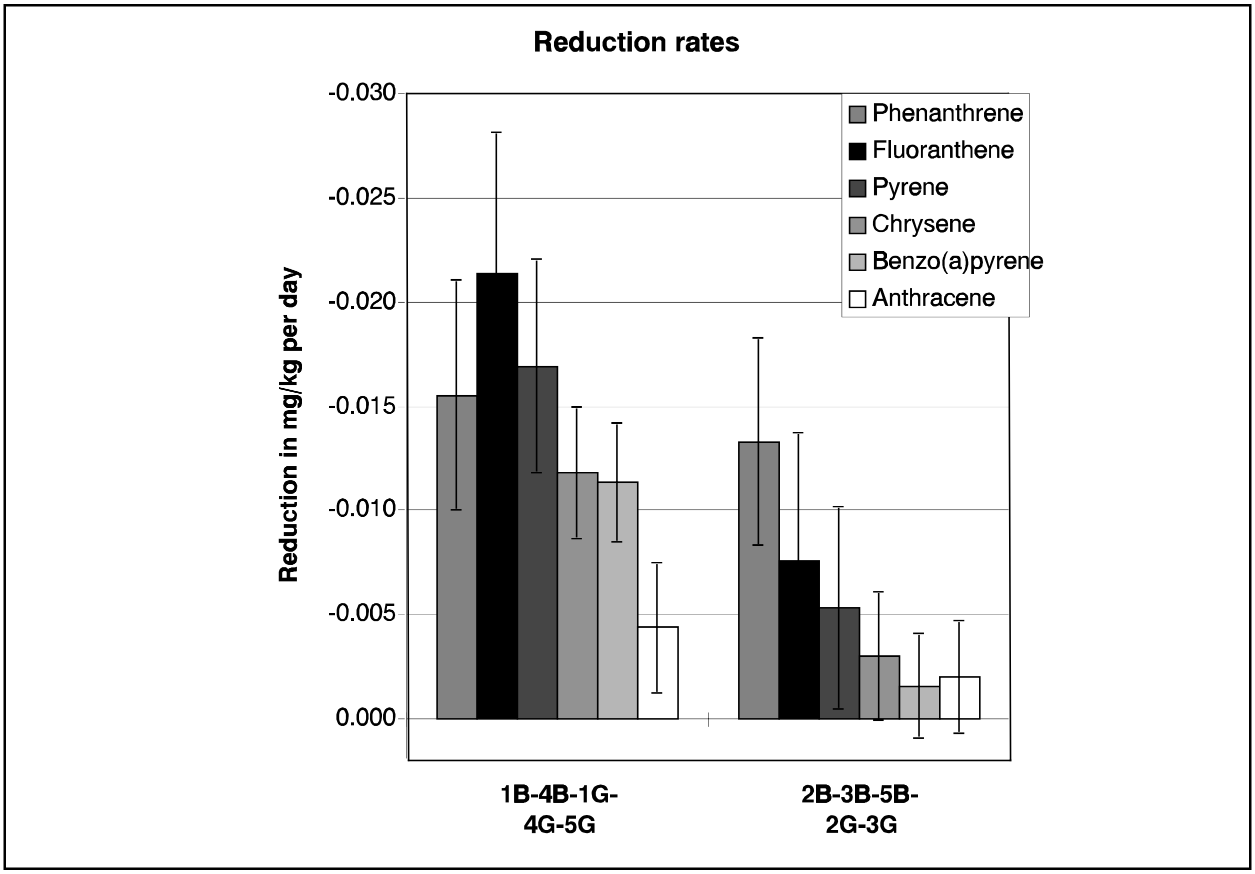
- Elution of PAHs to leachate. This is also not very likely because the content of PAHs was high during time period t_9-t_{11}. Moreover, a number of elution tests (bench-scale tests) established that the elution of PAHs from the soil was insignificant.

- The change of the soil consistency resulted in changes in bonding and adsorption, *etc.*, of PAHs to the soil particles so that the accessibility of PAHs in the soil from windrows 2G-5G was reduced. The ability of the extraction agent dichloromethane to extract PAHs is affected by the soil structure. Considering the results of the freeze-dried samples in which the content of PAHs in this period was the same for windrows located outside as for those located inside, this explanation is believed to be possible.

4.3.3 Estimate of the Amount of Degraded PAH

In test windrows 1B, 1G, 4B, 4G, and 5G, a 23.5-45.5% reduction in the content of the selected PAHs was estimated in the test period of 496 days (see Figure 2). An exception was anthracene. This corresponded to half-lives between 529 and 967 days for each PAH (see Table 5). In the group of test windrows comprising 2B, 2G, 3B, 3G, and 5B, there was a significant reduction of phenanthrene (39.3%, corresponding to a half live of 618 days), fluoranthene (18%, corresponding to a half live of 1,428 days) and pyrene (15.6%, corresponding to a half life of 1,494 days). No significant reduction was observed in anthracene, chrysene, or benzo(a)pyrene (see Table 5).

Figure 2. Reduction rates for PAHs and standard deviations for windrows 1B, 1G, 4B, 4G, and 5G, and windrows 2B, 3B, 3G, and 5B, respectively.



Generally, it can be expected that due to the chemical structure and physical and chemical properties (water solubility, log K_{ow}, etc.) the biodegradation of phenanthrene and anthracene will be greater than other PAHs. From Table 5, it appears that the conversion of anthracene is significantly smaller than the conversion of the other PAHs, which may be attributed to the low output concentrations or the great standard deviation of results, which may have overshadowed the effect.

Addition of ^{14}C-marked PAH substances to the test soil showed a relatively quick mineralization of phenanthrene, anthracene, and pyrene with a t½ of greater than 100 days. In the microcosm test, a reduction in the PAH content with a half-life of 110-133 days for each PAH was measured. After conclusion of the microcosm test, slurry tests (soil suspended in water on shaking table) were carried out for 69 days. The lowest and highest concentrations of the selected PAHs were 1-2 mg/kg DM anthracene and around 5 mg/kg DM fluoranthene, respectively. After the 69 days, no significant reduction in the content of each PAH could be registered. This indicates that a further reduction of the PAH content was not possible even if the microcosm test had been longer.

As mentioned above, a reduction of the PAH content with a half life of 529-967 days was observed in the field test. At the conclusion of the test on the 496th day, the content of each PAH was around 3-4 times higher than in the microcosm test (which was the initial concentration in the slurry test). It may well be that the lower concentrations for degradation of the PAH substances in the test soil had been reached in the field test. Thus, the achievable minimum concentrations are higher in the field test than in the bench-scale test, which can be explained by the fact that the soil in the field test is much more homogeneous and was manipulated less than the soil applied for the bench-scale test. This becomes obvious when looking at the significantly greater standard deviations observed in the analytical results from the field test, as compared with those of the bench-scale test. It should be noted that soil particles greater than 4 mm were removed from the bench-scale test soil, whereas particles greater than 80 mm were removed from the field test soil.

Table 5. Percentage of PAH removed from windrows 1B, 1G, 4B, 4G and 5G and windrows 2B, 2G, 3B, 3G, and 5B in the test period (496 days), calculated using regression equations.

Test Windrows	PAH	mg PAH/kg DM		%PAH Removed	$t_{1/2}$ (days)
		t = 0 days	t = 496 days		
1B, 1G, 4B, 4G, and 5G	Phenanthrene	19.444	12.996	33.2	627
	Anthracene	8.436	6.452	23.5	967
	Chrysene	13.156	7.204	45.2	556
	Fluoranthene	28.842	18.426	36,1	674
	Pyrene	21.527	13.095	39.2	636
	Benzo(a)pyrene	12.005	6.549	45.5	529
2B, 2G, 3G, 3B, and 5B	Phenanthrene	16.425	9.977	39.3	618
	Anthracene	-	-	-	-
	Chrysene	-	-	-	-
	Fluoranthene	21.683	17.715	18.3	1428
	Pyrene	15.922	13.442	15.6	1494
	Benzo(a)pyrene	-	-	-	-
	Note: $t_{1/2}$= half-life				

On the basis of the test, it is not deemed realistic to attempt a *complete* degradation/reduction of the selected PAH in the soil from the Frederiksberg Gasworks site through on-site biodegradation. This should be seen in the light of the results achieved in the present tests and results reported in literature. Whether the same is true for PAH-contaminated soil from other gasworks sites, and from other types of tar contamination, will to a great extent depend on the following factors:

- age of the contamination;
- “form” and distribution of the contamination in the soil; and
- soil composition. (Is the soil sandy or clayey with a high or low content of organic matter? Which qualitative properties does the organic fraction have? At old gasworks sites a relatively high content of coal and coke dust particles to which the PAHs can adsorb can be expected.

It was also concluded that it is doubtful whether the biodegradation of PAHs in contaminated soil can meet the limit values of 5 mg total PAH/kg soil DM and 0.1 mg benzo(a)pyrene/kg soil DM that currently exist in Denmark. At any rate, it is a precondition that the extraction in the chemical analysis is conducted with dichloromethane.

The report emphasizes that the part of the PAH reduction that can be attributed to biological processes (total and partial mineralization) has not been fully determined. Consequently, total mineralization of PAHs is often deemed less important than adsorption processes or than partial mineralization combined with adsorption processes. It has not been determined whether PAHs adsorbed to soil particles (which are not accessible to the chemical analysis) can be mobilized again at a later time and thereby become accessible to microbial degradation.

Toxicity investigations of PAH-contaminated soil have shown a lower toxicity in soils with a high content of organic matter, because PAHs are adsorbed to the organic fraction in the soil. In these tests, the PAH substances were not bound more than they could be extracted in the chemical analysis. The fact that soil with the same content of PAHs can have widely different toxicity is interesting and requires further examination.

5. CONCLUSIONS

The study showed shown that on-site biodegradation of the 3- to 5-ringed PAHs is a slow process. Moreover, none of the different treatments of the test soil (addition of wood chips, compost, detergent etc.) resulted in a significant reduction in treatment time. At many gasworks sites there will be large standard deviations in the results, even with a large number of chemical analyses conducted at the same time. This is believed to be due to the distribution of PAHs in the soil and the form of the PAH substances (*e.g.*, large or small tar residues etc.).

Analyses of the same soil at different times is deemed problematic as changes in the soil conditions (*e.g.*, soil consistency, including water content, *etc.*) affect the ability of the extration agent to extract PAHs and, thus, affect the analytical results. The field test, which was based on a large number of analyses (a total of 960 chemical analyses), has shown that more detailed standardized methods for determining the PAH content in soil are required. The standardization should include:

- pre-treatment of PAH-contaminated soil for chemical analysis;
- method of analysis, including choice of extraction agent and method;
- selection of PAHs representing the contamination; and
- the result should be compared with a standardized description of the soil.

Moreover, execution of intercalibrations between laboratories is required. Such intercalibrations could be part of an accreditation scheme for the laboratories.

As far as PAH-contaminated soil is concerned, an assessment of remedial action (*e.g.*, biodegradation) should not be based on measurement of total PAH concentration alone, but instead on individual PAH concentrations. Furthermore, due to the large standard deviations, it is insufficient to base remedial actions on a few chemical analyses or measurements in an area. In addition to a greater number of chemical analyses and measurements it is important to conduct a more detailed assessment of the physical and chemical properties of the soil. As a final basis for a decision on remedial actions, it may prove relevant to assess the toxicity of the soil.

6. REFERENCE

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Project No. 12

Groundwater and Soil Remediation at a Former Manganese Sulfate Production Plant

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1. INTRODUCTION

The former manganese sulfate ($MnSO_4$) plant in the Municipality of Tinglev, Denmark was found to contain severe sulfate (SO_4) and cyanide (CN) contamination of the soil and groundwater resulting from on-site disposal of about 45,000 m^3 of hazardous waste. The plant operated from 1932-1970, and industrial operations included the use of coal gasification wastes as a raw materia; the disposal of production residues and gasworks waste is the source of most of the site contamination. The production residues contaminated groundwater with manganese and sulfate (sulfate concentrations up to 1,600 mg/L), while the gasworks waste caused cyanide contamination.

Off-site incineration and off-gas treatment of the buried wastes was estimated to cost 8-13 million ECU. If this traditional remediation approach were taken at each of the estimated 125 gasification sites in Denmark, the total clean-up costs could be economically prohibitive. To reduce these costs a pilot-scale demonstration was initiated to evaluate alternative remedial designs.

2. EXPERIMENTAL STUDIES

2.1 Treatment Concept

The materials requiring treatment were the disposed solid wastes, leachate from the solid wastes that has infiltrated the unsaturated zone, and contaminated groundwater. Conceptually, the leachate and most contaminated groundwater could be collected for treatment by insertion of drains beneath the deposits. Treatment of the wastes could be achieved by accelerated leaching through installation of infiltration drains at the top of the wastes to introduce suitable treatment agents. It was estimated that if leaching at a rate of 2-3 L/S annually were achieved (40-60 times the natural rate), it would take 7-10 years for contaminants to be leached from the wastes. A total of 160,000-240,000 m^3 would have to be collected and cleaned each year. *Ex situ* batch processing of the wastes was also investigated.

2.2 Leachability of Wastes

Initial laboratory investigations focused on the leachability of the solid wastes present on the site. Results indicated that CN and SO_4 leaching was highest above pH 10 and at a liquid/solid ratio larger than or equal to 20. Pilot-scale leaching tests conducted on heaps of the production residue and the gasworks waste showed that sodium hydroxide effectively leached sulfate and cyanide from the production waste. However, fine particles in the gasworks waste resulted in clogging when the leachant was added, so the leaching tests with this waste were unsuccessful.

2.3 Treatment of Leachate and Groundwater

Five possible methods for cleaning the leachate and contaminated groundwater were evaluated: biodegradation, chemical precipitation, chemical oxidation, evaporation, and reverse osmosis. An evaluation of the economics of evaporation and reverse osmosis suggested that these approaches were too expensive. Furthermore, both methods have the drawback of producing small volumes of highly concentrated liquors. As a result, they were not evaluated experimentally.

Pilot-scale tests of biological treatment of the leachate required continuous supervision and were laborious, and the biomass was insensitive to fluctuations in pH. The treatment was not evaluated further.

Laboratory experiments examined the potential of chemical oxidation and precipitation to treat specific components of a contaminated leachate or contaminated groundwater. Experiments showed that ultraviolet (UV) light destroyed complex cyanides in the concentration range of 1-25 ug/kg within 10 minutes.

Precipitation of excess sulphate in the leachate using barium chloride suggested this approach would not be practical at a large scale. The procedure removed all sulphate by forming a barium sulphate precipitate. However, high levels of barium remaining in treated liquids prevented these liquids from being recirculated into the subsurface by infiltration drains because of the likelihood of precipitation. Also, the liquids could not be used downstream without further treatment. In addition to this technical disadvantage, the process was estimated to be too expensive.

2.4 Treatment of Solid Wastes

Treatment of the sulfate-rich solid waste was proposed as an *ex situ* batch or *in situ* remediation process. In the *ex situ* batch process, solid waste would be mixed with water in a "ponded" area to increase chemical solubility through intimate contact between solution and waste. Retention times were as high as 120 hours. An improved design consisted of a fluidized bed batch treatment which eliminated the need for stirring, and water rich in sulfate was constantly removed from the top of the reaction reservoir.

In situ treatment would involve accelerating the leaching process by using pH-neutral groundwater or an aggressive leachant (containing sodium hydroxide) on the waste, and collecting leachate in collection drains installed beneath the waste. It was suggested that at a liquid/solid ratio of 20, the leachate derived from pH-neutral water may have a concentration acceptable for being returned to the groundwater. A pilot-scale treatment facility was constructed onsite. Heaped waste was leached using a sodium hydroxide solution. Objections to this technology are linked to the use of chemicals during treatment. It was concluded that batch treatments are unlikely to be feasible due to high costs and long treatment times. Furthermore, disposal of effluent is costly. *In situ* may be more viable, but it will take a long time. Costs for disposing effluent may also make this approach unfavorable.

Treatment of the cyanide-contaminated waste was evaluated using accelerated *in situ* leaching and an *ex situ* batch process. *In situ* treatment was evaluated at pilot-scale, but was found to be unsuccessful since fine-sized particles present in the wastes rapidly reduced permeability of the heap to leachant additions. *Ex situ* batch processing was evaluated at bench-scale using water at pH 7 and aqueous sodium hydroxide. *Ex situ* batch processing was shown to be unworkable because subsequent solid/liquid separation proved extremely difficult. The use of water was not recommended by the authors, since the total leaching of the cyanide was not achieved. It was therefore concluded that treatment of the cyanide wastes was not feasible, at present, due to lengthy treatment times and high costs.

3. CONCLUSIONS

In conclusion, the sulfate-contaminated wastes could be treated by an *in situ* method, although the treatment times could be lengthy and disposal of effluent costly. A viable option may be to leave the material onsite and cover it with clean soil from other parts of the site. Growing plants on the surface will minimize infiltration of precipitation. A membrane cover may be another option. Regardless of the approach used, leachate and groundwater should be monitored. The cyanide-contaminated wastes are not suitable for on-site treatment and should be excavated and removed for incineration or treatment.

Future work at the site will involve modeling of the site hydrogeology to evaluate the groundwater threat.

Project No. 13

Rehabilitation of a Site Contaminated by Tar Substances Using a New On-site Technique

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1. INTRODUCTION

This on-site remedial demonstration project combining excavation of tar contaminated soil followed by on-site *ex situ* thermal desorption was conducted at an old gasworks site in a densely populated area of Copenhagen. Excavation was conducted inside a ventilated tent. The project was regarded as a demonstration of a new on-site technique.

2. BACKGROUND

The Valby Gasworks was one of the largest in Copenhagen with an operating capacity of up to 300,000 m^3 of coal gas per day. Site investigation showed a wide distribution of contaminants in the soil and groundwater, including coal tars, phenols, ammonium compounds, cyanides, and heavy metals. One area of the site contained two tar reservoirs that had been partially filled with demolition debris after site closure. A large amount of tar was left at the base of the reservoirs. The upper part was filled with rainwater mixed with tar substances. The total amount of contaminated material in the two reservoirs was about 12,000 tonnes.

The objective of the demonstration project was to remediate the heavily-contaminated soil and debris within and around the pits using an approach that minimized off-site migration (for example, as air emissions) since the site was located in an urban area.

The project was funded by the European Union LIFE-program (44%),the Danish Agency of Environmental Protection (22%), the City of Copenhagen (30%), a consulting firm, and several private contractors. The estimated total cost was 18M DKK (U.S.$2.6 M). Seventy percent of this cost was attributed directly to soil and groundwater treatment.

3. TECHNICAL CONCEPT

Free-phase tar and heavily-contaminated materials were excavated within the tent, which covered an area of 40 by 50 m (with a height of up to 10 m). The air within the tent was cleaned using three powerful (extraction) ventilators connected to a two-stage filter system consisting of particle and active carbon filters. About 60% of ventilation air was blown in actively as fresh air at the end of the tent away from the extraction fans; the remaining 40% came from general leakages.

Although on-site thermal desorption is claimed to be suitable for treating tar contaminants, it was considered uneconomical to treat all the excavated material in this manner. A soil washing system was therefore used to provide a volume reduction step by producing clean fractions in the particle size ranges greater than 50 mm and 2-50 mm through screening and high-pressure spray washing. All solid fractions were dewatered before further treatment or re-use with the contaminated process effluent, recycled, and subsequently treated before discharge. It was observed that tar removal efficiencies were increased through use of recycled water. This was believed to be due to elevated levels of ammonia in the recycled water (up to 20,000 mg/L) which assisted tar solvation. The contaminated fraction (<2 mm) was treated using the thermal desorption process.

The thermal treatment plant consisted of two separate indirect heat treatment units, the first operating at 250-300°C while the second operated at 800-900°C.

In the first stage, water and volatile substances were evaporated from contaminated materials The off-gas was treated using a particulate dust trap and an air/oil/water separator/condenser. The second stage, operating at the higher temperatures, was used to volatilize the heavier tar substances, which were recovered in an air/tar condenser. Each treatment unit was transported in a standard 12 x 9 m container and had a maximum operating capacity of 2.5 tonnes/hour. However, during operation, its practical operating capacity was only 1 tonne/hour, the limiting factor being the rate at which energy could be transferred from the reactor walls to the material. Treated material had a residence time of approximately 3 hours inside the reactors. After treatment, the decontaminated soil was cooled using a closed single-axle screw conveyor with a box cover to prevent dust emissions.

The first stage desorber was a specially designed indirectly-heated rotary unit operated in a strictly controlled atmosphere that was slightly overpressurized and secured by inert gas. The processor was heated by a closed loop thermal fluid (boiler). The slight overpressure led the gaseous hydrocarbons and steam to the controlled condensation stage. Non-condensable gases (nitrogen, argon, methane, hydrogen, *etc.*) were removed from the condenser and fed to the oil-fired burner of the stage-2 processor. Stage 2 employed a indirect rotary heat exchanger with an external shell temperature of 1,100°C produced by oil burners.

4. ANALYTICAL APPROACH

Soil samples were extracted for 60 minutes with dichloromethane, after addition of water. The extract was analyzed on a gas chromatograph with a flame ionization detector. Identification and quantification was done by comparison with known standards—in this case coal tar. Water samples were extracted with pentane and analyzed in a similar way. Identification and quantification was done by comparison with standards for polycyclic aromatic hydrocarbons (PAHs) and BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). For analysis of phenol, pentafluor-benzoylchloride was added to the sample prior to extraction with heptane. The extract was analyzed on a gas chromatograph with an electron capture device (ECD).

In Denmark, analysis for “total tar substances” is carried out by comparison with a “natural” coal tar as standard, rather than through determination of individual PAHs (*e.g.*, the U.S. Environmental Protection Agency's list of 16 PAHs).

5. RESULTS

Analysis of the “clean” products from the soil washing process proved difficult, due to the variable nature of the coarse material (comprising pieces of brick, concrete, and stones). Only limited chemical analysis of the coarse washed fraction (2-50 mm) was carried out. Reliance was largely placed on visual inspection. Tar concentrations in the wash water increased due to its recirculation, and washing efficiency decreased because at high tar concentrations, the water lost its ability to emulsify the tar.

Concentrations of total tars in the fine concentrate (<2 mm) passed to the thermal treatment plant were found to range between 1,500 mg/kg and 83,000 mg/kg. The material was regarded to be of optimal size and homogeneity for the thermal treatment.

Because of the variable nature of the feed material and the three-hour plug-flow operation, it was difficult to match input and output samples. The characteristics were therefore expressed statistically—the distribution of values for both was approximately log normal.

Treatment efficiency was reported to be on the order of 99.8%, with total tar concentrations reduced to 22 mg/kg from a median input of 11,000 mg/kg. Comparable performance was achieved for individual PAHs, including benzo(a)pyrene, which was reduced from a median value of 100 mg/kg to less than 0.1 mg/kg.

6. HEALTH AND SAFETY

During excavation, the release of volatile substances was very high. Although ventilation managed three air exchanges per hour, it was still necessary for workers within the tent to use personal protection. Two principal levels of protection were provided:

(1) chemically-resistant suits with fresh-air supplied through an air tube for manual work in the tent involving direct contact with heavily-contaminated material; and

(2) fabric coveralls and with a fresh-air mask with multifilter for all other work operations.

Excavator operators either used the latter level of protection or were supplied with a pressurized cabin with filtered air supply.

The effectiveness of the chemically resistant suits was checked. Volatile tar substances such as BTEX compounds, phenols, and naphthalene, could not be detected inside the suits.

Both of the desorber units were protected by two independent systems:

(1) Jets spraying water on the hot internal surface thereby producing steam, which has three functions:

- as a start-up procedure to remove air/oxygen from internal hot parts before feeding materials;
- to keep the system overpressurized, relative to atmospheric pressure during operation; and
- as back-up in shutdown situations, when steam production from wet material decreased.

(2) Nitrogen was automatically added to the processor if the internal pressure dropped below atmospheric.

7. ENVIRONMENTAL IMPACTS

One of the key elements of the project was to avoid emissions to atmosphere by using a ventilated tent. One of the project's key observations concerned the noise associated with the remedial process. Air emissions from the thermal treatment process were destroyed by feeding them to the stage-2 oil burner.

It was found that with a measured level of about 60 dB(A) at the working site, it was difficult but practical to meet the maximum permitted noise level of 50 dB(A) at the site boundary.

Water from the tar reservoirs was used in the soil washing process and/or sent to a treatment plant (1 m^3/hr capacity) that consisted of an oil skimmer, cellulose filter for particulates, and an activated carbon filter.

8. COSTS

The total project cost was about 18M DKK (about U.S.$2.6M), of which 15M DKK (about 70%) was for contracted clean-up costs. The cost breakdown was as follows:

- Personnel costs (consultant and contractor), 13 %
- Operation and maintenance, 7 %
- Establishment and rental of the tent, 7%
- Soil, air, and water cleaning, 70%
- Analytical costs, 1%
- Miscellaneous, 2%

9. CONCLUSIONS

- The tent was necessary during remediation of the tar reservoirs to protect surrounding areas against volatile tar substances.
- On-site remediation of soil is difficult in densely-populated areas, mainly because of possible noise nuisance.
- Soil washing of the coarse fraction was successful, providing efficient cleaning of coarse materials (>2 mm) contaminated with tar substances

- Water in the tar reservoirs was beneficial in the soil washing process, probably due to a high content of ammonia.

- The indirectly heated thermal treatment plant was capable of treating tar polluted soil with a cleaning effect greater than 99.8%.

- Protective masks and suits are essential and effective when working on old gasworks sites.

10. REFERENCES

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Project No. 14 Ozone Treatment of Contaminated Groundwater		
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1. INTRODUCTION

In 1991, ADEME, the French Agency for Energy and Environment, received responsibility for the remediation of an abandoned quarry located in Vaucelles, France. The quarry had been used from 1963 to 1972 for the disposal of various chemical wastes, including chlorinated solvents. By 1980, the first signs of pollution—including foul-smelling odors and dying vegetation—had appeared in the surrounding area.

This Pilot Study project showed that combining biological pretreatment with ozone/ultraviolet (UV) oxidation to groundwater containing organic contaminants achieves levels lower than regulatory limits set for drinking water or for discharge to a river. Results of the pilot-scale study will be used to design a full-scale application by 1996.

2. REMEDIATION PROGRAM

The remediation program consisted of three phases:

Phase 1: Site investigation.
Phase 2: Study of treatment feasibility and treatment selection.
Phase 3: Installation of a pilot-plant to test an ozone based treatment process.

Phase 1, started in June 1993, identified soil and water contamination. Over 20 toxic chemicals were identified in the groundwater, including chlorinated and non-chlorinated solvents, alcohols, petroleum hydrocarbons, aliphatics and aromatics, and volatile organic compounds (VOCs). Ethanol, phenols, chlorinated solvents, BTEX, acetone, and several aliphatic hydrocarbons were noted in concentrations between 0.8 and 360 milligrams per liter (mg/L). Chemical oxygen demand was 250 mg/L; total organic carbon was 60 mg/L; and AOX was 5.5 mg/L.

Contaminated groundwater was found to be emerging at the base of a limestone hill downgradient from the quarry, which is near the Autumn River Valley. Rainwater mobilized contaminants from wastes deposited in the quarry, into infiltrated site bedrock. Contaminants infiltrated the limestone strata is a sandstone drinking water aquifer that underlies it. The contaminated groundwater flowed from the aquifer directly into the Autumn River.

During Phase 2 (begun in September 1993), a treatment process was selected for reducing contaminant concentrations in the groundwater to acceptable levels. A key selection criterion was that the process should not form any hazardous by-products. The selected process consisted of two elements: (1) a biological pretreatment; and (2) a combined ozone/UV oxidation system. The biological pretreatment involved the degradation of organic compounds within the groundwater by microorganisms, in a process similar to that used in conventional sludge treatment. However, the activated sludge was separated from the purified water using a membrane filter which in principle reduced sludge production by a factor of five over the conventional process. In the second stage of treatment, a UV/ozone process was used to treat the waste water from the biological process since it was hoped that pretreatment would degrade contaminants into a form more amenable to photochemical oxidation.

Phase 3 of the study involved a pilot-scale assessment of this remedial scheme. First, a long and deep drainage trench was constructed at the base of the limestone hill to intercept the groundwater flow. The downstream wall of the trench was lined with an high-density polyethylene (HDPE) membrane to restrict groundwater flow beyond the trench. Contaminated water was pumped from the trench into an aeration reactor where microbes degraded organic compounds. As noted earlier, using a membrane filter produced one-fifth of the activated sludge produced in a conventional process. UV/ozone oxidation was then performed on the pretreated wastewater. The objectives of the pilot-test were to optimize treatment cost and performance and to determine dimensions of a full-scale plant. Tested treatment combinations were as follows:

- ozone, and ozone/UV without biological treatment; and

- ozone, ozone/UV, and ozone H_2O_2 after biological treatment.

3. RESULTS

The main results of the study were:

- Combined biological/chemical treatment was more effective than chemical oxidation alone;

- Ozone consumption was higher in the ozone/H_2O_2 system than in the ozone/UV system, but the treatment results were the same.

- Biological pretreatment combined with ozone/UV and having a flow rate of 30 L/hour reduced chemical oxygen demand by 90-95%, total organic carbon by 80%, and VOCs by 100%.

4. COSTS

Estimated costs for reducing the VOC concentration in the groundwater to acceptable drinking water limits were reported as FF15 million (capital cost) plus FF23.7 million annually (1992).

5. CONCLUSIONS

The project showed that applying a combined biological pretreatment with ozone/UV oxidation to groundwater containing organic contaminants achieves levels lower than regulatory limits set for drinking water or for discharge to a river. Results of the pilot-scale study will be used to design a full-scale application by 1996.

Project No. 15/45

Combined Chemical and Microbiological Treatment of Coking Sites/ Bioremediation of Soils from Coal and Petroleum Tar Distillation Plants

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In France, former disposal sites of petroleum refinery wastes, including coal tars, are often characterized by concentrations of total hydrocarbons of up to 2,200 mg/kg in soil and 4,800 mg/kg in settling ponds; 3-10 mg/kg phenols; 850-1,500 mg/kg polycyclic aromatic hydrocarbons (PAHs), and 10-300 mg/kg cyanides. During this Pilot Study project, PAH-degrading bacteria were identified and the practical bioremediation of PAHs in the contaminated soils evaluated. Furthermore, an oxidation-based pretreatment to enhance subsequent bioremediation was evaluated.

Pilot-scale assessments were conducted with five different fungi and nine bacteria isolates in a recirculating bioreactor. Biopiles were constantly mixed and aerated with amendments of straw, saw dust, and uncontaminated soil. Inorganic nutrients were added to the system using a proprietary time-release nutrient that the manufacturers claimed was specially formulated to speed up degradation rates. Three oxidizing pretreatments (hydrogen peroxide, sodium hypochlorite, and ozone) were assessed by mixing them as amendments into the biopiles during their construction.

The results after two months of the trial showed that only four of the bacterial isolates and none of the fungi showed significant PAH degradation. A practical problem encountered during the pilot-study was that the high concentrations of tar present in the soil made it difficult to turn and mix the material, which may have significantly reduced contaminant accessibility. Furthermore, it was speculated that a similar problem may occur with heavy clay-rich soils. Despite these difficulties, degradation rates of 75% for PAHs (800 to 200 mg/kg after 12 months), 75% of phenols (after 7 weeks), and 50% of cyanides (after 2-3 months) were reported. Unfortunately no information was provided on the relative success of each degrader organism.

Little information was provided on the success of the oxidizing pretreatments other than that considerable additions were required to observe any increased degradation of PAH concentrations. The addition of an oxidizing catalyst, such as ferrous sulfide, was found to reduce the amount of nutrients necessary for the system. In 19 weeks, 1,000 mg/kg PAH was reduced to 50 mg/kg with pretreatment, hydrogen peroxide, and a ferrous sulfide catalyzer.

No detailed written information has been provided for this project.

Project No. 16

Combined Vacuum Extraction and *In Situ* Stripping of Chlorinated Vapors

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1. INTRODUCTION

The NOVOC™, an *in situ* volatile organic compound (VOC) removal system, is based on an air-lift pumping technology that use air injection. A remediation system installed at a former pigment manufacturing facility located in Aubagne, France, consisted of a series of NOVOC™ wells and soil vapor extraction wells and blowers. ICF Environnement, ICF's Kaiser International's French subsidiary designed, constructed and operated the system for a period of 22 months, beginning in June 1994.

2. BACKGROUND

The facility specialized in the manufacturing of paint and pigments for paints, inks, plastics, and textiles. The pigment manufacturing process involved the use of metals-based colorants and solvents. The facility operated for approximately 50 years and closed in 1986. Contaminants present included perchloroethene (PCE) and heavy metals. Initial PCE concentrations ranged from 0.085 to 3.7 mg/L in groundwater and from 10 to greater than 5,000 mg/kg in soil. The negotiated cleanup levels for PCE were 1 mg/L in groundwater and 50 mg/kg in soil.

3. TECHNICAL CONCEPT

The NOVOC™ system employs a special well design that consists of a well within a well. The outer-fully screened well extends from ground surface through the unsaturated zone and terminates at the water table. The inner well extends from ground surface through the saturated zone and is screened in the zone of contamination. An air injection line is placed in the inner well where it releases bubbles through a diffuser above the zone of contamination. Contaminated water enters into the bottom well screen rising with the bubbles. As the bubbles rise, contaminants are transferred from the liquid phase to the gas phase (*in situ* air stripping). The VOCs are separated from the water at the top of the well and are collected by a vacuum system. The treated groundwater flows back to the aquifer through the top screened outer casing. The VOCs are treated above ground in a carbon adsorption unit. Figure 1 shows the system schematic.

Numerical modeling of the gas and water flow in the inner well provided estimates of flow patterns, pressure gradients, gas and water velocities, and mass transfer characteristics within the treatment scheme. The remediation system consisted of nine air extraction wells and three NOVOC™ wells. A total of four NOVOC™ wells (NV1, NV2, NV3, and NV4) were installed, however, only three wells were located in a productive aquifer. NV1, NV2, and NV3 were installed at depths of 20 m, 36 m, and 20 m, respectively. Intercepting highly productive aquifers proved to be a limitation during operation. Pits were constructed around NV1, NV2, and NV3 (60 m^3, 120 m^3, and 120 m^3, respectively). The pits were filled with washed gravel. A 650-mm diameter, 5 m long, screened PVC casing was installed at the top of each of the pits to the depth of the saturated zone to facilitate the reinjection of the pumped water. Six monitoring wells and two pumping wells were installed during the construction of the pits for system monitoring. The pits were lined at the surface with plastic to prevent vapors from escaping.

The system operated for a period of 22 months. System monitoring included measuring water levels daily, recording well depression values, and collecting and measuring the volume of PCE recovered from the decanter, stripper, and carbon unit condenser. NOVOC™ system efficiency was controlled quarterly and consisted of collecting water samples from monitoring wells located adjacent to the remediation wells. Static samples were performed quarterly

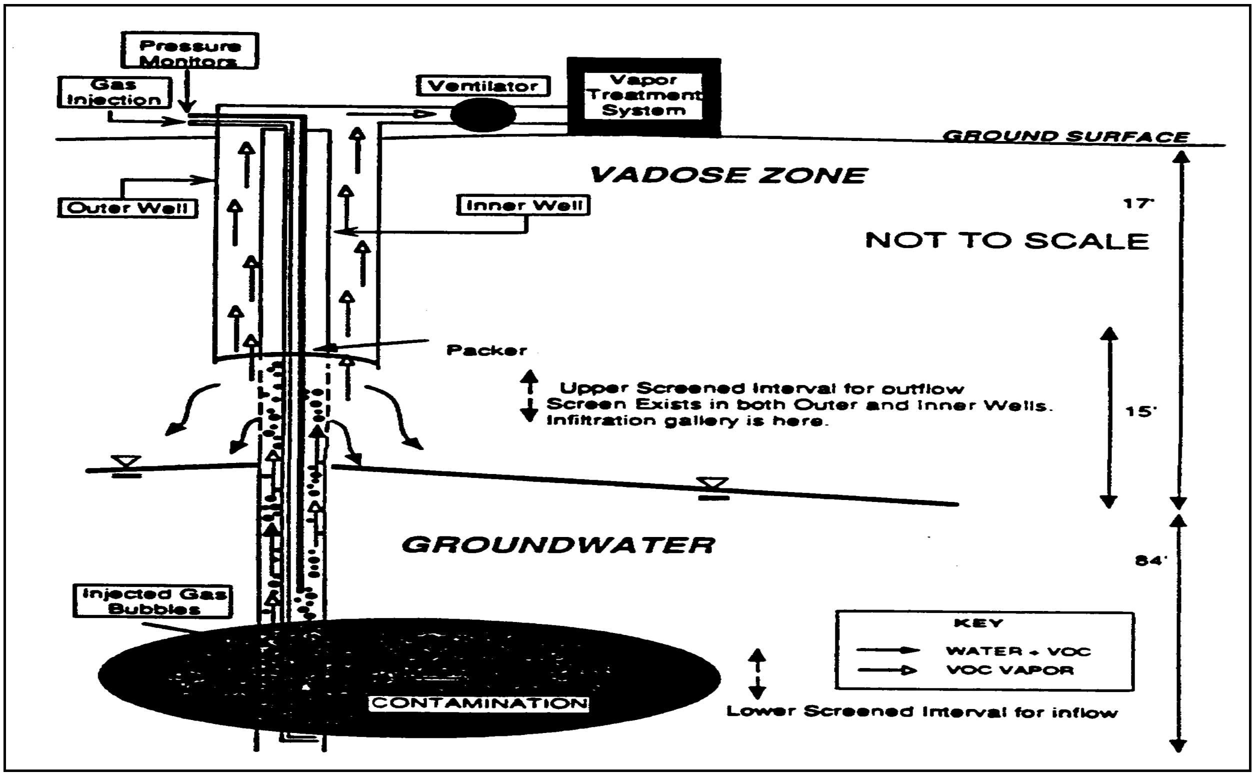

Figure 1: NOVOC™ system schematic

by turning off the soil vapor extraction wells, allowing them to equilibrate for two weeks, then sampling the soil gas from the well head. Results determined if the desired cleanup levels had been achieved and whether operation of the wells should be continued.

NV1 operated at 125 gallons per minute (gpm) and NV2 at 60 gpm. The zone of circulation was estimated to be 40 m radially from both NV1 and NV2. The circulation zone distance was determined by measuring dissolved oxygen (DO) levels in the groundwater. DO background levels were 1 to 2 mg/L, while DO levels in the circulation zone were measured at 5 to 8 mg/L.

4. RESULTS AND CONCLUSIONS

Only NV1 and NV2 wells were operated, due to the inability to pump a significant amount of water from NV3. The volume of PCE removed confirmed system efficiency. By March 1996, over 2,070 liters (3.4 tonnes) of PCE had been recovered. Results from the final soil and groundwater sampling conducted in March 1996 showed that the target concentrations of 1 mg/L in groundwater were achieved. PCE concentrations measured in the NOVOC™ wells after the system was turned off for a 1-month period were between 200 and 565 µg/L.

It has been suggested that advantages of this system over conventional pump and treat are a reduction in cost (between 10-15% cheaper than pump and treat), minimal maintenance requirements, and consolidation of contamination into a single treatable phase. Reported disadvantages include the dependence on favorable site conditions, potential cross-contamination of a any shallower aquifer and the impact of this process on local groundwater levels.

Project No. 17

Treatment of Polluted Soil in a Mobile Solvent Extraction Unit

Technical Contact:	**Country:**	**Project Status:**
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1. INTRODUCTION

The mobile *ORG-X* solvent extraction system has been developed as part of the EUREKA RESCOPP program to remediate a wide range of organic contaminants and soil types. It has been specifically developed to remediate high molecular weight compounds (for example, polycyclic aromatic hydrocarbons [PAHs] and tars), especially where contamination is associated with the silt and clay soil fractions. Under this Pilot Study project, the ORG-X process was combined with other technologies to treat PAHs, polychlorinated biphenyls (PCBs), petroleum hydrocarbons and heavy metals in a variety of soil types.

