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Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

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MODERN SOCIETY
Number 190

FINAL REPORT

Volume 2
Appendices

Part 2: Pages 663 through 1389

Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

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Participating Countries

Canada	Germany
Denmark	The Netherlands
France	United States

Observer and Other Countries

Austria	Norway
Italy	Turkey
Japan	United Kingdom

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The project reports included in Volume 2 are as they were presented. They have not been revised to bring to a consistent level of detail. For example, some project reports have little baseline data or little discussion of independent evaluations of the project. They are included here to provide general information about that type of technology.

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Keywords

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Encapsulation
Extracting agents
Extraction
Fixation
Fractured rock
Furan(s)
Ground water, contaminated
Ground water, contaminated, treatment
Hazardous waste
Hazardous waste site
High-pressure jet
Immobilization
In-situ
Incineration
Indirect heating
Infrared incineration
Kiln, rotary
KPEG
Landfarming
Leach testing
Microbial treatment
Microorganisms
Oxidation
PCB
Pesticides
Pozzonanes
Pyrolysis
Remedial investigation/Feasibility study
Remediation
Remedy selection
Separation
Soil, contaminated
Soil, contaminated, treatment
Solidification
Stabilization
Stack gas emissions
Thermal desorption
Thermal destruction
Trichloroethene

Foreword

The Council of the North Atlantic Treaty Organization (NATO) established the "Committee on the Challenges of Modern Society (CCMS) in 1969. The CCMS was charged with developing meaningful environmental and social programs that complement other international programs with leadership in solving specific problems of the human environment within the NATO sphere of influence; as well as transferring these solutions to other countries with similar challenges in environmental protection.

Ground water and soil contamination are among the most complex and challenging environmental problems faced by most countries today, and there is an ongoing need for more reliable, cost-effective cleanup technologies to address these problems. Many governmental and private organizations, in many countries, have committed resources to the development, test and evaluation and demonstration of technologies to meet this need. The ongoing challenge to these organizations is how to maximize the value of these technology advancements and effectively transfer the information to people responsible for making decisions and implementing remedial actions.

Consequently, a NATO Committee on the Challenges of Modern Society (NATO/CCMS) Pilot Study on the Demonstration of Remedial Action Technologies for Contaminated Land and Ground Water was conducted from 1986 through 1991. It was designed to identify and evaluate innovative, emerging, and alternative remediation technologies, and transfer technical performance and economic information on them to potential users. The Study was conducted under the joint leadership of the United States, Germany, and The Netherlands. In addition to these co-pilot countries, Canada, France, and Denmark actively participated throughout the five year study. Norway participated as an "observer" nation, and the United Kingdom, Department of the Environment was represented at conference and workshop meetings. Japan was represented at the initial International conference. Organizations from Hungary and Austria attended the Fifth International Meeting.

This is the detailed report of the findings, conclusions and recommendations produced by that Study. It is intended to serve as a reference to the state-of-the-technologies examined by the participants. It is not intended to be a manual on technology applications but as a guide to the potential application of different technologies to various types of soil and ground water contamination. The conclusions reached from this Study revealed both the strengths and weaknesses of current technologies as well as what efforts are needed to increase the effectiveness of remediation tools and their application.

There are several volumes to this report. Volume 1 is the report itself. Volume 2 is the Appendices, and comes in two parts. Part 1 contains overviews of national environmental regulations, and papers by NATO/CCMS Guest Speakers; it consists of pages 1 through 662. Part 2 contains the final reports of the NATO/CCMS Fellows, and reports of the individual projects; it consists of pages 663 through 1389.

A limited number of copies of this report are available at no charge from two sources: NATO Committee on Challenges to Modern Society, Brussels, Belgium; or U.S. Environmental Protection Agency, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, United States. When there are no more copies from these sources, additional copies can be purchased from the National Technical Information Service, Ravensworth Building, Springfield, Virginia 22161, United States.

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Abstract

This publication reports on the results of the NATO/CCMS Pilot Study "Demonstration of Remedial Action Technologies for Contaminated Land and Ground Water" which was conducted from 1986 through 1991. The Pilot Study was designed to identify and evaluate innovative, emerging and alternative remediation technologies and to transfer technical performance and economic information on them to potential users.

Twenty-nine remediation technology projects were examined which treat, recycle, separate or concentrate contaminants in soil, sludges, and ground water. The emphasis was on *in situ* and on-site technologies; however, in some cases, e.g., thermal treatment, fixed facilities off-site were also examined. Technologies included are: thermal, stabilization/solidification, soil vapor extraction, physical/chemical extraction, pump and treat ground water, chemical treatment of contaminated soils, and microbial treatment.

This report serves as a reference and guide to the potential application of technologies to various types of contamination; it is not a design manual. Unique to this study is the examination and reporting of "failures" as well as successes.

Acknowledgements

The Pilot and Co-Pilot Study Directors thank all who made significant contributions to the work of the Pilot Study:

Those representing their countries made a major contribution to the direction of the Study by recommending projects within their respective countries which would be of particular interest to this Study, and by discussing the regulatory and general environmental technology situations in their countries.

The various chapters were written by the respective authors after reviewing reports prepared on the Case Studies for the meetings of the Study Group.

Good use was made of the NATO/CCMS Fellowship Program to further enhance the value of the Study and a number of Fellows contributed directly to the preparation of this report. Robert Olfenbuttel of Battelle also served as the general editor for the report, supported by Virginia R. Hathaway of JACA Corp., editor.

Expert speakers, often supported by NATO/CCMS travel funds, participated in the workshops and conferences of the Pilot Study and contributed to the work of the Pilot Study Group.

Until his retirement, the NATO/CCMS International Staff was represented by the former CCMS Director, Mr. Terrance Moran. Dr. Deniz Beten replaced Mr. Moran and attended the Fifth International Meeting.

Ms. Naomi Barkley of the Office of Research and Development, Risk Reduction Environmental Laboratory, Superfund Technology Demonstration Division, U.S. Environmental Protection Agency served as Task Project Manager for this project.

The names and addresses of all participants in the Study Group are given in Volume Two.

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NATO/CCMS Fellow:

Alain Navarro, France

New French Procedures for the Control of Solidificated Waste

NATO/CCMS CONFERENCE

ANGERS

Wednesday November 7th

BULK AND SOLIDIFIED WASTE
AN ADAPTED PROCEDURE

I - INTRODUCTION.

The admission of hazardous industrial waste or waste, containing hazardous substances is the object of a regulatory procedure. Certain wastes can either be admitted directly or absolutely excluded. All other categories of waste must be submitted to an admission procedure. In France, this procedure includes a leaching test carried out according to the AFNOR standard.

The principle of this standard is to carry out a leaching test in order to determine the immeadiately soluble fraction when brought into contact with water. The results of this test therefore integrate both the solubility of the waste and the conditions of access of water to the waste. Hence, it is necessary to crush the waste to particle size of no greater than 4mm. Under these conditions, the test may primarily be considered as an arbitrary means of waste characterization, rather than a tool for predicting the mean or long term behaviour of the waste.

Two large categories of waste should be excluded from the field of application of this standard :

* ***Bulk waste** : the definition of bulk waste is, any waste that when produced consists of fragments greater than 4mm, on condition that this state be durable in time when under the influence of physical, mechanical or chemical agents.*
* ***Solidified waste** : the definition being waste, either liquid or solid originally, but which has undergone a solidification treatment by the addition of binders (cement, molten glass, organic binders) according to a specific procedure.*

In order to more accurately predict the behaviour of these 2 categories before admission to landfill (class I), the possibility of developing a better adapted leaching test was studied, rather than applying the AFNOR standard.