2. THE TREATMENT SYSTEM

The *ORG-X* treatment system is a continuous process using a combination of standard and patented equipment. It is based on several treatment steps. First, excavated soil and crushed debris are screened to remove oversized clean material (#4 mesh). Undersized material from the screens is passed to a solvent mixing tank where the soil and debris are mixed with solvent at ambient temperature. This provides the first solvent extraction stage. From the mixing tank, the slurry is passed to an inclined auger screw, which provides a second extraction stage in addition to solid-solvent separation. Coarse dewatered material is transferred from the top of the auger to a dryer which evaporates residual solvent, condenses it, and sends the condensate to a vaporizing recovery unit. The treated dry soil is then either stabilized, if contaminants such as heavy metals are present, or reused. Solvent exiting the base of the screw auger is further treated in a decanter to remove suspended soil fines, which are returned to the primary mixing tank. Spent solvent is treated in a vaporizer recovery unit to produce an organic contaminant concentrate and clean solvent. The recovered solvent is recycled to the initial mixing tank, while the concentrated contaminant oil requires off-site treatment. The composition of the proprietary solvent has not been reported, but it is claimed to be non-chlorinated, non-toxic, biodegradable, and oxygenated, and to have a low boiling point.

The feed rate of the *ORG-X* system depends on the soil type and ranges from 2 to 5 tonnes per hour. The system is transported in modular components on five separate trailers.

3. PERFORMANCE

Table 1 contains limited case study information presented for this technology. The ORG-X mobile solvent extraction unit operates best under optimum moisture content and grain size. In one case study, the soil moisture content of 20% made the soil difficult and more costly to treat. The process achieves higher efficiency on sandy material, but is being improved for fine-grained soils.

4. COSTS

Costs depend on the amount of material requiring further treatment, ranging from U.S.$ 200 per tonne of soil for quantities less than 2,000 tonnes to U.S.$ 90 per tonne for quantities of material over 100,000 tonnes (1994).

Table 1: Case Study Summary Information for the *ORG-X* Technology

Material Type	Principal Contaminants	Residual Contaminant Levels
Silty sand, 200 t	2-10 g/kg coal tar 250-2,000 mg/kg PAH	coal tar, not reported 6-30 mg/kg PAH
Loam soil, 12 t	200-500 mg/kg 2-4 g/kg BTEX	1-6 mg/kg PCB BTEX, not reported
Silty sand, 80 t	2,000 mg/kg heavy organics	20 mg/kg heavy organics

Project No. 18 Biological *In Situ* Remediation of Contaminated Gasworks		
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1. BACKGROUND

This Pilot Study project followed the progress of a three-year *in situ* bioremediation project of a former gasworks site in the German town of Karlsruhe. The specific test area was located beneath the location of a tar-ammonia separating sump, where spills and leaks had resulted in contamination of the underlying ground. Maximum contamination was located at a depth between 5-7 m. The <2 mm grain size soil fraction recovered from this zone contained a maximum of 55,000 mg/kg of extractable lipophilic organics and 14,000 mg/kg of polycyclic aromatic hydrocarbons (PAHs). The intention of this technology was to enhance natural degradation processes on site by providing an optimized environment through controlled addition of oxygen and nutrients.

2. TECHNICAL CONCEPT

The test area was isolated from its surroundings by sealing walls keyed into an aquiclude of impervious clay at 17 m depth, forming a test cell (Figure 1). The water level in the test cell was lowered below the level of contamination to enhance the air flow and promote aerobic degradation of hydrocarbons. A network of lances was sunk into the ground to serve as injection and extraction points for oxygen, to try to attain homogenous, horizontal, subsurface air flow. Above ground, an irrigation system was installed to allow vertical seepage of inorganic nutrients and moisture into the soil.

An objective of the study was to follow the changing concentration of leachable contaminants during the course of the experiment. This was achieved by large-scale flushing of the soil body at large intervals during the test period. Flushing was achieved by using a dedicated infiltration and an extraction well. This process was later used to introduce nutrients into the ground and to raise soil temperature by preheating the infiltration water.

3. RESULTS

Prior to field testing, considerable work was carried out by researchers to quantify the type and level of contamination, both horizontally and vertically, in the soil. Three cores were collected from the site and sampled at 1-m vertical intervals for chemical analysis. Principle methods included extractable lipophilic organics, infrared spectroscopy of hydrocarbons (IR-HC), and gas chromatography of the 16 PAHs contained on the U.S. Environmental Protection Agency list and the two methylnaphthalenes. Considerable disparity resulted from estimates of total contamination using the various assays. Detailed investigations (not elaborated for the Pilot Study) showed the non-specific parameter, lipophilic organics, to be the most suitable measurement.

After one year of bioremediation, a second set of cores was extracted from the site. The second cores were taken near the initial cores to minimize the influence of the inherent heterogeneity of contaminant distribution. Nonetheless, some paired samples showed decreases in contamination, while some actually showed increases. For technical reasons, the cores could not be closer than 0.5 to 1 m, which proved to be too far for comparison. In order to account for the very heterogeneous contaminant distribution observed in the soil, a new method was developed that gave more detailed information about the degree and distribution of contamination. Freezing the ground allowed the researchers to extract undisturbed soil cores as long as 12 m from the test area and also from the untreated (but

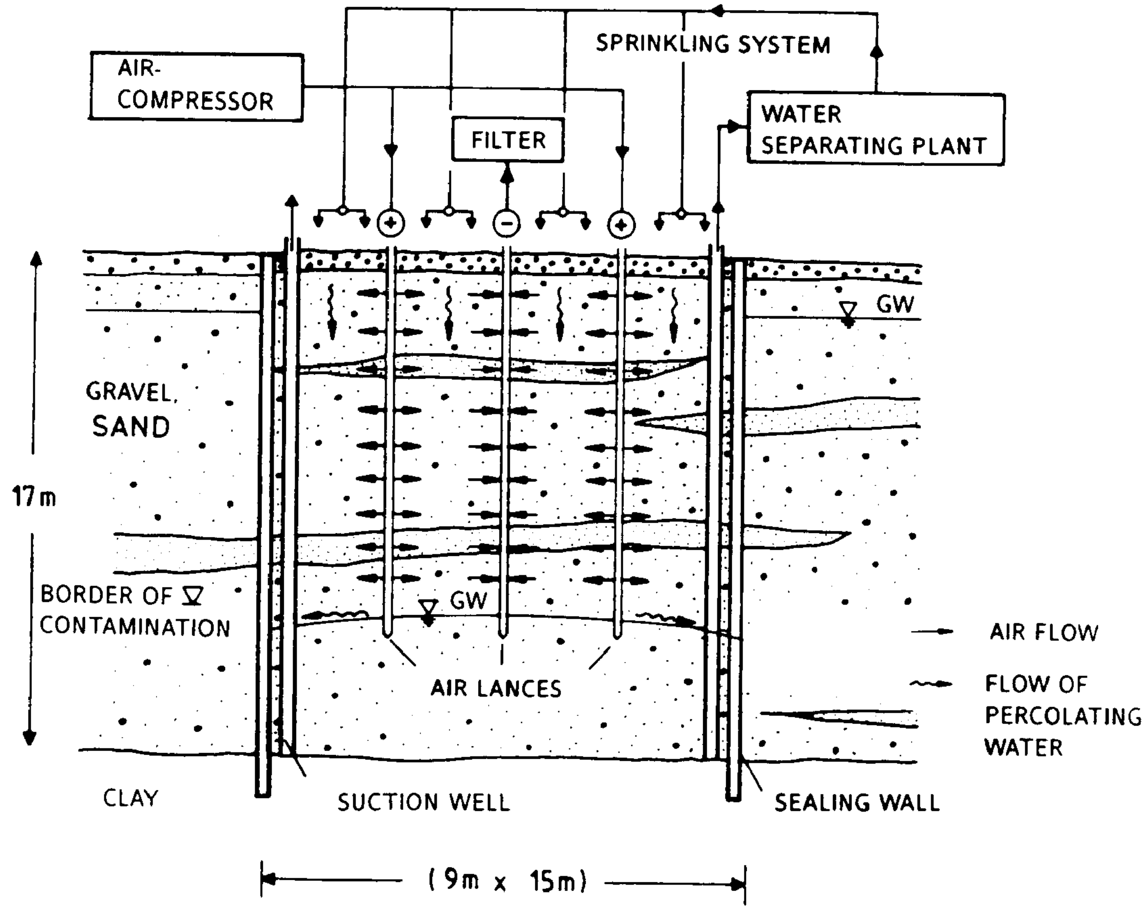

Figure 1: Illustration of principal surface and subsurface installations

uncontaminated) ground around the test site. Initial observation indicated that the tar composition between treated and untreated soils had changed during treatment. The viscosity of the tar in the treated soil was markedly higher than that of the untreated soil, suggesting a reduction in the lighter weight components. As an alternative measure of biodegradation, the authors suggested using the method of Douglas *et al.*, (1993). Assuming that in similar source material, the PAH composition remains relatively constant, and that during soil bioremediation, lower molecular weight compounds that are relatively easier to degrade than higher weight compounds will be destroyed first, then the ratio of higher to lower molecular weight compounds is an indicator of biodegradation. The authors used the 4-ring PAHs as an indication of initial concentration. Using this technique, the researchers reported that 54% of total PAHs present in the soil were degraded after 2.5 years of remediation.

Monitoring of CO_2 and O_2 over three years yielded an estimate of organic material decomposed, as well as certain conclusions about the factors which most influence degradation rates. Assuming that the hydrocarbons consumed were predominantly aromatic, the O_2 consumed and CO_2 produced account for 2,400 kg of organic material mineralized. Maximal degradation rates were seen when the soil was warmed either by flushing with warm air or water, or by natural warming during the summer months. Rapid degradation was also supported by supplying oxygen by air flushing, rather than as dissolved oxygen in water. This latter observation reinforced the desirability of lowering the water table below the level of contamination to facilitate aeration of the contaminant zone.

4. RESIDUALS

Apart from biomonitoring, determining contaminant emissions is very important for assessing the course and progress of the remediation process. It provides an indication of the hazard potential that the contaminated site still possesses.

Water was flushed through the contaminant zone approximately every three months to extract elutable contaminants. Chemical oxygen demand (COD) and dissolved organic carbon (DOC) in water samples obtained during these large-scale elution experiments are of particular interest. Because the water used for flushing was repeatedly passed through the body of contaminated soil (10-20 fold flushing of mobile soil pore water volume), it became enriched with contaminants. During the 3 years of bioremediation, the COD peaks thus obtained were reduced by about 83%, while the DOC peaks dropped about 76%. During the same period, there was a parallel decrease of 97% in the concentration of PAHs.

5. COST DATA

No cost data are available for this study.

6. CONCLUSIONS

Exactly assessing the efficiency of bioremediation in the field was difficult due to the extreme heterogeneity of the soil. Analysis of contaminant composition suggested that the more available components of the tar oil were readily biodegraded. The main limitation to biodegradation appeared to be the bioavailability of contaminants.

Bulk removal of 54% of PAHs were mirrored by large reductions in elutable components. Large-scale elution tests showed a reduction of 89% for DOC and COD, and 97% for PAH. Although in some places the soil still contains relatively high concentrations of PAH, the hazard potential of the site has been reduced considerably. Determining the extent of contaminant reduction for soil not receiving special treatment will be an important subject of further studies.

7. REFERENCE

Douglas, G.S., R.C. Prince, E.L. Butler, and W.G. Steinhauer (1993). "*The use of internal chemical indicators in petroleum and refined products to evaluate the extent of* biodegradation," In Hinchee, R.E., B.C. Alleman, R.E. Hoeppel, and R.N. Miller (Eds.), *Hydrocarbon Bioremediation*, Lewis Publishers, Ann Arbor, MI.

Project No. 19

Cleaning of Mercury-Contaminated Soil Using a Combined Washing and Distillation Process

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1. ABSTRACT

About 57,000 tonnes (metric tons) of soil and debris were successfully treated in a combined soil washing/vacuum distillation process. Soil and debris were contaminated with mercury at concentrations between 300 and 5,000 mg/kg (dry weight), with an average concentration of about 500 mg. Although in this specific project the treatment objective was to treat the soil and debris to meet the treatment criterion of 50 mg/kg to allow for landfilling, trial runs and plant optimization resulted in residual contaminant concentrations of well below 20 mg/kg. The treatment cost was estimated to be 480 Deutsche Marks (U.S.$320) per metric ton. The system is a full-scale, containerized, and transportable plant equipped with treatment systems for process water and off-gas. The daily throughput capacity amounts to 150 metric tons. Process residuals to be disposed or recycled offsite are condensed mercury, spent ion exchange resin, and a fine-grained precipitation sludge from the water treatment unit.

2. CHEMISCHE FABRIK MARKTREDWITZ SITE BACKGROUND

2.1 The Site

The Chemische Fabrik Marktredwitz (CFM) site occupies 0.5 square kilometers and was previously operated as a chemical production facility. It is located in the city center of Marktredwitz, Bavaria, Germany. Founded in 1788, CFM was one of the oldest chemical manufacturing facilities in the world. The facility was closed in 1985 because the subsurface soil and groundwater was severely contaminated. Mercury was processed at the CFM site for the production of pesticides, herbicides, and other mercury-containing products. There were accidental spills of used solvents, chemical wastes, and treatment residuals that were stored onsite. The primary contaminant of concern at the site is mercury in the concrete and brick-structures of the buildings and in the subsurface soil; concentrations between 300 and 5,000 mg/kg were detected. In 1988, the state of Bavaria decided to fund the remedial action on the site. The County of Wunsiedel, a co-founder of the project, was charged with the management of the remedial action project.

2.2 Site Remediation

In 1988, the development of a concept for comprehensive remediation of the CFM site was initiated with the objective of allowing the site to be developed as a housing and shopping area. The remedial concept consists of applying the innovative Harbauer technology to clean up the soil and debris to an extent that allows landfilling of the treated solids. The remedial approach incorporates the following elements:

- Protection of the nearby creek, “Kösseine,” by installation of a vertical groundwater barrier and a groundwater pump-and-treat system;
- Demolition of technical facilities and buildings;

- Soil excavation and backfilling (The soil on the site had to be excavated to an average depth of 4 m below the original ground surface. The excavation pit was backfilled with clean soil);

- Soil and debris treatment (A total mass of 57,000 metric tons of excavated soil and debris contaminated with greater than 50 mg/kg mercury was treated in the off-site Harbauer treatment facility); and

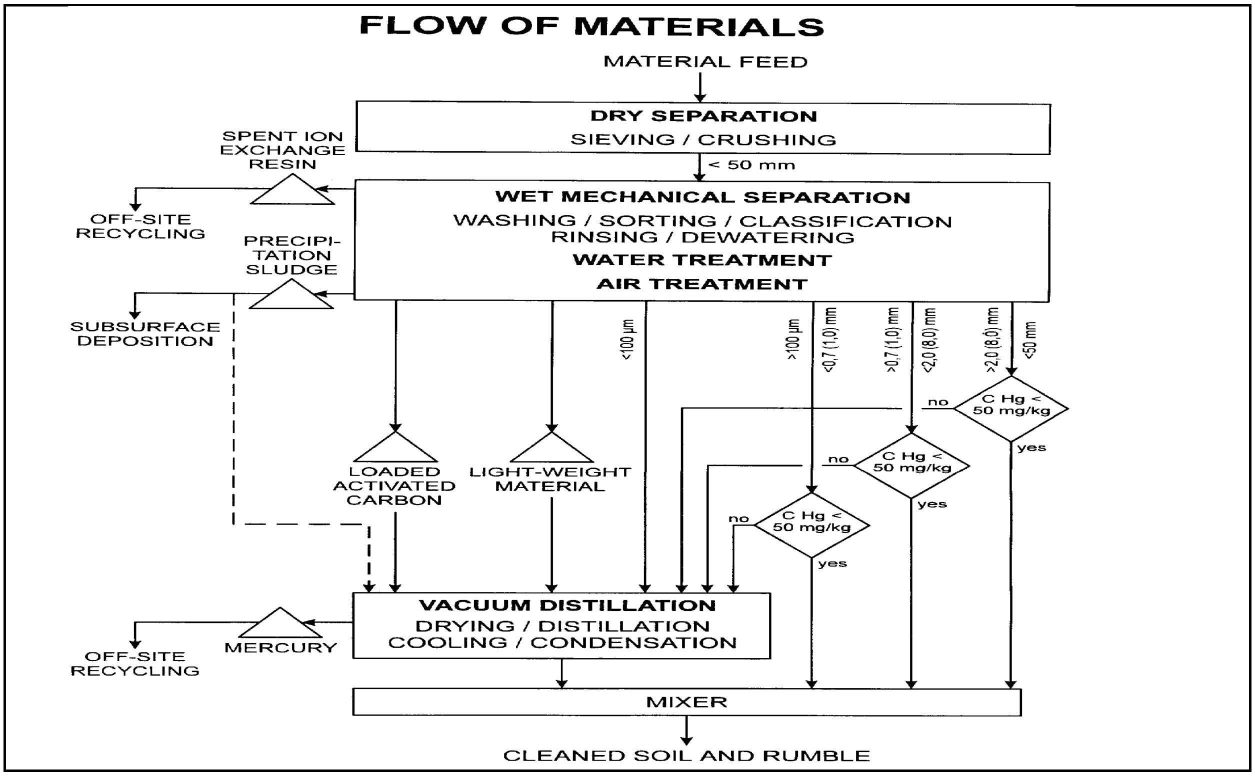
- Landfilling of treated soil near the soil treatment plant (Excavated soil from the site containing less than 50 mg/kg mercury was landfilled directly).

3. HARBAUER TREATMENT TECHNOLOGY

3.1 Plant Description and Treatment Principle

The Harbauer treatment system consists of two main processes: soil washing and vacuum distillation. The principle of this combined treatment process is to concentrate the mercury in the fine-grained portion of the soil by soil washing and to clean the resulting highly-contaminated, fine particle fraction using vacuum distillation (a thermal evaporation process) as a downstream treatment. Figure 1 shows the flow of material, in principle. The feed stream enters the facility on the top-most point and passes the process units downward without pumping.

Figure 1. Material flow



The fine-grained, highly-contaminated fraction of soil that is separated in the soil washing process is transferred into the vacuum-distillation process. This technology involves heating the soil to a temperature high enough to volatilize mercury. The Harbauer vacuum-distillation process heats the soil to temperatures between 350-450 °C at a pressure of 50-150 hPa. These low-pressure conditions reduce the boiling points of the contaminants, resulting in lower energy consumption of the entire system and a small flow of process gas amounting to only 3-5% of the gas flow, which is usual for incineration plants. Thus, process gas treatment systems with much smaller capacities are needed, resulting in significantly lower investment and operational costs. Furthermore, vacuum distillation is a low-oxygen process that is assumed to avoid the generation of dioxins or other unwanted oxidation products. The relatively moderate heating temperature is considered to cause no severe changes in the mineral structure of treated soils.

The Harbauer soil treatment plant is a full-scale, commercial, transportable plant configured as shown in Figures 2 and 3. The plant is a modular system, and the process units are preassembled in about 60 containers (3-m wide, 3-m high, 10-14 m long). The plant is gas-sealed; internal air is kept and treated; noise-reduced equipment is used; and the subsoil of the operation site is protected by a bottom-sealing system.

Figure 2

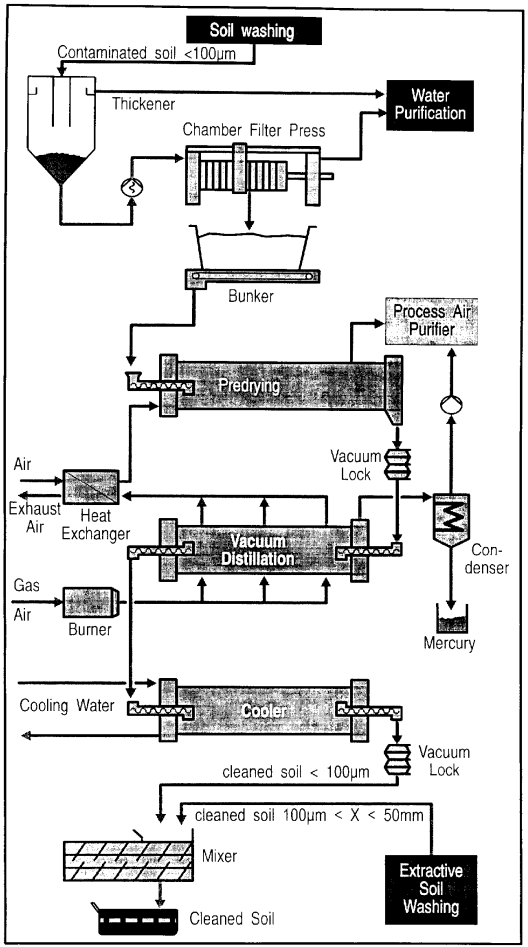
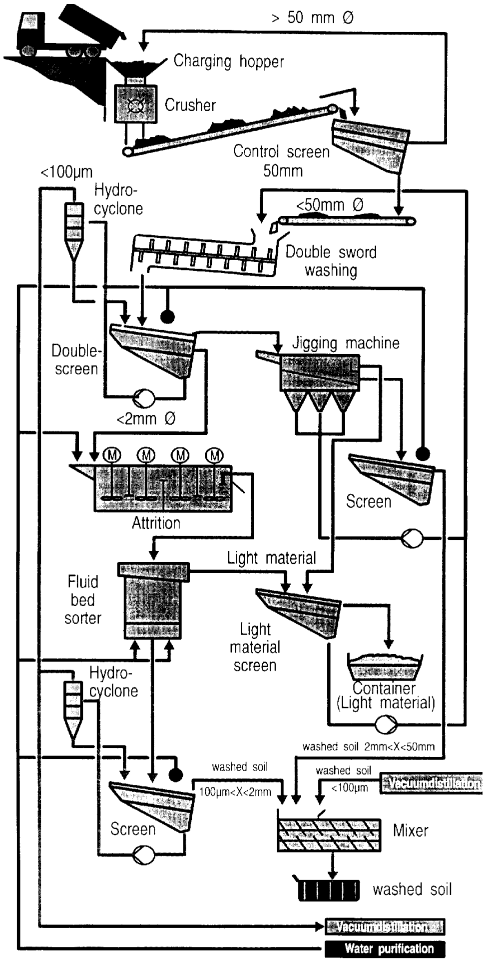


Figure 3



In addition to soil washing and vacuum distillation, the Harbauer treatment system incorporates water treatment and process air treatment. All processes are described in the following sections

3.2 Technology Description

3.2.1 Soil Treatment

Simplified flow charts of the soil washing and vacuum distillation stages are shown in Figures 2 and 3. The contaminated material is transported from CFM to the soil treatment plant in closed containers. Here, it is crushed and screened at 50 mm and then conveyed to the soil washing unit.

Blade washers and an attrition scrubber dislodge the mercury and other contaminants from the soil particles. The mobilized contaminants are separated by means of classification, sorting, rinsing, and dewatering. After the washing process, the sand and debris fraction is discharged as cleaned material. The fine-particle fraction is concentrated in thickeners, dewatered in chamber filter presses, and then transported continuously to the vacuum distillation unit using belt-conveyors and a bucket conveyor.

The vacuum distillation process consists of the following primary units: a dryer, vacuum distillation unit, and cooler. The contaminated solids are fed to a rotating drum dryer that is heated indirectly to approximately 100 °C by steam produced in a non-contact heat exchanger. Soil exiting the dryer has a residual moisture content of less than 1% by weight. The dried soil is fed through a vacuum lock to the vacuum distillation unit, which consists of a rotating drum heated indirectly by propane burners. Under low pressure conditions of 50-150 hPa and an average temperature of 350 to 400°C, the mercury and other compounds are volatilized from the solids. After passing the vacuum distillation unit, the soil is transported to a cooler, a water-cooled rotation drum. The cooled soil (temperatures less than 50°C) passes a vacuum lock and is transported to a mixer where it is mixed with washed coarse-grained material. The treated soil was disposed in the CFM landfill located near the treatment facility.

3.2.2 Water Treatment

The process water runs in circuits and is reused after treatment. Process water from the vacuum distillation unit and from the soil washing stage is first pumped into thickeners, where small soil particles are separated. The thickener overflow is pumped into a buffer tank. This tank ensures a constant flow rate in the water treatment unit and reserves a buffer volume in case of technical problems. From the buffer tank, the contaminated process water is pumped to the flocculation/precipitation stage, which consists of five stirrer vessels. In the first two vessels, $Ca(OH)_2$ or HCl is added to adjust the pH. In the next precipitation vessel, precipitation agents like Epofloc, $FeClSO_4$, and $FeCl_3$ are added. If required, HCl and $Ca(OH)_2$ are also added to adjust pH. In the next step, the process water is pumped to a plate separator.

Before entering the plate separator, flocculants are added to the process water in a flocculator to form larger particles that can be separated in the plate separator. From there, the process water is pumped to a sand filter followed by two activated carbon filters. The sand filter is used to separate the remaining very fine particles, and the activated carbon filters used to adsorb any organic contaminants in the process water. The sand filter and the activated carbon filter need to be backflushed from time to time, so a washwater vessel is filled with cleaned water coming from the activated carbon filters is used. After backflushing, the water is pumped into the washwater vessel to be treated again in the whole water treatment stage. The precipitation sludge separated by the plate separator is mechanically dewatered using filter presses. Flocculants are added to achieve good dewatering results.

The final treatment step for the process water is an ion exchanger. This requires the pH of the process water to be lowered in an acidification stage. Screen filters are used to protect the ion exchanger against plugging. The cleaned water may be discharged to the sewer with the pH adjusted to meet local requirements.

Typically, all the cleaned process water is reused in the soil treatment process. For this purpose, it is pumped into the process water tank. The desalting water (which is regarded as clean) of the cooling towers is also collected in the tank. From the process water tank, the cleaned water is pumped to the mixer and is used for the batching tanks of chemicals.

3.2.3 Exhaust Air Treatment

A dustfilter and activated carbon filter are the main units of the exhaust air treatment unit. Approximately, 25,000 m^3/h of air are extracted from the receiving hall. The dust is separated from the air in the dustfilter and is conveyed to the material feed of the vacuum distillation. The stream (20,000 m^3/h) of exhaust air from the vacuum distillation process is combined with the de-dusted stream from the dust filter, and the whole stream of 45,000 m^3/h is treated in the activated carbon filter stage. Impregnated activated carbon is used to separate the mercury. To avoid condensation in the filters, the contaminated air is heated in a heat exchanger.

After the activated carbon filter station, the cleaned air is released to the atmosphere via a stack where the mercury concentration is monitored. The height of the stack depends on local conditions.

4. TREATMENT RESULTS

4.1 Results of Routine Plant Monitoring

Thorough monitoring of the plant has shown that all requirements were met during operation of the system. Emissions were found to be well below the specified criteria. Long-term plant monitoring has shown that residual concentrations are well below 50 mg/kg, even if peaks of very high input concentrations amount to more than 5,000 mg/kg mercury (Table 1).

Besides the routine monitoring, a technology demonstration according to the U.S. Environmental Protection Agency's (USEPA) Superfund Innovative Technology Evaluation (SITE) Program protocols has been done. The demonstration results are summarized in Section 4.2.

Table 1. Mercury Concentrations in Treated Waste Streams

Unit	Period	Avg. Conc. of Mercury in Feed Stream (mg/kg)	Avg. Conc. of Mercury in Treated Stream (mg/kg)	Treatment Criteria
soil washing plus vacuum distillation	Sept. 93 - Oct. 94	average = 500 peaks up to 5,000	23	50 mg/kg
	Nov. 94 - Oct. 95		19	
	Nov. 95 - Feb. 96		7.9	
vacuum distillation	Oct. 95 - Apr. 96	-	3.6	-
water treatment	1993-96	-	(see Section 3.2)	10 µg/L
stack gas	1993-96	-	(see Section 3.2)	50 µg/dscm

About 57,000 metric tons of soil were successfully treated between 1993 and 1996; the daily average throughput amounted to about 150 metric tons.

4.2 Results of a Technology Demonstration under USEPA's SITE Program

The Harbauer Treatment System has undergone a technology demonstration in a joint project of the German Federal Ministry of Science, Education, Research and Technology and the USEPA. The technology demonstration was done according to the SITE protocols during routine operation of the plant. Based on the SITE demonstration results, the following conclusions were drawn about the Harbauer soil washing and vacuum distillation soil treatment technology:

- Average total mercury concentrations in the treated sandy loam and loam soils were reduced from 875 mg/kg to less than 18 mg/kg (95% confidence level).
- Average total mercury removal efficiencies for the soils ranged from 98-99%.
- Average Toxicity Characteristic Leaching Procedure (TCLP) mercury concentrations in the soil leachates were reduced from 82 µg/L to less than 6 µg/L.
- The average mercury concentration in treated process water discharged to the municipal sewer was 5 µg/L.
- The average mercury concentration in the treated stack gas discharged to the atmosphere was 2.92 µg per normal cubic meter (these measurements were not made during the same test runs as the demonstration soil samples that were collected).
- The estimated treatment cost is 480 Deutsche Marks (DM) per metric ton, which is approximately U.S.$320 per metric ton (assuming a 1.5 DM to 1 U.S. dollar exchange rate).

4.3 Process Residuals

- Lightweight particles separated in the soil washing process and spent activated carbon from water and off-gas polishing are collected in containers and treated in the vacuum distillation unit in batches.

- Precipitation sludge from the water treatment system is disposed to subsurface hazardous waste storage facilities.

- Spent ion exchange resin is reactivated offsite for recycling.

- Condensed mercury is disposed offsite for reuse or proper disposal. During plant operation, nearly 30 metric tons of mercury were recondensed and disposed.

- Treated wastewater and treated offgas were released with the mercury concentrations listed in Table 1. Both streams were subject to constant on-line monitoring.

5. SCOPE OF APPLICATION OF THE TECHNOLOGY

5.1 General

The modular design of the plant allows adaptation of the system to a wide range of applications that might be very different from the conditions at the CFM site. Although the soil washing and the vacuum distillation can also be operated separately, the combination of these two processes is considered to be the main advantage. In many cases, clean-up criteria cannot be met economically by using only one type of technology.

For the CFM site, a soil clean-up criterion of 50 mg/kg mercury (dry weight) was specified by the authorities because the soil was designated to be landfilled in a monofill. The soil was not used for backfilling at the CFM site. In the future, it can be expected that in other remedial projects, reuse of the treated soil will be required. For these cases, a residual mercury concentration of 50 mg/kg can be assumed to be too high. Therefore, optimization of the plant operation during test runs was performed. The results show that the combined Harbauer process allows for substantially lower residual contaminant concentrations (well below 10 mg/kg) for the combined coarse- and fine-grained stream exiting the plant (see Table 1). The soil stream treated by vacuum distillation from October 1995 to April 1996 was 3.6 mg/kg dry weight in average. Long-term monitoring of the plant has shown that the soil treated by vacuum distillation had residual concentrations well below 10 mg/kg dry weight. Trial runs done with mercury-contaminated soil from another site showed that a clean-up criterion of 2 mg/kg can be reliably met using an appropriate plant configuration.

5.2 Applicability to Contaminants

The technology is suitable for volatile contaminants with boiling points between 350-450°C at pressure ranges between 50-150 hPa. The results of trial runs with a small-scale pilot plant, serving as a model for the full-scale systems, are listed in Table 2.

Table 2. Results of Trial Runs Using a Small-Scale Pilot Plant

Contaminant	Feed Soil Concentration (mg/kg)	Treated Soil Concentration (mg/kg)
PAHs (sum of 16)	32,000	< 1
Total Hydrocarbons	102,000	< 10
Cyanide	1,728	< 10
Mercury	8,000	0.5 - 4
Lindane	3,400	0.002
TNT	100,000	0.4

5.3 Applicability to Soil Types

The soil washing separation point between the fine-particle fraction to be treated in the vacuum distillation unit and the coarser fraction, which is discharged as cleaned material, can be adjusted according to the contaminant load of the different grain size fractions. Adjustments can be made in the range between 100-µm and 8-mm particle sizes.

Three years of routine operation of the plant have shown that the vacuum distillation process is very insensitive to variations in soil type. Gravel, sandy soils, fine-grained soils (up to 90% silt and clay), slags, concrete, bricks, and other solids with mechanical characteristics similar to soil can be treated effectively and efficiently with this technology.

Project No. 20 Fluidized Bed Soil Treatment Process—*BORAN*		
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1. INTRODUCTION

The *BORAN* thermal fluidized bed soil treatment process has been designed to treat slurry residues from soil washing plants. The system is designed to treat contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The plant is operated by the designers and manufacturers of the plant, and while intended to be a commercial operation, is also intended to be used as a full-scale test bed for design modifications. The basic technology is already in use for waste treatment and a number of other applications. Due to difficulties with the feed mechanism, progress in becoming fully operational was delayed. The project will consequently be continued in the Phase III Pilot Study.

2. PROCESS DESCRIPTION

Before contaminated soil is fed into the furnace, it is screened in a vibrating bar sizer with a cut-point at 20 mm. Material greater than 20 mm in diameter is transferred elsewhere for alternative treatment and safe disposal. Material less than 20 mm is fed into the furnace.

The furnace is fitted with two overbed screw feeders for soils and four in-bed feed points for fine residues. At the design conditions, fuel oil is supplied to the bed at the rate of 725 L/hr to maintain the bed temperature at 900°C, which reportedly ensures that the organic content of the soil is fully oxidized and destroyed. The combustion chamber is rectangular with one side wall inwardly inclined to act as a deflector plate and limit bed expansion. Preheated air is injected into the chamber to ensure that feedstock (contaminated soil), combustion gases, and bed materials are circulated rapidly in an elliptical path within the combustion chamber. It is claimed that the controlled circulation produces lateral mixing and turbulence, which enhance combustion efficiency.

Immediately downstream of the reactor is a hot gas cyclone capable of removing up to 85% of the soil and fines expected to be carried by the fast moving off-gas stream. The cyclone is designed to remove up to 7.5 tonnes of particles per hour. This material is cooled using water-cooled screw feeders from around 900°C to 180°C before it is transferred to three storage silos as a clean product. The majority of the treated soil is collected at this stage, although some of the coarser particles sink to the base of the fluidized bed within the furnace and are collected as an heavy ash product.

After the hot gas cyclone, the off-gas stream passes to an afterburner where it is heated to 1,200°C by an oil-fired heater. The flue gas enters the treatment chamber at the top and passes down the center of the chamber to the exit at the base. The afterburner gases are directed tangentially at high velocity to the flue gas stream to mix turbulently with the flue gas at the top of the chamber. At the base of the chamber, a water bath with an immersed screw feeder extracts any soft entrained material. When the afterburner is in use, the following quench chamber reduces the temperature of the flue gas back to 900°C. A heat exchanger system uses the flue gases to preheat air about to be injected into the main furnace.

The flue gas cleaning plant consists of a primary and a secondary system. Primary absorption of inorganic gases such as hydrogen chloride and sulfur dioxide is achieved by mixing finely-powdered limestone into the flue gas stream. The limestone is subsequently collected in a bag house. In the secondary absorption system, any residual organics, including dioxins and furans, are collected by activated brown coal coke filters. Fouled coke is incinerated in the furnace. No performance data for this technology are available at present (July 1997).

The plant was not in operation during a visit by some members of the Pilot Study in September 1996 because it was undergoing modification to improve the feeding mechanism—the original version not being well-suited to handling clayey soils. The plant is located on a very restricted site, and the main limiting feature appears to be the very limited storage capacity for material awaiting treatment.

Project No. 21

Mobile Low-Temperature Thermal Treatment Process

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Many commercially available thermal treatment plants for contaminated soil are based on rotary kilns operating at temperatures above 500°C. However, some hydrocarbons are volatile at temperatures below 300°C offering the possibility of significantly reducing the environmental and economic costs of treating some soils. This project concerned the design and evaluation of a mobile low-temperature thermal treatment technology. The results reported were obtained from a pilot-scale plant. Although a full-scale plant has been designed, one has yet to be built.

1. BACKGROUND

Ruhrkohle Umwelttechnik GmbH (RUT) has operated thermal treatment facilities for contaminated soil since 1986. In 1990, RUT initiated development of a mobile low-temperature treatment system for a range of soil contaminants (such as volatile hydrocarbons, chlorinated solvents, and mercury) with the following aims: to reduce overall treatment costs compared with high temperature treatment; to reduce plant transport costs in order to increase applicability of on-site treatment to smaller remediation projects; to improve performance and cost effectiveness of thermal treatments for fine-grained and especially clay-rich soils; and to reduce project initiation times by producing a process that did not require regulatory permitting for any off-gas or effluent emissions.

2. PROCESS DESCRIPTION

2.1 Pilot Plant

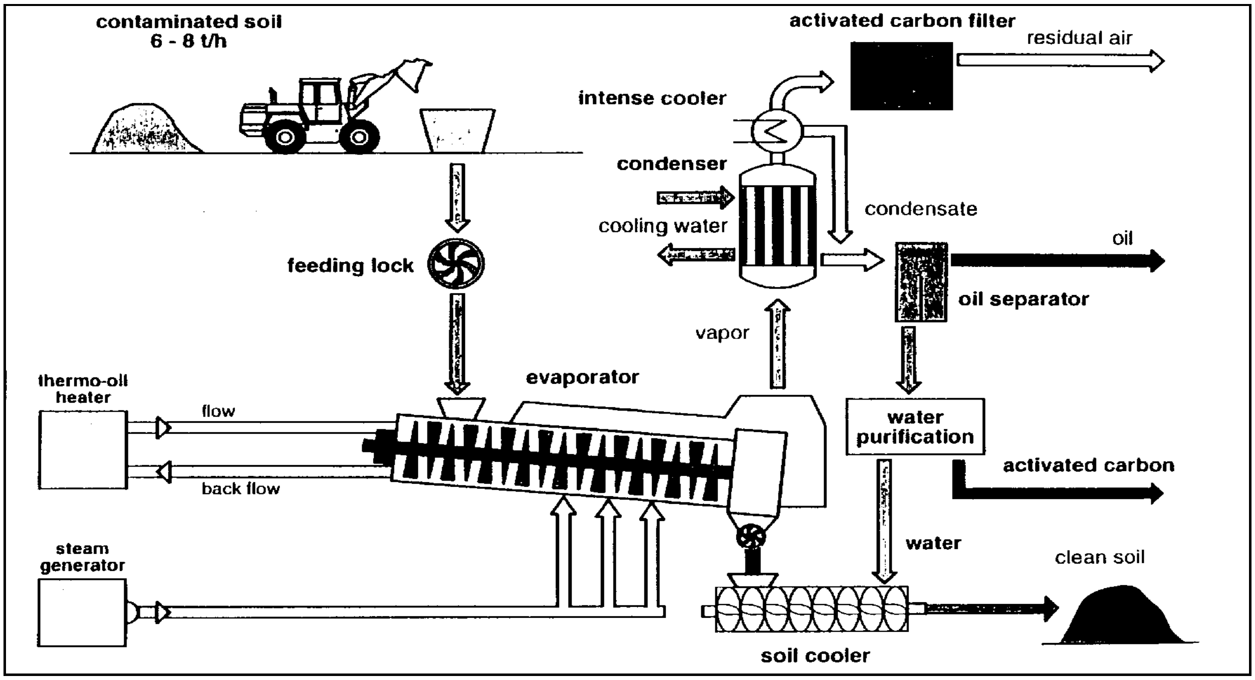
The pilot plant has a capacity of 150 kg/hr and is housed in two containers. The process, which is shown schematically in Figure 1, involves heating soil (<15 mm grain size) in a gas-tight evaporator at temperatures in the range of 200-330°C (lower temperatures can be employed for BTEX compounds—see below) under continuous agitation for about 45 minutes. The soil is indirectly heated via thermal oil, which acts as the heat transfer medium. During the first five minutes, the soil is dried and then heated to the required temperature. Contaminant removal is aided by steam injection.

The exhaust gases from the evaporator contain a large proportion of steam. Volatilized contaminants are collected from the off-gases by a multi-step condensation system. Contaminants such as chlorinated solvents and mercury are separated from the condensed steam, which is cleaned and recycled. Further contaminant separation may be carried out to produce low boiling point and high boiling point products to increase their recycling value. The cooled off-gas (at about 5°C) is further cleaned using an activated carbon filter for organic contaminants (this is regenerated using steam) and an unspecified chemical adsorption unit for inorganics (such as mercury) before discharging to the atmosphere. The treated soil is cooled to about 60°C and water added to raise soil moisture content to 7-10%.

2.2 Concept for a Commercial Scale Plant

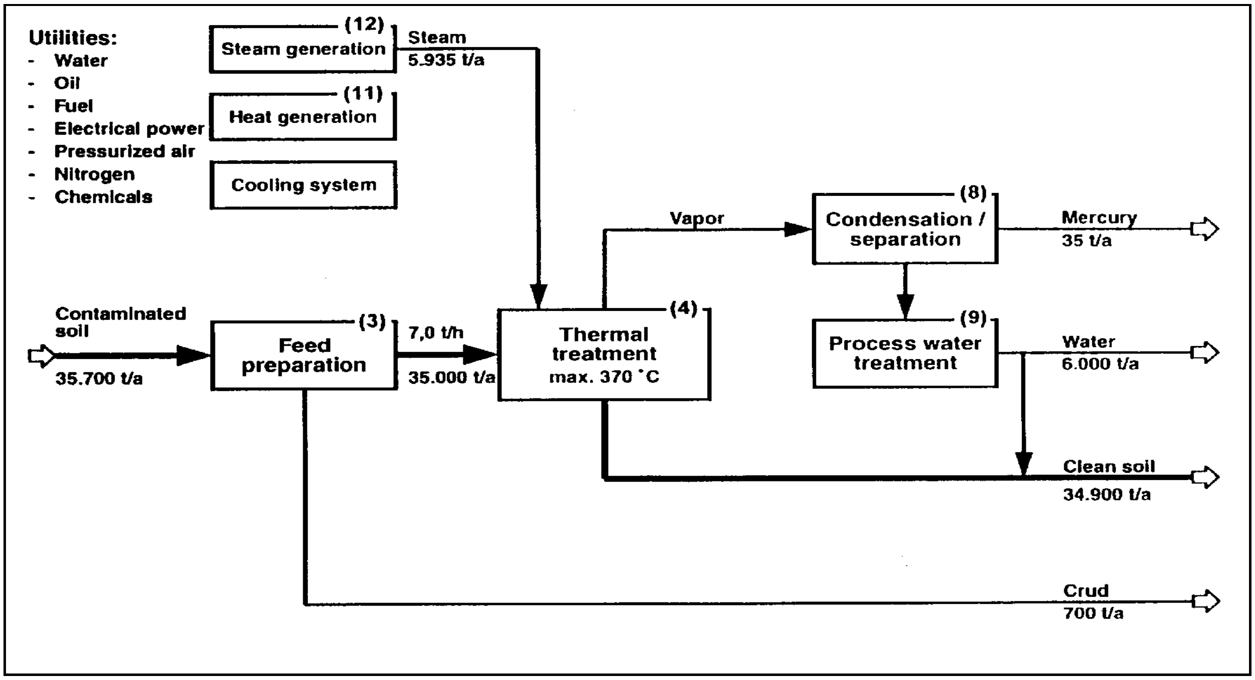
By the end of 1995, the basic engineering for a commercial plant for treating mercury-contaminated soil was completed. The plant has a capacity of 6-7 tonnes/hr. Its relatively large size results from the need for safety devices to comply with environmental protection regulations and worker safety protection rules. Plants for treating oil-contaminated soil, however, can be smaller. One major factor is that they do not require the safety devices needed for mercury. All in all, the plant requirements may be reduced to a level of approximately 65%, with consequent reduction in operating costs.

Figure 1: RUT TERRA•POR™ mobile low temperature soil cleaning system



The concept of the commercial plant to treat mercury-contaminated soil is illustrated in Figure 2:

Figure 2: Flow sheet for full scale plant



- Prior to continuous feeding to the thermal treatment unit, contaminated soil or rubble is freed from any nibs or metallic fractions.

- In the evaporator, the contaminants are evaporated by indirect heating and water vapor stripping. Then, the treated soil is cooled and remoistened with purified process water. The contaminated vapors are de-dusted with a cloth filter.

- The heat gradient required for the thermal treatment of the contaminated material is created in a thermo-oil heater. This unit houses the fuel oil tank and the facilities for the intermediate storage, feeding, and emptying of the heat transfer medium.

- The process steam plant is where the stripping steam is raised and superheated. The unit also contains facilities for the softening, degassing, and preheating of the feed water.

- Condensation involves a multi-step cooling of the hot and de-dusted vapors from the evaporator. The residual gas is finally purified with the help of activated carbon and then blown off. The contaminated residues, a mixture of water and mercury, are separated by gravimetric settling. The mercury is salvaged, and the water is cooled and used in the condensation process as quench water. Any excess water is fed to the process water treatment unit.

- The resulting process water contains mercury—both in dispersed and ionic forms. Process water treatment ensures physical and chemical purification of the water to meet the required effluent standard(s). The purified water is used for moistening the cleaned soil. Excess water is discharged.

3. RESULTS OBTAINED ON PILOT-PLANT

Pilot-scale trials (Table 1) were conducted during 1994 and 1995 to evaluate process performance and to aid design of a commercial-scale plant. The effect of steam injection was to enhance volatilization of certain contaminants at a particular temperature. Results showed that at 270°C and low steam injection rates, a treated soil sample still contained up to 35 mg/kg of polycyclic aromatic hydrocarbons (PAHs) with 5 or 6 aromatic rings. At higher injection rates, but at the same temperature, this residual concentration dropped to about 10 mg/kg. In many cases, the observed concentration of contaminants in the process water was low or below detection limits.

Table 1: Summary Results of Pilot-Scale Trials.

Contaminant		**Temperature (°C)**	**Stripping steam (kg/hr)**	**Input concentration (mg/kg)**	**Output concentration (mg/kg)**
Mineral oil in clay soil		240	6	38,000	60
Heavy mineral oil		270	5	22,000	1,000
Light tar oil (PAH C_2 - C_4)		270	6	4,500	2
Tar oil (PAH C_2 - C_6)		240	6	5,000	20
Mercury	in sandy soil	280	4	300	5
	in clay soil	330	6	900	25
	in clay soil	320	6	11,000	85
TNT		210	8	180	4.5

An additional set of experiments was set up to study to what extent the contaminant residues in treated soil are available to the biosphere. For this purpose, eluate analyses were performed. The experiments with mercury showed that although there was significant variation in treatment results (5-85 mg/kg), eluate concentrations never exceeded the detection limit.

Figure 3 illustrates the effect of temperature. In soil contaminated with PAHs (2,000 mg/kg), contamination was reduced to 70 mg/kg at 210°C, whereas it was reduced to 30 mg/kg at 270°C. For 2- and 3-ring aromatics, treatment has almost reached its maximum efficiency at 210°C, whereas for higher-boiling aromatics, significant improvement was observed at temperatures up to 270°C.

Figure 3: Results in relation to temperature

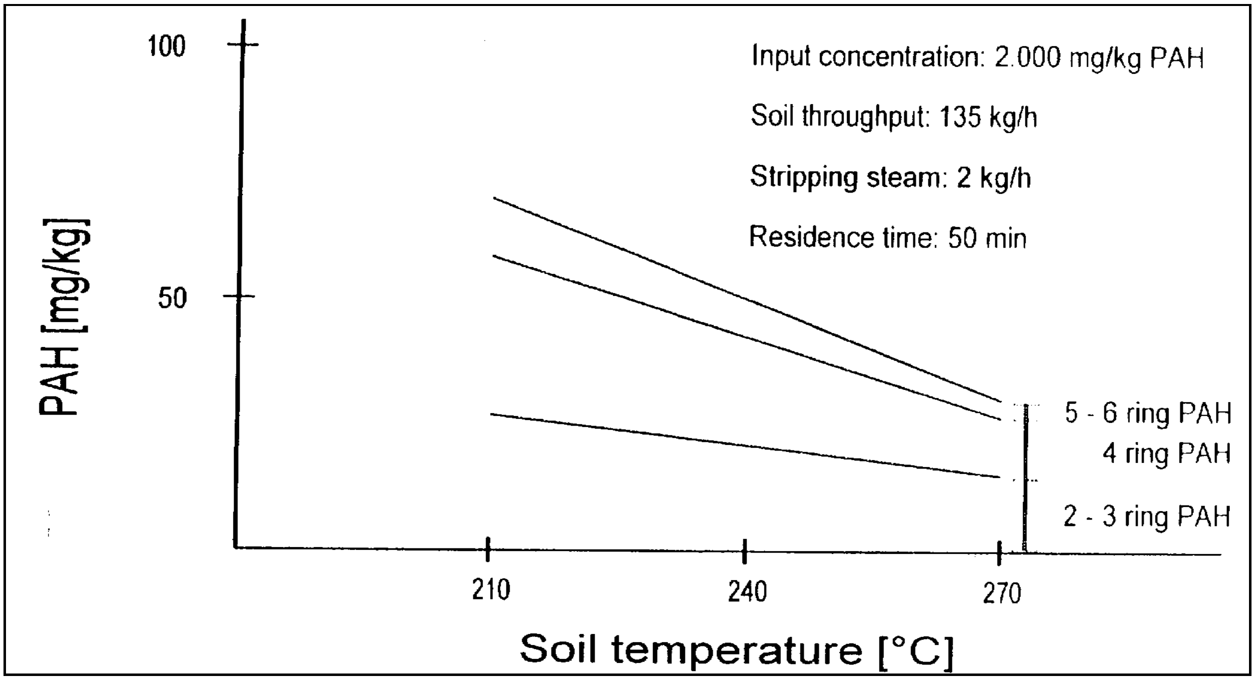


Figure 4 shows how increasing the amount of steam at a fixed temperature (270°C) increased the effectiveness of the process. Thus, the same effectiveness can be achieved at a lower temperature.

Figure 4: Results in relation to amount of steam

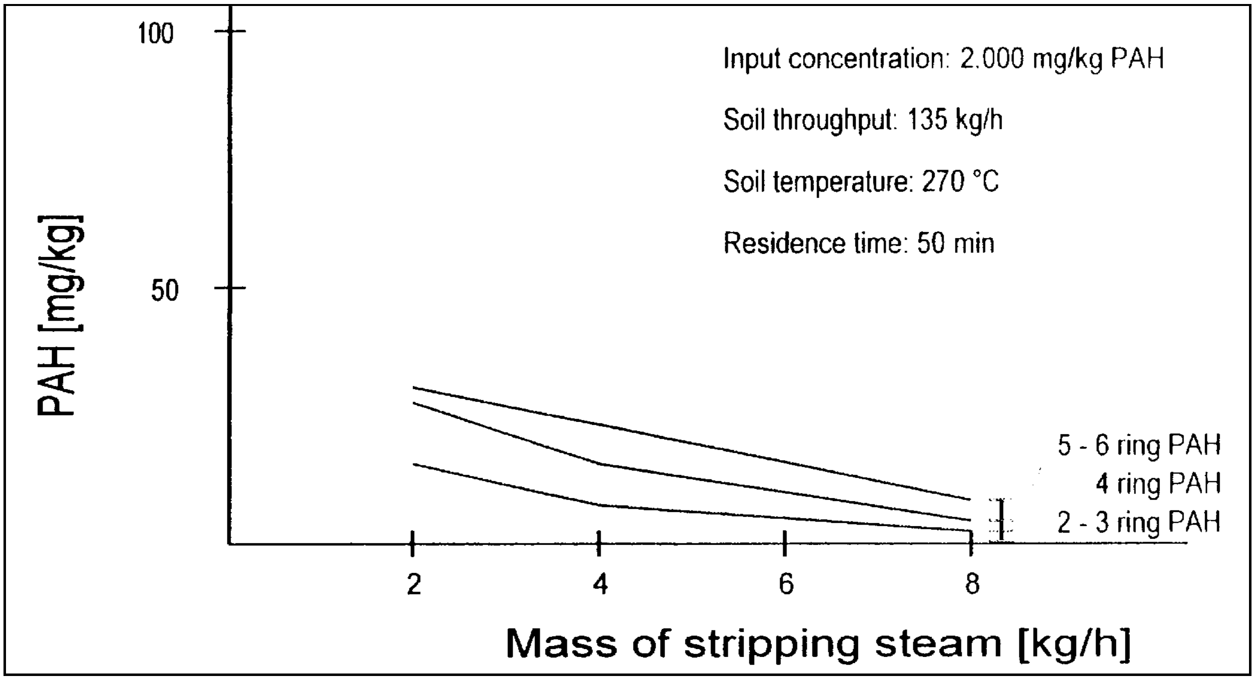
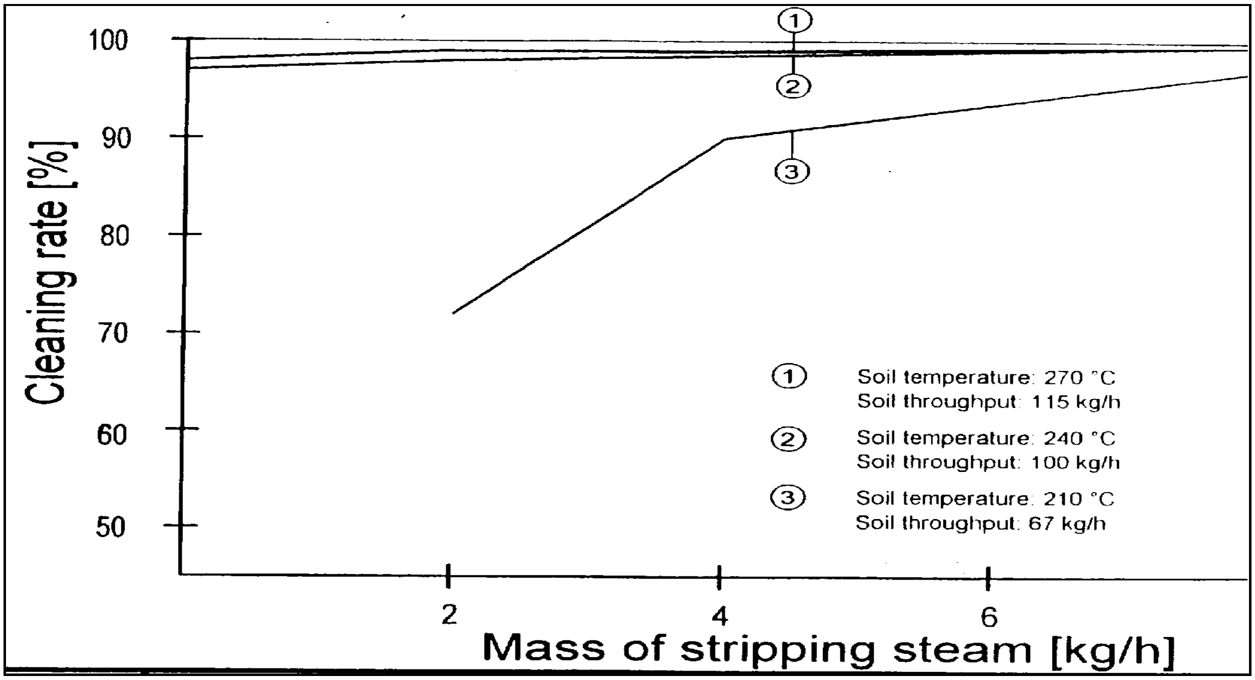


Figure 5 illustrates the impact of steam on PAH removal at various temperatures. The effect of steam was insignificant between 240 and 270°C, whereas a clear effect occurred at 210°C. Application of 8 kg/hr steam at this temperature resulted in a similar degree of PAH removal as at 270°C without steam.

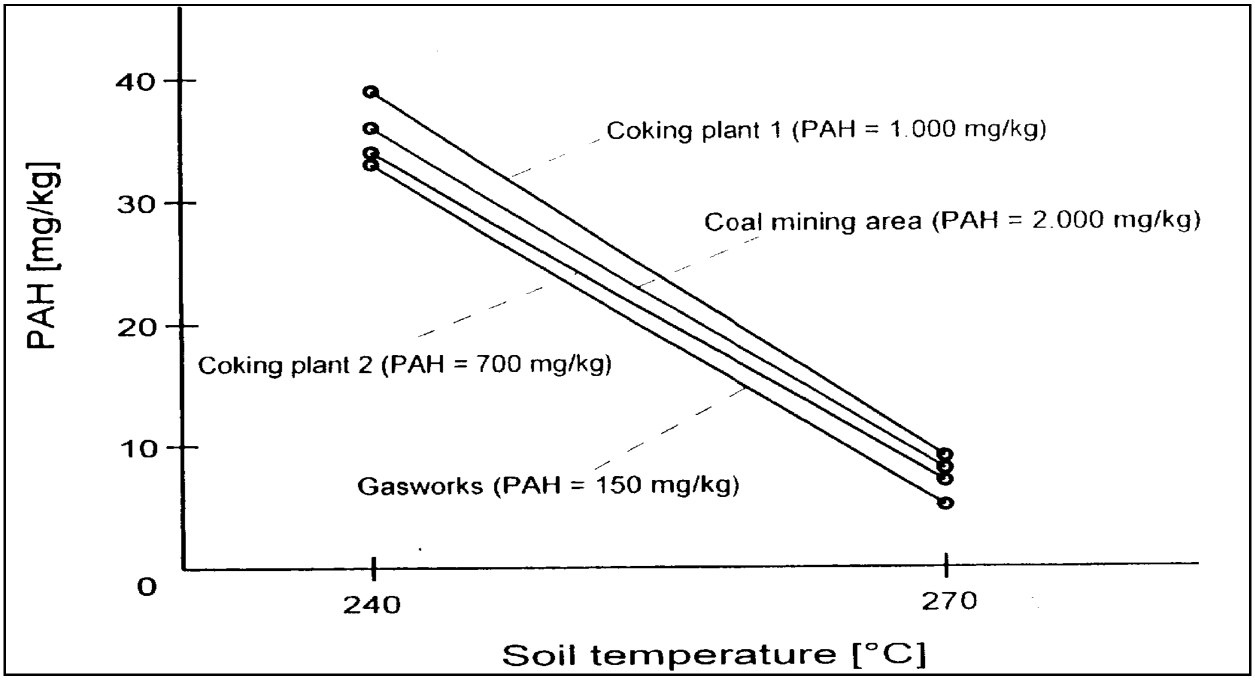
In 1996, additional experiments were carried out on a variety of PAH-contaminated soils from a number of coking plant and gas works sites in the Ruhr area. The soils were treated under otherwise identical test conditions (residence

Figure 5: Results in relation to temperature and amount of steam



time and quantity of steam) at temperatures between 240°C and 270°C. Analytical results of the treated soils were very similar (see Figure 6), thus confirming the wide applicability of this process. In addition, soils contaminated with lignite tar oil could be treated successfully at 270°C in the pilot plant. The results are presented in Table 2.

Figure 6: Results for different PAH-contaminated soils



Treatment was extended to include bulk material and activated carbon loaded with BTEX compounds (benzene, toluene, ethyl benzene, and xylenes). Treatment of activated carbon was investigated to determine if the process might be a cost-effective alternative for the well-established regenerative process. The presence of BTEX compounds and activated carbon required special explosion protection measures. The experiments were performed with high steam loadings (8-12 kg/hr), and the dust filter was de-dusted with the help of nitrogen, instead of compressed air.

Table 2: Test results for 1996

Material treated	Conditions (residence time: 40-60 mins.)		Input (mg/kg)	Output (mg/kg)
	Temperature (°C)	Stripping steam (kg/hr)		
Soil with lignite tar oil	270	8	MKW 1,500 KW 17,000	MKW 80 KW 750
Bulk material with BTEX	90	8	4,500	40
Activated carbon with BTEX from air treatment	270	12	7,600	45
Activated carbon with BTEX from water treatment	270	12	45,200	850

The low-boiling BTEX compounds were successfully removed from the bulk material when steam stripped, even at treatment temperatures of 90°C (Table 2). Such lower treatment temperatures save energy and also preserve the physical structure of heat-sensitive bulk material. Quantitative separation of BTEX compounds from activated carbon required a temperature of 270°C (Table 2). The considerably higher temperature, compared to the bulk material, results from the higher adsorption power of activated carbons.

4. COSTS

According to RUT, the costs of cleaning soil using a full-scale plant based on this process would be about 150-250 Deutsche Marks (U.S.$90-160) per metric ton, depending on the contaminant(s). The cost depends on the plant equipment required and waste disposal costs (which vary according to the contents of the harmful substances and the composition of the soil).

An important cost-related factor is the quantity of soil to be treated at a particular site. A mobile plant cannot really compete with stationary plants when only a small amount of soil is to be treated. However, for larger quantities of soil, treatment of the above contaminants in the mobile plant is less expensive, because on-site cleaning does not involve any transport costs for the soil and does not require any expenditure for obtaining permits. Another advantage of the mobile plant is that it may be installed rapidly and operated for up to 12 months under German law without the necessity for time-consuming applications for approvals to set up and operate.

5. REFERENCE

Fortmann, Jürgen, Peter Jahns, and Klaus Kossmann. *Mobile low temperature thermal soil treatment process.* Paper presented at NATO/CCMS meeting, Golden, Colorado, 1997.

Project No. 22

Environmental Evaluations of Former Soviet Military Bases in Hungary

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1. INTRODUCTION

After the withdrawal of the former Soviet army from Hungary in 1990, the Hungarian Ministry for Environment conducted an environmental assessment and damage survey. Hydrocarbon soil contamination was found to have affected 2.7-3.0 million m^3 of soil and between 1.0-1.2 billion liters of groundwater.

Tököl airbase was one of the sites identified as needing prompt remediation since it is located just 600 m from the Danube River, and on top of the aquifer that supplies Halásztelek with about 5% of its municipal drinking water. Site investigations determined that the groundwater was contaminated by free-phase and dissolved hydrocarbons from a jet fuel storage area. Contaminated groundwater from the airfield was migrating slowly towards the abstraction water boreholes for Halásztelek.

Remediation at Tököl was accomplished in phases between August 1991 and June 1993 in cooperation with the Danish Environmental Protection Agency. Free product was separated from contaminated groundwater by depressing the water table to speed flow of groundwater to extraction wells, pumping, and on-site water/oil separation.

2. BACKGROUND

After the withdrawal of the former Soviet army from Hungary in 1990, the Hungarian Ministry for Environment conducted an environmental assessment and damage survey following a method acceptable to both the Hungarian and Soviet governments. One hundred seventy-one garrisons, 340 settlements, 6,000 major buildings, and 46,000 ha of land were included in the survey. Hydrocarbon soil contamination was found to have affected 2.7-3.0 million m^3 of soil and between 1.0-1.2 billion liters of groundwater. During the assessment, between 5.5 and 6.5 million liters of hydrocarbon product was found as non-aqueous phase liquids (NAPLs) floating on the surface of groundwater.

Due to time and funding constraints, work was begun in 1991 at the 20 most-polluted bases, with an objective to contain the pollution. By the end of 1993, eight sites were fully remediated, while the remaining 12 major sites were completed in 1994. The goals of the 1993-94 assessment were to identify those remaining sites that required remediation and those sites where only monitoring is necessary.

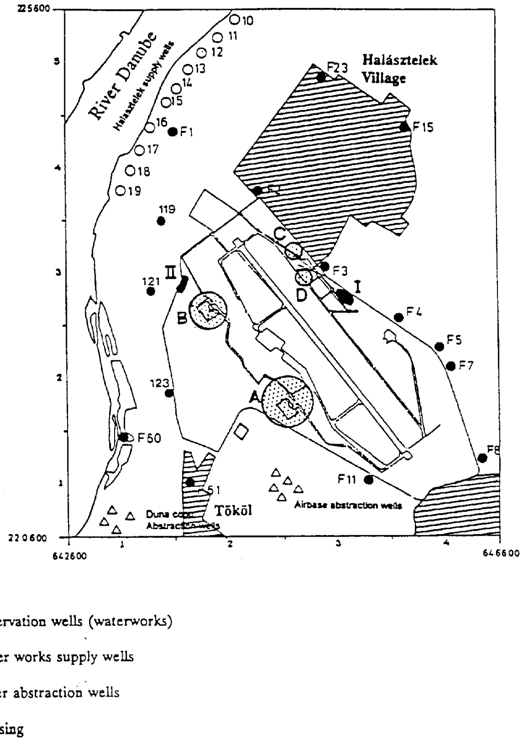
Site investigations at Tököl airbase determined that the groundwater was contaminated by free-phase and dissolved hydrocarbons from a jet fuel storage area. Contaminated groundwater from the airfield was migrating slowly towards the abstraction water boreholes for Halásztelek.

3. TÖKÖL AIRBASE

3.1 The site

The Tököl airbase is situated in the northwestern part of Csepel Island, about 1 km from Halásztelek and about 1.2 km from Szigethalom and Tököl (Figure 1). The airbase is about 2.5 km long and contains a 60-m wide concrete runway.

Figure 1: Location of Tököl Airbase (not to scale shown)



Location of Tököl Airbase, Halásztelek and Tököl Village (1:40.000)

Forty-two hangars are arranged in three blocks. Between the hangars are shelters and ammunition stores. A fuel storage and filling station (capacity approximately 6,000 m^3) is located in the southwestern part of the airbase.

The airbase overlies a major aquifer (capacity about 600,000 m^3/day) that supplies drinking water to the local population. The hydrogeological structure of the aquifer consists of a clay layer about 15-20 m below the surface overlain by a 10-15 m sand and gravel layer. The water abstraction wells of the Halásztelek well field are drilled and filtered in this layer. Fine sand and sandy silt, between 2-5 m in thickness overlie the sand and gravel layer. The groundwater level is about 4-5 m below ground level. Water levels are influenced by the level in the Danube River, by precipitation rates and by abstraction from the aquifer. Groundwater flows in a west and northwest direction at a rate of about 40-50 m/year.

3.2 Investigation, Assessment, and Remediation

The Hungarian Institute for Environmental Management began investigating the airbase in August 1991. On the basis of the investigations, 12 recovery wells and 46 infiltration wells were drilled in the second half of 1992. Recovery operations were continued in four locations until June 30, 1993.

Recovery of free product and groundwater containing dissolved hydrocarbons was carried out by:

- separating water and free product using 150 mm small-diameter Filter Scavenger pumps in large-diameter recovery wells.
- depressing the groundwater table in the vicinity of recovery wells to speed up the flow of free product.

From November 1990 to June 1993, approximately 280,000 m^3 of contaminated groundwater were pumped out. Approximately 224,000 liters of free product were recovered. By April 1994, the volume of recovered jet fuel had reached about 700,000 liters.

3.3 International Collaboration

A group of Danish firms were commissioned by the Danish National Environmental Protection Agency to assist the Hungarian authorities in the investigation and remediation of Tököl airbase. The Danish input was made in close cooperation with the Hungarian authorities and using Hungarian sub-contractors, such as laboratories and drilling companies. Danish input was provided in two phases:

Phase 1: investigations and preventative water abstraction; pumping tests; procurement, delivery and installation of pumps; sampling and analysis of water samples.

Phase 2: support through five workgroups: the Risk Group, the Recovery Group, the Monitoring Group, the Model Group and the Bio Group. The work of the five workgroups is summarized below:

Workgroup	**Area of Work**
Risk Group	Assessment of potential human health and environmental impact of contamination and the need for and extent of any remedial action. Work has included collection and assessment of data, monitoring, hazard assessment, and review of international and Hungarian standards for contaminated soil and groundwater. Assessment indicated that the main potential impact of the airbase was on the Halásztelek aquifer; ecological effects were judged to be insignificant.
Recovery Group	The main purpose of this group was to minimize further dispersion of contamination and maximize free-phase recovery of jet fuel. Work has involved data collection, delivery and installation of equipment, training, evaluation of recovery strategy and associated data, and maintenance of equipment.
Monitoring Group	The purpose of this group was to monitor the status of the contamination present at the airbase, together with any trends over time. Data obtained on groundwater levels, thickness of free-phase product, and contaminant concentrations in soil and groundwater samples are fed into a database from which graphic representations of the subsurface conditions can be made.
Modeling Group	Two separate models have been used: the SHE model for groundwater flow and contaminant transport; and the ARMOS model for migration of free-phase product. The SHE model was used primarily to predict the dispersion of contaminated groundwater to local receptors (*e.g.*, Danube and abstraction wells at Halásztelek). The ARMOS model was used primarily to optimize the free product recovery operation. Model predictions (conservative) suggested that the dissolved hydrocarbon contamination (from Zone B of the airbase) would reach the water catchment area with 6 - 8 years and from Zones C and D within 12 - 18 years; and that contamination from Zone A will reach the Danube in 12 - 18 years. The potential for biodegradation of dissolved hydrocarbons in groundwater has also been investigated using the SHE model.
Bio Group	The purpose of this group was to explore the potential for biodegradation and to create a basis for implementation of *in situ* biological remediation. Work activities have included the establishment, operation and monitoring of a pilot scale *in situ* biological treatment plant; laboratory tests and field measurements to identify an appropriate test field; monitoring of pilot scale operations and recommendations on the development of a full-scale biological treatment plant.

3.4 Costs

The total cost for remediating the Tököl site has been estimated to be U.S.$600M (1994).

3.5 Conclusions

1. Large quantities of free-phase jet fuel have been recovered from the Tököl airbase and immediate risks to a major potable water supply source at Halásztelek have been reduced.

2. However, free-phase jet fuel cannot be recovered by pumping operations alone, and contamination adsorbed onto soil in the unsaturated zone is also present at the airbase, posing a long-term source of water contamination.

3. Pilot scale *in situ* biological treatment was successful and was recommended as an effective method for securing further reduction of the risks to groundwater quality posed by the airbase.

4. REFERENCES

1. Reiniger R. and Z. Horvath. *Environmental problems at former Soviet military bases in Hungary* Paper to NATO/CCMS meeting 1993.

2. Anon. *Danish assistance in the remediation of Tököl airbase near Budapest, Hungary, Phase 2* (Final report: summary, prepared for Danish Environmental Protection Agency, June 1994).

Project No. 23 Modeling and Optimization of *In situ* Remediation		
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1. INTRODUCTION

In situ remediation of contaminated soil and water is widely perceived to offer the greatest potential for enhancing performance and reducing the cost of treatment. However, its commercial implementation has been limited by the perception that current methods are unreliable and their treatment duration unpredictable. The unpredictability of full-scale *in situ* treatment is not solely due to the complex heterogeneity of field sites, but also due to economic and time constraints on the preliminary collection of field data. Treatment design and predicted performance are often based on bench-scale studies used in combination with models incorporating subjective default data values. The results are often misleading and overly optimistic. This Pilot Study project reports on several aspects of an investigation into the modeling of *in situ* treatment with an overall goal of enhancing and optimizing treatment performance.

2. THE MODELS STUDIED

2.1 Soil Vapor Extraction

A predictive model for soil vapor extraction (SVE) was the first model discussed (Budapest meeting, 1992). A literature survey revealed that although several groundwater models existed, there had been relatively little development of soil air models for predicting the performance of SVE. The presentation focused on a spreadsheet model which had been developed by *Tauw Milieu* to predict SVE performance for sites contaminated with up to three volatile organic compounds (VOCs). The model consisted of differential equations linked to a mass balance based spreadsheet. Model outputs included the cumulative amount of contaminants extracted and soil contaminant concentration (both as a function of time). The model output was used to determine expected treatment durations. Parameters and expressions within the model accounted for equilibrium sorption to organic matter, transfer from liquid to vapor phase and contaminant interactions, diffusion, biodegradation, and time dependence. Four case studies were evaluated using the predictive model: one laboratory-based study, two on-site studies, and another conducted *in situ*.

2.2. *In situ* Soil Flushing

A model developed to predict the treatment duration of *in situ* soil flushing has also been discussed (Quebec City meeting, 1993). This model examined change in contaminant concentrations in extracted water as a function of time which is an important parameter in determining treatment cost and equipment requirements for above-ground water treatment. The model methodology reportedly improved the handling of uncertainty within the site and contaminant invariability in data across a site. Predictive results for a remediation scenario where monochlorobenzene had contaminated soil and groundwater at a model site were presented. A simple predictive model (a first-order approach) combining transport factors with an expression for the linear adsorption of organic compounds by soil organic matter was linked with a statistical simulation to model heterogenous site distributions of organic matter and adsorption coefficients. Assuming a homogenous distribution of site parameters, soil flushing duration was predicted to achieve the remedial target for groundwater contaminant concentration in three years. However, modeling site parameters more realistically using an heterogenous distribution increased treatment times to the order of decades. The authors stressed that a higher quality of soil investigation was necessary in order to generate a realistic prediction of remediation duration and cost.

2.3 *In situ* Bioventing

A model developed to investigate the effectiveness of *in situ* bioventing was presented at the NATO/CCMS Oxford meeting in 1994 and the Adelaide meeting in 1996. A mechanistic model, dubbed ECOSAT, was developed and calibrated with data from laboratory batch and column bioventing tests. The advantage of mechanistic models over simplified empirical models is that they allow for scenario calculations. Scenario calculations, in turn, may help to develop site specific soil investigation strategies, to evaluate different combinations of remediation techniques, and to design and optimize the process control of the selected techniques.

The calibrated model was used to predict bioventing performance and the predictions were compared to ten full-scale soil venting projects. Ideal assumptions were made: (1) the aquifers were homogeneous and sandy; (2) the contaminants mobile and easily biodegraded; (3) non-aqueous phase liquids were absent; (4) that average measured values represent degree of contamination and permeability; (5) retardation factor and K_d are constant; and (6) zero or first order decay adequately describes the kinetics of the process. Comparison with field data revealed that predictions based on averaged properties are too optimistic—the duration of the remediation is longer than predicted. In full-scale remediations, the initial gas phase concentration is somewhat higher than estimated, and after a first rapid concentration decrease, the rate of the venting process changes considerably. As a result, the remediation process stagnates. The deviation between the estimated and observed duration of remediation differs by at most one order of magnitude. The stagnation of biotreatment suggests that a significant fraction of contaminants is unavailable to the treatment process.

Following up on the results presented at the Oxford meeting, the authors used the ECOSAT model to more fully investigate the stagnation phenomenon. The model was used to investigate whether availability of the substrate was reduced by non-linear contaminant sorption, heterogeneity or spatial variability in site parameters, or non-equilibrium phenomena. The study concluded that non-equilibrium phenomena, particularly diffusion-controlled mass transfer from areas of the soil where convective flow is absent, were the dominant factors in treatment stagnation. This finding was supported by the anecdotal field observations that vapor-phase concentrations of contaminants often increase when vapor extraction is interrupted. The model was also used to compare continuous vapor extraction with intermittent extraction (*i.e.*, for one day in ten). Results showed that for either method, treatment times were approximately the same since they were dependent upon the slowly diffusing contaminant fraction. However, the intermittent extraction technique provided oxygen to the bioavailable water-soluble fraction of contamination much more efficiently, promoting biodegradation as the dominant contaminant removal process. In contrast, the continuous extraction method rapidly reduced the concentration of available contaminant through physical volatilization and not through biodegradation.

3. CONCLUSIONS

The use of average values as input variables for remediation models has been shown quite often to underestimate the duration and cost of the remediation program. By properly accounting for variabilities in site properties, such as permeability, organic content, contaminant distribution, *etc*., more realistic predictions of cost and duration can be achieved. A high quality of soil investigation is necessary in order to generate realistic predictions.

Project No. 24

Combined Remediation Technique for Soil Containing Organic Contaminants: Fortec®

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1. INTRODUCTION

In some cases, biological remediation of soils contaminated with petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) is only partially successful. In order to improve biotreatment effectiveness for these contaminants, *Heidemij Realisatie* is developing an innovative treatment system called Fast Organic Removal Technology (*Fortec*®). The *Fortec*® process is a combination of several reportedly proven techniques for soil and sediment treatment. This Pilot Study project described the development of the *Fortec*® process from bench- to full-scale.

2. THE PROCESS

The objective of the *Fortec*® process is to improve treatment effectiveness through increased biodegradation rates; decreased residual contaminant concentrations; and increased applicability to recalcitrant pollutants. *Fortec*® consists of three unit operations combined in series: (1) multi-step hydrocyclone separations; (2) UV/hydrogen peroxide photochemical pretreatment; and (3) slurry-phase bioremediation.

In many cases, organic contamination is found to be concentrated in the finer soil and sediment fractions, such as in silt and clay. Hydrocyclone separation is used to separate the coarser sands and gravels, which are treated as “clean,” from the finer silts and clays to form a concentrate for further treatment. *Heidemij* claim efficiency of separation is improved by using a series of hydrocyclones in a multi-stage configuration. Photochemical oxidation of the fines concentrate is an optional process. The combination of ultraviolet (UV) light and hydrogen peroxide is intended to partially oxidize organic contaminants in the soil slurry to enhance subsequent bioremediation, especially of the more recalcitrant pollutants such as higher molecular weight PAHs. The slurry is treated batch-wise within a UV/hydrogen peroxide reactor module. Organic contaminants (and their breakdown intermediaries from photochemical oxidation) are degraded in a slurry-phase bioreactor operating at between 10-25°C with a slurry containing from 3-15% solids. The bioreactor is aerated using a compressor, which injects air into the reactor through a perforated plate at the bottom of the treatment chamber. Nutrients are mixed into the slurry prior to entering the bioreactor at a level appropriate to the concentration of contaminants present. Mixing within the bioreactor is achieved by pumping the slurry from the bottom to the top. The bioreactor is operated on a batch-wise basis, with typical residence times in the order of 3-20 days. After treatment, the slurry is transported to a settling tank and dewatered by a belt filter press. The coarse and fine treatment products may be recombined, if appropriate.

3. RESULTS

Development of the *Fortec*® process has resulted from bench-scale, pilot-scale (25 and 50 m^3 volume bioreactors), and demonstration (300 m^3 volume reactor) tests. All stages of scale-up have been supported by further laboratory studies to measure biological activity during testing. Bench- and pilot-scale tests have focused on biodegradation with and without photochemical pretreatment for soils contaminated with mineral oils, PAHs, chlorophenol and the pesticide lindane (β-HCH). Mineral oil contaminants were strongly degraded by the bioreactor (reductions from 5,000 mg/kg to <100 mg/kg in 3-8 days) with no significant photochemical oxidation observed (presumably the high bioreactor degradation rates were an important factor). However, photochemical oxidation was found to be highly effective at enhancing subsequent PAH biodegradation. PAH concentrations were reduced from 30 mg/kg to 5 mg/kg in 15 days. Biodegradation without chemical pretreatment showed no PAH degradation over the corresponding period. It was reported that enhanced degradation was due to the breakdown of the soil organic matter on which the PAHs were sorbed (thereby increasing availability) rather than oxidation of the PAH molecules themselves. Biodegradation of lindane was ineffective with or without photochemical pretreatment. It was suggested that lindane was too recalcitrant to either chemical or biochemical reactions.

Based on the initial studies, a full-scale *Fortec*® Bioreactor was designed and built. This was integrated with the *Heidemij* fixed full-scale soil washing plant at Moerdijk (capacity 30-50 tonnes per hour) for demonstration tests. A quantity (unspecified) of sandy soil contaminated with heavy crude oil (up to 14,500 mg/kg) was tested using the soil washing plant and bioreactor. Soil washing separated two “clean” fractions: a coarse fraction (10.5% by soil weight) and a sand fraction (87.5% by soil weight with an average contaminant concentration of 130 mg/kg). The fines fraction (12.5% by soil weight) had an initial contaminant concentration of 110,000 mg/kg, which was reduced to 22,000 mg/kg after treatment in the bioreactor (residence time of 40 days). After treatment, the soil fractions were recombined. In a second demonstration, sediments contaminated with up to 2,000 mg/kg of PAHs were treated with a final concentration of <300 mg/kg. No cost data was included for either demonstration.

Project No. 25 Slurry Reactor for Soil Treatment		
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1. INTRODUCTION

This project focused on the treatment of excavated clay soils and sediments contaminated with organic compounds, such as mineral oil and polycyclic aromatic hydrocarbons (PAHs). The treatment technology described is the Slurry Decontamination Process (SDP), which combines separation processes with a microbiological slurry reactor. The objectives of this project were to:

- design and construct a pilot plant;
- establish all controlling process parameters;
- determine a cost per tonne of clay; and
- design a full-scale plant and secure funding to build it.