The first phase of this study was to carry out a literature survey followed by a procedure proposal. The proposed procedure is now being tested in the laboratory, and it is only when this second phase has been completed that any official decision can be made.

The first phase of this work will be discussed here.

II - THE AFNOR STANDARD

(see overhead 1)

III - LITERATURE SURVEY.

The new procedure must achieve 2 objectives.

* *to be adapted to the specific case of bulk or solidified waste, concerning the transfers which take place between the waste and water, and to the structural integrity.*

* *to be coherent with the AFNOR standard.*

The literature survey shows that we have a large number of operational tests at our disposal, on a national and international level to :

- *appreciate the physical and mechanical properties which govern the state, in the long term, of bulk and solidified waste.*

- *evaluate the leachability of waste, in particular, solidified radioactive waste.*

1) Principal results of leaching test.

Globally, leaching tests can be divided into 3 main categories.(see overhead 2)

THE AFNOR STANDARD X31 210
September 1988

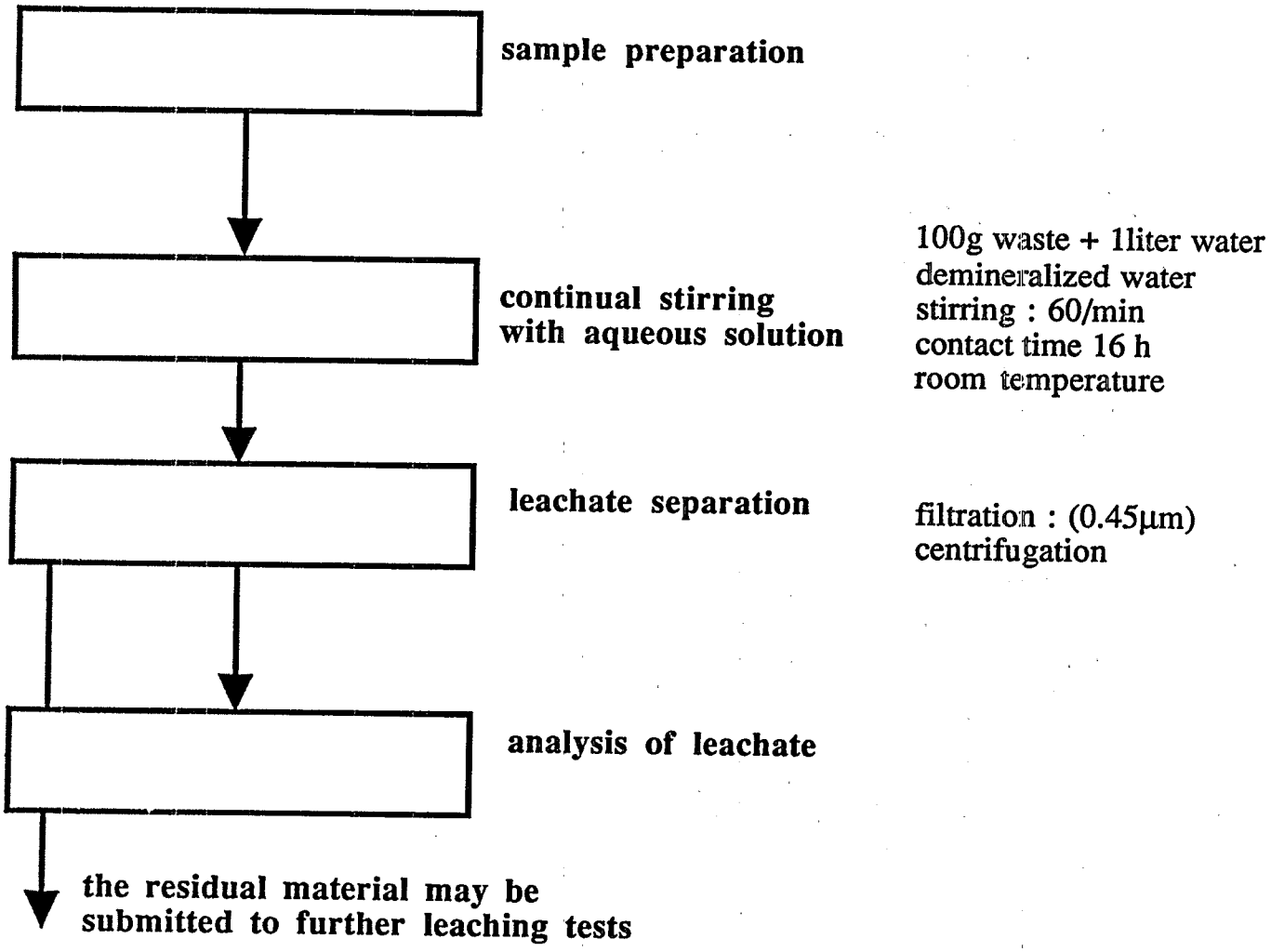
This standard describes a leaching test to obtain, under defined conditions, a soluble fraction which can be analysed for characterization purposes.