2. THE PROCESS

The flowsheet for the SDP system begins with soil pretreatment. Vibrating grizzly bars are used to remove debris (particle sizes >60 mm). The undersize particles from the bar screen are fed to a micro-pulverizer. After grinding, the soil is transported to a sieve where the coarse gravel fraction (>4 mm) is separated. In this wet screening section, both recirculation water and the nutrient addition are used as washing water.

The first bioreactor is a DITS (Dual-Injected-Turbulent-Separation) reactor. In addition to biological degradation, the slurried feed soil (particle sizes between 1 and 4,000 µm) is separated into coarse and fine fractions. Slurry is injected at the bottom of the reactor creating a controlled turbulent mixing within the suspended slurry. The coarse fraction settles at the bottom of the reactor while the fine fraction is kept in suspension. Slurry from the top of the reactor is pumped to a solid-liquid separator where particles larger than 100 µm are removed, and the treated slurry is re-injected at the reactor bottom.

From the base of the first reactor, the coarse fraction from the DITS reactor is fed directly to a dewatering plant where it is used to aid subsequent filtration of the treated fines. Fine particles from the top of the reactor are further treated in a cascade of suspension bioreactors. Approximating plug flow, a cascade of three equally-mixed tanks are optimized for first-order kinetics of contaminant degradation. Due to the removal of the coarse fraction at the beginning of the process, the designers do not expect any settling problems within the cascade reactors, which are agitated by injecting air through the base.

After being treated in the cascade, the slurry is dewatered by means of filtration. As a filter aid, the coarse fraction from the DITS-reactor is used. From the dewatering section, percolated process water is recycled to the beginning of the process. Approximately 75% of the process water is recycled. Additional water input comes from the supply of nutrients to the system. Process water temperature is maintained at 30°C by transfer of excess heat from the air compressor. Therefore, biodegradation within the bioreactors is optimized by careful control of temperature, air and nutrient supply, and slurry pH. To prevent escape of fugitive air emissions from the treatment plant, air outlets are directed to a biofilter.

3. RESULTS

The pilot-scale plant has demonstrated a reduction of 3,000 mg/kg oil to 200 mg/kg oil in 60 days; the remediation proceeded very rapidly with concentrations reduced to 500 mg/kg after 25 days.

4. CONCLUSIONS

The designers have concluded that this technology has the potential to treat polluted wet clay and peaty soils from either a mobile or fixed installation. However, the technology is restricted to the treatment of organic contaminants and will cost more than other biological technologies such as landfarming.

[Note: No final report was provided on this project].

Project No. 26

Treatment of Creosote-Contaminated Soil
(Soil Washing and Slurry Phase Bioreactor)

Technical Contact:	**Country:**	**Project Status:**
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1. INTRODUCTION

This Pilot Study project reports on an investigation into the remediation of soil contaminated with three- and four-ring polycyclic aromatic hydrocarbons (PAHs) using a process that combines soil washing (especially froth flotation) with slurry-phase bioremediation. The project consisted of two phases of work: bench scale treatability studies and pilot scale remediation trials.

The Norwegian State Railways cooperated with the Norwegian Pollution Control Authority to support the technology evaluation and develop the project. The Railways owns several former wood preserving facilities and wished to evaluate options for treating possible creosote contamination where total polycyclic aromatic hydrocarbon (PAH) concentrations exist at levels between 270 and 51,000 mg/kg.

2. BENCH-SCALE STUDIES

Bench-scale biological treatability studies consisted of two steps: (1) screening of isolated “native” soil organisms to determine their tolerance and ability to degrade PAHs; and (2) experiments to determine optimum conditions for biodegradation of selected isolates in aerated slurry reactors (1 dm^3 in size). SBP Technologies, Inc and the U.S. Environmental Protection Agency (USEPA) in Gulf Breeze, Florida characterized the microbial populations. Five different test soils contained 270 to 51,000 mg/kg (dry weight) PAHs. These soils were investigated at 20°C under pH-controlled conditions. PAHs were extracted from soils by four serial extractions using boiling hexane. The investigators noted that the PAH data reported here may be 2-5 times greater than those derived from the 16-component standard used by the USEPA SW-846 Method 8100.

Studies to isolate enhanced PAH degraders showed that the five soils contained degraders for phenanthrene and fluoranthene, and these were closely related to organisms isolated earlier in the U.S. Tests to evaluate the effect of added nitrogen and phosphorus revealed that at optimal concentrations of these nutrients, acclimated microbial cultures degraded 94% of the PAHs within 7 days. In contrast, the control achieved only 20% degradation in the same period.

The bench-scale soil washing investigations showed that the most effective combination of one of the cationic collectors and a foamer removed 90-95% of PAHs for sandy soils. Increased water temperature or pH provided no significant benefits and were incompatible with downstream biological treatment.

3. PILOT-SCALE STUDIES

The pilot-scale plant set up at the Norwegian State Railways site in Lillestrom, Norway combined froth flotation as a pretreatment for soil washing, a 1 tonne/hour soil washing plant and a 454-liter bioslurry reactor. This phase of work examined four excavated soils made up of sand, silt, clay, and sawdust/sand from the railways site, as well as two soils from another location. Initially, the soil was screened at 2 mm to remove potentially “clean” coarse material and as a pretreatment for the froth flotation process. Evaluated variables for froth flotation included single and blended commercial anionic and cationic surfactants used with a foamer, while soil washing variables consisted of temperatures between 10-50°C and pHs between 7 and 11.

At the pilot scale, soil washing at a loading rate of 550-859 kg/hour removed 20-90% of PAHs from two clay soils. The cleaned fraction contained 15-1500 mg/kg PAH. In terms of overall performance, clayey soils impaired the efficiency of soil washing and resulted in less than optimum performance.

The pilot-scale biotreatment phase of the study tested indigenous microorganisms as well as patented degraders. Amendments for biostimulation included nitrogen and phosphorous, pH, aeration, surfactants, and temperature. Tests were conducted with five 60-liter batches of sludge resulting from soil washing two clayey soils. During treatment of these sludges containing 14-20% solids, PAH concentrations fell by up to 97% after 6 days. Oxygen uptake decreased during this time and corresponded to a lowering of bioavailable PAHs in the bioreactor. An interim report noted that the native populations of PAH degraders "appeared to be sufficient to achieve residual PAH concentrations ranging from 55-200 mg/kg after a 6-day retention time." The investigators attributed pilot-scale results—better than those achieved at the bench scale—to better mixing and aeration and a higher operating temperature (28-32°C).

A Microtox 15-minute bioassay revealed that the combined soil washing and biological treatment reduced toxicity by a factor of 10. Soil washing itself reduced the relative toxicity only slightly. The bioreactor treatment accounted for most of the reduced toxicity.

4. COSTS

Costs (in U.S.$ per cubic meter) for various aspects of the remediation were estimated at $160 for excavation, sorting and backfilling; $300 for washing; and $530 for biological treatment.

Project No. 27

Soil Washing and Chemical Dehalogenation of PCB-Contaminated Soil

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1. INTRODUCTION

Leakage from PCB-containing insulator oils from stored transformer equipment contaminated soils with up to 2,000 mg/kg of PCBs at a site in Oslo, Norway. The shallow distribution of contamination meant that groundwater pollution had not occurred and that the most heavily polluted soils (>10 mg/kg PCBs) could be excavated for treatment and disposal. In Norway, the cost of incinerating PCB-contaminated materials ranges from U.S.$5,000-$7,500/tonne; thus, soil pretreatment techniques such as soil washing were viable economic options. This report summarizes the Pilot Study project on the development of an on-site treatment for PCB-contaminated soils that combines soil washing (as a volume reduction step) with chemical dehalogenation.

The three-year project included bench-scale studies on soil washing (completed in 1993), followed by pilot-scale and full-scale washing in 1994 and 1995, respectively. Dehalogenation investigations began at the bench-scale in 1995 and ended at the full-scale in 1996.

The Pilot Study focused on a combined system of water-based soil washing and dehalogenation because of its unique application to Norway. Both processes were new in that country, and reductive dehalogenation was considered innovative.

2. TECHNICAL CONCEPT

2.1 Soil Washing

The principal objective of this project was to treat the 1,288 tonnes of excavated PCB-contaminated material. Volume reduction was achieved by separating debris (>0.05 m) from soil and by treating the soil in a washing plant. A total of 11.9 tonnes of scrap iron, plastic, and wood were separated from the excavated material and hand sorted into porous and non-porous components. Non-porous debris was surface washed to remove contamination (<5 µg PCB /100 cm^2) and disposed in an on-site landfill. Porous material was sent for incineration. Soil was treated in a washing plant whose design was based on bench- and pilot-scale testing. The aim of soil washing was to achieve a contaminated volume reduction of 70%. This objective was based on size characterization of the soil, which suggested that the heavily contaminated silt and clay fraction (<0.1 mm size) represented 30% by volume of the total soil.

The washing plant had an operating capacity of 1.5 tonnes per hour and comprised three basic processes for particle size classification and surface cleaning. Contaminated soil was first slurried with water and a cationic surfactant in an attrition mill (operating at a pH of 10-11 and a temperature of 35-50°C). Size classification was carried out using a spiral separator, which produced a clean coarse fraction (>0.1 mm) and a contaminated fines concentrate (<0.1 mm) for further treatment. The fines concentrate was treated in a double air flotation cell using a proprietary collector and methylisobutylcarbanol as flotation reagents with the floated concentrate collected, coagulated, thickened, and filtered for further treatment. All coarse "clean" fractions were sampled and re-treated if contamination exceeded 10 mg/kg PCB. After treatment, the coarse fraction was returned to the original excavation area which was subsequently capped. Process water from the effluent plant was treated, as necessary, before discharged to the sewage system.

The full-scale washing was completed in 1995 with the concentrated fine contaminated sludge from the flotation process being stored until the chemical dehalogenation plant was ready. The biggest problem with full-scale washing at the site resulted from the occurrence of higher than expected levels of fines (<0.1 mm) in the excavated soil as a result of initially unrepresentative site characterization. The presence of up to 63% fines in the input stream caused significant material handling problems for the washing plant and made the 70% volume reduction target impossible to achieve. The final volume reduction was claimed to be 60% with 780 tonnes of clean soil and 400 tonnes of PCB-enriched sludges being produced. Treatment lasted approximately 6 months.

2.2 Chemical Dehalogenation

Three chemical dehalogenation systems were evaluated at bench scale by technology vendors, and one was selected for pilot-scale operation at the site. Details of the treatability study and the exact nature of the treatment technologies were not presented. However, all three bench-scale systems were based on the use of a reductive reagent that acted on the contaminated sludge (<10% moisture content) in a closed chemical reactor. Results for soils containing around 250 mg/kg (dry weight) PCBs showed that for two of the three processes tested at the bench scale, residual soil levels of PCBs were less than 1 mg/kg. The unsuccessful third vendor attributed the failure to interferences by the soil washing additives.

Treated soil contained residual PCBs, byproducts formed during treatment, and chemicals used to promote dehalogenation of PCBs. All of these compounds posed possible environmental hazards. To evaluate these hazards, a suite of ecotoxicological tests was conducted on leachate generated from samples treated according to the U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP). The interim report did not contain results of these tests to evaluate the risk associated with clean and treated soil to be redeposited at the site.

The dehalogenation technology tested at the pilot scale involved first drying soil to 10% moisture, then adding a nucleophilic agent and exposing the mixture to a reducing environment. The final report documenting results was not available.

3. COSTS

The capital costs of the soil washing plant were reported to be about U.S.$750,000 with operating costs in the order of U.S.$380 per tonne, which included all material handling and chemical analysis. Operations include handling materials and analyses (approximately 20% of operational costs). Costs for dehalogenation were not available.

Project No. 28

Use of White-Rot Fungi for Bioremediation of Creosote-Contaminated Soil

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1. INTRODUCTION

Lignin is resistant to degradation by many types of natural microorganisms. An exception to this are white rot fungi, which are able to degrade lignin and other natural recalcitrant compounds through production of powerful free radical extra-celluar enzymes. The enzymes produced by white-rot fungi are non-specific in their degradation mechanisms, and their potential to degrade difficult to degrade contaminants such as polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol, and polychlorinated biphenyls (PCBs) has been the increasing focus of research. This Pilot Study project reports on the evaluation of two species of white-rot and one species of brown-rot fungus for their potential to degrade high molecular weight PAHs in soil.

2. BACKGROUND

From 1994-95, samples for initial and bench scale testing were collected from an abandoned wood preservation site in Southern Norway, which is contaminated with creosote. The initial total PAH concentration was reported to be 2,400 mg/kg (based on 40 PAH compounds and heterocyclic compounds). The proportion of PAHs that were 2- or 3-ring compounds was less than 16%, reflecting the age of the contamination. The remainder was accounted for by 4-, 5-, and 6-ring compounds.

Pilot-scale testing was scheduled to take place between 1995-96 using soils from an abandoned mine in Norway, but has been delayed.

3. TECHNICAL CONCEPT

The contribution that fungi appear to make to bioremediation is in the degradation of poorly-soluble high molecular weight compounds by extra-cellular lignolytic systems. The fungi of interest are primarily basidiomycetes, and most studies have been carried out using the white rot fungi. The ability of these fungi to degrade these compounds (which were reported to include DDT, TNT, PCBs and PAHs) derives from the non-specific nature of their attack on wood.

Wood is comprised largely of lignocellulose in cell walls around xylem tissue,which is used for water transport and structural support by plants. For white rot fungi, hyphae are able to grow in the xylem lumen, but are unable to grow into the cell walls. The cell walls are also resistant to penetration by large molecules such as enzymes. The main energy source for these fungi is cellulose in the cell walls. Consequently, the degradation of wood is initiated by low molecular weight compounds such as hydrogen peroxide, metal ions, and veratryl alcohol. However, the cellulose in the cell walls is associated with lignin, which is a polymer that does not have a regular structure. Hence, no specific enzymes have evolved to degrade it. Rather, degradation of lignin takes place via a nonspecific array of enzymes and free radicals. As the fungal hyphae cannot (at least initially) penetrate the cell wall, and because of the highly damaging and non-specific nature of the degradation system, the enzymes and other compounds are excreted outside the fungal hyphae to do their work. Thus, there are advantages of fungal lignolytic degradation for treating toxic compounds because:

- the degradation system is not specific so many compounds are susceptible to attack; and

- the degradation takes place outside the cell so less soluble and larger compounds can be degraded—compared with bacterial degradation, which is generally an intracellular process.

Two outstanding fundamental questions for fungal degradation are:

- Do fungal types other than white rot fungi have similar effectiveness (hence the test of a brown rot fungus)?; and

- What are the products of the degradation process?

The technical approaches being considered by the testing encompassed:

- fungal degradation activity;

- the impact of compost—for example, the possibility of immobilizing PAH in the humic fraction; and

- pre-treatment of samples to allow degradation of readily-degradable materials by indigenous types prior to inoculation with fungi.

4. INITIAL FINDINGS

Initial studies were designed to investigate the manipulation of parameters such as substrate type, humidity, temperature, and pH in order to optimize fungal biodegradation of contaminants. Lignin-degrading enzymes are generated by the fungus only when other nutrient sources are limiting and when lignin is also present as a substrate. Nitrogen availability is a key determining factor.

Screening tests were conducted using the white-rot fungi *Pleurotus ostreatus* and *Trametes versicolor* and the brown-rot fungus *Lentinus leptinus*. The tests were used to evaluate different lignin substrates, such as wheat straw, wood chips (birch or pine), and newspaper, and to determine the influence of pH, aeration, and adding compost. Tests were carried out either on petri dishes or in 1-L Erlenmeyer flasks. Following these tests, *Pleurotus ostreatus* was investigated further using wheat straw as the lignin substrate.

Contaminated soils were incubated with straw and fungus for 8 weeks at 20°C. A range of supplements were added (peat, compost, and potato pulp). Degradation performance was dependent upon the number of aromatic rings in each PAH compound, ranging from up to 70% degradation for 3-ring PAHs to less than 35% for 5-ringed compounds (such as benzo(a)pyrene).

Further bench studies (using 60-liter batches) investigated the impact by degradation of indigenous microbial populations as a pre-treatment, followed by fungal inoculation. The pre-inoculation incubation period was two months. After inoculation samples were incubated for a further three months. Samples incubated with bark prior to fungal inoculation exhibited the greatest PAH degradation, and this benefit was reduced if fertilizer was also added during the pre-inoculation incubation period. Degradation of PAHs was greater at 20°C than 8°C. However, the benefit of preliminary incubation with bark was greater for the lower temperature. Compared with the controls, degradation of PAHs was enhanced by the fungal inoculation, but degradation of heterocyclic compounds was not.

Radiolabeling of the PAH compounds enabled tracing of treatment metabolites. The results produced the contradictory findings that indicated no accumulation of intermediate metabolites, yet low rates mineralization.

Project No. 29

Sorption/Solidification of Selected Heavy Metals and Radionuclides onto Unconventional Solvents

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1. INTRODUCTION

The project involved a laboratory-scale investigation of the use of solid wastes, such as red muds and coal fly ashes, to absorb toxic heavy metals and radionuclides from water (a fixation or stabilization process) followed by solidification of the metal-loaded solid wastes in a cement-based system.

2. BACKGROUND

Cadmium (II) (Cd^{2+}), lead (II) (Pb^{2+}) and copper (II) (Cu^{2+}) are toxic heavy metals that pose a serious threat to the fauna and flora of receiving water bodies when discharged in industrial wastewater. Cesium-137 (^{137}Cs) and strontium-90 (^{90}Sr), with half lives of 30 years and 28 years, respectively, pose significant threats to the environment as a result of fallout from nuclear bomb tests and reactor accidents. In recent years, land burial of radioactive wastes has become a common practice, also posing a radioactive contamination risk to groundwater. In Turkey, ^{137}Cs became a matter of public concern after the Chernobyl accident, especially due to contamination of tea-growing areas on the Black Sea coast. Milk products and other biological materials containing Cs were also extensively investigated for possible ^{90}Sr contamination.

Various treatment technologies have been developed for the removal of these metals from water. Processes available include ion exchange, electrodialysis, reverse osmosis, membrane filtration, sludge leaching, electrowinning, solvent stripping, precipitation, and common adsorption. The cost of adsorptive metals removal processes is relatively high when pure sorbents, such as activated carbon or hydrated oxides, are used. Consequently, there is an increasing trend toward substitution of pure adsorbents with natural byproducts or stabilized solid waste materials. Such materials may also be useful for constructing “natural barriers” around radioactive waste disposal sites, especially for facilities involving shallow-land burial of low-level wastes , in order to prevent the leakage of radionuclides from the facility to the environment.

The aim of this Pilot Study project was to develop cost-effective unconventional sorbents, preferably metallurgical waste solids, for heavy metal and radionuclide removal from contaminated water. The removal capacities of heavy metals (Cd, Pb, and Cu) and radionuclides (^{137}Cs and ^{90}Sr) and the sorption modeling of red muds and fly ashes were studied in this regard. The irreversible nature of sorption needs to be shown so as to guarantee non-leachability of metals from the metal-loaded sorbents.

3. SCOPE OF THE STUDY

Metal uptake (sorption) and release (desorption) were investigated by thermostatic batch experiments using bauxite red muds and coal fly ashes. The distribution ratios of metals between these solid sorbents and the aqueous solution were determined as a function of sorbent type, equilibrium aqueous concentration of metals, and temperature. The breakthrough volumes of the heavy metal solutions were measured by dynamic column experiments so as to determine the saturation capacities of the sorbents . The sorption data were analyzed and fitted to linear adsorption isotherms.

The materials used were red muds (alkaline leaching wastes of bauxite from the Bayer process for the manufacture of alumina) and fly ash from a coal-fired power station. The red muds comprise a mixture of minerals, including sodium aluminosilicates, kaolinite, chamosite, iron oxides (hematite), and iron hydroxides. 94% of the mud had a grain size less than 10 µm. About 99%of the fly ash passed a 200-mesh sieve (74 µm grain size).

Both materials were strongly alkaline when leached with water. The red muds were washed with water to a neutral pH, and then dried and sieved before use. Portions of the red mud were subjected to acid treatment. A portion of this was, in turn, subjected to heat treatment at 600°C for 4 hours. The raw fly ash was washed with distilled water 5-6 times (washing removed about 40% of the initial fly ash by weight), filtered, and dried. A portion of the water-washed ash was acid-treated, washed with water, and then dried at 100°C.

The heavy metal solutions contained up to 10,000 mg/L of Cd, Pb, or Cu made from the corresponding nitrate salts. No further pH adjustment was made. Solutions containing ^{137}Cs and ^{90}Sr were made up by dilution of flacons of standard solutions supplied by Amersham International Ltd.

Desorption studies were carried out using distilled water, saturated aqueous carbonic acid (pH=4.75), and H_2CO_3/$NaHCO_3$ buffer solutions (pH=7.0) so as to simulate carbonated groundwater conditions for the purpose of risk analysis around waste disposal sites.

4. SOLIDIFICATION OF THE HEAVY METAL-LOADED SORBENTS

The sorbents may also serve as effective fixation agents for removing heavy metals from water prior to solidification for disposal. Although stabilization tests were conducted on the fly ash and red muds, as well as on the adsorbents after they were loaded with contaminating metals, the detailed results are not described in the final project report. Solidification of the red muds and fly ash was accomplished by addition to a mixture of cement, standard sand, and carefully measured water. When metal-loaded solid waste was added (up to 20% by mass) to Portland cement-based formulations, the fixed metals did not leach out from the solidified concrete blocks over extended periods with the exception of Cu^{2+} which reached a concentration of 0.4 mg/kg after 8 months in water of pH 8-9. In concentrations below 20%, the compressive strengths and shear strengths of the doped concrete did not significantly differ from the control concrete. However, there is a critical weight percentage of 10-20% additives above which the strength declines dramatically.

5. CONCLUSIONS

The bauxite wastes of alumina manufacture (*i.e*., red muds) are hydrous oxide-like adsorbents capable of removing the radionuclides ^{137}Cs and ^{90}Sr as well as other heavy metals from water. Radiocesium and strontium adsorption on red mud may be represented by B.E.T.-Langmuir isotherms. Acid- and heat-treated red muds are more effective in Cs removal than water-washed red muds, but heat-treatment is detrimental to the surface -SOH sites important for ion-exchange sorption of ^{90}Sr. Cesium uptake is predominantly irreversible and exothermic and increases with the specific surface area of the sorbent, though some retained Cs^+ may be released with H^+ and Na^+ ions from the surface. A rise in pH favors the exchange sorption of Sr, while the specific adsorption of Cs is negatively affected.

Coal fly ashes of thermal power plants are composite adsorbents capable of removing radiocesium and radiostrontium, as well as other heavy metals from water. The adsorption of these radionuclides may be represented by Langmuir isotherms as an approximation of multilayered adsorption expressed by the B.E.T. equation. Although acid treatment of fly ash has shown no improvement in adsorption capacity, it is recommended to prevent trace pollutant leach-out from the adsorbent into water.

In investigating the possibility of using metallurgical solid wastes as sorbents in heavy metal removal from contaminated water, red muds and especially fly ashes have been shown to exhibit a high capacity for heavy metals with the sorption sequence Cu > Pb > Cd in accord with the order of insolubility of the corresponding metal hydroxides. An empirical Langmuir approach could approximate isotherm modeling of metal sorption. Essentially, the metals were held irreversibly and would not leach out into carbonic acid or bicarbonate-buffered solutions.

The metal-loaded solid wastes could be solidified to an environmentally safe form thereby serving the two-fold aim of water treatment and solid waste disposal. A two-fold aim of heavy metal fixation and metallurgical solid waste disposal would then be achieved with the constraint that fly ashes better serve the purpose of heavy metal fixation than red muds.

Red muds and fly ashes, along with other metallurgical solid wastes and clay minerals, may be utilized for constructing "natural barriers" around shallow-land burial sites of low-level radioactive wastes and heavy metal-containing products.

6. REFERENCE:

Apak, R., G. Atun, K. Güçlü, E. Tütem, M. Hugül, J. Hizal and S. Ayhan. *Sorption/solidification of selected heavy metals and radionuclides from water*, Final Report to NATO/CCMS meeting Golden, March 1997.

Project No. 30

Using Separation Processes from the Mineral Processing Industry for Soil Treatment

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1. INTRODUCTION

This report summarizes a project carried out to investigate the general application of particle separation techniques from the mineral processing industry to the treatment of contaminated soils from the U.K.

Physical separation techniques can be used to divide contaminated soil into fractions that can be relatively easily treated. Physical treatment can also act as an early process in a treatment train involving subsequent chemical, biological, or thermal processes to reduce the volume of material requiring subsequent remediation and to convert the material into a more suitable form (such as a slurry).

The project was included in the NATO Pilot Study because it aimed to design and operate a soil washing plant to treat contaminated soil which had attributes unique to the U.K. The Warren Spring Laboratory[a] carried out the work on behalf of the U.K. Department of the Environment and the U.S. Environmental Protection Agency.

The study comprised two phases: laboratory characterization tests, and pilot-scale tests. These are described in Sections 2 and 3, respectively.

2. LABORATORY CHARACTERIZATION TESTS

Laboratory characterization tests were developed to ascertain treatability potential by physical segregation alone or in combination with other treatment technologies. Soil samples (5-20 kg) were collected from various UK locations for characterization. Sites included former gasworks, coke works, canal dredgings, chemical works, metal reprocessing and pickling plants with principal contaminants including heavy metals, inorganic cyanides, polycyclic aromatic hydrocarbons (PAHs), and phenols.

Bench-scale laboratory characterization tests were carried out to determine the preferential distribution of the majority of the contamination to specific particle fractions of the soil, leaving the bulk of the soil depleted in contaminants. These tests were based on differences in grain-size distribution; settling velocity (hydrocyclone separation); abrasion by using attrition scrubbing to abrade contaminant coatings, followed by hydrocycloning; specific gravity distribution using sink-float tests with heavy liquids; surface chemical properties, specifically hydrophobicity using froth flotation; and magnetic properties assessed using the Franz Isodynamic Separator.

Results from the laboratory tests showed that most of the examined U.K. soils displayed some degree of preferential distribution of contaminant to particular soil fractions but:

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[a] *In 1994 Warren Spring Laboratory was merged with the Environmental Division of AEA Technology to form the National Environmental Technology Centre. AEA Technology has more recently been privatized.*

- the level of contaminants in the depleted fractions was not always sufficient for the fractions with the lowest concentration of contaminants to be considered suitable for reuse as inert fill; or
- the proportion of soil in the contaminant depleted fraction was not always large enough for commercial exploitation.

The results from two of the soils from the laboratory treatability studies were used to design treatment circuits, which were tested at pilot scale.

3. PILOT-SCALE TESTS

Pilot-scale tests were conducted with the Warren Spring Laboratory's National Environmental soil washing plant. Tested contaminated soils (up to fifty tonnes) came from the sites of a former metal reprocessing works and gasworks. Material from both sites consisted of building rubble, wastes, and soil. A relatively high clay content of around 30% made handling this material difficult.

The throughput of the pilot plant was 0.5 tonnes of soil per hour with the selected remedial scheme based on the exploitable separation features ascertained in the characterization tests. This plant compared froth flotation and a Multi-Gravity Separator for separating fine particles. Altogether, treatment processes consisted of particle release and coarse sizing, further sizing, attrition scrubbing and classification, and contaminant concentration. The plant featured process water containment and recirculation, and carbon filters to extract volatile contaminants from emissions. Wastes and sludges from the plant received further treatment at downstream processes or were shipped to a licensed landfill.

The level of contaminant reduction, when compared to the original soil, measured the effectiveness of the process. In the pilot-scale tests using froth flotation, residues with low levels of contaminants (*i.e.*, treated material) made up around 48% by weight of the original feed. For tests with the Multi-Gravity Separator instead of froth flotation, residues with low levels of contaminants totaled around 50% of the original feed. Compared to their respective feeds, both residues contained markedly lower levels of PAHs, petroleum hydrocarbons, cyanide, lead, and arsenic. Comparing the residues themselves, those derived from froth flotation contained higher levels of PAHs and petroleum hydrocarbons but lower levels of lead and cyanide. Arsenic levels did not differ much in the two.

Samples from the former metal reprocessing works produced a small portion of dense material (specific gravity >2.8) with marked concentrations of contaminants. Despite this separation into the dense fraction, the remaining bulk of treated material contained unacceptable levels of contaminants. According to a report, rather than consider absolute concentrations only, researchers evaluated Toxicity Characteristic Leaching Procedure (TCLP) data to assess this soil in terms of mobile and non-mobile contaminants. The researchers reconsidered the role of physical treatment to reduce hazards presented by this soil. An option would be to combine physical separation with a mild acid leach to reduce the mobile contaminants in the soil to below an indicative leachability criteria (in this case, TCLP). Concentrates from the physical separation and precipitates from downstream processing of metal-rich solutions could then be potentially stabilized or treated to recycle the metals.

With a soil from a former gasworks, the maximum volume reduction would be expected to be 60% with an optimized treatment circuit. The authors suggested that the reason for this was that the clay and fine silt fraction (<0.01 mm) of the soil represented approximately 30% of the total weight of material. Treatment of the clay and silt fraction using a slurry phase bioreactor could potentially reduce the organic contaminants in the soil. Physical separation within this treatment train would have acted as a pretreatment stage not only to reduce the volume of material requiring downstream treatment, but also to present the material to the downstream process in a more appropriate form, that is for example, as a slurry not as a mixture of contaminated rubble combined with clay.

Project No. 31 Decontamination of Metalliferous Mine Spoil		
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1. INTRODUCTION

Metals in discarded spoil can be solubilized by rain or shallow groundwater, or can be dispersed into sensitive environments when dry spoil is blown. Traditional reclamation systems focus on containment, not decontamination. These systems rely on impermeable strata below waste, and/or a cap consisting of low-permeability materials like clay.

The objective of this Pilot Study was to determine if current metal-processing techniques for extracting metal-rich ores from less valuable waste material could be used to reprocess old metalliferous spoil materials to recover metals of some value and to reduce the environmental impact of the spoil. For a period of three years starting in 1990, work was conducted to evaluate methods for decontaminating metalliferous spoil from abandoned mines in central and north Wales. The investigation focused on lead-zinc mining in Wales—these metals are of particular significance in current and former mining operations across Europe.

The Water and Environment Division of the Welsh Office commissioned the study. Richards, Moorehead and Laing Ltd. undertook the work in association with the School of Engineering (Materials and Minerals) within the University of Wales College, Cardiff.

2. THE STUDY

Laboratory-scale studies were conducted to evaluate the mineral processing techniques on lead-zinc mine spoil materials from five unreclaimed former metal mines. The evaluation of techniques represented the first phase of a two-part study to identify promising treatment options to be examined in detail during the second phase of the study. During the study, researchers first characterized spoil material and then examined techniques involving gravity separation, froth flotation, chemical leaching, and biological extraction.

The mine spoil was characterized to determine the mineralogy of contaminated particles and the distribution of contamination according to particle size. Concentrations of lead and zinc in the whole spoil samples were up to 20% and 15% by mass, respectively, but copper and cadmium concentrations were in the range of parts per million. Lead was observed to concentrate in the finer particle sizes of the spoil.

The nature of the spoil influenced minerals produced by weathering. A fine-grained, compact, clay-like spoil saturated with water created anaerobic conditions that inhibited oxidation of the minerals. Under these conditions, the minerals retained their sulfide forms. In contrast, a sandy spoil allowed extensive oxidation to occur and convert lead and zinc minerals to their more easily leached sulfate forms.

Mineral processing techniques exploit physical and chemical differences between contaminated and uncontaminated particles. In this study, differences in particle density and surface chemistry for the separation of spoil particles were evaluated using dense media (so called “sink and float”) and froth flotation tests.

A multi-gravity separator (MGS) was used to further evaluate density separation at the pilot scale. Laboratory-based density separation resulted in consistently reduced metal concentrations (<2% by weight) in the lighter spoil fractions representing over 90% of the total sample weight. The heavier concentrate contained up to 32% lead and 5% zinc by weight. Although significantly cleaner than original spoil, these levels still greatly exceeded U.K. soil guidelines. The pilot-scale MGS treatment produced similar results on the less than 0.5 mm fraction of spoil. Results showed that the MGS can concentrate almost 70% of the metals into a mass of less than 10% of the original spoil, leaving a combined metal assay of 2.5% in the residue.

For most of the tested spoils, froth flotation performed poorly but achieved reasonable performance where spoils remained unoxidized. Additives showed little promise in terms of producing marketable concentrates or tailings with significantly lower metals contents. The effectiveness of this technique depended critically upon the mineralogy of the spoil. Unweathered material that was rich in sulfides showed better segregation of contaminants into the concentrate.

Leaching of metal contaminants from the spoil by a variety of chemical agents such as sulfuric acid, sodium hydroxide, and diethylenetriamine, and by using ferric bacteria inoculum was evaluated on unprocessed spoil and treated fractions from the density and froth flotation tests. Effective chemical leaching depended on the degree of spoil weathering. Generally, sulfuric acid and diethylenetriamine, leached 2-33% of the lead, and 12-64% of the zinc. Sodium hydroxide leaching of weathered spoil mobilized 25-92% of the lead and 3-23% of the zinc in unprocessed spoil.

To evaluate the extent to which metals remaining in reprocessed (by gravity separation or froth flotation) residues would be leached and, hence, be of environmental concern, the residues were subject to chemical and biological leaching. This leaching removed only 2-5% of the remaining contaminants, indicating a resistance to leaching in residual material. Bacterial leaching of lead proved to be ineffective, but significant movement of zinc from the spoil was recorded.

It was recommended that future work focus on the applicability of alkaline leaching and its integration with gravity separation methods for the treatment of this type of metalliferous waste. Further work on the pilot-scale assessment and optimization of the MGS was also suggested.

Project No. 32

CACITOX™ Soil Treatment Process

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1. INTRODUCTION

CACITOX™ is a multi-component leaching process using a proprietary combination of highly selective and environmentally tolerant reagents. It is used in conjunction with a soil washing pretreatment and effluent recovery system called the *EXCEL*CR*™ Soil Treatment Plant. The *CACITOX*™ reagent comprises low concentrations of carbonate, oxidants, and complexing agents. This mixture, used at near neutral pH and at ambient temperature, reacts with contaminated materials and converts insoluble or absorbed contaminants such as heavy metals and transuranic elements into soluble complexes. The low reagent concentrations and their high selectivity are designed to minimize secondary waste.

The leaching process is considered an emerging technology because it represents an innovative way to chemically treat contaminated soils. One of the objectives of the process is to treat soils with significant clay and silt content for which conventional soil washing techniques are not cost-effective. The technology can potentially treat contaminated soils and sediments, without depositing unacceptable by-products into the soil matrix or destroying the matrix itself.

2. THE PROCESS

The project consisted of three phases: (1) evaluation of the process with heavy metals; (2) evaluation with radionuclides; and (3) engineering design for a mobile *ex situ* soil treatment plant. Early testing using spiked synthetic soils demonstrated the effectiveness of the *CACITOX*™ process in reducing contaminant concentrations to regulatory levels, even in the high-clay soils. There are four stages to the process: (1) size classification, where oversize materials are sorted out and contaminated soil volume is reduced; (2) soil leaching using the *CACITOX*™ reagent, with laboratory-optimized parameters for the particular soil and contaminant conditions of the site; (3) soil/leachate separation using a bank of hydrocyclones, followed by dewatering with filters; and (4) leachate treatment using precipitation and ion exchange processes. Precipitated contaminants are ultimately treated by containerization, encapsulation, or dewatering. The pilot-scale transportable plant has a capacity of 10 kg/hour, with easy scale-up to 100 kg/hour.

3. PERFORMANCE

Performance evaluation was accomplished at bench scale using synthetic test soils spiked with aqueous solutions of the nitrate form of commonly encountered metals. Seven heavy metals and six radionuclides were evaluated at “low” and “high” concentrations. Since clay soils proved the most intractable, most testing was conducted with fine-particle soils. In general, all heavy metals partitioned in a similar manner in the various soil size fractions. While the clay and silt fractions contained the bulk of the spiked contamination, 26% of the contaminants were contained within the coarse sand/gravel fractions. For the “high” spiked samples, the coarse fraction exceeded the Dutch “B” Values[a] or Canadian residential levels for all metals except cadmium and arsenic. Thus, conventional soil washing alone,

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[a] These values have now been superseded.

which relies on particle size classification, would be ineffective in treating these soils. Soil pH did not appear to significantly affect contaminant removal. While the bench-scale tests failed to meet regulatory levels for soils spiked with 1,000 mg/kg cadmium or arsenic, it was reported that further optimization of the reagent formulation would enable target values to be achieved. Similarly, the addition of organic contaminants had little effect on initial leaching efficiencies, and 98% of the organic contaminants were removed from the soil. Removal efficiencies were comparable to leaching with mineral acids, but *CACITOX*™ dissolved less than 10% of the soil matrix (compared to 40% for acid washing).

During the leaching trial for removing radionuclides from test soils, a single contact with the *CACITOX*™ reagent mixture removed 52-76% of the plutonium, americium, neptunium, strontium and radium, but only 2% of the cesium. Limited data for removal of radionuclides from a contaminated site showed how repeated contacts could improve removal.

4. CONCLUSIONS

In summary, the *CACITOX*™ technology can process materials containing high levels of fine-grained particles like silt and clay and can selectively dissolve actinides and heavy metals from other wastes. Because the *CACITOX*™ process treats inorganic contaminants, it requires other technologies for treating mixed wastes. The final report mentioned that using low concentrations of mild chemicals resulted in low costs, but did not provide supporting data.

Project No. 33

In-Pulp Decontamination of Soils, Sludges, and Sediments

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1. INTRODUCTION

This project reports on a collaborative program of bench-scale and demonstration plant-scale development of a treatment technology by Davy and Kommunekemi of Denmark. The project receives funding from the U.K. and Danish governments under EUREKA EUROENVIRON, and has been accepted into the U.S. Environmental Protection Agency's Emerging Technology Program. The NATO/CCMS accepted this project in 1992 for its novel application to “in-pulp” adsorption of heavy metal contaminants.

The process combines conventional *ex situ* soil washing techniques with an innovative chemical treatment stage. A major advantage expected for this approach is the ability to remove contaminants from fine-sized soil fractions such as silt and clay. Two techniques are used to extract contaminants:

(1) leaching using acidic or alkaline reagents followed by adsorption to activated carbon or ion exchange resin; and

(2) adsorption by activated carbon or cation exchange resins in direct contact with a soil slurry.

Contaminants may then be desorbed from the recovered activated carbon or ion exchange resin, which is subsequently recycled.

2. TEST PROGRAM

Test materials consisted of contaminated soils and sediments. The soils came from:

- a reclaimed site contaminated with arsenic;
- a gasworks facility containing zinc and lead;
- a wood preserving site contaminated with copper, chromium and arsenic; and
- chlor-alkali and gas metering sites with mercury contamination.

In addition, a sediment sample containing zinc, lead, and iron was collected from Hamilton Harbour in Ontario. Zinc, lead, iron, and manganese levels in the sediment exceeded Ontario’s “severe effect” guidelines, while copper, chromium, and nickel levels ranged between the “severe effect” and “limited effect” levels.

This summary highlights work done on samples from the wood preserving site, the chlor-alkali site, and the harbor. Project reports did not contain information on the other samples.

Initial tests focused on the physical and chemical characterization of the contaminated materials. This characterization included determining the contaminant distribution according to soil particle size. Since contamination existed in all fractions of soil collected from the wood preserving site, leach tests were carried out on samples of the whole soil.

The leaching work was based on small pilot-scale experiments. These examined various inorganic and organic acids, alkalis, and chelating reagents under various conditions. A 300-g sample of soil was stirred constantly with 1 liter of leaching fluid for a period of 24 hours with the concentration of contaminants in the leachate and soils periodically monitored. It was concluded that mild leaching was inadequate for obtaining target contaminant concentrations in the solid residue. Sulfuric acid was the most effective leaching agent, removing 90-97% of the contaminants from the soil. Copper, zinc, and chromium were removed to below target levels, but arsenic concentrations exceeded the target of 30 mg/kg.

Adsorption tests on leachate from soils from the wood preserving site were carried out with various ion exchange resins, activated carbon, and magnetite to treat the leachates produced by the leaching procedure. Compared with the other adsorbents, the ion exchange resins were shown to remove the most copper, chromium, and zinc from the leachate. Acid resins adsorbed from 75-100% of the copper, chromium, and zinc from the leachate but only 20-60% of the arsenic. It was suggested that arsenic was difficult to treat using resins since at the low pH values where arsenic acid is most soluble, it does not normally exist as ionic species. At high pHs, the ion exists in solution but adsorbs onto iron precipitates found under these conditions. A further complication was the competitive adsorption of bulk metal ions, such as calcium and iron, which necessitated a change in flow sheet design to include a chemical precipitation step to remove these ions prior to adsorption.

A 10-kg sample of the soil from the wood preserving site was treated at bench scale using the unit operations of physical separation and chemical leaching that had been identified from the experimental studies. The metal content in the treated soil was lower than in the feed material: copper (22 vs. 360 mg/kg), chromium (74 vs. 621 mg/kg), zinc (68 vs. 414 mg/kg) and arsenic (102 vs.1,204 mg/kg). Only arsenic exceeded its preliminary treatment target of 30 mg/kg. Further work on arsenic removal has been conducted on a different soil sample. Focusing on protocols that take account of arsenic speciation, chelating agents were shown to leach a maximum of 52% of arsenic from the soil. A combination of flotation, screening, and hydrocycloning achieved 60% removal in 80% of the soil, but this still exceeded the target level. Multiple acid leaching was able to reduce arsenic from 650 to 22 mg/kg, but at a relatively high cost. The degree to which using such strong acids destroyed the soil matrix was not mentioned but is likely to be a significant effect. An alternative suggestion involved raising the leachate pH to co-precipitate arsenic acid with iron, but no test results for this technique were reported.

Trials with the mercury-contaminated soil used oxidative and complexing conditions such as nitric acid, hydrochloric acid, and sodium hypochlorite. To improve extraction of mercury, the approach included size separation to remove fines and was operated at higher temperatures. Ion exchange resins developed for mercury adsorbed the metal slowly. As a result of difficulties with this approach, a thermal option was investigated. Preliminary tests revealed that by heating contaminated materials to around 800°C, treated soils achieve regulatory targets for mercury.

Work with Hamilton Harbour sediment aimed to demonstrate the technology, obtain necessary data for pilot plant design, and show that the Ontario guidelines for sediment could be met. Leaching tests were conducted with mineral and organic acids. During leach screening tests, strong mineral acids dissolved contaminants, as well as calcium and iron, in 90 minutes. These two metals and organic contaminants would compete with the metal contaminants during adsorption. A two-stage leaching approach was tested as a way to eliminate this competition. This approach involved a mild acid to dissolve iron first, followed by a strong acid to attack the contaminants. The presence of organic contaminants had little impact on the removal of metals.

Tests with several adsorbents pointed to chelating resins as the likely candidate. These resins proved to be more selective than activated carbon or magnetite for the contaminant ions over the other metal ions. The high level of iron in solution inhibited the adsorption of contaminants, and thus required pretreatment such as magnetic separation to remove iron from the sediment before leaching. Precipitation to remove metals from the leachate was somewhat ineffective because some metal remained in solution and required further processing.

3. RESIDUALS AND EMISSIONS

The process generates a variety on residuals and emissions, some of which require further treatment or disposal. Decontaminated solids may require final treatment, such as pH adjustment and dewatering, before being disposed. For most metal extractions, acid is used to remove metals from the resin, resulting in a concentrated solution of metals. These solutions may be treated by precipitation, reduction, or electrowinning to recover metals, or may be disposed at a secure disposal site or encapsulated. In the case of sediments, the leach stage may produce gas emissions if anaerobic activity produces sulfides. These emissions, noted during leach tests with sediments from Hamilton Harbour, may require gas scrubbing in a commercial plant. Decanted water from excavated sediment may also have to be treated. Finally, cleaned soils and sediments may introduce anions to their disposal site.

4. COSTS

Little information is available on cost. If the process demands aggressive leaching with oxidative and complexing agents as well as elevated temperatures for enhanced leaching, the treatment plant will have to be built of unique materials. Under these conditions, treatment costs are expected to be high (no data or expected costs were provided).

“In-pulp” processing, used alone or combined with other physical processing techniques, offers an option to treat soils chemically to achieve low absolute values of metals. If a leachability standard is required, a chemical treatment may be attractive provided the leaching agent is more severe than the standard requires. Thus, applicability of the technology would depend on its ability to achieve regulatory requirements.

5. CONCLUSIONS

Although applicable to metal contamination, the technology may be adapted to handle organic contaminants by using carbon as an additional adsorbent. Plans to develop the technology further include investigating surfactants, solvents and other agents to extract organic contaminants and to combine this with adsorption by activated carbon.

Project No. 34

Chemical Fixation of Soils Contaminated with Organic Chemicals

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1. INTRODUCTION

Conventional stabilization/solidification methods, such as those based on cementitious and pozzolanic materials, have been applied with limited success to treating soils with organic contaminants. Hydrocarbon chemicals can have detrimental effects on cement hydration and structure formation. This project involved the development of a range of modified organophilic clays with the aim of overcoming these limitations in an advanced *in situ* stabilization/ solidification application based on cementitious binders. This technology has been tested at field scale on a site contaminated with a variety of inorganic and organic substances.

2. PROCESS DESCRIPTION

The Envirotreat process is an *in situ* technology developed with the financial support from the U.K. Department of the Environment's Environmental Technology Innovation Scheme (ETIS). The research and development has been carried out in collaboration with the former Warren Spring Laboratory, the University of Birmingham, and May Gurney Ltd., a U.K.-based civil engineering contractor.

The stabilization/solidification process uses specialized modified smectite clays that contain reactive species. These clays are claimed to have diverse potential environmental applications and to be compatible with conventional stabilization/solidification process materials. The clay technology is primarily targeted at organic contaminants, but also has the capability to treat both cationic and anionic heavy metal species by a combination of ion-exchange processes and chemical interaction with pillaring agents and other intercalatants.

The technology uses modified continuous-flight auger drilling and injection techniques. The treatment materials are injected in a slurry form into the contaminated ground and mixed with the soil *in situ*. The primary challenge is to ensure that the contaminated soil and treatment media are mixed homogeneously. Envirotreat is now evaluating the *in situ* process as an "active containment system" and is considering a number of options, including the application to permeable barriers/reactive treatment walls.

3. BACKGROUND

Commercially available organophilic clays are typically made by substitution of quaternary ammonium salts into phyllosilicate clay matrices (*e.g.*, montmorillonite). The clays are commonly employed in the paint and oil industries as sorbents for organic chemicals. The primary objective of this project was to modify these clays through intercalation (*i.e.*, substitution of the cations between clay layers) to improve stabilization of organic contaminants by:

(1) increasing the size of the interlamellar spacing within the clays to accommodate larger-sized molecules such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), the effective surface area and the potential reactivity by the introduction of selected pillaring agents;

(2) optimizing the polarity of the interlamellar environment in order to increase absorption and adsorption of organic contaminants;

(3) providing a reactive environment on interlamellar clay surfaces to chemically bind contaminants permanently; and

(4) providing an active medium for effective treatment of heavy metals (both cationic and anionic) and other inorganics by cation exchange processes and/or interaction with the intercalated species (which can then be immobilized within the cementitious matrix following alkaline precipitation).

Certain intercalating agents, such as transition metal complexes and organometallic cations, are known to have a pillaring effect on clays, acting as molecular props or “pillars” between clay lamellae to create a two-dimensional porous interlayer structure. This improves clay stability to excessive dehydration and widens interlamellar spacing to allow larger organic molecules such as PAHs to enter. By using iron- and aluminum-based pillaring agents, a variety of chemically reactive sites can be created inside the interlayer spacing. For example, the presence of aluminum ions (Al^{3+}) adjacent to the interlamellar spacing provides an effective site for Lewis acid/base reactions with chlorinated and heterocyclic hydrocarbons. In addition, numerous other forms of chemical bonds may be possible between the intercalated organophilic clay and the contaminant, including van der Waals, dipole, and hydrogen bonds. Diagrammatic representations of the *generic* modified clays are shown in Figures 1 and 2.

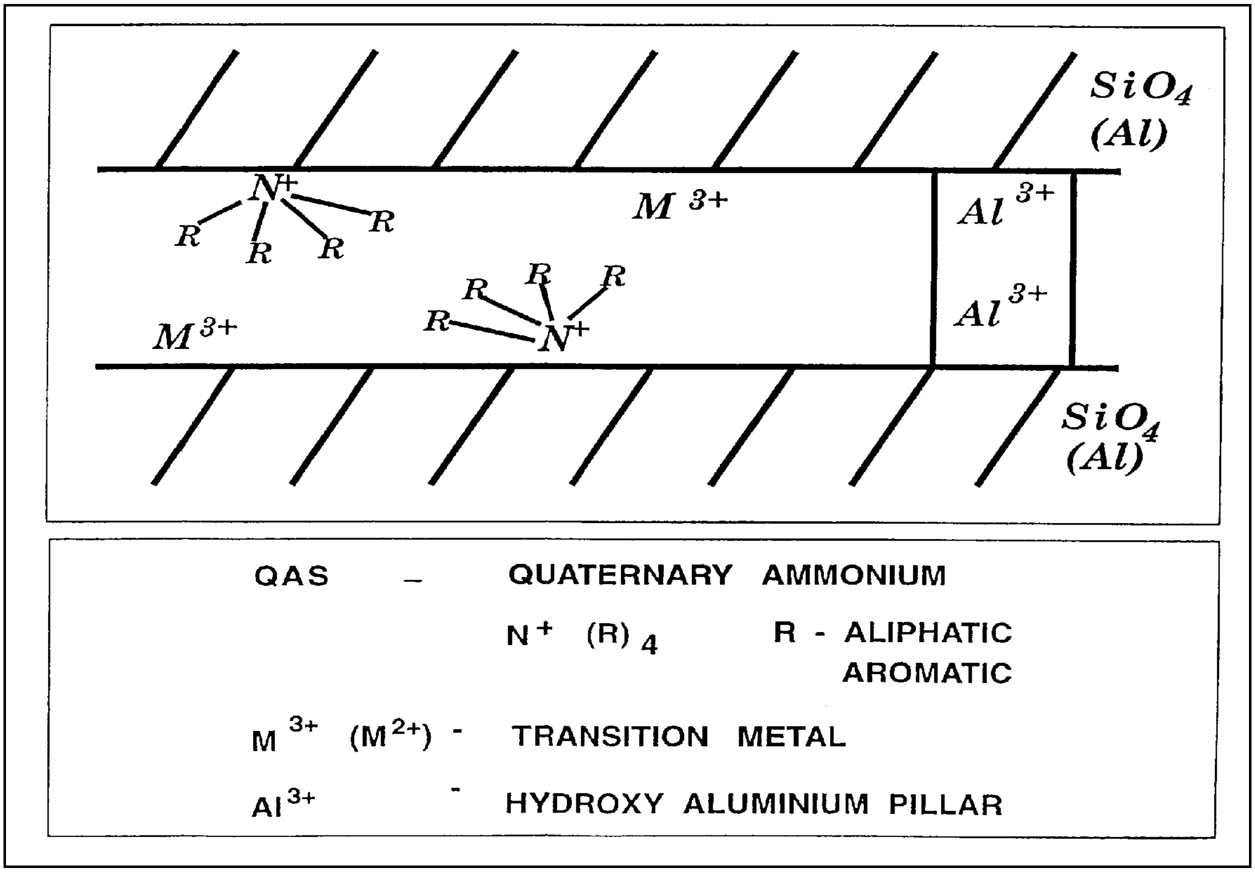

Figure 1: Schematic of modified clay

An advantage of using tailored organoclays is that a clay can be manufactured to treat a specific group of contaminants by manipulating the type and amount of intercalating agents used. By selective use of available smectite clays and intercalation of appropriate quaternary ammonium ions in conjunction with other relatively low-cost agents (principally Fe and Al compounds), it is possible to produce highly-efficient and multifunctional treatment media. Envirotreat’s aim was to produce a range of clays with varying hydrophobicity and chemical composition to deal with five groups of organic compounds:

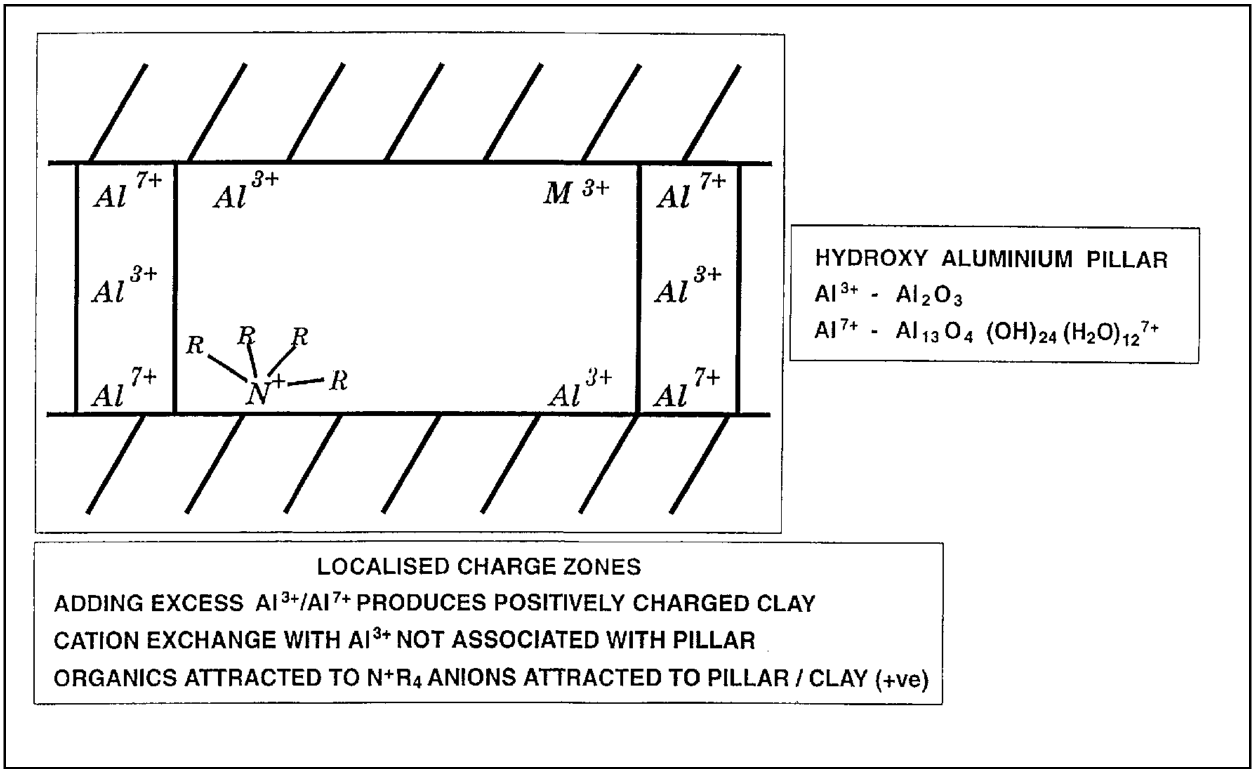

Figure 2: schematic of modified clay (positive)

- PCBs, dioxins, chlorinated hydrocarbons;
- PAHs;
- benzene, aryl compounds, benzene derivatives;
- hetrocyclics, organophosphorus/sulfurous compounds; and
- polar compounds, phenolics.

It was acknowledged that this approach would not cover all eventualities. However, it was felt that most organic contaminants likely to be encountered at sites would react to some extent with one of the modified clays. Where there is more than one type of organic contaminant at a site, the intention is to use more than one clay formulation, as deemed appropriate.

4. INITIAL LABORATORY ADSORPTION TESTS

Adsorption tests were carried out on three representative organic compounds: benzene, orthodichlorobenzene, and pyridine. Benzene and orthodichlorobenzene have low solubilities in water and were well adsorbed by all clay formulations. In contrast, the results for pyridine indicated that the more hydrophillic (inorganic) clay formulations are generally more effective in removing organic compounds of high solubility. The results confirmed the need for a range of modified clays.

Further sorption tests were carried out at the University of Birmingham. This research focused on the ability of pillared clays to sorb humic acids, which are common organic constituents of groundwater. When groundwater is chlorinated, humic acids can react to formation mutagenic or carcinogenic substances. It was concluded that aluminum and aluminum+phosphoric acid pillared clays were most effective in sorbing fulvic acid (a light humic acid) from water. Iron pillared clay was generally less effective, and a combined iron/aluminum pillared clay was the least effective (probably due to its low surface area).

Conventional smectite clays have cation exchange properties that can be used in the treatment of cationic species (*e.g.*, toxic heavy metals) under controlled conditions. They are not, however suitable for the treatment of problematic anionic and complexed species, in particular chromates and dichromates, arsenates, and ferriferrocyanides, *etc*. However, modified pillared clays were shown to be effective for the treatment of hexavalent chromium solutions. Untreated bentonite was ineffective in absorbing CrO_4^{2-}. The modified clay formulation provided a reactive medium for the treatment of both cationic Cr^{3+} and anionic $CrO_4^{2-}/Cr_2O_7^{2-}$.

5. AUGER DEVELOPMENT

The four main challenges of auger development were:

- the piling rig should remain largely unaltered;

- the standard injection system for conventional flight augers need to be modified to inject smaller volumes at higher pressures;

- the auger system needs extensive modification to inject smaller volumes and needs to be adapted to ensure that the *in situ* mixing process produces homogeneously treated soil without significant displacement of the soil to the surface; and

- the auger system and supporting ancillary equipment have to be “purpose designed” to accommodate the injected cementitious material containing the modified clays.

Several prototypes of the auger system were developed and tested for mixing efficiency prior to the field trial of the stabilization/solidification system.

6. FIELD TRIAL

5.1 The Site and the Program

The technology was tested at field scale on a contaminated U.K. Ministry of Defense site located in West Drayton, Middlesex. A variety of chemical plants has existed on the site since the turn of the century, including a chemical waste “quarantine store,” chemistry laboratory, flammables store, battery bank, engine testing areas, underground storage tanks and nucleonic laboratory. Likely contaminants include, flammable materials, solvents, concentrated sulfuric acid, oils, petrol, and radioactive species. Following investigation, the principal contaminants of concern were judged to be PAHs (7-12 mg/kg) and, in particular, benzo(a)pyrene.

Prior to field operations, a laboratory program was carried out to determine the type of intercalated clay to be used, the cement/fly ash/clay ratio for the grout, and the optimum soil/grout ratio.

The grout was injected using a prototype auger fitted to a conventional piling rig that produces 900-mm diameter columns either individually or overlapping. For this demonstration, columns with 50% overlap were chosen and several different optimized mixes were evaluated in adjacent columns.

Cored material aged 50 days (taken at 44 days), 70 days (taken at 57 days) and 1 year (presumed to have been taken at 57 days) from each column were tested in the laboratory against the treatment criteria outlined below.

6.2 Site Characterization

Previous chemical analysis records provided some data on the concentration of a number of heavy metals and referred to general organic contamination with a specific reference to acid tars in the vicinity of the trial pit.

The ground consisted of 1.7 m of fill material (sand and sandy-clay containing fragments of bricks, timber, metal, concrete, and glass), overlying 0.3 m gravelly-sand underlain by sandy gravel to the base of the trial excavation. Soil samples were collected from depths of 0.5, 1.5 and 2.3 m from the trial pit. The analytical results are summarized in Table 1.

Table 1: Concentrations of PAHs and heavy metals in soil samples from field site

Depth of soil sample	**m**	**0.5**	**1.5**	**2.3**	**Accuracy**
pH		7.5	7.1	7.3	
Cadmium	mg/kg	3.4	4.4	4.2	+/- 0.2
Copper	mg/kg	460	310	635	+/- 40
Chromium	mg/kg	ND(b)	45	62	+/- 2
Lead	mg/kg	1,560	2,300	3,330	+/- 160
Nickel	mg/kg	84	37	53	+/- 4
Zinc	mg/kg	564	600	785	+/- 40
Total of 6 PAHs (a)	mg/kg	7.4	10.2	12.0	+/- 0.02

Note: (a) fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene
(b) not determined

The results indicated there were potentially 17 PAHs present in the soil. Those investigated in detail were fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, which are specified by the World Health Organization (WHO) and the U.S. Environmental Protection Agency (USEPA) as proven or suspect human carcinogens. The total concentration of the six WHO PAHs ranged from 7.4-12 mg/kg of dry soil with the most abundant PAH being fluoranthene with a concentration of up to 4.3 mg/kg.

6.3 Performance Criteria

The effectiveness of the various treatments in the laboratory and field was assessed against:

- unconfined compressive strength (UCS) by an ASTM method (greater than 350 kPa after 28 days curing);
- leachability, based on the USEPA Toxicity Characteristic Leaching Procedure (TCLP), which uses an aggressive acid leaching medium, with respect to six WHO PAHs (total PAHs less than 10 µg/L and benzo(a)pyrene less than 0.5 µg/L) and chromium, copper, lead, and zinc with target levels of 50 times U.K. drinking water limits; and
- a final leachate pH in the TCLP test (between 8-10 following 28 days curing) to ensure low metal solubility (this was later amended to a pH of 7-11).

Durability (freeze/thaw and wet/dry) and permeability tests (less than 1×10^{-9}m/s) were used as secondary evaluation criteria. ASTM test procedures were used for the initial freeze/thaw tests on laboratory prepared materials, but the test method was subsequently modified as it was judged to harsh in relation to typical U.K. weather conditions.

6.4 Treatment Optimization in the Laboratory

6.4.1 Preparation of modified clays

Seven modified clays were prepared from a conventional Ca^{2+} bentonite clay (premixed with 5% w/w sodium carbonate):

- Al^{3+} pillared;
- Fe^{3+} exchanged and Al^{3+} pillared;
- Fe^{3+} exchanged, Al^{3+} pillared and then treated with benzyl quaternary ammonium salt (QAS);

- Fe^{3+} exchanged, Al^{3+} pillared and then treated with 2HT (aliphatic) QAS;
- Al^{3+} pillared and Fe^{3+} exchanged (spiked);
- Al^{3+} pillared and Fe^{3+} exchanged (spiked) and then treated with benzyl QAS; and
- Al^{3+} pillared and Fe^{3+} exchanged (spiked) and then treated with 2HT QAS.

X-ray diffraction analysis of the clays showed that all had been effectively pillared/intercalated. The modified clay was produced as a suspension water (0.5 g clay/10 g of liquid).

6.4.2 Tests on synthetic soils

The treatment/optimization trials were conducted in two stages: first on synthetic soils intended to model site soils and then on actual site soils. The model system comprised a mixture of sand and clay with pyrene added at a concentration of 20 mg/kg, this being the average PAH content of the site soils. The pyrene was added to the pre-mixed clay and sand as a powder because of its low water solubility. The non-carcinogen pyrene, which was present on the site, was judged a satisfactory substitute for the six WHO PAHs.

The following treatment materials were used:

- ordinary Portland cement (OPC);
- power station fly ash (known in the U.K. as pulverized fuel ash);
- modified clays; and
- quick lime (as an alternative to cement for raising the pH).

The treatment materials were combined in a grout with the clay suspension as the source of water. The grout mixes were added to the prepared soil and thoroughly mixed to obtain a pumpable consistency (by inspection).

Initial development work focused on OPC/fly ash mixes. Parameters that affect the properties of the soil-grout mix, such as cement/fly ash ratio, soil/grout ratio, water/cementitious materials (OPC+fly ash) ratio and the amount of modified clay added were considered. Uncontaminated soil was used as a control to determine if contaminants affected performance/properties.

6.4.3 Tests on site soils

Following the tests on the model soils, a limited number of soil-grout mixes were prepared using site soils. These latter tests indicated that the real soil/grout mixes produced treated soils with a UCS of about 50% of the model soils. Physical examination showed a similar degree of homogeneous mixing for all three different soil-grout ratio mixes tested. Consequently, a decision was made to proceed with further tests using a soil/grout ratio of 5:1, thereby using the minimum amount of grout to achieve the overall objective with regard to UCS.

Two options were considered for raising the pH: (1) increasing the amount of OPC in the grout; and (2) adding quick lime to the grout. Following initial trial and error experiments six mixes were selected for detailed evaluation. The addition of quick lime retarded strength development and significantly reduced strength at 28 days. Examination of the pH data led to the target range be amended from 8-10 to 7-11. Leachate results for pyrene were all satisfactory.

On the basis of these results, four mixes were selected for further testing with a view to use in the field trial.

6.5 On-site Trial

6.5.1 Installation

An area of 6 m^2 to a depth of 2.5 m was treated in the trial. As indicated above, four mixes were selected following extensive laboratory development work, and two further mixes were added to extend the range of material combinations (see Table 2). One was replicated.

The clay formulation used was Al^{3+} pillared and Fe^{3+} exchanged (spiked) and then treated with benzyl QAS. The modified clay was produced as a suspension at Birmingham University and transported to site in steel drums. The clay concentration was 20 g/L (2.5 times more dilute than used in laboratory treatment trials).

A grid treatment plan was prepared as shown in Figure 3. The approach adopted with the six soil-grout mixes was to designate specific columns for each mix, with a minimal overlap of nominally 50% to determine the rate of spoil generation in the worst-case scenario. The site trial took place over two days. The solid line columns in Figure 3 were installed on day one, and the dotted line overlapping columns were installed on day two.

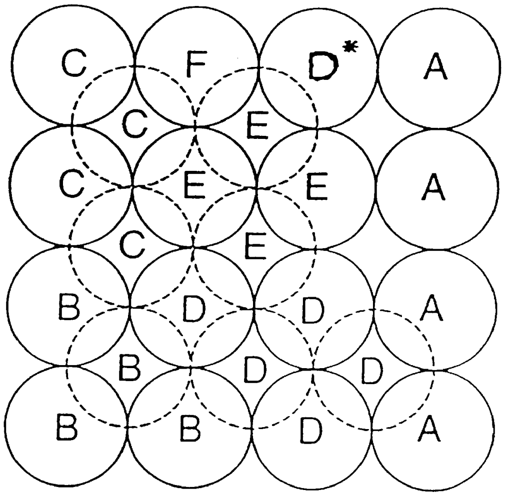

Figure 3: Plan of the soil-grout overlapping columns showing the mix used in each column

The columns were formed by advancing the auger into the soil to the required depth of the column, mixing the soil in place during the auger descent and then injecting the grout slurry into the soil with simultaneous mixing on the auger withdrawal. The overall volume increase was measured at the end of the second day to be about 1 m^3, which is an increase of about 6.5%.

6.5.2 Sample collection

The properties of the stabilization/solidification soil-grout material were investigated for single as well as overlapping column areas to ensure that homogeneous mixing had taken place and that no weak areas or areas of preferential flow had been created during column formation.

Cores were collected at 44 and 57 days (logistical problems prevented sampling at 28 days as originally planned). UCS, pH, leachability, durability and permeability testing were conducted on the cored material. The total curing times, including storage at Birmingham University before testing, were 50 and 70 days, respectively.

Table 2: Composition of Mixes Used in Field Trial

Mix		**A**	**B**	**C**	**D**	**E**	**F**
Fly ash	kg	80	80	80	80	80	-
Cement	kg	30	30	25	25	20	80
Lime	kg	-	1	4	4	-	-
Bentonite	kg	-	-	-	-	-	8
Water							
clean	L	26	26	26	30	23	110
clay suspension	L	20	20	20	16	17	30
Total	L	46	46	46	46	40	140
Soil:grout (solids+water)	w:w	5	5	5	5	5	5
Grout (solids only):soil	%	14	14	13.5	20	14	8
Modified clay	kg	0.4	0.4	0.4	0.32	0.34	0.6
Total solids	kg	660	661	654	654	600	528
Modified clay:solids	g/kg	0.61	0.60	0.61	0.49	0.57	1.14

Mix		**A**	**B**	**C**	**D**	**E**	**F**	**D***
Soil in column	kg	1,200	1,200	1,200	1,200	1,200	1,200	1,200
Dry grout in column	kg	240	240	240	340	240	240	340
Fly ash in grout column	kg	125	120	125	175	140	-	175
Cement in grout column	kg	46	46	40	55	35	85	55
Lime in grout column	kg	-	1.5	6	10	-	-	10
Bentonite in grout column	kg	-	-	-	-	-	85	-
Water in grout column								
clean water	L	40	40	40	70	40	120	40
clay suspension	L	30	30	30	30	30	30	30
Total	L	70	70	70	100	70	150	70
modified clay/column	kg	0.6	0.6	0.6	0.6	0.6	0.6	0.6
modified clay/kg soil	g	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Notes:
1. The density of the soil taken to be 1,700 kg/m^3.
2. The column is 0.6 m in diameter and 2.5 m high.
3. The concentration of the modified clay suspension is 1 kg clay/50 liters.
4. Replication of mix D is denoted as $D^{*.}$

6.5.3 Results

The results of testing are summarized in Table 3. All UCS values exceeded the target value of 350 kPa and were greater than the equivalent (28-day) laboratory results. This was particularly true for the mixes containing quick lime.

The leaching results were all satisfactory. All mixes satisfied the pH range of 7-11 and tended to be at the alkaline end of the range. The total concentrations of the six WHO PAHs in the leachates were all below 2 µg/L and often below the 0.02 µg/L detection limit. The individual leachate values for benzo(a)pyrene were also within the target value of less than 0.5 µg/L. All results for chromium, copper, lead, and zinc were satisfactory. Subsequently, more detailed analyses also showed satisfactory performance with respect to a wider range of metals.

The samples survived a modified freeze-thaw test—the ASTM method being considered too aggressive following the laboratory trials for U.K. conditions. The wet-dry test results were also satisfactory.

Only one sample satisfied the permeability criterion of less than <1x10^{-9} m/s. This was likely due to the presence of natural bentonite.

Table 3: Results on Cores taken at 44 days and 57 days

Mix	Strength (kPa)	TCLP leach results		Durability tests		Permeability (x10^{-9} m/s)
		pH	PAHs (µg/l)	wet/dry mass loss (%)	freeze/thaw mass loss (%)	
44 days						
A1	1,332 1,239	11	<0.5			
B1	1,037	7.4	<0.5			
C1	1,458	11	<0.5			
D1	1,212	10.2	<1.1			
E1	690	9.1	<0.6			
F1	1,533 1,876	10.4	<0.5			
D1*	-	-	<1.0			
57 days						
A2	1,989	9.6	<0.5	-1.46	-1.13	1.82 3.46
B2	823	10.1	<0.6	1.77	1.72	0.15 1.23
C2	1,340 955	10.9	<1.6	1.32 1.71 2.55	0.95 1.03 1.83	5.04 2.56
D2	1,692	10.3	<0.8	-1.24	0.1	3.5 6.92
E2	1,523 1,381 1,494	10.8	<1.9	0.41 0.35	-0.09 -0.09	0.81 3.17
F2	1,156	11	<0.6	-0.46	-1.5	0.8 0.6

6.5.4 Medium term performance

Cored samples collected during the site trial were cured under laboratory conditions for 12 months. they were wrapped in wet cloth and kept in a humidity room. The cores had diameters ranging from 75 to 150 mm and a maximum length of 400 mm.

Samples from all mixes showed an increase in UCS cured for 12 months, compared to those cured for 70 days. Permeability values decreased as expected due to continuing cement hydration processes. Wet-dry durability testing gave similar results after 12 months, and freeze-thaw testing was largely inconclusive (all samples failed at very low temperatures as previously experienced). The results for UCS and permeability are given in Table 4. In general, the results indicated that physical properties improve with aging.

Table 4: Results for 2 months and 14 months(a)

Mix	Compressive strength (kPa)		Permeability ($\times 10^{-9}$ m/s)	
	2 months	14 months	2 months	14 months
A	990	2,325	2.64	0.39
B	1,332	2,812	0.69	0.18
C	1,231	2,180	2.56	0.10
D	1,274	2,570	2.21	0.52
E	1,480	1,712	1.99	1.30
F	1,335	ND(b)	0.64	0.19
D*	1,365	1,875	0.70	0.12

Notes: (a) cores taken at 57 days and stored in the laboratory under humid conditions for 12 months
(b) not determined

7. REFERENCE

N. A. McLeod. *Chemical fixation of soils contaminated with organic chemicals* (final report for NATO/CCMS Pilot Study), Envirotreat Limited, Kingswinford, U.K., 1997.

Project No. 35

In Situ Soil Vapor Extraction within Containment Cells Combined with *Ex Situ* Bioremediation and Groundwater Treatment

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1. INTRODUCTION

The former Derwenthaugh Cokeworks site is located adjacent to the River Derwent, near Gateshead, Tyne, and Wear. Investigation of the site identified a 7.9-ha area that was significantly contaminated with coal carbonization wastes from the original plant including BTEX (benzene, toluene, ethylbenzene, and xylenes), polycyclic aromatic hycrocarbons (PAHs), phenols, heavy metals, and cyanides. The site was underlain by fill, sand, and gravel to a depth of 2-4 m. Groundwater contamination was severe and included the presence of free floating product shown to be seeping into the adjacent river. This Pilot Study project reported on the remediation scheme adopted at the site; the project was funded by a Land Reclamation Grant from the U.K. government.

In summary, the remedial scheme involved four stages of work: (1) installation of a cut-off wall to protect the adjacent river from further pollution and to allow safe excavation (to a depth of 5 m) of the contaminated ground; (2) installation of wells for dual-phase vapor extraction (DVE) to remove volatile organic compounds (VOCs) and free-phase product; (3) use of wells to extract contaminated groundwater for surface treatment; and (4) excavation and treatment of contaminated soil.

2. BACKGROUND

Built in 1928-29, the former Derwenthaugh Cokeworks site is situated about 2 km southwest of the confluence of the Rivers Tyne and Derwent in Northeast England, and lies between the River Derwent and the A694 Rowlands Gill to Blaydon Road. The site lies within the valley of the River Derwent and follows the course of the river for approximately 2.5 km, covering a total area of about 55-hectares. The cokeworks carbonized coal with by-products including tar, ammonium sulfate, benzole, and town gas. Prior to the closure of the plant, 475,000 tonnes of coal per year were being used to produce foundry coke.

Site investigation works indicated the area to be underlain by variable fill material overlying fine-to-medium sands and a persistent gravel layer, usually at about 2-4 km below ground level. Groundwater was encountered in monitoring wells installed in the gravel during the initial investigation. The contours suggested a general hydraulic gradient running from south to north with a fall in level of about 3 m across the site. The original site investigation indicated that a high level of contamination was present in both soil and groundwater. In particular, the groundwater was found to be contaminated with phenol, oil, and PAHs across the entire site. A floating layer of free oil was evident at certain locations, and oil was observed to be seeping into the River Derwent at several places along the river bank. Benzene and other VOCs were also detected in significant concentrations.

3. TECHNICAL CONCEPT

3.1 Overall Scheme

A deep cut-off slurry wall was installed, enclosing the area to be treated in order to allow safe excavation to up to 5 m depth (with minimal dewatering) and to prevent outflows of contaminants directly into the river. The cut-off wall was taken down to a sufficient depth to form an aquiclude to minimize: (1) river water entering the site; and (2) the flow of pollutants from the site to the river.

A well point system was installed. Dual vacuum extraction was conducted, to dewater the site and remove vapor contamination (including benzene and VOCs) and free-phase product. Extracted groundwater was treated prior to discharge. The treated liquid had to conform to strict default criteria (devised by the National Rivers Authority (now the Environment Agency) before discharge into a soakaway adjacent to the river was permitted.

Following dewatering, the solid material was excavated. Solids unsuitable for treatment were placed directly into an on-site encapsulation facility. Other material was screened and either air dried and reused or treated by *ex situ* bioremediation to remove oil and PAH contamination. Suitably treated materials were used as backfill to reinstate the excavated contaminated area.

3.2 Slurry Wall

The first stage of treatment was to install a cutoff wall using a vibratory emplacement technique along the boundary of the remedial works. Laboratory investigations optimized the slurry used (about 34% solids), which consisted of bentonite, ordinary Portland cement, ground granulated blast furnace slag (a cementitious material), and water. The average thickness of the emplaced wall was 0.132 m, and it had a permeability of at least $1x10^{-8}$ m/s and strength of 200 kN/m^2.

3.3 Dual Phase Vapor Extraction (DVE)

Following testing, DVE was implemented by dividing the area into a series of treatment cells. Initially 30 0.1-m inner diameter wells were installed to a depth of 4.5-5 m below ground level, but this was increased to 37 m following discovery of complex strata differences between the whole site and the original field test area. DVE uses an applied subsurface vacuum to draw contaminant vapors and free product to the surface for separation and treatment. At the surface, free product was separated from the groundwater in a separator tank and volatile organic vapors were adsorbed onto activated carbon filters. In order to facilitate free product removal, dewatering trenches were dug in some sectors of the site (see below).

3.4 Groundwater Treatment System

Extracted groundwater was generated at a rate of 75 m^3 per day. Groundwater treatment consisted of several phases designed to sequentially treat contaminant components using a succession of holding lagoons and reactors: (1) reception/buffer lagoons (floating product removed by skimming); (2) heavy metal removal by hydroxide precipitation; (3) cyanide oxidation; (4) sulfide oxidation; (5) pH correction; (6) sand filtration; (7) activated carbon filtration; and (8) biological oxidation of ammoniacal nitrogen. Treated groundwater was discharged to a soakaway along the Derwent.

3.5 Treatment of Excavated Materials

The excavated solid material varied in composition. Excavated materials were classified on the basis of past work on the site based on physical appearance, location, and depth of the excavation, and previous analytical data for that site sector. Material judged unsalvageable was sent to an on-site encapsulation area. The remainder of the material was screened at 100 mm and left in piles to air dry. Oversized material was crushed and reused on site, if analysis indicated this would be acceptable. Undersized material was sent for biological treatment using “biopiles.” The design of the biopiles was based on preceding laboratory and field scale tests (see below). The biopiles were constructed over a high density polyethylene (HDPE) membrane and clay liner. Runoff was collected via an HDPE-lined ditch and was reapplied to the biopiles. Aeration was provided via a network of air injection pipes. The biopiles were clearly identified and delineated to allow determination of process effectiveness by material batch. Forced aeration was provided on a continuous basis. Effectively treated material was reused onsite. A total of 28,000 m^3 of material was treated in four batches of 7,000 m^3. Treatment duration was 2-3 months, depending on the time of year.

4. FINDINGS

4.1 DVE Process

The DVE process was operated for 46 weeks, during which time the total mass of VOCs recovered was in excess of 150,000 kg. Severe weather conditions often caused problems during DVE treatment because of freezing of supporting pipework and equipment. The objective of the treatment was to remove free product and reduce concentrations of VOCs—particularly benzene—to safe levels for excavation rather than as a complete remedial treatment in itself. This objective was achieved; however, the contractor regarded the following points as noteworthy:

- Pipework requires protection from severe weather conditions.
- The variable ground conditions meant that assumptions made based on a field trial in one sector were not valid for the whole site, and further wells had to be retro-fitted.
- The volume of liquid requiring extraction exceeded the capacity of the DVE system, and slit trenches with surface pumps were required to remove groundwater and free product. The pumps were more effective for this, and the vacuum effort was then focused on the removal of VOCs.
- Over the project, there emerged greater-than-anticipated requirements for process monitoring, in part because of the complexity of the site conditions. Much of this was carried out by hand. It would have been far more efficient to have installed capability for centralized or remote process monitoring when works were begun.

4.2 Groundwater Treatment

Consent limits for water treatment discharge was one of the major regulatory controls on this project . A particular difficulty was coping with seasonal variation in water volumes, ranging from conditions with low treatment volumes containing high concentrations of pollutants, to high volumes with low concentrations. The variability of groundwater quality required a higher degree of monitoring than originally was envisioned. Furthermore, at times the volume of groundwater requiring treatment exceeded the design capacity of the system, necessitating its storage in “buffer” lagoons.