It consists of :

1) general recommendations for waste sampling, either at the production or disposal stage.

2) sample preparation procedures for laboratory tests

3) procedures for leaching tests



4) an official experimental report

A - Tests without renewal of contact solution.

A known quantity of liquid is brought into contact with a known quantity of waste for a given period of time. 3 subcategories can be distinguished :

- *tests with stirring*
- *tests without stirring*
- *tests with sequenced extraction*

B - Dynamic tests.

The solution is renewed, either continuously or periodically. 3 subcategories can also be distinguished :

***BATCH TESTS** : the waste is in particle form in a confined medium.*

***FLOW AROUND TESTS** : the waste is in block form and the solution flows round it.*

***FLOW THROUGH TESTS** : the waste is in block form and the solution percolates through it.*

C - Hybrid tests.

These can be divided into 2 categories :

- *saturation tests*
- *extraction tests (SOXHLET for example)*

All these categories can be distinguished by their different operating conditions :

**** Nature of the solution :***

- *water or dilute aqueous solution (natural, distilled, deionized, acidified)*
- *more concentrated aqueous solutions (acids, brine)*

It would seem better not to use brine (particular case of seawater) and strong acids, which correspond to unrealistic situations.

Deionized water would be a better solution, eventually acidified with acetic acid (case of mixed waste containing biodegradable waste.

**** Sample preparation :***

All crushing must be excluded but certain wastes are of a dimension that special standard samples must be made either by moulding (solidified waste) or by cutting out (bulk waste). In the case of bulk waste of dimensions smaller than the chosen standard sample, a standard volume was considered.

**** Mode of contact with water :***

Systems with stirring are the best adapted to our approach : mechanical stirring (backwards and forwards) using a bar magnet, or a rotor, or by bubbling gas through the solution (nitrogen or carbon dioxide).

**** Liquid/solid ratio :***

This ratio can easily be expressed for dry waste ; it must be more precisely defined for wet waste. In the literature, the ratio solution / waste varies from 1 : 1 to 100 : 1.

**** Contact time :***

It can vary from 16 hours to 1 year. The AFNOR standard fixes this time at 16 hours.

**** Final separation of leachate :***

In the case of tests without stirring, separation is carried out by filtration. In other cases, the separation is often described precisely (choice of filtration mode, centrifugation, filter size. etc...

2) Tests used to evaluate the structural integrity of the bulk materials.

- *visual appreciation : a rigourous nomenclature must be defined concerning fragmentation, softening, fissuring, colour changes, reduction to dust, etc...*

- *mechanical strength.*

The mechanical behaviour of the waste has to be known in order to qualify it as "bulk waste" and to predict its behaviour at the time of testing.