The treatment process generated a number of waste streams, some of which were disposed of offsite, others of which were encapsulated onsite.

The biological treatment plant, which consisted of a nitrification lagoon, was a retro-fit forced by changes in the composition of the ammoniacal nitrogen in the groundwater as work on site progressed. Initially, this nitrogen was found as NH_3. However, as time went on, free ammonia levels fell and NH_4^+ concentrations increased. Inoculum from a local sewage works was found to perform far better than commercially available inocula.

A reed bed is planned to treat residual contamination following site reinstatement. It is envisioned that the reed bed will need to accommodate a groundwater flow of 30-50 m^3 per day.

4.3 Excavated Materials

Over 130,000 m^3 of solid materials were excavated during the remediation. Of this total, 51,000 m^3 were able to be reused as fill following screening and drying. 55,000 m^3 were targeted for bioremediation, of which 28,000 m^3 were reportedly treated. Of this 28,000 m^3, 4,000 m^3 failed to reach the required standard and were encapsulated (the required treatment targets were not reported). The balance of the materials (20,000 m^3) was also encapsulated. A significant proportion of the material sent to biological treatment was demolition rubble. 30% of the treatment volume was removed by screening at 100 mm prior to placement in the biopiles.

4.4 The Biopile Trials

Preliminary investigations based on plate counts implied that an adequate range of PAH-degrading bacteria was already present in the site soil. Aeration and addition of nitrogen and phosphorous were found to enhance biodegradation rates in solid phase laboratory-scale tests. Throughout the tests, levels of naphthalene did not greatly decline, whereas levels of higher molecular weight PAHs (*e.g.*, acenaphthene and fluorene) did decline. It was suggested that naphthalene was being produced as an intermediate breakdown product from the degradation of higher PAHs.

Field-scale tests were carried out using small-scale biopiles with forced aeration to test the effect of covering them with insulating materials and the effect of water and supplement addition. The results of these trials indicated no significant benefit from either nutrient addition or insulation. Degradation rate did appear to decline with lower ambient temperature.

Following the main works, the following points were noted:

- the main factors affecting the degradation process were aeration and ambient temperature. Attempts to replicate laboratory conditions that were indicated as beneficial showed no cost effective benefits at full scale;
- significant reductions in the contaminant levels were achieved through redistribution and volatilization;
- often these processes alone were enough to achieve the specified criteria, with no further action required; and
- a key contribution to success is careful management of material batches and screening.

5. MATERIALS TREATED

The materials treated have been described above and include:

- rubble that was separated by screening and dried;
- undersized material, which was treated biologically or sent for on-site encapsulation;
- extracted groundwater, treated by a series of physical, chemical, and biological processes; and
- extracted soil air treated by activated carbon filtration.

6. PROCESS RESIDUALS

6.1 Range of Residuals

Residuals included the materials encapsulated onsite and material deemed to have failed to meet treatment targets following its biopile treatment, which was also encapsulated on site. Treatment process residuals from the air and water treatments were:

- oil from the reception lagoon, which was disposed offsite;
- sludge from the settlement lagoon (following hydroxide dosing), which was encapsulated onsite;
- oil from the DVE separator, which was disposed offsite;
- sludge from the DVE separator, which was encapsulated onsite;

- sludge following pH correction, which was encapsulated onsite; and
- spent carbon, which was encapsulated onsite.

The sludges typically contained 3% solids.

6.2 Water

The final report presented a typical groundwater composition prior to treatment, discharge consents, and concentrations following treatment as documented number of groundwater monitoring reports (Table 1).

Table 1: Composition of Groundwater Prior to and Following Treatment

Analyte	Concentration (ppm)		
	Typical Pretreatment Values	NRA Effluent Discharge Criteria	Range in Reports
Cyanide	3.8	0.1	<0.1 (free)
Chloride	373	-	-
Sulfates	1,520	-	-
Phenol	21.8	1	<0.05
Sulfide	71.7	5	<0.02 (free)
PAH	-	1	<1-2
Lead	<0.02	0.02	<0.01-0.3
Cadmium	0.01	0.002	<0.001-<0.01
Zinc	0.9	0.09	<0.01-0.03
Arsenic	<0.01	0.01	<0.01-0.03
Iron	-	5	<0.01-0.23
NH_4	260	5	0.2-34 (saline as N)
Suspended solids	-	60	25-1,420
COD	-	500	7-270
pH	6.1-9.3	5-9	7.1-12.5
total hydrocarbons	6,220	-	-

Note: * = toluene-extractable material

7. COSTS

The contract for the remedial works described for the cokeworks site was let at £2.9 million (1994). The cost of the overall project was originally estimated at £8 million and was funded by a derelict land grant via English Partnerships, a regeneration agency in the U.K. The Final Report quotes an overall investment of £10 million, rather than £8 million. No further breakdown of costs is provided, and no detailed costs are provided for the processes described above.

8. SAFETY

The principal safety concern, apart from the general hazards of working in a civil engineering project involving excavation, was the ambient VOC level—particularly benzene. Monitoring included background monitoring and personal exposure measurements and record keeping, in accordance with U.K. COSHH (control of substances hazardous to health) Regulations.

Project No. 36

Enhancement Techniques for *Ex Situ* Separation Processes Particularly with Regard to Fine Particles

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1. INTRODUCTION

Ex situ soil separation processes (often referred to as soil washing) are widely used in Northern Europe and North America for the treatment of contaminated soil. They mostly use separation processes from the mineral processing industry to remove contaminated concentrates from soils and produce relatively uncontaminated soil fractions that may be suitable for reuse as relatively "inert" fill. At present, commercial soil separation is mostly restricted to the removal of fine fractions (for example, <0.063 mm), which normally contain the highest concentration of contaminants, leaving the coarse fractions (>0.063 mm) relatively uncontaminated. In this approach, the separation of the contaminated fines often results in a net cost saving to the overall treatment process since, for example, it can significantly reduce the volume of contaminated material requiring landfill disposal. However, in cases where contaminated soils have a high silt and clay content (>30-40%), the financial benefits of volume reduction are diminished to the point where conventional soil washing is considered uneconomical. For such soils, enhancement of soil separation processes and the development of downstream treatment of fine fractions are felt necessary to increase the range of soil types treatable by soil washing and to reduce the volume of secondary wastes that require disposal.

The study was carried out under a contract to the U.K. Department of the Environment by AEA Technology's National Environment Technology Centre.

2. THE STUDY

This Pilot Study project investigated the feasibility of extending *ex situ* soil washing processes to soils that contain a high proportion of fine particles through the use of physical separation techniques and equipment normally used for the treatment of fine mineral ores and industrial minerals.

A laboratory study and pilot-scale study were conducted on the treatment of two fines-rich soils containing organic contaminants. One soil from a former industrial site contained 62% soil particles less than 0.063 mm and was contaminated with diesel fuel. The other soil, from a former gasworks facility, had up to 43% soil particles less than 0.063 mm and was contaminated with polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPH), and complexed cyanides. The project examined key processes such as disaggregation of agglomerated fines, particle sizing and classification, attrition scrubbing to remove fine particles attached to surfaces of coarser particles; density concentration, dewatering, and integration of the aforementioned processes with slurry-phase biological treatment.

Results of the investigation showed that both soils could be disaggregated using a tumbling mill partially filled with steel balls or pebbles. Subsequent attrition scrubbing of silt- and sand-sized particles from both soils had little effect on the contaminant content of these particles, even after extended periods of time and after the addition of various dispersant reagents (to prevent fine particles re-coating larger particles). The surfaces of these particles in both soils were therefore thought to be relatively free of persistent fine coating contaminants.

During screening and classification, the contaminants in the diesel-contaminated soil were markedly concentrated in the fraction less than 0.002 mm. Removal of entrained or misplaced ultrafines (<0.002 mm) from the coarse soil fractions was found to be essential to achieve low levels of contamination in the gravel, sand, and silt-sized fractions. Froth flotation of the fraction less than 0.01 mm did not significantly reduce contamination in the non-floating product.

The contaminants in the gasworks soil were more evenly distributed in the various size fractions, and removal of entrained soil particles made little difference in the contaminant content of the fractions. With this soil, other physical separation processes could substantially reduce PAH and TPH contamination, but not complex cyanide contamination. For the fine particles, a combination of classification at 0.01 mm with froth flotation or specific gravity concentration was reported to substantially reduce the contaminant content of the treated product. Froth flotation proved best on the 0.01-0.63 mm fraction, producing a non-floating fraction weighing 69% of the untreated material. Three stages of froth flotation reduced PAH contamination by 61%, TPH by 54%, and cyanide by 39%. By comparison, specific gravity separation on the 0.01-0.63 mm fraction reduced PAHs, TPH and cyanide contamination by 68%, 76%, and 14%, respectively. Despite substantial reductions, however, the products still contained significant residual contamination, which made them unlikely to be suitable for re-use.

In-slurry biological treatment of the contaminated fine fractions from the diesel-contaminated soil removed over 80% of the TPH contamination present. Despite this reduction during the 28-day treatment, treated fines retained relatively high levels (2,300 mg/kg) of TPH. It was suggested that further work was required to reduce the time period for treatment and the level of residual contamination in the treated product so that the process could be more effectively integrated with physical pretreatment. With the fine fraction from the gasworks soil, in-slurry biological treatment for 28 days achieved only a 40-50% reduction in PAHs, 25% reduction of TPH, and virtually no cyanide degradation. The operation of the bioreactor, especially system pH, was found to be difficult to control and further work was suggested to improve treatment performance.

3. RESIDUALS AND EMISSIONS

Residuals from the combined process include treated soil materials and others that did not achieve remediation guidelines. Clean material could be reused onsite, while partially clean materials would have to be dewatered and disposed. Water from soil washing and bioslurry treatment would also have to be treated before disposal.

4. COSTS

The report detailed fixed costs as well as costs for maintenance, administration, *etc*., but provided an operational cost of £UK 29-43/tonne for the soil separation process. In practice, the overall operational costs would also include the cost of disposal or the further treatment of the contaminated concentration. Thus, if disposal of the concentrate costs £100/tonne and the concentrate amounts to 35% of the original mass, the overall treatment costs would be £74-88/tonne. In a U.K. context, considering typical disposal cost of 50/tonne, the overall treatment cost would be £47-61. Thus, the process would be only marginally cost effective, unless a smaller amount of contaminated concentrate were produced, or a cheaper means of treating the concentrate were technically feasible.

5. CONCLUSIONS

The main conclusions of the study were that physical separation processes may be appropriate for soils containing a high fines content provided that a substantial fraction of the soil of grain size greater than 0.002 mm is contaminant free, and that material less than 0.002 mm comprises less than 30-35% by weight of the soil. It was recommended that the separated fraction less than 0.002 mm should also be dewatered to minimize disposal costs.

Project No. 37

Bioventing of Hydrocarbon-Contaminated Soil in the Subarctic Environment

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1. INTRODUCTION

Petroleum hydrocarbons such as JP-4 are generally considered biodegradable, if indigenous microorganisms receive an optimal supply of oxygen and nutrients. Bioventing is a technique that aerates subsurface soils using a series of injection and extraction wells in order to stimulate *in situ* biodegradation on sites where oxygen is limiting the degradation rate. Bioventing in this instance is outwardly similar to soil vapor extraction (SVE) except that the air flow is controlled to reduce the physical vaporization of contaminants. Its objective is to avoid the costs of off-gas treatment, which may occur with SVE (estimated as U.S.\$33-\$39/m^3 of contaminated soil). So far as stimulating *in situ* biological activity is concerned, bioventing has two advantages over aqueous oxygen delivery systems (*i.e.*, pump and treat). First, on a mass basis, less air is required than water to deliver an adequate amount of oxygen. Second, the permeability of soil to air is much larger than the permeability of soil to water. This Pilot Study project reports on the application of bioventing in cold climates where the basic approach is combined with soil warming.

2. EXPERIMENTAL DESIGN

Eilson Air Force Base (AFB) is an operational base located in the Alaskan interior. The climate is subarctic, with an average annual temperature near 0°C (ambient temperatures range from -30°C to +30°C). The technology demonstration was conducted on a 0.4-ha area, designated Site 20, which had been contaminated to a depth of nearly 3 m with JP-4 from suspected leaking pressurized fuel lines. The site soil consisted of a mixture of sand and gravel, with increasing silt content to 3 m, which was the depth of the water table. TPH levels ranged from 100-3,000 mg/kg. A field evaluation of bioventing was undertaken at Site 20 to determine whether and to what degree soil warming can enhance the effectiveness of bioventing of JP-4 and to determine whether soil warming promoted a higher rate of biodegradation all year round.

In the summer of 1991, a bioventing system was installed at Site 20 consisting of an air blower plumbed into air injection/extraction wells spaced at 10-m intervals. Air movement in bioventing can be achieved by blowing air into the ground (injection bioventing) or by creating a vacuum to draw air out of the soil (extraction bioventing) with the latter approach more commonly adopted. The majority of this study used injection bioventing with a blower forcing air into the ground at a rate of 0.015 m^3 per minute. The demonstration area was divided into four test plots where the bioventing system was combined with different soil warming techniques:

(1) Warm Water System test plot: Groundwater collected by an extraction well was pumped through an electrical heater and warmed to around 35°C before reinfiltration. Insulation was placed over the ground surface to retain heat;

(2) Heat Tape System test plot: Strips of tape heater were buried to a depth of 1 m in the test plot and warmed at a rate of 16 W/m^2. Insulation was placed over the plot to retain heat;

(3) Solar test plot: Insulation placed over the ground during the winter months was replaced with plastic mulch sheeting during the spring and summer to capture solar heat and passively warm the soil; and

(4) Control test plot: No soil warming. Both the warm water and heat tape systems were operated for two years from summer to summer over the demonstration period (1991-94). The solar and control plots were monitored for 3 years.

The monitoring program consisted of three major elements: (1) an evaluation of system performance, which included measurement of soil gas composition, soil temperature, microbial respiration and contaminant levels; (2) an evaluation of environmental impact of measuring of surface air emissions; and (3) a cost evaluation.

3. RESULTS

Bioventing significantly increased oxygen levels in the soil gas with a corresponding decrease in carbon dioxide and hydrocarbon concentrations. Soil temperature in the warm water and heat tape test plots were consistently 10°C higher than in the solar heated and control plots. The average biodegradation rates in the warm water and heat tape treated plots were between 3 and 4 times higher than those in the solar and control test plots. It was interesting to note that after switching off the heating systems, biodegradation rates in these plots decreased below that of the control suggesting that the microorganisms may have adapted to the higher temperatures. TPH removal in the warmed plots was an order of magnitude higher than in the solar-heated and control plots.

4. EMISSIONS

In general, air emissions of benzene in the control plot were higher when the bioventing system was on than when it was off. Emission rates were 0.00038 and 0.0001 kg/day with and without air injection. Although bioventing increased emissions, they were well below regulatory limits. Using the data provided by the demonstration, costs were evaluated for remediation of a 5,000 m^3 site with an average TPH level of 4,000 mg/kg using bioventing with or without a soil heating system.

5. COSTS

The evaluation showed a trade-off between cost and treatment time with a basic bioventing system costing U.S.$25.5/$m^3$ over 9.4 years operation, compared with a cost of U.S.$24-26/$m^3$ for a bioventing system using either a warm water or heat tape system operating for up to 3.4 years.

Project No. 38 Demonstration of Peroxidation Systems, Inc. *Perox-Pure*^{TM} Advanced Oxidation Technology		
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1. INTRODUCTION

The Peroxidation Systems, Inc., *perox-pure*^{TM} is a chemical oxidation technology that destroys dissolved organic contaminants in water using an oxidation process based on ultraviolet (UV) radiation and hydrogen peroxide. The basic concept of the treatment system is that a variety of organic chemicals can be effectively oxidized by the combined use of two oxidants such as UV radiation and hydrogen peroxide, UV radiation and ozone, or ozone and hydrogen peroxide. The most direct method for the generation of hydroxyl radicals is through the cleavage of hydrogen peroxide. Photolysis of hydrogen peroxide produces two hydroxyl radicals, which react rapidly after formation with organic contaminants present.

This summary highlights the technology demonstration at the Lawrence Livermore National Laboratory site in California, which was completed under the Superfund Innovative Technology Evaluation (SITE) program. Participants in this SITE demonstration included the U.S. Environmental Protection Agency (USEPA) Risk Reduction Engineering Laboratory, USEPA Region 9, Lawrence Livermore National Laboratory, Peroxidation Systems, Inc., the German Federal Ministry of research and technology, and the PRC Environmental Management, Inc. SITE team. Peroxidation Systems Inc. was responsible for delivering, setting up, operating, and demobilizing the treatment system. The PRC SITE team and others collected and analyzed samples. Under a U.S.-Germany bilateral program, the German Federal Ministry of Research and Technology reviewed the demonstration plan and asked for additional analyzes.

2. THE PROCESS SYSTEM

The technology consists of four modular units that are skid-mounted and portable: the UV/oxidation unit, hydrogen peroxide feed module, acid feed tank, and the control panel unit. Two cartridge filters are placed upstream of the system to remove suspended solids present in the groundwater.

Several operating parameters influence the performance of the system including hydrogen peroxide dose, influent pH, tube cleaner operation, and influent flow rate (hydraulic retention time). During the demonstration, each of these operating parameters was varied, and its impact on system performance observed. The authors claimed that a unique feature of the *perox-pure*^{TM} system is the circular wipers attached to the quartz tubes housing the UV lamps (5 kW mercury vapor lamps). The wipers are designed to improve system performance by minimizing the loss of UV radiation caused by the formation of a chemical coating on glass surfaces from contaminant oxidation.

3. THE DEMONSTRATION PROJECT

3.1 Introduction

During the demonstration at the Lawrence Livermore National Laboratory, testing was carried out on shallow groundwater contaminated with volatile organic compounds (VOCs). The 32-ha site was part of the laboratory’s General Services Area. Trichloroethene (TCE) and tetrachloroethene (PCE) were the principal groundwater contaminants with concentrations of about 1,000 and 100 µg/L, respectively. Information from a remedial investigation and feasibility study and data from treatability studies were used to identify three primary objectives for the demonstration: (1) determine the VOC removal efficiencies of the *perox-pure™* system; (2) determine whether treated groundwater meets applicable discharge limits at the 95% confidence level; and (3) estimate treatment costs, including process chemical dosages and utility requirements. A secondary objective was to obtain information on the type of by-products formed during treatment.

3.2 Results of the Demonstration Project

The *perox-pure™* system generally produced an effluent with TCE and PCE levels below detection limits, and 1,1,1-trichloroethane (TCA) and chloroform levels slightly above detection limits. The system achieved maximum removal efficiencies of greater than 99.9, 98.7, and 95.8 % for TCE, PCE, and 1,1-dichloroethane (DCA), respectively. The system also achieved removal efficiencies of up to 92.9 and 93.6 % for TCA and chloroform, respectively. The treated effluent met California drinking water action levels and Federal drinking water maximum contaminant levels for all VOCs at the 95% confidence level.

3.3 Residuals

Gas chromatograph and mass spectrometer analysis of influent and effluent samples for VOCs indicated that no toxic intermediate organic compounds were created during treatment. Although the toxicity of the effluent to water flea and fathead minnow was found to be greater than for the influent, this was assumed by the authors to be due to residual hydrogen peroxide being present.

4. OTHER PROJECTS

Information on how the technology performed at three other facilities provide additional performance data to support findings of the SITE project. For these studies, the technology was used to treat wastewater containing acetone and isopropyl alcohol (IPA), groundwater contaminated with TCE, and groundwater contaminated with pentachlorophenol (PCP).

The first case study at the Kennedy Space Center in Florida tested the oxidation system as a replacement for the existing carbon adsorption treatment for wastewater containing acetone and IPA. The replaced system could not achieve the required discharge level of 0.5 mg/L. In contrast, effluent from the new oxidation system met all of the discharge criteria, including the demineralization discharge standards in less than the specified 24-hour maximum treatment time. The system was efficient enough to allow treatment of the wastewater in a flow-through rather than a batch mode at a flow rate of 5 U.S. gallons (18.9 L) per minute (gpm), a hydrogen peroxide dosage of 100 mg/L, and 10 kW of power for a period of 20 hr/day.

For the second case study, the perox-pure™ technology was used to treat well water containing 50-400 mg/L of TCE. Because the well was located in the middle of a large residential area in Arizona, the treatment was chosen because of its low-visibility and quiet operation. When treatment was conducted at a flow rate of 135 gpm (510 L/min) and 15 kW of power, TCE was consistently treated to a level below the analytical detection limit of 0.5 ug/L.

A full-scale *perox-pure*™ system treated groundwater contaminated with PCP at levels up to 15 mg/L for the third case study conducted on the property of a chemical manufacturing company in Washington in 1988. Continued operation confirmed that the *perox-Pure*™ system could destroy the PCP to below the target level of 0.1 mg/L. To obtain this result, the system operated at a flow rate of approximately 70 gpm (265 L/min), a hydrogen peroxide concentration of 150 mg/L, and a power requirement of 180 kW. High levels of iron required a pretreatment system to oxidize and remove this metal. To reduce the tendency for scaling, acid was added to lower the pH of water to around 5, and the oxidation system featured automatic devices to keep the lamps clean.

5. COSTS

Cost analysis of the demonstration project indicated that the groundwater remediation cost for a 190 L/min *perox-pure™* system would range from U.S.$2-3/m^3 (1992), depending on contaminated groundwater characteristics. Of this total cost, the *perox-pure™* system direct treatment cost would range from U.S.$0.80-1.30/m^3 (1992).

Treatment costs for three of the other four projects ranged between U.S.$3.60 and U.S.$5.00 per 1,000 U.S. gallons (U.S.$0.95-1.3/m^3). Treating well water for the second case study cost only U.S.$0.28 per 1,000 U.S. gallons (U.S.$0.07/m^3). These costs exclude those for capital.

Project No. 39

Management of Soil Vapors at the Basket Creek Site

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1. BACKGROUND

The Basket Creek Surface Impoundment site (Basket Creek) is located in Douglasville, Georgia, USA. The site was contaminated during the 1960's when it was used for the illegal disposal of hazardous wastes. At that time, an intermittent stream bed was dammed with soil to form a surface impoundment. The impoundment measured 35 feet (10.7 m) by 50 feet (15.2 m). It ranged in depth from 6-12 feet (1.8 to 3.7 m).

Liquid refinery and other hazardous wastes were reportedly disposed in the impoundment over a number of years; however, detailed information on the quantity and specific composition of the wastes was not available. The wastes were accidentally ignited in July 1970 and burned for several days. Subsequently, local officials required the landowner to cease disposing waste and cover the impoundment with soil.

In 1989, the EPA conducted a Hazard Ranking System evaluation for Basket Creek, but the site did not qualify for the National Priorities List. Emergency action, however, was initiated in 1991. The site was found to contain high soil concentrations of lead, mercury, and organic compounds (trichloroethene, toluene, methyl isobutyl ketone and methyl ethyl ketone).

Several different remedial strategies were evaluated. Off-site remediation was rejected on the grounds of cost. Treatability studies were carried out for two on-site treatment technologies: *in situ* soil vapor extraction (SVE) and low temperature thermal desorption. *In situ* SVE was ruled out on the basis of the soil's low permeability. Low temperature thermal desorption was rejected after the soil sample ignited during trials.

The selected technology was *ex situ* SVE, which involved excavation, processing, and stockpiling of contaminated soil on the site. The stockpiled soil was then treated using SVE. Soil excavation and treatment was carried out under cover of a large ventilated enclosure; exhaust gases were passed through a thermal oxidizer (fume incinerator) before discharge to atmosphere.

2. TECHNICAL CONCEPT

The treatment technology comprised four main components:

(1)	Metal enclosure, 60 ft (18.3 m) x 120 ft (36.6 m)	Designed to totally enclose the impoundment and stockpiled soil and to contain processing operations.
(2)	Soil handling plant	Track-mounted excavation equipment and power screen. Soil was excavated and placed directly onto the power screen, which shredded soil clumps. Screened soil was transported to the stockpile using a covered stacking conveyor.

(3)	SVE system	Comprised seventeen, 4-inch (100-mm) diameter slotted well screen strings positioned horizontally in the soil stockpile. Chemical resistant screens were placed over the well screen to prevent soil from clogging the slots. The vacuum for each well screen row was supplied by a vacuum pump fitted with a filter canister and silencer.
(4)	Air emission control equipment	Vapors drawn out of the SVE system were routed via PVC piping to the thermal oxidizer. This was a three-chamber, propane-fired unit designed to treat 10,000 ft/min^3 (283 m^3/min) of vapors with a greater than 99% destruction and removal efficiency. In addition, a moveable fume hood collected vapors at the excavation point and at the power screen. The vacuum was provided by a draft blower located outside the enclosure. A baghouse filter plant was used to remove particulates (down to 0.5 microns) from the air stream. Air exiting the baghouse was routed to the thermal oxidizer.

3. MATERIALS PROCESSED

Samples of material from the impoundment were collected in March 1990, May 1991, and January 1992 and analyzed for organic compounds and metals. Samples collected in May 1991 were subjected to the USEPA Toxicity Characteristic Leaching Procedure (TCLP). The total concentrations and TCLP concentrations of the primary contaminants are listed in Table 1.

Table 1: Concentrations of Primary Contaminants

Contaminant	**Concentration**	
	Total (mg/kg)	**TCLP (mg/L)**
Trichloroethene	BDL - 8,600	11.0
Toluene	9,300 220,000	BDL
Methyl ethyl ketone	BDL - 23,000	280
Methyl isobutyl ketone	1,400 - 66,000	BDL
Lead	668 - 4,400	32.6
Mercury	38.2 3,554	0.1
BDL = below detection limit		

Key characteristics of the host matrix were:

- Particle size distribution of 16.4% clay, 34.4% silt, 40.8% sand, and 8.4% gravel
- Moisture content of 16.9%;
- Air permeability of 1.5 x 10^{-7} cm/s;
- Porosity of 0.316;
- Bulk density of 112.5 lbs/ft^3 (1,800 kg/m^3); and
- pH of 5.46.

4. SYSTEM OPERATION

A trial burn of the thermal oxidizer took place in October 1992. Soil in the impoundment was exposed and stirred to liberate volatile organic compounds (VOCs). The vapor was routed to the thermal oxidizer which was operated at approximately 1,600°F (870°C). Mass emission rates were calculated for VOCs, semivolatile compounds, dioxins and furans, and were reported to the Agency for Toxic Substances and Disease Registry (ATSDR). The ATSDR determined that predicted emissions from the oxidizer would not pose a threat to public health.

Full-scale operations began in November 1992. The contaminated area was divided into 48, 10 ft x 10 ft (3 m x 3 m) grids. Excavation was carried out in individual blocks to minimize the surface area of exposed soil. Rocks and debris larger than 2 inches (50 mm) were rejected by the power screen and placed in roll-off boxes. Excavation (up to 14 feet (4.3 m)) was halted when solid homogeneous rock was encountered.

The SVE system was operated continuously, and that associated with excavation and screening was operated an average of 25-30 hours/week. In February 1993, excavation and backfilling of the 48 grid sections was complete. The SVE system was operated for an additional three weeks after excavation to complete treatment of the soil. Approximately 100 U.S. short tons (90 tonnes) of rocks and debris from power screening, 18 yd^3 (13.8 m^3) of excavated metal and crushed drums and approximately 4,250 gallons (16.1 m^3) of decontamination water from health and safety activities were disposed at appropriate off-site facilities.

Site restoration involved dismantling and removing the enclosure and process equipment. The site was then regraded using site soils and seeded with grass. Site restoration was completed in August 1993.

5. RESULTS

The action memorandum covering remediation activities at the site defined treatment targets for treated soils as shown below. In addition to these targets, the thermal oxidizer was required to be at least 95% efficient for VOC destruction.

Parameter	Soil Treatment Target
Trichloroethene (TCLP)	0.5 mg/L
Tetrachloroethene (TCLP)	0.7 mg/L
Benzene (TCLP)	0.5 mg/L
Methyl ethyl ketone (TCLP)	200 mg/L
Lead (TCLP)	5.0 mg/L
Mercury (TCLP)	0.2 mg/L
Total halogenated organic compounds	1,000 mg/kg

Analytical data for the treated soil showed that soil treatment targets were met for all contaminants after the six months treatment period. Total VOCs in treated soil ranged from 0.142-1,571 mg/kg, and approximately 72,000 lbs (32,688 kg) of total VOCs were recovered from the soil. Toluene accounted for the largest proportion of recovered VOCs (approximately 80%) with methyl isobutyl ketone accounting for the next largest (11%). The destruction efficiency of the thermal oxidizer was at least 95%, and reached 98% for three months of system operation.

Airborne concentrations of VOCs inside the enclosure occasionally approached 500 ppm (the stop work condition) and regularly ranged between 200-400 ppm. However, no VOCs were detected during hourly air monitoring surveys outside the enclosure or in off-site high volume air samplers.

6. COSTS

Total project costs were approximately U.S.$2.2 million broken down (according to the inter-agency Work Breakdown Structure, WBS) are set out in Table 2. Costs directly attributable to treatment activities (U.S.$660,000) correspond with a treatment cost of U.S.$413/yd^3 ($540/m^3) of soil treated (1,600 yds^3 or 1,223 m^3 of soil in surface impoundment) or U.S.$275/U.S. ton ($271/tonne) of soil treated and U.S.$9.20/lb ($20.28/kg) of VOC removed.

7. HEALTH AND SAFETY

One of the main health and safety concerns of the project was the potential for the build-up of VOCs inside the enclosure from soil excavation and screening activities, and the possibility of a fire or explosion. Various protective measures were taken including:

- A site safety officer was present inside the enclosure at all times during excavation.

- Level B personal protective equipment (PPE) for workers (supplied breathing apparatus, fire resistant overalls, disposable outer suits and boots, and hard hats).

- Reusable PPE was decontaminated onsite.

Table 2: Costs Summary

Cost Element			**Estimated Costs (U.S.$)**
(i)	Before Treatment Costs		
	•	Monitoring, sampling, testing, and analysis	$260,000
	•	Site work (excavation and soil preparation	$390,000
	•	Air Pollution/gas collection and control (enclosure, air handling system, part of incinerator)	$650,000
		Subtotal	**$1,300,000**
(ii)	Treatment Costs		
	•	Operation (short term, up to 3 years) (operating costs and personnel)	$130,000
	•	Cost of ownership (SVE system, part of incinerator)	$530,000
		Subtotal	**$660,000**
(iii)	After Treatment Costs		$130,000
	•	Disposal at a commercial facility	
	•	Site restoration	$22,000
	•	Demobilization	$68,000
		Subtotal	**$220,000**

The atmosphere inside the enclosure was monitored using a combustible gas indicator. A limit of 10% of the lower explosive limit (LEL) was set as an automatic cease-work condition, and workers were required to evacuate the enclosure. A photo-ionization Detector (PID) was also used to monitor airborne contaminants as total hydrocarbons in air. A limit of 500 ppm total hydrocarbons was also set as a cease-work condition.

Potentially explosive atmospheres were also monitored in the air handling system (inside and outside the enclosure) including vapor extraction piping, flexible duct work and steel duct work. Detectors signalled an audible alarm at 15% of LEL (excavation stopped); a reading of 20% of LEL caused automatic interlocks to activate, which shut down the blower. The 15% LEL level in duct work was exceeded several times per day during excavation of the highly contaminated areas. Several times during the project, the 20% LEL level was exceeded. Air monitoring was also conducted at the perimeter of the enclosure and using off-site high volume samplers.

8. CONCLUSIONS

- Data for samples collected from the soil stockpile showed that soil treatment targets were met in all 14 sampling grids after six months of treatment although there were variations. For example, total VOC data showed a range over four orders of magnitude (0.142-1,571 mg/kg).
- A total of 72,084 lbs (32,730 kg) of total VOCs were recovered of which 75-80% were from the soil stockpile and 20-25% from excavation and screening.
- VOC recovery varied during the course of treatment, peaking during weeks 7, 8 and 9 at 11,000 lbs/week (4,994 kg/week). Variations are thought to reflect those in soil concentrations within the impoundment.
- Recoveries varied for different VOCs with toluene and methyl isobutyl ketone (measured at the highest concentrations prior to remediation) accounting for approximately 80% and 11% of the total recovered VOCs, respectively.
- The destruction efficiency of the thermal oxidizer was at least 95% over 12 weeks of operation, reaching 98% during 3 months when monthly average inlet concentrations were greater than 100,000 ppmv.
- Although VOC concentrations inside the enclosure were elevated, they never exceeded the stop-work thresholds of 10% of the LEL or 500 ppm total hydrocarbons. No VOCs were detected outside the enclosure or at off-site sampling locations.
- Although no pre-treatment data for stockpiled soils were available, TCLP concentrations for trichloroethene and methyl ethyl ketone in treated soil were lower than those in pre-excavation samples. Concentrations of lead and mercury in soils were also lower following treatment, although it is believed that pre-excavation sample results for these metals may not be representative of the contaminated area as a whole.
- The choice of *ex situ* soil vapor extraction resulted in lower costs than would have been expected for off-site incineration of soil. The cost is estimated between U.S.$6-6.7 million.

9. LESSONS LEARNED

- Excavation and power screening greatly increased soil permeability.
- There were limitations associated with the construction materials used for the soil stockpile. Spacing of horizontal wells was difficult because they were made of PVC and would bend under the weight of the soil. Carbon steel pipes would have been more rigid, but more expensive.
- It is important to oversize the air handling system for venting the enclosure. This helps prevent the development of explosive conditions in the enclosure and ductwork.
- Excavation within the enclosure took much longer than it would have done outside due to space constraints. Excavation within the enclosure at Basket Creek took 3 months compared to an estimated 4 days had it taken place outside.

Project No. 40

An Evaluation of the Feasibility of Photocatalytic Oxidation and Phase Transfer Catalysis for Destruction of Contaminants from Water (*In Situ* Treatment of Chlorinated Solvents)

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1. INTRODUCTION

Photocatalysis is an emerging treatment technology that uses an advanced oxidation process based on generating hydroxyl radicals using UV light in the presence of a semi-conductor catalyst, such as platinum-coated titanium oxide. The Hand D process uses a fixed-bed catalyst with the semi-conductor fixed to a silica gel support. Pretreatment of groundwater by removing suspended matter and inorganic ions is conducted by a series of filters and ion-exchange columns. Dissolved oxygen levels are increased, as necessary, to supply oxidants for the destructive oxidation process. The UV light is provided by natural sunlight.

The project researched development of highly photoactive catalysts and a fixed-bed photocatalytic process to destroy toxics in air and water. It also researched development of a treatment process using adsorption to remove contaminants and advanced oxidation processes (AOPs) to regenerate spent adsorbents. The developed technologies were field tested at Tyndall Air Force Base (AFB), K.I. Sawyer AFB, and the Wausau Water Treatment Plant.

2. LABORATORY STUDIES

Some of the photocatalysts used in the laboratory studies were modified on their surfaces with noble metals, or changed by doping with transition metals to extend the photocatalyst's response to visible light. Artificial light and UV sources and solar radiation were used to evaluate the photoactivities of these catalysts for destroying model compounds. Results showed that platinum-coated Aldrich titanium oxide (Pt-Aldrich-TiO_2)—a surface-modified catalyst—performed best for destroying hydrophobic compounds. The laboratory-developed, platinum-coated Michigan Technology University TiO_2 catalyst performed best for hydrophilic compounds.

The supports tested for fixed-bed photocatalysts consisted of random packing and structured materials. These supports were chosen for their adsorption capacity, UV transmission, and mass transfer properties. Silica-based materials were included to test how they performed at destroying organic compounds, and some of them were surface-modified to increase their adsorption capacity. Investigations excluded electron-rich materials that could scavenge reactive radicals and diminish the efficiency of photocatalysis. Researchers developed a unique procedure involving heating and annealing to prepare supported catalysts for fixed-bed reactors. During solar experiments, the fixed-bed processes were optimized with respect to the type of catalyst and dosage, support type and size, and preparation methods. Destruction of a model compound was tested under various UV irradiance, influent concentration, pH, and hydraulic loading. Tanning lamps tested on the same fixed-bed process tested the destruction of several other compounds in air and water. Two reactor designs consisted of a catalyst added as a slurry and passed through a lighted reactor, and a catalyst attached to a support in a lighted fixed-bed reactor.

Tests with the fixed-bed photocatalysts revealed that Pt-Aldrich-TiO_2 supported on silica gel completely mineralized TCE in water (8 mg/L) in one contact time of 1.3 minutes. This destruction rate was 16 times better than observed for an optimized slurry of a commercially-available photocatalyst (Degussa P25).

Increasing the adsorption capacity of a silica-based support improved the overall destruction kinetics. Silica gel modified to increase surface hydrophobicity and the adsorption capacity for non-polar organic water pollutants increased the adsorption capacity for trichloroethene (TCE) in water by more than a factor of five. When used as a support for Pt-TiO_2, the modified silica gel showed faster overall degradation kinetics for TCE than did the unmodified silica gel.

For experiments with contaminants in the gas-phase, results showed faster destruction kinetics than in the aqueous phase. This suggests the option to strip volatile compounds followed by gas-phase destruction by photocatalysis. For trichloroethane (TCA), a relative humidity of 25% yielded the best destruction rate. On the other hand, toluene destruction increased with increasing vapor content. The fixed-bed approach provided high light efficiency. The reported ratio of organic molecules destroyed to UV photons required was 40%—much higher than the 5% value commonly reported. Phosgene and carbon monoxide, two major toxic by-products in air-phase photocatalysis, were not found above regulated levels.

Developing the combined processes of adsorption followed by regeneration consisted of using a fixed-bed system adsorber to remove and accumulate organic compounds, and regenerate the spent adsorbent using homogeneous AOP, photocatalysis, or a combination of steam and photocatalysis. For homogeneous AOP, hydrogen peroxide/ozone and UV light/hydrogen peroxide were used for destructive adsorbent regeneration. Both of these options consumed three to six times more oxidants in the regeneration process than would be needed to destroy the contaminants in water directly by conventional AOP. Regeneration appeared to be limited by adsorbate desorption from the interior to the exterior adsorbent surface. Neither option is feasible because the desorption rate is too slow, and therefore too much oxidant is required to regenerate the adsorbents.

In testing photocatalysis for destruction of adsorbed contaminants and regeneration of adsorbents simultaneously, the catalysts were impregnated onto the adsorbent before being used to adsorb organics. The first test consisted of using UV illumination to test photocatalysis alone for regenerating the spent adsorbents and destroying the contaminants. Results showed that desorption of adsorbates from the interior to the exterior of an adsorbent limited the regeneration process. Thus, temperature played a leading role in photocatalytic regeneration, and increasing temperature enhanced regeneration rate much more effectively than increasing light intensity. Using heat to increase the desorption rate and match the photocatalytic oxidation rate is one way to maximize the photolytic regeneration efficiency.

Saturated steam was used to overcome this problem of slow desorption rates. Heating promoted the kinetics of photocatalysis and AOP processes by desorbing organic contaminants on the interior of the adsorbents and moving them to the exterior for oxidation. Thus, steam followed by photocatalysis was found to be an effective way to regenerate spent adsorbents and to clean up the regeneration fluid (off-steam or steam condensate).

3. FIELD TRIALS

At Tyndall AFB, a solar photocatalytic process was used to remediate fuel-contaminated groundwater containing BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) at greater than 2 mg/L. Two options were tested: (1) a solar photocatalytic fixed-bed process using Pt-TiO_2 supported on silica; and (2) fixed-bed process with Pt-TiO_2 impregnated adsorbents alone or combined with Pt-TiO_2 supported on silica gel. During option 1, ionic species fouled the catalysts and inhibited destruction, so the water was pretreated to remove suspended particulates and ionic species and to increase dissolved oxygen. Following pretreatment, catalyst photo-activity continued undiminished after 25 days of operation. The BTEX compounds were destroyed with 6.5 minutes of empty bed contact time on rainy days. Test results with various flow rates, reactor diameters, influent concentrations, solar irradiances and weather conditions confirmed the potential application of the process. Treatment cost was estimated at U.S.$5.52/1,000 U.S. gallons (U.S.$1.46/$m^3$).

During option 2, two different reactor design configurations were tested. The first design was a continuous flow configuration with three fixed-bed reactors in series. The first and third reactors were packed with platinum-coated TiO_2 supported on silica gel supports. The second reactor was packed with a photocatalyst-impregnated adsorbent. In daylight, the incoming organic compounds were destroyed in the first reactor. At night, the organics were adsorbed onto photocatalyst-impregnated adsorbent in the second reactor; the adsorbed organics were either mineralized or partially mineralized in the second reactor during daylight. The remaining organics or destruction by-products were destroyed in the third reactor. Because organic compounds can be adsorbed during periods of insufficient sunlight, the process can treat water continuously. Like option 1, option 2 was also affected by catalyst fouling. After four days of operation, the process was apparently unable to destroy any more BTEX compounds. An ion exchange unit was added to the system and satisfactory BTEX destruction was resumed; however, the third reactor still did not perform well, presumably due to fouling species desorbed from the second reactor.

In the second design, a reactor packed with photocatalyst-impregnated adsorbents was used to remove the organics during darkness. During daylight, the adsorbent was taken off-line and regenerated by passing heated water through the reactor. The hot water was then passed through a fixed-bed reactor packed with platinum-coated TiO_2 supported on silica gel supports to destroy any residual desorbed organics or by-products. The strategy behind this design was to have an 18-hour adsorption period followed by a 6-hour regeneration period during which the solar irradiance is strong enough to destroy most contaminants.

The spent adsorbents were regenerated in the presence of sunlight while passing hot water (90°C) counter-current to the flow direction during the adsorption process. The desorbed organics from the regeneration process were destroyed in the subsequent fixed-bed photoreactor. The process was examined for 10 adsorption and regeneration cycles. The efficiency (ratio of organics removed and destroyed to organics adsorbed) of the process to regenerate the adsorbents was examined for each cycle. Overall, 21% of the total influent BTEX was destroyed, and 98% of the BTEX was removed from the waste stream. The detention times required for 99.9% destruction of TCE (5 mg/L), TCA (5 mg/L), and toluene (115 mg/L) were 2.15 seconds, 11.2 seconds, and 40 seconds, respectively. While the process appears to be effective for 10 cycles, more cycles are required to determine whether steady-state is achieved.

At K.I. Sawyer AFB, the unit used a fixed-bed photocatalyst and a solar panel made up of 80 tubular reactors to treat chlorinated compounds in groundwater. The design included a water pretreatment unit, which included a turbidity filter, a bubble-less oxygen contactor, and ion-exchange columns. The reactor was a modified solar thermal reactor panel with 80 plastic tubes mounted in parallel. The capacity for each reactor panel was designed as 0.25 U.S. gallons per minute. On a sunny afternoon, the panel destroyed 95% TCE, which was present in groundwater at 100 µg/L, within a two-minute contact time.

At the Wausau Water Treatment Plant, fixed-bed adsorption removed and accumulated organic compounds. The spent adsorbents were regenerated off-line with steam followed by photocatalysis. The groundwater contained chlorinated compounds and BTEX. Direct photocatalytic oxidation was not effective for regenerating spent adsorbent loaded with contaminated groundwater because nuisance substances in the water fouled the catalyst. Tests combining steam regeneration followed by photocatalysis of steam condensate showed that carbon adsorbent was not effectively regenerated and lost a significant amount of capacity. Background organic matter in the water may have caused this loss of efficiency. Based on the results of chloride yield with all the tested adsorbents, steam regeneration did not appear to destroy significant amounts of the sorbed chlorinated compounds.

Project No. 41

In Situ Microbial Filters

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1. INTRODUCTION

This technology exploits the capability of resting-state methanotrophic bacteria to degrade trichloroethene (TCE) oxidatively. Bacteria are produced in bioreactors and injected through a borehole into the subsurface where they attach to the solid rock matrix creating an inoculated subsurface zone. Contaminants dissolved in groundwater are biodegraded by bacteria as the groundwater passes through the "biofilter." The Pilot Study followed a field demonstration at the Kennedy Space Center, Florida where groundwater is contaminated with TCE. In the field demonstration, the biofilter was established by injecting bacteria into the contaminated aquifer through a borehole, and the filter function was tested by withdrawing groundwater through the same borehole.

2. TECHNICAL CONCEPT

Three major engineering issues were considered for the performance of the *in situ* biofilter:

(1) Groundwater residence times in the microbially enhanced zone must be sufficient to allow degradation to take place;

(2) Nutrients are not supplied to the bacteria, and the oxidative transformation of contaminants consumes cellular resources, which are not replenished; therefore, a fixed mass of contaminants can be biodegraded by each resting-state bacterial population, which must be periodically replaced;

(3) The efficiency of microbial attachment to subsurface soil and rock matrix depends on site-specific parameters.

Laboratory study of these considerations led to development of empirical mathematical models for predicting site-specific *in situ* conditions. Saturation, attachment rates, entrainment rates, and enzymatic longevity functions were included, providing quantitative data for qualitative limits on engineering parameters.

3. RESULTS

This technology has been tested at field scale at the Kennedy Space Center on groundwater contaminated with TCE. Indigenous TCE-degrading bacteria were collected from the site groundwater and grown in culture to increase their numbers. Bench-scale testing revealed that the degradation capacity of bacteria at the site was about 0.25 g of TCE per gram of bacteria. When sufficient bacteria were produced, the organisms were mixed with site groundwater and reinjected into the subsurface around the borehole. An estimated 10% of injected bacteria attached to subsurface rocks around the borehole. Contaminated groundwater was repeatedly flushed through the biofilter zone by extraction and reinjection through the same borehole to greatly increase contact residence times between bacteria and groundwater. Nutrients were not supplied so that the contaminants were the only potential carbon source.

The thickness of the established biofilter was found to vary according to the rate of groundwater flow and the TCE concentration, with values ranging from under 10 mm to over 500 mm at 20°C and 10^8 cells/gram of sand. It was concluded that a 100-mm thick biofilter established at the site provided complete breakdown of TCE for a period of 8 weeks, and had a reduced degradation capacity for an additional 8 weeks.

The demonstration was reported as being “successful” but regulatory guidelines for TCE were not met in the treated water. The authors concluded that this was due to a high concentration of co-contaminants, including chlorofluorocarbon and methane, which were preferentially degraded to TCE.

4. COSTS

Remedial costs were claimed to be lower than pump and treat (up to 50%), with the most economical problems being associated with large fast-flowing plumes with low contaminant concentrations (<10 mg/L).

5. CONCLUSIONS

The authors suggested limitations to the potential use of this technology: a minimum subsurface pore size of greater than 10 µm to permit microbial transport; groundwater pH near neutral; concentrations of TCE in groundwater should not exceed 25 mg/L, since higher levels are toxic to the microbial degraders; and dissolved oxygen levels must be in the range 0.37 to 1.28 mg/L to support the microbial community, depending on the specific contaminant and its concentration.

6. REFERENCE

R. T. Taylor, et al. *In Situ Bioremediation of Trichloroethylen-Contaminated Water by a Resting-Cell Methanotrophic Microbial Filter*; Hydrology Science Journal, 38(4), pp. 323-342, 1993.

Project No. 42

Integrated Pneumatic Fracturing and *In Situ* Bioremediation

Technical Contact:	**Country:**	**Project Status:**
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1. INTRODUCTION

This *in situ* technology incorporates extending and creating fractures to increase permeability in tight soils to enhance *in situ* treatments such has bioremediation. The U.S. Environmental Protection Agency (USEPA) conducted pilot-scale demonstrations under the USEPA Superfund Innovative Technology Evaluation (SITE) program(1). USEPA reviewed the research and development of hydraulic and pneumatic fracturing technologies to remove contaminants from soil and groundwater(2).

2. BACKGROUND

A field-scale pilot study conducted under the SITE Emerging Technology Program investigated using pneumatic fracturing to enhance microbial processes. Fracturing and nutrient injections took place over a one-year period. This study was completed in March 1995.

3. TECHNICAL CONCEPT

Tight soils hamper *in situ* technologies such as soil vapor extraction, bioventing, air sparging, and other air and nutrient injection techniques. Hydraulic and pneumatic fracturing are enhancement technologies to increase treatment efficiency of *in situ* techniques. Hydraulic fracturing utilizes pressurized water, while pneumatic fracturing utilizes pressurized air to create cracks in low-permeability and over-consolidated sediments. By increasing the permeability of the soil to liquids and vapors, removal of contaminants by soil vapor extraction and biodegradation can be accelerated. Aerobic processes dominate at the fracture interfaces and, to a limited distance, into the soil away from the fracture.

Initial site characterization indicated low-permeability soils and benzene, toluene, and xylene (BTX) contamination. Over a one-year period, the site was pneumatically fractured, and periodic injections of nitrate and ammonium salt to enhance aerobic and anaerobic biodegradation were performed. Offgases from monitoring wells were analyzed for BTX compounds along with carbon dioxide, methane, and oxygen to evaluate treatment efficiency. Additional soil cores were analyzed to measure change in the extent of site contamination during remediation. Carbon mass balances were performed to evaluate treatment efficiency.

4. RESULTS AND CONCLUSIONS

Fracturing increased subsurface permeability by up to 40 times within an effective radius of approximately 20 feet (about 6 m). Results from soil sampling at the end of the demonstration showed a 79% reduction in soil-phase BTX concentrations. Cores from three distinct depths taken before and after remediation showed the total mass of BTX removed to be 22 kg. Based on periodic soil gas sampling, the mass of BTX removed during soil vapor extraction was computed to be 3.1 kg. Other BTX losses accounted for 0.8 kg of BTX. The total BTX mass removed due to biodegradation during the 12-month period was calculated to be over 82%.

References

1. U.S. Environmental Protection Agency. *Hydraulic Fracturing Technology Application Analysis Report* National Risk Management Research Laboratory, Cincinnati, OH, September 1993, EPA/540/R-93/505.

2. U.S. Environmental Protection Agency. *In Situ Remediation Technology Status Report: Hydraulic and Pneumatic Fracturing*, Office of Solid Wasted and Emergency Response, Technology Innovation Office, Washington, DC, April 1995, EPA542-K-94-005.

Project No. 43 Multi-Vendor Bioremediation Technology Demonstration Project		
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1. INTRODUCTION

The "Multi-Vendor Technology Demonstration" project took place at the "Sweden 3 Chapman" site, Sweden, New York, which was an abandoned hazardous waste disposal area containing very high concentrations of chlorinated and non-chlorinated solvents such as trichloroethene (TCE), tetrachloroethene (PCE), 2-butanone (MEK) and toluene. Specific technical objectives of this study were: to determine whether the use of naturally-occurring microorganisms can effectively remediate volatile organic compounds (VOCs) present in unsaturated soils at the site; generate field data for simultaneous evaluation of different biological processes; permit an evaluation of *in situ* and *ex situ* approaches; and evaluate performance of each demonstrated technology in meeting site specific remedial objectives. A protocol for conducting pilot-scale demonstrations of bioremediation technologies at the Sweden site was prepared at the University of Buffalo, and this was used as the core of the invitation given to technology vendors. Of thirteen technical proposals submitted, three different technologies were selected for demonstration:

(1) *Biovault* (ENSR Consulting and Larsen Engineers): an *ex situ* biopile-based treatment;

(2) *In Situ Field Bioremediation Treatment System* (R.E. Wright Environmental): an *in situ* bioventing and co-metabolic bioventing technology.

(3) *In Situ UVB (Vacuum Vaporized Well) Process* (SBP Technologies/Environmental Laboratories [ELI]): a system-based treatment within and around wells.

2. SITE BACKGROUND

The Sweden 3 Chapman site is in a rural residential area, where homes are serviced by private wells. The site operated from 1970-78 and received industrial, municipal and construction wastes. In 1991 a State Superfund Interim Remedial Measure removed over 2,500 drums of waste and 2,270 tonnes (2,500 U.S. tons[a]) of contaminated soil. The treated area was graded and capped. However, unacceptable amounts of VOC contamination remains on site. An estimated 9,800 m^3 of contaminated soil remained in the demonstration area.

The site is planned to be remediated by *ex situ* treatment using low-temperature thermal desorption, along with some "limited" groundwater treatment. Demonstrated technologies were to be considered as alternatives, if their trials were successful.

The site consists of a clay capping layer over a mixed fill layer, comprised of the disposed materials. Beneath the fill material is a thin silty-clay soil layer (0.4 to 2.1 m) with numerous fine silty sand lenses. Beneath this layer lies sandy-silt glacial till. Work during the trial revealed that a plastic liner had been placed between the fill material and the natural soil, creating a perched water table.

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[a] *The original US text refers to "tons," which the editors have interpreted as short tons (2,000 pounds).*

3.0 TRIAL CONCEPT

The project was a partnership of State and Federal agencies, universities and technology vendors. The technical objectives of the project were to:

- demonstrate that the use of naturally-occurring microorganisms could effectively remediate VOCs onsite;
- generate field data to allow the simultaneous evaluation of different biological processes;
- permit an evaluation of *ex situ* and *in situ* approaches; and
- evaluate the performance of each technology in meeting the established clean-up goals.

Clean-up goals were set by the N.Y. State Department of Environmental Conservation for six VOCs: acetone, 200 µg/kg; MEK, 600 µg/kg; methyl isobutyl ketone (MIBK), 2,000 µg/kg; PCE, 2,500 µg/kg; TCE, 1,500 µg/kg and dichloroethene (DCE) 600 µg/kg *soil*. 90% of tested samples were to meet these targets to achieve compliance (success). Toluene concentrations were also monitored.

Prior to selection of demonstration technologies, a detailed test protocol was drawn up by a panel of experts and used as part of the technology tendering. Sampling and analysis was carried out by a university and an independent consultant was retained by the U.S. Environmental Protection Agency (USEPA). Three sampling events were carried out. The demonstrations started in August 1994 and were completed for two of three projects by December 1994. The UVB technology was demonstrated over a longer time period (approximately 14 months).

Each vendor was allocated a trial area to carry out a demonstration-scale test. However, large differences between contaminant concentrations in the material treated complicated comparisons between technologies. Interpretation of results was further complicated by higher than expected detection limits for target analytes because of interference in the measurements from other VOCs. In some cases, detection limits exceeded treatment targets.

4. TREATMENT TECHNOLOGY DESCRIPTIONS

4.1 R.E. Wright *In Situ* Treatment

This technology was essentially a co-metabolic bioventing approach consisting of extraction wells linked to a central blower (Figure 1). The output of the blower was connected to the injection wells via ports to allow inputs of: ambient air, methane and anhydrous ammonia. The methane was intended to boost co-metabolic processes degrading chlorinated VOCs. The ammonia was intended to boost available nitrogen. The blower operated for approximately 2 hr/day for about five months. The system was designed to treat an area of 535 ft^2 (50 m^2) to a depth of 6 ft (1.8 m). The radius of influence of each well was estimated to be 10 ft (3 m). The treated material turned out to be less contaminated, with many samples meeting treatment targets in advance of treatment. The installation of the technology was complicated by the presence of the plastic liner and perched water, which were not anticipated based on available site investigation information.

4.2 ENSR/Larsen Biovault

Biopiles were constructed on twin layers of high density polyethylene (HDPE) supported by earth berms (Figure 2). The HDPE was covered by a layer of sand for protection and drainage. Approximately 100 yd^3 (76 m^3) of graded material was placed on a geofelt liner over the sand. The area of the pile was around 40 by 40 ft (12 x 12 m), and its height was about 3 ft (0.9 m). The surface of the pile was covered by a similar felt, sand, and HDPE construct. Aeration was via extraction pipes in the bottom sand layer connected to a fan with passive air injection pipes in the top sand layer. Liquids could be percolated into the biopile via a sprinkler system. Air and liquid movement was intended to optimize conditions for biological activity within the piles.

Two piles were set up, one with continuous aeration and one with discontinuous aeration intended to allow the development of alternating periods of aerobic and anaerobic activity within the piles. The materials treated within the piles were the most grossly contaminated site materials. The treatment was made more difficult by the fine-

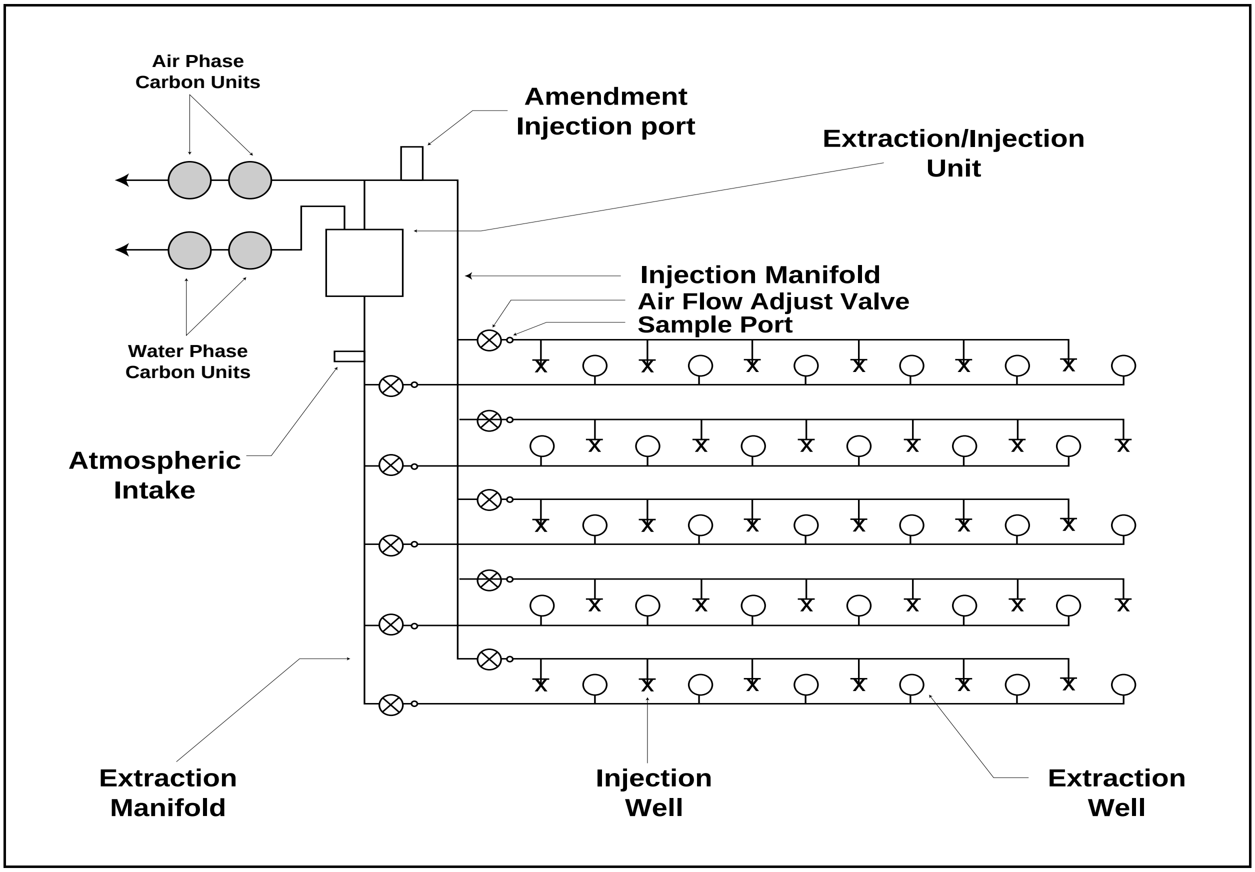

Figure 5. Schematic of R.E. Wright *In Situ* Treatment

grained texture of the soil being treated which impeded aeration and water movement. The vendor also claimed that the intermittent aeration pile did not achieve conditions suitable for anaerobic activity.

4.3 UVB Process

A schematic of the process is given in Figure 3. The basic unit was a 16-inch (400-mm) diameter steel water well with upper and lower screens inserted to a depth of 26 feet (8 m) below the ground surface. A submersible pump in the bottom zone of the well pumped ground water through an in line bioreactor packed with granular activated carbon. The treated water was discharged back into the soil from the top zone of the well. The bioreactor unit was integrated with an air stripping function, both to remove VOC, and to oxygenate the groundwater prior to its discharge. The discharge (coupled with the pumping of water from the lower zone) is intended to circulate water around the well and so create a zone of enhanced stripping and biodegradation activity around the well. The assembly included monitoring wells and nutrient addition.

One well assembly was tested during the trial. The unit was designed to treat approximately 1,000 cubic yards (760 m^3), covering an area of about 280 yd^3 (230 m^2). The radius of action of the well was estimated to be 35 ft (11 m). Installation of the well was complicated by the plastic liner and an unexpectedly shallow water table, due to high rainfall.

4.4 General

All three treatments included the capacity for treating offgases and liquid effluents generated.

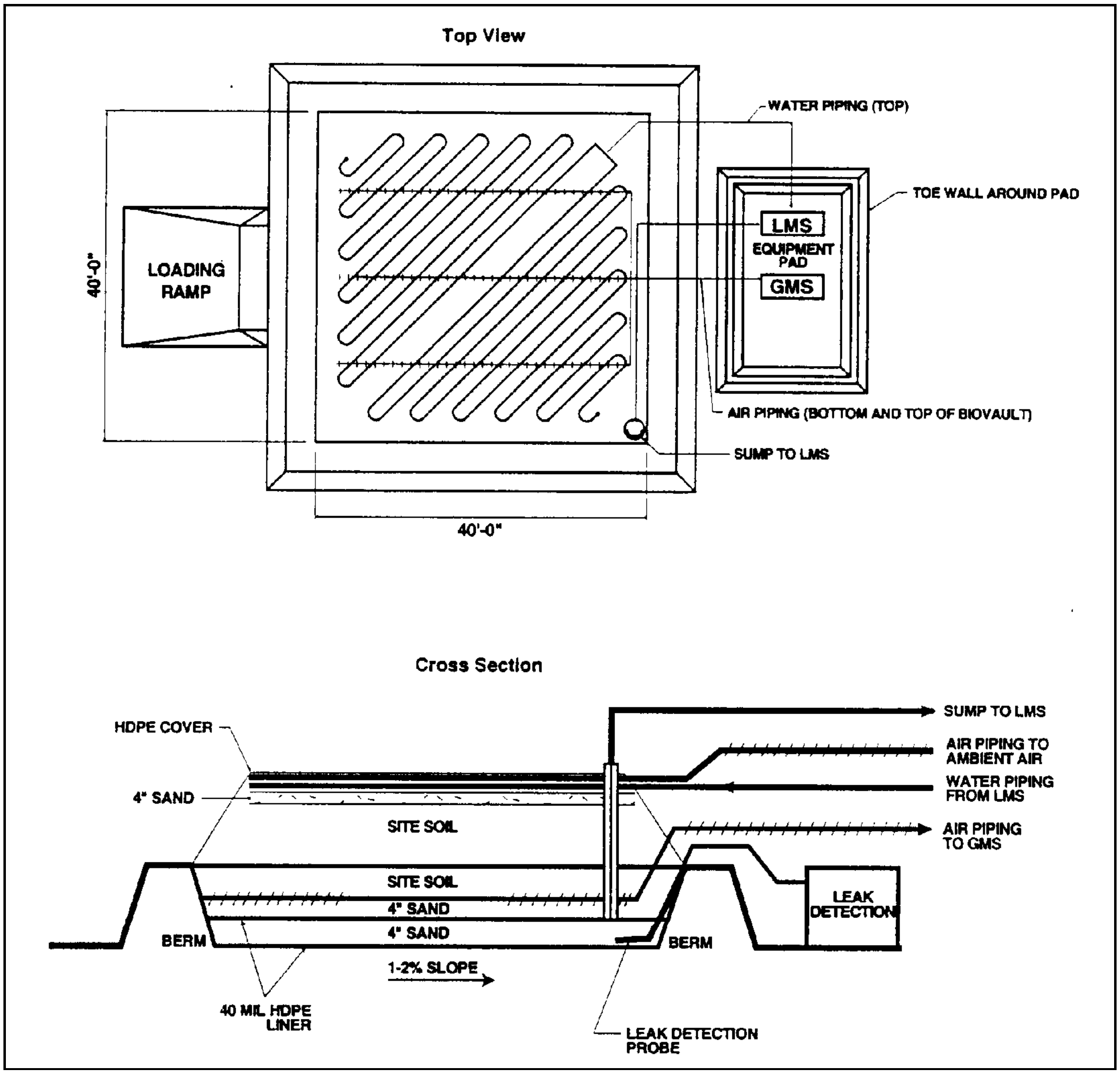

Figure 2: ENSR/Larsen biovault system: plan view and cross-section

5. RESULTS

VOC removal results for each technology are summarized in Table 1. Note that the results are still subject to verification by the USEPA.

5.1 R E Wright *in situ* System

The system achieved the compliance target. However, contaminant levels—particularly for MIBK and PCE—were already low in the test area, and data for acetone and MEK could not be interpreted because of difficulties with their detection limits. However, residual concentrations of toluene remained high. The estimated starting mass of toluene in the test volume was estimated to be 14 kg, and the finish mass to be 7 kg. MEK and MIBK data were not used in compliance assessment.

5.2 ENSR/Larsen System

Neither the continuously or intermittently aerated biopiles achieved compliance (79% of samples met targets), although both achieved substantial degradation of VOCs. As well as the difficulties with soil texture and aeration regime already mentioned, low ambient temperatures during the latter part of the treatment period may also have

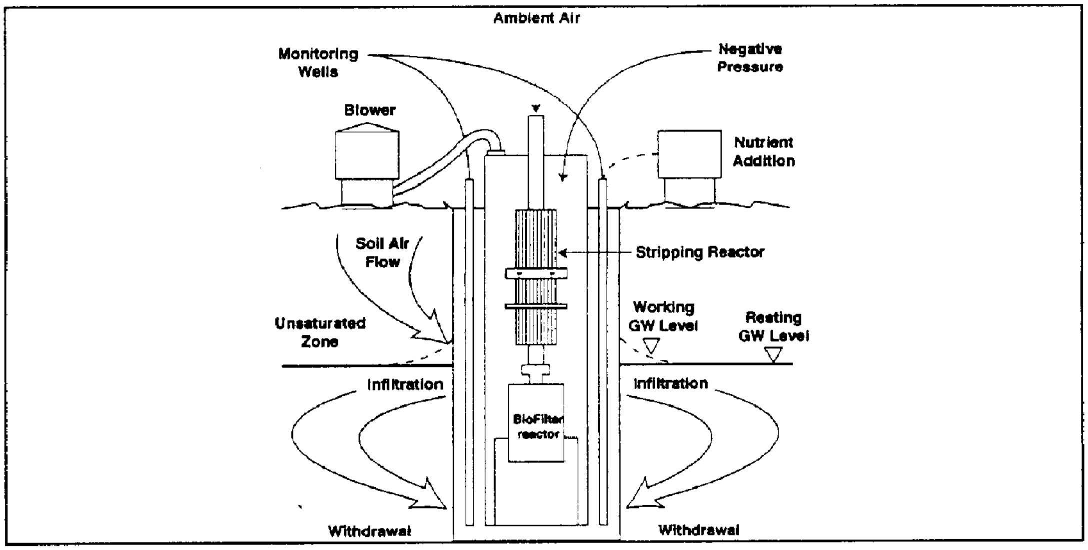

Figure 3: Schematic of SBP/ELI *in situ* UVB process

reduced biopile effectiveness. Interpretation of acetone and MEK data was complicated by difficulties with detection limits. Compliance assessment for other contaminants was based on 6-9 usable data points.

5.3 UVB

After 5 months, when the other trials were completed, samples from the UVB treatment area did not indicate significant contaminant reduction. Compliance was achieved for PCE only. A longer treatment period was considered appropriate for this technology. After 14 months compliance was also achieved for MIBK and TCE, (based on 45 usable data points).

Table 1. Overview of %VOC Removals

Treatment	**Acetone**	**MEK**	**MIBK**	**DCE**	**TCE**	**PCE**	**Toluene**
R. E. Wright: bioventing[1]	-	-	-	-	-	-	-
ENSR Larsen: intermittent aeration biopile	72	59	60	45	88	22	43
ENSR Larsen: continuous aeration biopile	83	71	79	57	99	45	51
ELI/SBP: UVB (after 14 months of operation)[1]	-	-	-	-	-	-	-
Note: [1]Data not provided							

5.4 General

Insufficient evidence was collected from any of the treatments to conclusively determine the relative contributions of biodegradation and volatilization to contaminant removal. However, monitoring of indicators of biological activity implied that degradation was taking place. Significant amounts of DCE, TCE, and toluene were collected from the offgases from the biopile and bioventing systems. Mass balance determinations indicated generation of DCE, presumably through biotransformation of TCE during both of these treatments. Smaller amounts of TCE and DCE were collected for the UVB treatment, and DCE accumulation was not detected. Evidence of *in situ* biodegradation was also more scant for the UVB treatment. The system design does not permit easy on line monitoring of O_2 use and CO_2 generation.

The heterogeneous nature of the site posed particular problems in both monitoring and performance assessment. General site information, such as direction of groundwater flow, did not always reliably predict the local conditions encountered the test plots.

Over the course of the demonstration, elevated levels of vinyl chloride (a degradation product of TCE) were noted in the groundwater downgradient of the test sites. It was not clear whether or not this was associated with the *in situ* treatment demonstrations taking place.

6. COSTS

The cost and duration of treating the estimated 9,800 m^3 of contaminated material at the Sweden 3 Chapman site were estimated by the vendors as follows, based on the demonstration tests (Table 2):

Table 2. Demonstration Test Treatment Costs

Technology	Total Cost (U.S.$)	Cost per m^3 (U.S.$)	Duration
R.E. Wright	For 8,100 m^3, $381,000	$52 ($39.50/yd^3)	12 months
ENSR Larsen	For 9,800 m^3, $695,000	$71 ($54.40/yd^3)	40 weeks
ELI/SBP UVB	-	$240 ($185/yd^3)	14 months

The cost basis was not the same for each estimate. For example, the R.E. Wright estimate included costs associated with permitting and the UVB estimate did not.

Project No. 44

Enhanced *In Situ* Removal of Coal Tar: Brodhead Creek Superfund Site

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1. INTRODUCTION

Past waste management practices at a former gasworks site at Brodhead Creek resulted in the contamination of soil and groundwater with polycyclic aromatic hydrocarbons (PAHs) and BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). During plant operation, waste coal tars were disposed onsite in an open pit. Over time, the coal tars migrated into the subsurface where they collected in a natural depression formed at the geological boundary between coarse gravels and silty sands. Site investigation identified a layer of free product coal tar covering an area of 0.12 ha which was shown to be polluting an underlying aquifer and a nearby river. A larger 3-acre (1.22-ha) area of residual contamination contains dissolved contaminants.

Remediation efforts have focused on the free product because it was believed to represent the major source of groundwater pollutants. After construction of a slurry cutoff wall to protect the river from further pollution, it was decided to remediate the free product area. Due to unspecified problems, excavation of the contaminated ground was not considered practical, and an innovative *in situ* treatment was selected. This Pilot Study project reported on the remedial operations that were initiated in July 1995 with an expected completion date of March 1996. The site was remediated under the U.S. Environmental Protection Agency (USEPA) Superfund Program.

2. PROCESS CONCEPT

The selected technology known as Contained Removal of Oily Wastes (CROW) is a thermally-enhanced *in situ* recovery process. It is a technique developed from the recovery of petroleum from oil shale deposits. It uses hot water injected into the contaminated region to reduce the density and viscosity of tar deposits to a level where they can be pumped to the surface for further treatment and disposal. The rate at which the heated water is injected into the ground is used to control the displacement and temperature of the tar material so that it is forced towards a series of extraction wells. Lateral containment is achieved by carefully controlling injection and extraction rates to isolate the affected area hydraulically. A layer of cooler water above the area of active recovery prevents mobilized fluids from migrating vertically. This cooler water also absorbs volatile contaminants if they are released.

3. TREATABILITY STUDIES

Preliminary treatability studies on coal tar samples were used to determine the optimum temperature and injection/extraction rates required for full-scale operation. These studies indicated that coal tar in soils could be reduced to a residual saturation of 60-70%.

4. FULL-SCALE APPLICATION

Full-scale operation was based on a pattern of six injection wells surrounding two extraction wells in the center of the contaminated zone. Screens were used in each well to focus injection and extraction flows at the depth of contamination. Plans in the original design included injection of heated water (93°C) at a rate of 378 L/min for recovery of water/coal tar mixtures at a rate of 435 L/min. However, shortly after full-scale operation began, much lower injection rates were observed than had been anticipated. Iron precipitate that formed around the injection well screens significantly reduced operational performance. Although this problem was partially solved by installing agitators in the injection wells, flow rates remained low (114-132 L/min). The lower flow delivered less energy than planned to the aquifer, so the system operated at 71°C instead of the expected 93°C. A water heater designed for high flows did not heat the water to the required temperatures at the lower flows. Replacing the heater solved this problem. Also, the reduced flow rate and lower operating temperature extended the treatment times from four to eight months. A higher injection temperature of 96°C was achieved in January 1996 (presumably due to installation of the new heater).

Specifications for performance required treatment to continue until results showed that there was less than 0.5% additional recovery of coal tar per pore volume of water flushed through the contaminated zone. During December 1995, a cumulative flow of 3.1 times pore volume of water resulted in recovery of 602 L of tar. This was based on previous operational experiences at a similar site where achieving this specification meant that 98.5% recovery of recoverable tar had been attained. Planned groundwater sampling will assess the effectiveness of the treatment.

The report did not mention how extracted liquids were treated or disposed. However, the proposed treatment involved pumping recovered waste product to storage tanks for further treatment such as flotation and settling to recover light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs). Most of the clarified water was to be reheated and reinjected, but the rest was to be treated biologically, then passed through a granular activated carbon filter before being discharged to the surface.

In summary, hot water was injected into the subsurface over 7 months to remove free coal tar. The project was considered successful although it did not achieve expected operating conditions and recovery of contaminants. Sampling groundwater in the future will assess the overall effectiveness of the treatment.

Project No. 45

This was an accidental replication of Project 15

Technical Contact:	**Country:**	**Project Status:**

Project No. 46 Project withdrawn		
Technical Contact:	**Country:**	**Project Status:**

Project No. 47

In Situ Electro-osmosis (Lasagna™ Project)

Technical Contact:	**Country:**	**Project Status:**
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1. INTRODUCTION

The Lasagna™ process is intended to overcome the significant technical problem of delivering treatment agents to contaminants in low-permeability soils, and render *in situ* treatments more feasible in such soils. The technology provides an integrated *in situ* remedial process by combining electroosmosis to move dissolved contaminants, and treatment zones to degrade or adsorb the contaminants.

In 1994, a consortium consisting of Monsanto, E.I. Dupont de Nemours (Dupont) and General Electric signed an agreement with the USEPA to jointly develop an integrated, *in situ* remedial technology referred to as the Lasagna™ process. In 1995, funded in part by the U.S. Department of Energy, the vertical configuration of the process was tested at the Paducah Gaseous Diffusion Plant in Paducah, Kentucky.

The project was accepted into the NATO Pilot Study to recognize the project's partnership of government and industry participants and to show the potential of a relatively low-cost technology to treat water-soluble organic compounds, inorganics, and mixed wastes occurring in low-permeability soils.

2. TECHNICAL CONCEPT

This *in situ* process can be operated in horizontal or vertical configuration but does not require injection or extraction wells. The vertical configuration consists of outer layers that act as either positively- or negatively-charged electrodes. Vertical treatment zones lie between the outer electrodes. Sheet piling, trenching and slurry walls can be used to create vertical treatment zones. In the horizontal configuration, treatment layers installed by hydraulic fracturing or related methods occur between the upper and lower layers that make up the electrodes. These electrodes may contain graphite or other granular electrically-conductive materials.

The Lasagna™ process depends on electroosmosis, treatment zones, and switching electrical polarity. Electroosmosis relies on a low voltage electrical current applied to the electrodes to create an electric field to flush contaminants from low-permeability soil into or through the treatment zones. These zones, installed in close proximity through the contaminated material, contain appropriate materials (*e.g.*, sorbents, catalytic agents, microbes, oxidants, buffers, *etc.*,) to sorb or degrade contaminants. Placing the treatment layers close to each other minimizes the time for electroosmosis to move liquids from one layer to the next. Laboratory tests show that water movement by electroosmosis is very slow, typically about 25 mm/day. Switching electrical polarity reverses liquid flow and appears to increase the efficiency of contaminant removal as well as allowing complete sorption and degradation by passing contaminants through the treatment zones several times. Reversed flow minimizes the high pHs and low pHs that occur at the cathode and anode respectively when the system is operated in one direction.

Characteristics of the site and contaminants determine the configuration. In general, the vertical configuration is more applicable to shallow contamination within around 50 ft (15 m) of the surface. The horizontal configuration works best for deeper contamination.

3. CCMS CASE STUDY

3.1 Overall Program

The NATO/CCMS case study was limited to the field demonstration of electroosmosis, using the vertical configuration, to transport and adsorb TCE at the Paducah Gaseous Diffusion Plant. The case study was carried out in two phases:

- Phase I, conducted between January and May 1995, evaluated the overall effectiveness of coupling electrokinetics and carbon adsorption treatment zones.

- Phase IIa, commercial-scale demonstration conducted in 1996 examined iron filings in the treatment zone to dehalogenate TCE. This work was conducted to depths of up to 15 m and with a wider spacing between the treatment zones.

The full-scale Phase II cleanup (not included in the CCMS study) will then take place if the Phase IIa tests successfully reduce TCE levels in soil to 5.6 mg/kg.

3.2 Study Site

The site covers an estimated area of 6,000 ft^2 (557 m^2)and extends to a depth of 45 ft. TCE concentrations are as high as 1,523 mg/kg, but average around 84 mg/kg. Concentrations increase with depth, and the highest concentrations are believed to occur at depths between 20-30 ft (6.1-9.1 m). The contamination resulted from cylinder drop tests conducted at the site in the 1960s and 1970s to test the structural integrity of steel cylinders used to transport and store uranium hexafluoride. TCE was used as a refrigerant during the tests contaminated the soil.

3.3 Phase I Study

The field study for remediation of chlorinated solvents, conducted at the Paducah Gaseous Diffusion Plant, lasted for 120 days and ended in May 1995. A key objective was to successfully demonstrate coupling electroosmosis to flush TCE from the clayey soil (hydraulic conductivity $<10^{-7}$ cm/sec) and adsorption to remove the contaminant from the pore water. The test site was 15 ft x 10 ft (about 4.6 x 3 m) and 15 feet deep (4.6 m). A control area was built next to the test area and isolated from it hydraulically. The vertical configuration tested at the site consisted of steel panel electrodes and treatment zones made of wick drains containing granular activated carbon.

A direct current of around 0.4 volt/cm applied to the electrodes caused groundwater to flow from the anode to the cathode at a rate of about 13 mm/day. The induced pH gradient caused problems such as soil drying and cracking, and metal and mineral deposits at the cathode. Pumping water from the cathode to the anode reduced these problems.

During the 120-day demonstration, the area was covered with plastic. A vent fan directed soil offgas to an in-line filter for TCE analysis. Operating parameters during this period were:

• Power after one month:	105 volts, 40 amperes
• Electroosmotic flow rate:	4-5 L/hour
• Average soil temperature:	25-30°C

Soil samples collected throughout the demonstration site before and after the test showed that the process removed 98%-99% of the TCE from the tight clay. TCE levels in the soil were reduced from 100-500 mg/kg to an average of 1 mg/kg. Sampling and analyzing the carbon revealed how much dissolved TCE was adsorbed in the treatment zones and provided mass balance data. These carbon samples accounted for around 50% of the original TCE. The unaccounted TCE may be attributed to passive diffusion (5%), evaporation (5%), *in situ* degradation of TCE, non-uniform distribution of the contaminant in the soil, or incomplete extraction of the compound from the activated carbon before analysis.

Results suggest the process is effective for removing residual dense non-aqueous phase liquid (DNAPL) as well. At most soil sampling locations with TCE concentrations of greater than 225 mg/kg indicative of residual DNAPL in soil pores the process reduced these levels to less than 1 mg/kg.