The literature shows that , to our knowledge, no specific procedure exists for waste, for this aspect , and that we have to use procedures applied to construction materials. For example we can quote tests such as :

- *tensile strength*

- *compressive strength , for which a number of devices exist together with very rigourous procedures.*

3) Freeze/thaw tests

A number of procedures have been listed. The parameter "material" (porosity and tensile strength) and the operational parameters (water content at the time of freezing, temperature gradient, number of cycles) must be taken into account.

4) Wetting/drying tests

The water content and water absorption capacity are the two essential parameters which must be known in order to carry out this test. The various tests in the literature differ in their operating modes and as well as in the criteria chosen to evaluate the structural integrity.

5) Resistance to biological agents test.

The freeze/thaw tests and the wetting/drying tests have given rise to diverse protocols adapted to waste. This is not the case for biological tests which have been very little used. It is necessary to refer to tests concerning the biodeterioration of materials.

- *bacterial corrosion of metals,*
- *biodegradation of plastic, paint, fuel, tarmac, rubber,*
- *composting of municipal and industrial waste,*
- *bioleaching of ores,*
- *biodegradation of diverse materials (piping systems, joints, surfaces) in contact with drinking water.*

6) Diverse ageing tests.

Procedures exist related to the nature of the concerned materials and to their mechanisms of physico-chemical degradation.

IV - SPECIFICATIONS FOR THE DEVELOPMENT OF AN ADAPTED LEACHING TEST

In France, there is a standardized test for waste prior to landfill. As bulk and solidified waste have been excluded from the field of application of this test, it is important to develop a specific procedure for these two categories.

To define the new test it is important to :

a) to define the conditions which differentiate classical waste from bulk or solidified waste.

b) to determinie the shape of the standard sample to be adopted.

c) to adopt a leaching procedure which can be common to both bulk and solidified waste and also as close as possible to the existing standard procedure.

d) to define the list of complementary tests which allow us to predict the behaviour of these wastes in their ultimate disposal site.

e) once this list of tests has been determined, to choose the techniques and tools adapted to each of these tests.

V - EXPERIMENTAL PROTOCOL

At the end of this study, and after discussion with the laboratory representatives concerned, a provisory protocol was elaborated. This protocol which we will describe here is presently being tested in the framework of an experimental programme, and it is only after this second phase that a definitive protocol will be elaborated.

It is important to remind you here that :

1) this protocol is common to both bulk and solidified wastes.

2) It has tried to remain coherent with the existing french standard procedure.

3) *It does not have the ambition of being a trustworthy simulation of the behaviour of waste, but is to be considered as a tool, easy to implement, reliable and applicable to these types of waste of any origin.*

4) *it must not be considered as a test destined to "validate" solidification technologies in general. However such validation work could include the principles of these tests.*

5) *carrying out this test does not mean that the analytical operations for waste characterization are no longer necessary.*

VI - CONCLUSION.

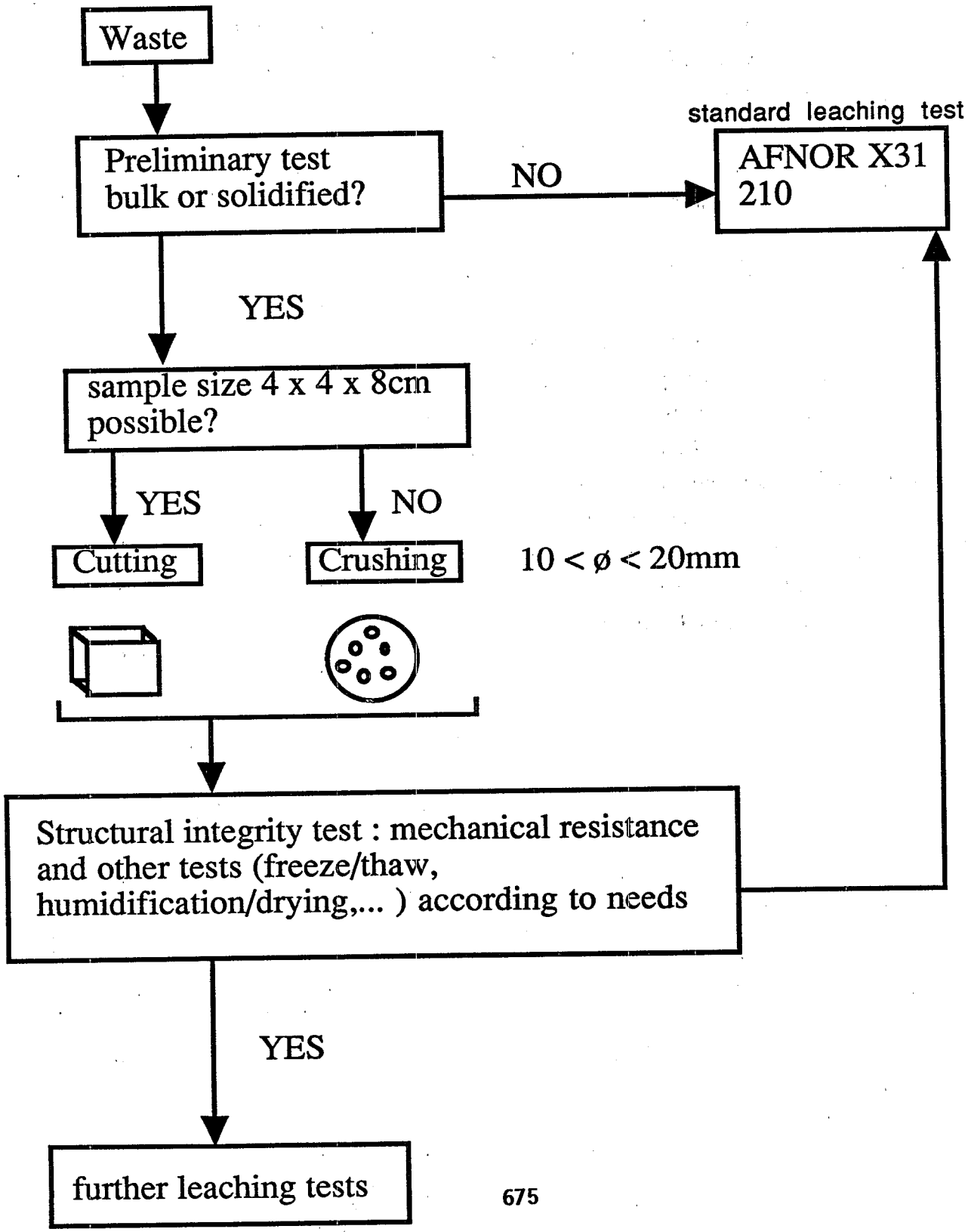
The procedure presented here cannot be considered as defintive. It is in the process of being validated and may undergo modification at the end of the experimental phase. Taking into account the probable evolution of conditionning techniques and management strategies of landfills which accept industrial waste (class I), it is necessary to have such control tools at our disposal.

It must be noted that this procedure, which has been voluntarily simplified, cannot, by itself, be used as a technique for the validation of solidification processes in general.

Finally, by confronting this procedure with procedures used abroad , the ultimate objective may be achieved, which is to elaborate a common international procedure.

A. NAVARRO 1990

TEST PROTOCOL



NATO/CCMS Fellow:

Peter Walter Werner, Germany

Biodegradation of Hydrocarbons

Report on activities in the frame of the
NATO/CCMS Fellowship Programme

Title:

Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

Aspects of In Situ Removal of Hydrocarbons from Contaminated Sites by Biodegradation

by Peter Werner

Dr. Peter Werner

Report on activities in the frame of the NATO/CCMS Fellowship Programme

Title: Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

Activities: 1987: Participation in the SETAC-Conference in Pensicola (Florida)
November, 9, 1987