3.4 Phase IIa Study

The success of the Phase I study led a more extensive field investigation incorporating reactive treatment zones such as iron filings to destroy TCE *in situ*. The first part (Phase IIa) of this two-stage (Phase IIa and Phase II) investigation conducted on 20 times more soil than was treated in the preliminary field investigation will try to resolve scale-up questions, verify cost estimates for treatment, and evaluate how the zero-valent iron performs. Preliminary results of the Phase IIa demonstration at the site in Kentucky show that treatment zones with iron filings can dechlorinate TCE, producing relatively innocuous end-products such as chloride ion, ethane and ethene. Other potential intermediate products like dichloroethene and vinyl chloride are associated with the surface of the filings.

4. POSSIBLE TECHNICAL LIMITATIONS

Extended operation of electroosmosis could dry out soil, change pH in the soil, and precipitate metals and minerals near the negatively-charged electrode eventually stopping the process. Reversing the polarity of the electrodes causes the water to flow in the opposite direction and may resolve these problems. Pumping the high pH water to the surface and recycling it to the anode may provide a convenient way to maintain neutral conditions at the electrodes.

5. RESIDUALS AND EMISSIONS

Residuals and emissions include offgases resulting from evaporation, and the treatment layers. At the Kentucky test site, TCE losses by evaporation accounted for 5% of the mass balance. These off-gases did not require treatment. If treatment layers are determined to be a hazardous waste, removing and disposing of them may be an issue.

6. COSTS

An engineering evaluation and cost analysis for the vertically configured process estimates a treatment cost of U.S.$40-90/yd (U.S.$52-118/m^3) of clay soil containing TCE at a depth of 40-50 feet and over an area of 1-2 acres (0.4-0.8 ha). With optimized electrode spacing, improved ability to install treatment zones and electrodes at closer spacing, and mass-produced prefabricated materials resulting from wider use of the technology, costs are expected to fall to U.S.$20-40 per cubic yard U.S.$26-52/m^3). These costs exclude those for analysis, waste disposal, *etc*.

7. FUTURE DEVELOPMENTS

Work on the horizontal configuration has focused on developing long-lasting electrical and fluid connections between the electrodes and the treatment zones and preventing gases from building up in the electrodes. The University of Cincinnati is conducting laboratory and field research on hydrofracturing and biodegradation to develop the horizontal configuration. Laboratory investigations are focusing on optional treatment processes for other types of contaminants, such as DNAPL, heavy metals, and mixed wastes.

In a horizontal unit in the field, the treatment zone consists of granular activated carbon seeded with a microorganism and nutrients. This microorganism, isolated from a group of organisms, was chosen for its ability to degrade TCE. This test, conducted in the spring and summer of 1996, examined how well methanotrophic microorganisms survived in a treatment zone under the conditions required for electroosmosis to occur.

8. CONCLUSIONS

The Lasagna™ process offers promise for treating water-soluble organic and inorganic contaminant, and mixed wastes in low-permeability soils as well as in groundwater. For highly non-polar contaminants, surfactants introduced into groundwater or incorporated into treatment zones will solubilize the organic compounds. The process has been shown to be effective in treating residual DNAPL as well. Larger scale demonstrations need to be conducted to confirm the effectiveness of using zero-valent iron to degrade contaminants. The horizontal configuration using biological treatment zones needs to be evaluated as well.

Project No. 48

Project withdrawn

Technical Contact:	**Country:**	**Project Status:**

Project No. 49

Characterization of Residual Contaminants in Bioremediated Soil and Reuse of Bioremediated Soil

Technical Contact:	**Country:**	**Project Status:**
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1. INTRODUCTION

Certain residual pollutants remain after soils contaminated with oil products have been bioremediated. The emission levels to be expected during the reuse of remediated soil were estimated by means of laboratory and field tests. These were so low that the risk of harm to protected materials may be considered extremely low. Nevertheless, the validity of this claim would need to be checked in each individual case.

2. BACKGROUND AND PROJECT OBJECTIVE

Mineral oil products are major pollutants found at contaminated sites in Switzerland. The revised *Umweltschutzgesetz* (USGrev, the Environmental Protection Act) and the relevant ordinances (*e.g., Technische Verordnung über Abfälle*, the Technical Waste Ordinance) require excavated material contaminated with pollutants to be treated, wherever technically feasible, ecologically beneficial and economically viable. Thus, whether the soil has to be treated or dumped depends largely on the quality of the products obtained from the treatment process and the options for reuse. Biological treatments leave residual contaminants in the soil whose potential risk to the environment is largely unknown.

Since the unsaturated zone of subsoil has not been defined as a protected material in Swiss legislation, no tolerance values or limits are provided in the corresponding ordinances for pollutants in the unsaturated zone. As a result, Swiss environmental legislation can only offer limited guidance in the evaluation of soil contaminated with oil products. The limit for hydrocarbons in drinking water is specified as 0.02 mg/L in the *Fremd-und Inhaltsstoffverordnung* (FIV, the Ordinance on Foreign Substances and Constituents) and the *Schweizerisches Lebensmittelbuch* (SLB, the Swiss Food Book). As regards the dumping of waste, the Technical Waste Ordinance does not specify any limits for hydrocarbon levels in dumped material, but does set limits for the leachate of inert substances (0.5 mg HC/L) and residual substances (5.0 mg HC/L). The quality target for running waters is 0.05 mg HC/L. Wastewater with an HC content of up to 10 mg/L may be introduced into surface waters, while those with an HC content up to 20 mg/L have to pass through a wastewater treatment plant.

The lack of a legal basis for evaluation has prompted a number of cantons to define their own tolerance limits for the assessment of excavated material. Thus, for example, a tolerance limit of 50 mg HC/kg applies to uncontaminated excavated material in the canton of Zurich. Material with HC levels exceeding 500 mg/kg may not be dumped in inert material landfills. However, the HC residual content of bioremediated material can range from 100-5000 mg/kg, depending on the oil product involved, the initial content, the degree of weathering, and the soil type. This means that the soil cannot usually be freely reused after bioremediation and must therefore be sent to a landfill. But since bioremediation with subsequent dumping of the treated material is neither ecologically beneficial nor economically attractive, biological remediation technologies are only used in rare cases. The soils contaminated with mineral oil products are much more likely to be treated by a soil washing process, used as an aggregate in cement works, or depending on the canton involved, sent directly to a landfill.

The purpose of this project was to investigate the environmental acceptability of bioremediated soil by means of a risk analysis. The project was subdivided into the following operational stages:

- physical and chemical characterization of the residual contaminants;
- environmental behavior of the residual contaminants;
- effects of the residual contaminants on the environment; and
- evaluation of the environmental acceptability by means of a risk assessment.

3. CHARACTERIZATION OF RESIDUAL CONTAMINANTS

First of all, various extraction methods were evaluated with the aid of reference substances. Soxhlet extraction with tetrachloromethane proved to be the most effective method and was therefore used for all subsequent investigations. Infrared spectroscopy (according to DIN 38’409-H18) and gas chromatography were used to quantify the HC content.

- Infrared spectroscopy (according to DIN 38’409-H18) *(1)*;
- Gas chromatography with a hydrocarbon mixture as the calibration solution; and
- Gravimetric assay (according to DIN 38’409-H17) *(2)*.

Similar total hydrocarbon (THC) contents in bioremediated soil material were obtained for all three methods. Infrared spectroscopy was subsequently used routinely, while the other quantifying methods were employed primarily for comparison purposes. With each measurement a differentiation was made between the total solvent extractable material (TSEM) and the total petroleum hydrocarbon (TPH) content. The TPH was obtained by using (alumina) to separate all the compounds with polar functional groups (*e.g.*, acid-alcohol groups) contained in the TSEM.

The remediated soil material used for all tests originated from various minor oil spills (primarily involving EL heating oil) that was combined before being sent to a bioremediation plant. The contaminant content in the fine material (<2 mm) was 780 mg/kg of TSEM and 430 mg/kg of TPH, in each case related to the dry content of the sample. The content of polycyclic aromatic hydrocarbons (PAHs) was below 2.8 mg/kg and was not subsequently measured.

The residual contaminants in the bioremediated soil were chemically analyzed and characterized. These residual contaminants were then separated into individual compound classes on the basis of their polarity using two different methods: column chromatography on silica gel and a two-dimensional separation by means of high performance liquid chromatography coupled with gas chromatography. Most of the residual contaminants consisted of apolar, low-volatility compounds (boiling points >280°C). Small quantities of polar compounds (*e.g.*, fatty acids and long-chain alcohols) were also detected in individual fractions. On the whole, however, the compounds were very hydrophobic, with a very high octanol/water partition coefficient (K_{ow}) of over 10^6.

4. ENVIRONMENTAL BEHAVIOR OF THE RESIDUAL CONTAMINANTS

The second phase of the project involved the investigation of the environmental behavior of the residual contaminants in the bioremediated soil after being applied as topsoil. The processes investigated were biodegradation, leachability due to precipitation, and volatilization.

4.1 Leachability of the Residual Contaminants

The leachability of the residual contaminants through percolating water was investigated in laboratory tests by means of shake and column leachate tests and by means of a lysimeter test outdoors. The initial THC content was 0.09 mg THC/L, as measured by both the column and lysimeter tests, and rapidly declined thereafter. After approximately 60% (column tests) and 95% (lysimeter test) of a theoretical annual precipitation, the THC content in the percolating water was already below the drinking water limit of 0.02 mg/L. The leached quantity of pollutants corresponded to

0.1% of the THC content in the soil material. Extrapolation of these measurements indicated that only approximately 1% of the residual contaminants would leach out even after one hundred years' precipitation.

Similar percolating water contents were determined for a given water/solids ratio in both test designs. With the German DIN-S4 leachate test, a TPH content of 0.1 mg/L was obtained with a water/solids ratio of 10:1. This figure was above the percolating water contents of approximately 0.09 mg TPH/L measured at the start of the column tests. It was also approximately 10 times higher than the average THC content in percolating water with the same water/solids ratio. This difference is probably due largely to the break-up of lumps of soil caused by shaking in the DIN-S4 leachate test and the resulting greater leachability of the residual contaminants. The DIN-S4 leachate test can therefore be considered as a highly conservative test that greatly overestimates the actual percolating water contents in the field.

Another important parameter is the dissolved organic carbon content (DOC). This includes all the polar and apolar organic compounds dissolved in the water. Whereas the DOC of 4.3-15 mg/L in the bioremediated soil was similar to that found in gravel (6 mg/L), the DOC of plant earth was much higher at a level of 107 mg/L. These results indicate that a large part of the soluble compounds in all the investigated materials consisted of polar compounds (lipids, humic substances, *etc.*). Experience has shown that the DOC is an indicator of the degree of microbial degradation of a material, as demonstrated by the high DOC levels in compost, sewage sludge, or spinach. A low DOC, on the other hand, means that low oxygen depletion can be expected in groundwater.

4.2 Air-borne Emissions

Air-borne emissions were investigated by gas chromatography (atmospheric measurements). Since the residual contaminants exhibited a very low vapor pressure ($<10^{-6}$) any air-borne emissions can be considered to be negligible.

4.3 Degradability of the Residual Contaminants

The degradability of the residual contaminants was investigated in laboratory degradation tests. Under optimized conditions, the remediated soil material was incubated, and both the TPH content and CO_2 formation were monitored. During the test period of 3 months, the residual contaminant content decreased by approximately 20%; approximately 85% of this decrease in TPH content was converted into CO_2.

A CEC degradation test was conducted in order to investigate possible further biodegradation of these residual pollutants in aqueous solution. After 21 days, the quantity of residual contaminants present at the start of the test had declined by about 20%. This indicates that the bioavailability was either greatly reduced as a result of the low water solubility or else that these residual contaminants were poorly degradable.

The long-term biodegradation was investigated in a 28-month field trial under near-natural conditions. Accordingly, approximately 2,000 m^3 of remediated soil was homogenized and applied as a 1-meter-thick layer. Three repetitions of four types of cultivation were investigated: (1) planting with red clover; (2) planting with rye-grass; (3) fallow; and (4) soil tillage with regular plowing. Twenty samples from 0-25 cm and 25-50 cm were taken from each plot of land and composited. The average reduction in concentration of the residual contaminants over these 28 months was approximately 13%, and no significant differences were observed between the individual cultivation types. Since only small quantities of residual contaminants leached out or were emitted into the air over the entire trial period, the reduction in the TSEM and THC contents can be attributed to biodegradation.

5. EFFECTS OF THE RESIDUAL CONTAMINANTS ON THE ENVIRONMENT

5.1 General

Relatively little is known about the mammal toxicity of individual hydrocarbon compounds. Given the metabolism of hydrocarbons in mammals, n-hexane can be considered as a relevant substance in toxicological terms; the toxicity of other alkanes (*e.g.*, n-heptane, i-octane, *etc.*) is much less relevant. Since low molecular weight hydrocarbons (*e.g.*, n-hexane) are no longer present in bioremediated soil, the residual hydrocarbons are probably not very relevant toxicologically. Higher molecular weight hydrocarbons and other compounds observed in remediated soil (fatty acids and alcohols) are also naturally occurring compounds (*e.g.*, in plant material) and are therefore not considered to be toxicologically relevant.

5.2 Effect on Plants and Soil Organisms

The germination and growth of 36 plant species on both remediated soil and plant earth (control) were investigated in greenhouse trials. The plants developed normally on both soil materials and showed no phenotypical changes of any kind.

In a second series of tests the effect of the residual contaminants on the plant yield of eight crops and eight wild herbs grown with plant earth that had been deliberately contaminated with residual pollutants (TSEM dissolved in 1,1,2-trichloro-trifluoroethane and sprayed on the soil material). Uncontaminated material and material treated with solvent were employed for reference purposes. After 30 test days the plants were harvested and the yield (fresh weight) determined gravimetrically. On average, a 25% increase in plant yield was observed in the contaminated plant earth, compared to the control plants. Although the effect was not statistically significant given the considerable variation, these results show that the contaminants added to the soil did not inhibit growth.

Since a wide variety of plant species was used, adverse effects on other plant species are unlikely. This was further confirmed by the diverse plant communities that grew on the fallow fields. Normal growth was also observed in the plants employed in the field trials, and the typical root nodules of the red clover were well developed. Uptake of the residual contaminants by the plants was not investigated since similar compounds also occur naturally in plants (see above) and higher molecular weight hydrocarbons are absorbed by the plants only to a very limited extent.

While the effect on soil organisms was not specifically investigated, a high worm density was observed in the field trial, particularly on the cultivated plots.

5. 3 Effect of soil leachates on water-fleas and bacteria

Dilution series of DIN-S4 leachates and percolating water samples from the above-mentioned lysimeter tests were used to investigate the effect of aqueous soil leachates on the water-flea (*Daphnia magna*) and on the bioluminescent bacteria *Vibrio fischeri*. However, no significant acute toxic effects on these aquatic organisms were observed.

6. RISK ASSESSMENT FOR REMEDIATED SOIL

A risk assessment based on the data from the tests described above was performed. A mass flow analysis was conducted in order to determine the emissions expected during the first year after the application of bioremediated soil material as topsoil. Leaching into groundwater, volatilization, uptake by cultivated plants, and losses due to biodegradation were all taken into account. Over 99% of the measured reduction in THC content from 430 mg/kg to 407 mg/kg was attributable to biodegradation. Leaching produced the highest emission of approximately 0.4%. However, since the leaching rate showed a clear decline in the second year after application of the remediated soil material, almost no emissions would likely be detected after the first year. Those residual contaminants that are soluble in percolating water should be more readily degradable than the insoluble residual contaminants, thus resulting in reduced groundwater contamination.

To conclude, these results can be illustrated quantitatively taking the example of n-hexane as a “worst case” scenario. Assuming that the measured emissions in percolating water relate to n-hexane, Table 1 shows that leachate levels of 0.11-0.15 mg/L would be expected. This would exceed the SLB drinking water threshold of 0.02 mg/L. However, if the maximum permitted level of n-hexane is consumed by an adult in drinking water (70 kg bodyweight; 2 L drinking water/day intake) with a reference dose (RfD) level of 0.06 mg/kg/day) this gives a permitted concentration of 2.1 mg/L. This corresponds to one hundred times the SLB threshold and more than ten times the measured initial values in percolating water. These calculations demonstrate that this evaluation of potential risks based on leachate tests and compared with drinking water values is very conservative, particularly since the actual concentrations decline rapidly (Figure 1) and this percolating water undergoes further dilution before being used as drinking water.

The exposure to humans and the environment from emissions is so low that, considering the toxicity of these residual contaminants, no adverse effects can be expected for humans or the environment.

Estimates of potential emissions for various applications (backfilling, filling of trenches, *etc.*) and groundwater conditions indicate that protected goods would not be impaired, even if reused in sensitive locations (*e.g.*, protected watersheds).

7. CONCLUSIONS

The residual contaminants in successfully bioremediated soil are hardly soluble, difficult to volatilize, and undergo further biodegradation only over prolonged periods. Since the anticipated emissions are very low, no adverse effects to humans or the environment are expected. Nevertheless, bioremediated soil should not be evaluated on the basis of the residual content of THCs. Rather, maximum emissions should be used as a basis for evaluation, and these can be determined according to the planned reuse of the soil material. Leachate tests and gas volume measurements are suitable for determining such emissions and should include, in addition to the aliphatic hydrocarbons, other contaminants of possibly greater relevance (*e.g.*, PAHs).

After undergoing quality control measures bioremediated soil might be used for a variety of purposes, although sensitive applications (*e.g.*, use in agriculture or as fill in groundwater areas) would require prior thorough testing for all relevant contaminants.

8. ACKNOWLEDGEMENTS

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9. REFERENCE

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Bioremediated Soils from Oil Spills: Waste or Product?

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Project No. 50

Integrated Rotary Steam Stripping and Enhanced Bioremediation for *In Situ* Treatment of VOC-Contaminated Soil (Cooperative approach to application of advanced environmental technologies)

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1. INTRODUCTION

This project involved technology demonstrations at the Department of Energy's Pinellas Northeast Site located in Largo, Florida, USA. Concentrations of chlorinated VOCs in the sandy surficial aquifer at the site range from 10-1,000 mg/L. In January 1995, the following three technologies were selected for pilot tests at the Pinellas site:

(1) groundwater pump and treat with a pervaporation system to remove VOCs from the pumped groundwater, which eliminated air emissions and the need for costly groundwater pretreatment;

(2) *in situ* rotary steam and air stripping to treat the highest concentrations of VOCs in soil and reduce them to a level of 100 mg/kg; and

(3) nutrient injection to enhance *in situ* anaerobic bioremediation of soil with VOC concentrations of 100 mg/kg or less.

A potential cost savings of U.S.$5-10 million was anticipated over the proposed baseline remedial design, which was a standard 30-year pump-and-treat system using groundwater recovery wells and an air stripper. Furthermore, the proposed baseline remedial design was not expected to reduce the most concentrated areas of VOCs to below drinking water standards.

2. PERVAPORATION TECHNOLOGY EVALUATION

Evaluation of the pervaporation pilot test was conducted from 1995-1996. Two recovery wells pumped groundwater to the system, which used membranes for preferential permeation of VOCs. Transport of VOC vapors through the membrane was induced by maintaining a lower vapor pressure on the permeate side of the membrane than on the side of the influent groundwater. This pressure difference was achieved by cooling the permeate vapor to make it condense.

The pilot system was capable of treating 1-2 U.S. gallons (3.8-7.6 liters) of groundwater per minute. Approximately 6,250 U.S. gallons (23.6 m^3) of groundwater with VOC concentrations ranging from 500-1,000 mg/L were treated during the pilot test. Effluent contaminant concentrations were reduced to 1-4 mg/L under optimum operating conditions; however, the efficiency of the system was lowered due to membrane fouling caused by the precipitation of iron gel. Moderate success was achieved by modifying the system and adding chemicals to reduce membrane fouling. The only wastes produced during the pilot test were the permeate and the spent filters used to inhibit membrane fouling. VOCs were successfully concentrated in the permeate, eliminating air emissions. Full-scale system capital costs for the pervaporation system to treat 20 gallons per minute are expected to range from U.S.$200,000-$275,000; operating costs are expected to range from U.S.$10-$20 per 1,000 U.S. gallons ($2.6-$5.2/m^3) of treated water.

3. ROTARY STEAM AND AIR STRIPPING TECHNOLOGY EVALUATION

Evaluation of the rotary steam and air stripping pilot test is currently being conducted. The stripping system injects steam and hot air through a rotating auger to volatilize VOCs sorbed onto soil particles. The off-gases are transported by the injected steam and air to a metal hood at the ground surface where they are treated using a catalytic oxidation system for the destruction of contaminants and an acid-gas scrubber to eliminate air emissions.

Thus far, the system has effectively reduced the concentrations of chlorinated VOCs in soil from 1,000-6,000 mg/kg, to 100-300 mg/kg, which was the goal for this site. However, several operational problems were experienced with the total system. In particular, the catalytic oxidation system was unable to handle the quantity of the vapors generated by the stripping system. As a result, some vaporized VOCs initially escaped from the metal hood. This problem was subsequently controlled by reducing the injection pressures. The only wastes generated by the system were from the scrubber. The initial results of the pilot test indicate that the operational costs will range from U.S.\$70-200/yd*3* (\$90-260/m^3).

4. NUTRIENT INJECTION TO ENHANCE *IN SITU* ANAEROBIC BIOREMEDIATION

The *in situ* anaerobic bioremediation system recently began operation and has not yet been evaluated. The system involves a series of horizontally installed wells and infiltration galleries to control the hydraulic gradient and supply nutrients to the contaminated zone.

Project No. 51

Soběslav, South Bohemia Wood Treatment Plant

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Since the 1870s, a wood processing plant has been operating on the outskirts of the town of Soběslav, located 120 km south of Prague, Czech Republic. Wood products such as railway sleepers and telegraph poles were treated at the Soběslav wood processing plant either by immersion in boiling tar (“black” impregnation) or by coating with a mixture of heavy metal salts (“white” impregnation).

In 1990, following a decision to install and upgrade existing process equipment, a site investigation was performed to determine the extent of soil and groundwater contamination resulting from industrial operations at the plant. This investigation was completed in December 1996. Soil and groundwater contaminated with polycyclic aromatic hydrocarbons (PAHs) and metals were identified in an area of approximately 1-2 km^2. Contamination at the site resulted from on-site disposal of tar sludges in poorly lined pools, discharge of untreated effluent into the Lužnice River, and discharges of chemicals from treated products staged at the site prior to transportation.

Initial concerns about site pollution centered on the foul odors emanating from local drinking water wells. The odors prompted an investigation by the local environmental health authority, which examined the results of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and non-polar extractable organic analyses of surface water and groundwater samples. The more comprehensive investigation initiated in 1990 included a detailed site walkover survey, aerial imaging, inspection of plant life, installation and logging of monitoring wells, chemical sampling of soil and groundwater, and pump testing to determine subsurface permeability. Although originally intended to be completed in 14 months, the investigation was extended to 35 months because of financial, analytical, and regulatory difficulties.

During the walkover survey, the principal sources of contamination were identified as a leaking creosote oil storage tank and seepage from unlined disposal lagoons in the southeast part of the site. Nearly 100 boreholes were drilled, and sandy to sandy clay soils overlying sedimentary clays were found to underlie the site. Monitoring of the groundwater indicated a light non-aqueous phase liquid (LNAPL) layer up to 0.7 m thick at the site. Extensive analysis of soil and groundwater samples confirmed elevated concentrations (unspecified) of PAHs, heavy metals, and phenols.

An initial investigation of remedial options was carried out by a German consultant, which studied the effectiveness of biotreating the contaminated soils. Results showed that an initial decrease in PAH concentrations was followed by a greater increase to concentrations destroying the degrading organisms. The study concluded that microbial activity had caused rapid desorption of contaminants and increased bio-available concentrations to intolerably high levels. Although more success was achieved with bench-scale testing using *in situ* groundwater biotreatment, the technique was unsuccessful during field-scale tests. As a result, it was concluded that soil encapsulation in combination with pumping and treating groundwater using gravel filters was the most cost-effective remediation solution.

Project No. 52 Permeable Treatment Beds		
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Conventional methods for groundwater treatment have often been based on pump and treat systems. Pump-and-treat involves groundwater extraction, above-ground treatment (using established effluent treatment processes), and subsequent discharge of the treated water to the subsurface or to a local sewage drain. There is a growing consensus, however, that pump-and-treat systems often incur excessive treatment costs because of their potential for continuous operation over long periods of time. This Pilot Study project reports on the development of an alternative *in situ* treatment approach, which may provide lower operating costs and enhanced treatment performance over pump-and-treat.

WCI Umwelttechnik GmbH are developing an *in situ* permeable treatment bed that can be used on a site to prevent off-site migration of contaminated groundwater or to provide long-term source treatment of the contaminated soil or non-aqueous phase liquid (NAPL) in groundwater. This type of treatment system has also been investigated by the U.S. Environmental Protection Agency, the University of Waterloo (Canada), and the U.K. Department of the Environment, and has also been called “active containment.”

In the *WCI Umwelttechnik GmbH* concept, a permeable treatment bed is installed within an aquifer as either a permanent, temporary, or exchangeable structure perpendicular to the migrating contaminated groundwater. As the contaminated groundwater passes through the treatment bed, contaminants are transformed, destroyed, or immobilized within the bed matrix. Beds based on transformation or destruction of contaminants, such as the dehalogenation of organic solvents using zero-valent iron, are said to be *reactive*. Beds that immobilize contaminants are called *sorption* beds. The material from which the permeable bed is constructed is termed the *filling.* The physical and chemical nature of this material is highly dependent upon the type of contaminant and hydrogeological environment to be treated.

The *WCI Umwelttechnik GmbH* system consists of an excavated ditch to which the appropriate filling is added. An open ditch may be suitable for treatment depths up to 12 m, while a diaphragm wall with steel caissons may be required for depths up to 50 m. The filler material can be exchanged (for example when the sorbent is exhausted) without the ditch collapsing by the construction of a double-wall within the ditch into which the filler material and monitoring equipment can be placed.

A proposed system has been suggested by *WCI Umwelttechnik GmbH*, although no pilot- or field-scale studies have been carried out or proposed. Excavation of the ditch to the appropriate depth (usually keyed into an aquiclude) is carried out conventionally with drawdown of the local water table as necessary. A concrete base to the ditch is installed to act as a clean and strong platform for bed wall installation. The bed itself is constructed from a prefabricated unit consisting of two vertical slabs connected by horizontal bars that are stacked until the height of the ditch is reached. These prefabricated elements must have a hydraulic permeability higher than the surrounding aquifer, a long-term stability to physical and chemical stresses, and low production costs. The gaps between the installed prefabricated units will provide sufficient overall permeability.

The dimensions of the proposed system are governed by site-specific parameters, such as the rate of groundwater flow and the contaminant concentration flux into the treatment bed, as well as by intrinsic parameters of the bed itself, such as its sorption capacity and reaction rate. These characteristics are important to determine the residence time required for complete contaminant treatment. The monitoring requirements for an installed system include monitoring wells downstream of the treatment bed to determine performance effectiveness and periodic sampling of filling to verify that physical and chemical properties (such as permeability and sorption capacity) still meet operating guidelines.

Treatment cost for such a system has been suggested to lie in the range of 500-700 Deutsche marks per square meter of bed over an operating lifetime of 50 years.

Project No. 53

In Situ Bioremediation of Chloroethene-Contaminated Soil

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1. INTRODUCTION

In the Netherlands, between 20-30% of heavily contaminated sites have chlorinated hydrocarbons—in particular, trichloroethene (TCE) and tetrachloroethene (PCE)—as a principal constituent. On some sites, the depth to contamination makes *ex situ* treatment technically difficult and uneconomical. Therefore, there is a need to develop *in situ* remedial techniques for this type of contamination. Biotreatment is particularly attractive since it offers the potential for remediation without generating any secondary hazardous waste for further treatment or disposal. However, biodegradation of chloroethenes is technically and microbiologically complex, and might prove difficult to achieve under field conditions. This Pilot Study project reports on the development of an *in situ* biotreatment for chloroethenes from bench-scale studies to a pilot-scale field application.

2. TECHNICAL CONCEPT

The *Tauw Milieu* approach to treating chloroethenes exploits both aerobic and anaerobic microbial processes. Although chloroethenes such as PCE are persistent under aerobic conditions, they can be dechlorinated sequentially by anaerobic bacteria to TCE, dichloroethene (DCE), vinyl chloride, and ultimately to ethene. Since the dechlorination of DCE and vinyl chloride are the rate-limiting steps, these compounds are accumulated under anaerobic conditions as intermediate breakdown products of PCE. In contrast to PCE, however, less-chlorinated ethenes can be co-metabolically mineralized by aerobic bacteria. The *Tauw Milieu* process degrades PCE through stimulation of bacteria in spatially separated aerobic and anaerobic zones. PCE is degraded anaerobically to TCE and DCE, which are transported downstream to an aerobic zone where they are mineralized to ethene.

3. LABORATORY STUDIES

By February 1996, the process had been demonstrated and verified for PCE at the bench scale. These studies showed that under anaerobic conditions, using formate and methanol as carbon and electron-donor sources respectively, PCE and TCE were readily dechlorinated to DCE and other intermediaries. In addition, using toluene or phenol as a co-substrate, TCE, DCE, and vinyl chloride were readily degraded aerobically. Flask studies with indigenous bacteria from a proposed pilot-scale test site had similar results.

In order to evaluate degradation kinetics, a series of column experiments were performed using 0.7-L columns of site soil through which 200 mL of site groundwater was recirculated. The soil column was operated anaerobically, spiked with PCE, and supplied with formate or methanol as a carbon source and electron donor. PCE concentrations initially decreased due to sorption onto column material, but dechlorinated breakdown products were noted approximately three weeks after start-up. Although degradation was observed using both formate and methanol, it was concluded that methanol would be used for the pilot-scale system because of its lower cost and more stable pH profile. The aerobic column was set up in a similar way to the anaerobic column. It was spiked with PCE and its breakdown products (TCE, DCE, and vinyl chloride). The daughter products were readily degraded with the addition of phenol to the column, but PCE degradation was not observed.

3. PILOT-SCALE STUDY

The pilot-scale remediation study was conducted from August 1995 to September 1996 at a former dry cleaning facility near the town of Breda. Soil and groundwater was contaminated with PCE over an area of 1,800 m^2 to a depth of 10 m. Concentrations of PCE in groundwater ranged up to 10,000 µg/L. The unsaturated zone was remediated using soil vapor extraction, and the saturated zone and groundwater were remediated by a combination of aerobic and anaerobic biodegradation.

The anaerobic biodegradation zone was created by the extraction and injection of groundwater (up to 250 m^3/day) to which methanol and nutrients were added. A total of about 1,100 kg of methanol was injected. By carefully controlling the hydrogeological environment, anaerobic conditions were created within the recirculating "groundwater loop." Downstream of this loop, aerobic biodegradation was supported by slow infiltration of phenol (acting as a co-metabolite) through a series of wells. A well downstream of the anaerobic treatment zone was used to extract up to 150 m^3 of groundwater per day, in order to prevent the contamination spreading and to provide water for the phenol infiltration process. Extensive monitoring was conducted to determine the effectiveness and kinetics of the degradation processes and to mitigate the migration of the contamination plume. Methanol was detected in all monitoring wells in the anaerobic zone, in concentrations ranging from 120 to 800 µmol/L. As soon as the methanol was detected, anaerobic degradation was observed. PCE was degraded rapidly to DCE; TCE, vinyl chloride, and ethene were present but did not accumulate significantly.

Under anaerobic conditions, PCE was dechlorinated at rates comparable to those found in the laboratory, and evidence of complete anaerobic degradation to ethene was found. The aerobic process also proved successful, with complete degradation of phenol and DCE. The limiting factor associated with *in situ* biodegradation of chloroethenes appears to be the availability of suitable electron donors rather than the presence of microorganisms.

5. PROGNOSIS

The pilot study proved so successful that the site owner is continuing the remediation, which is expected to take two to three years.

Project No. 54

Treatment of PAH- and PCP-Contaminated Soil in Slurry Phase Bioreactors

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1. INTRODUCTION

EkoTec, a Swedish engineering company, has carried out several full-scale remedial actions at contaminated sites across Sweden. EkoTec currently is involved in two biotreatment projects that use slurry-phase bioreactors. This Pilot Study project reports on the use of these reactors to treat 3,000 metric tons of creosote-contaminated soil containing 1,000 to 10,000 mg/kg polycyclic aromatic hydrocarbons (PAHs) and 100 metric tons soil contaminated with 500 to 1,000 mg/kg pentachlorophenol (PCP).

Small-scale bioreactors were used to treat approximately 1 m^3 of each contaminated soil. The pilot-plant treatment of PCP-contaminated soils lasted from October 1995 to February 1996. Treatment of creosote-contaminated soils began in December 1995 and continued until March 1996.

The full-scale biological treatment of PCP- and PAH-contaminated soil is scheduled for completion in 1996 and 1997, respectively. Full-scale treatment will be designed on the basis of the pilot-scale work and will use large bioreactors with and operating capacity of 150 m^3.

2. TECHNICAL CONCEPT

Biodegradation of PAHs is accomplished aerobically, while PCP degradation uses a combination of aerobic and anaerobic conditions. Reductive dechlorination of PCP is reported to occur under anaerobic conditions, with an aerobic phase required to mineralize the dehalogenated breakdown products. During each study, oxygen and nutrient inflow to the reactor is carefully monitored along with slurry pH and operating temperature. The concentration of VOCs in the bioreactor headspace is also measured continuously to determine the extent of any gaseous emissions. The process water from the bioreactors is recirculated in order to maintain slurry moisture content with minimum water amendments. The water is treated with an activated carbon filter, which will be incinerated after treatment is completed. Where possible, operating parameters and contaminant concentrations are determined using field-portable measuring equipment.

Full-scale treatment will be designed on the basis of the pilot-scale work and will use large bioreactors with an operating capacity of 150 m^3. It is expected that soil pretreatment will be required and a vibratory screen will be used to remove material coarser than 2-3 mm. Further screening and hydrocyclones will reduce material input for the bioreactors to a uniform size distribution.

3. PILOT-SCALE STUDY

A 28-day respiration test followed by degradation tests at bench scale demonstrated the ability of slurry-phase reactor to degrade of PAH compounds by more than 90%. Design and implementation of the 1 m^3 pilot-scale bioreactor concentrated on evaluating different methods of supplying oxygen, stirring, and dispersion. Soil with PAH concentrations of 859 mg/kg were treated in the bioreactor, using a commercial mixture of nutrients and microorganisms from the bench-scale tests. Sodium carbonate and potassium phosphate were added to control pH, and water was added to maintain the moisture content. After 28 days, the PAH concentration decreased to 75 mg/kg.

A second phase test was run after the reactor was modified and equipped with a cooling system to maintain the slurry at an optimum temperature of 24-28°C. A degradation test was also carried out in a 450-L EIMCO Biolift reactor, using the same soil and contaminants as in the EkoTec reactor. Although the contaminant concentration in the EkoTec reactor was 313 mg/kg, compared to 164 mg/kg in the EIMCO reactor, residual PAH concentrations were similar: 48 mg/kg for the EkoTec, and 32 mg/kg for the EIMCO. Residual concentrations declined to 22 mg/kg in the EkoTec after 36 days and to 15 mg/kg in the EIMCO after 45 days. Laboratory analyses documented an anomalous increase in PAH concentrations during some phases of treatment. This may have been caused by mechanical grinding that increased the surface contact area or by secondary formation of PAH compounds during degradation.

A third pilot-scale test is underway using the EkoTec reactor and soil with an initial PAH concentration of 4,000 mg/kg. Treatment will be completed and evaluated during 1997. Results to-date have shown that the EkoTec reactor is more reliable than the EIMCO reactor. Pyrene was more resistant to degradation than other PAHs, and a specific growth substrate was added to the slurry to compensate. VOC emissions from the slurry were negligible. A residence time of 28 days appears to be sufficient to achieve treatment of the PAH-contaminated soil.

Soil contaminated with 126 mg/kg of PCP was treated by composting in a static sheltered warehouse with controlled pH. After four months, soil residual levels declined to 75 mg/kg. Soil with an initial PCP concentration of 630 mg/kg was treated in a pilot-scale bioreactor, first anaerobically and then aerobically. After six weeks, the PCP concentration dropped to 80 mg/kg. Results to-date demonstrate that PCP can be degraded either with composting or in a bioslurry. Static composting may be accomplished successfully——even in cold climates. Preheating process air and encapsulating the treatment pile are important factors.

Project No. 55

Czechowice Oil Refinery Project

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This project reports on a working partnership between the U.S. Department of Energy (DOE) and the Institute for Ecology of Industrial Areas (IETU), an independent organization under the Polish Ministry of Environmental Protection. The objective of this partnership is to foster cost-effective, innovative research and development activities to address contamination problems in Poland, with particular emphasis on environmental characterization, risk assessment, and remediation methodologies that may be beneficial to Eastern Europe. Each phase of the project aims to demonstrate the technology and decision-making processes involved in site remediation.

The first project initiated by the partnership was the environmental characterization, risk assessment, and remediation of the Czechowice Oil Refinery, which has operated for nearly 100 years near the city of Katowice in southern Poland. The refinery uses a catalytic cracking process to refine crude oil. Wastes from the cracking process were deposited in site lagoons, which are now filled with a thick viscous sludge. Leakage of the lagoons has contaminated soil and groundwater with several organic compounds.

Environmental characterization of the refinery will consist of a two-phased expedited approach utilizing low-cost, simple rapid-response technologies to obtain general site information, followed by quantitative sampling using direct push technologies for data collection. Risk assessment will involve the development and refinement of potential exposure scenarios. The scenarios will be combined with the expedited site characterization results to quantify potential risks from the site to humans and the environment. The estimates of risk will be compared to appropriate benchmark concentrations for the contaminants.

Based on preliminary site information, bioventing and biosparging have been proposed to remediate the lagoons. Bioventing involves the injection of oxygen and nutrients into the subsurface to aerobically stimulate the indigenous microorganisms to degrade hydrocarbons to carbon dioxide and water. Vertical injection wells will be installed around the perimeter of the lagoons to aerate and remediate the contaminated vadose zone. Biosparging will be conducted to treat the lagoon sludge. Biosparging is similar to bioventing except that the air and nutrients are injected into a liquid, in this case a lined basin filled with process water. Sludge that has been pH-adjusted or mixed with a surfactant will be added to the basin in batches. In the implementation of both remediation technologies, the level of microbial activity, pH, contaminant concentrations, and rate of degradation will be carefully monitored.

Project No. 56

Spolchemie a.s.—Mercury-Contaminated Site

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The town of Űsti nad Labem lies in a region of North Bohemia known as the “black triangle,” so named for the severity of its environmental problems. The *Spolek pro chemické a hutni vyroba* (Company for Chemical and Industrial Production), also known as “Spolchemie,” is one of the most contaminated sites in this region. Spolchemie was founded in 1856 for the production of chlorinated lime and sodium bicarbonate. The company has since produced pesticides, including DDT and “Agent Orange,” and a variety of other chemicals. More than 30 separate production facilities are known to have operated at the site, which occupies over about 500 hectares (1250 acres).

Mercury has been used in electrolysis operations at Spolchemie since 1890. Based on an environmental audit, it is estimated that the total release of mercury at the site has been greater than 500 tonnes. Liquid mercury has been observed during soil excavations.

Site investigations have been conducted near the electrolysis plant to assess mercury contamination in soil and groundwater. Mercury concentrations in nine groundwater samples collected in January 1996 ranged from <0.1 µg/L to 154.1 µg/L, and concentrations in 39 soils samples ranged from <0.0001 mg/kg to 707 mg/kg. Concentrations in all but one of the groundwater samples exceed 0.1 µg/L, which is the Ministry of Environment's Category A threshold concentration for mercury, and four samples exceed 5 µg/L, which is the Category C threshold. Furthermore, nine of 39 soil samples exceed the Category A threshold concentration of 0.3 mg/kg for mercury in soil; six samples exceed the Category C threshold of 10 mg/kg.

Up to several hundred micrograms per liter of chlorinated hydrocarbons and slightly elevated concentrations of zinc and copper were also detected in samples at Spolchemie. Remedial options are being studied.