Visit of the Eglin Airbase site
November, 10, 1987

Participation in the NATO/CCMS Meeting in Washington, DC
November, 11-13, 1987

1988: Participation in the TNO/BMFT Congress in Hamburg (Germany)
April, 14, 1988

1989: Visit of the institute of Erik Arvin (Department of Environmental Engineering in Copenhagen, Denmark)
May, 11, 1989

Participation in an International Symposium on Processes and Governing the Movement and Fate of Contaminants in the Subsurface Environment, Standford University
July, 24-26, 1989

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Introduction

In the late 70's, the public interest in contaminated sites increased rapidly. First aid measures consisted in replacing the polluted soil with non-polluted material. The more people investigated soil and groundwater, the more contaminated areas could be found. Gradually, the public became more and more aware of the problems. Together with an increasing feeling of responsibility, a large industry of remediation measures developed during the 80's.

Besides landfill, encapsulation, extraction, and incineration, which are just mentioned here, there is a strong interest in biological methods to remediate contaminated sites. The target of these methods using microbial activities is a complete mineralisation of the pollutants [1, 2].

The technical aspects of biological remediation using on-site and in-situ methods are described in a great number of publications of which only a few are refered to here [3, 4, 5, 6, 7].

The task of my fellowship programme is not to repeat things and facts which have already been described in different journals or presented at different congresses. Nor is it good to believe everything announced in advertising brochures of firms which offer biological remediation already commercially.

As a microbiologist, I want to focus especially on problems still existing in the field of biological processes used for remediation of contaminated sites. This will help us to get a better understanding for the ongoing processes. Moreover, it is necessary to regard biological processes on a realistic base. It is not worth exaggerating these methods not knowing enough about the background. The knowledge on biodegradation itself must be increased before the methods can be applied realistically. We must be aware of the problems and must admit that we do not know enough about them. Otherwise we might be blamed later on for having dealt amateurishly with difficult question such as the remediation of contaminated sites. Certainly, it is very useful to apply biological methods where they really seem useful. But it is impossible to solve all problems with microbiology. The aim must always be a combination of

different methods.

The reputation of microbial processes in the frame of remediation methods still is very good and we should take care that it remains like that.

In order to increase the possibilities to use microbial activities for the elimination of contaminants, I put the main interest in the fellowship programme on two problems which prohibit the biodegradation processes.

1) Bioavailability of the contaminants
2) Question of oxygen sources (air, oxygen, nitrate, hydrogenperoxide)

For a better understanding of the problem, I have to restrict my explanations to the biodegradation of hydrocarbons.

1) Bioavailability of the contaminants

Contaminations of subsurface by oil products in general result from accidental spills or leaking underground storages. Even when mobile oil has been removed by pumping, residual trapped oil can be a long-lasting source of water contamination by soluble hydrocarbons which therefore should be removed. Enhanced biodegradation should be used with the support of other means, described elsewhere [7].

For the application of in-situ measures the following preconditions must be guaranteed:

Table 1: Requirements for biological in-situ treatment

MICROBIOLOGICAL POINTS OF VIEW:

Biodegradability of the contaminants
Concentration of the contaminants
Absence of toxic substances (e. g. heavy metals)
Solubility of the contaminants

HYDROGEOLOGICAL POINTS OF VIEW:

Hydraulic conductivity 5×10^{-4} m/s
Flushing circuit
Water treatment before infiltration
Homogenious distribution of the contaminants
Prevention of spreading of the contaminants
Homogenious flushing through the contaminated soil

A detailed description of the procedure is given in [2].

Among the different factors, which limit biodegradation, listed in Table 2, I first want to focus on the bioavailability of the contaminants for the bacteria.

Table 2: Limiting factors for the biodegradation in contaminated sites

1) Physiological conditions (composition of inorganic nutrients, concentration of the nutrients)
2) toxic substances (e. g. heavy metals)
3) biodegradability of the pollutants themselves (kinetic data)
4) bioavailability (solubility, spatial separation)

The problem of bioavailability is characterized in just four words, given in Figure 1.

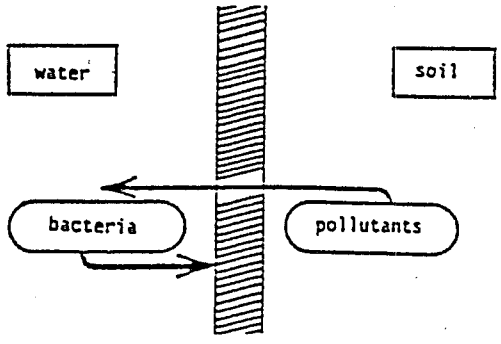

Figure 1: Distribution of pollutants and microorganisms in polluted soil

To enhance the biodegradation of contaminants, it is necessary to bring microorganisms and pollutants into close contact. Normally, the contaminants are very well attached to the soil or even integrated into the soil matrix - as it is known in the case of clay. We have to consider that the pollution of the soil normally takes a very long time (in the case of coalgasification plants about 50 years) and so diffusion plays a predominant role. We cannot expect that the organics are released within a short period of time. So it is an urgent task to increase the concentration of the pollutants in the aqueous phase to enable the bacteria to biodegrade them. In my opinion, it is not worth increasing the number of bacteria artificially because they are not able to penetrate the soil, at least in the case of clay.

The first step of remediation is to establish and maintain conditions which allow biodegradation. The second step is done by the bacteria themselves: if they find acceptable physiological conditions they will settle and proliferate voluntarily.

In order to illustrate the problem, an example of a laboratory experiment is described here. A column has been filled with sand that had been contaminated artificially with a consortium of 10 different PAH's. The initial concentra-

tions of the soil used in the experiment are given in the first row of the next table.

Table 3: Concentrations of PAH's during biodegradation in a laboratory pilot plant [8]

Substance	Concentration (mg/kg) Operation Time (d)				
	1	35	56	87	137
Naphthalene (NAP)	265.11	1.21	0.64	nn	nn
Acenaphthylene (ACY)	318.66	13.52	9.93	1.37	0.94
Acenaphthene (ACE)	356.45	43.42	16.78	3.03	2.30
Fluorene (FLO)	378.19	146.76	88.79	13.10	7.53
Phenanthrene (PHE)	379.42	226.13	171.80	23.52	12.55
Fluoranthene (FLA)	400.13	357.27	398.88	55.62	29.56
Pyrene (PYR)	397.68	385.36	339.42	58.27	30.47
Benzanthracene (BZA)	40.53	44.65	35.93	11.60	11.26
Chrysene (CHR)	41.74	36.15	37.82	19.66	17.28
Benzo(a)pyrene (BZP)	40.99	38.52	36.65	24.39	22.95
Sum	2619	1293	1137	211	135

Some results of the experiment are shown in Figure 2 on which the number of hydrocarbondegraders is plotted with respect to the operation time. As a proof for the bacteria, the incubation was done with naphthalene as a single carbon source. In the beginning, there is an increase in the population of 2 orders of magnitude, followed by a plateauphase which is almost constant over a period of 5 weeks. The concentration of the PAH's during this time is about 23 mg/l in water and 2.6 g/kg in soil. After the plateauphase, there is a decline of the number of bacteria combined with a decrease in the concentration of PAH's in water to a minimum of 0.03 mg/l. The concentration of PAH's in the soil, however, still is very high (1.0 mg/kg soil).

In the experiment presented here, we added 0.5 % acetone to the system and were thus able to increase the concentration of hydrocarbons in the water. The result was another increase in the number of bacteria in the system. The microorganisms where neither prohibited by acetone nor were they able to biodegrade it. At the end of the experiment, a concentration of about 140 mg/kg soil could be detected. The value is given separately because there was another step done at the end of the experiment which should be discussed in another scope. In order to increase the biodegradability we used UV-radiation.

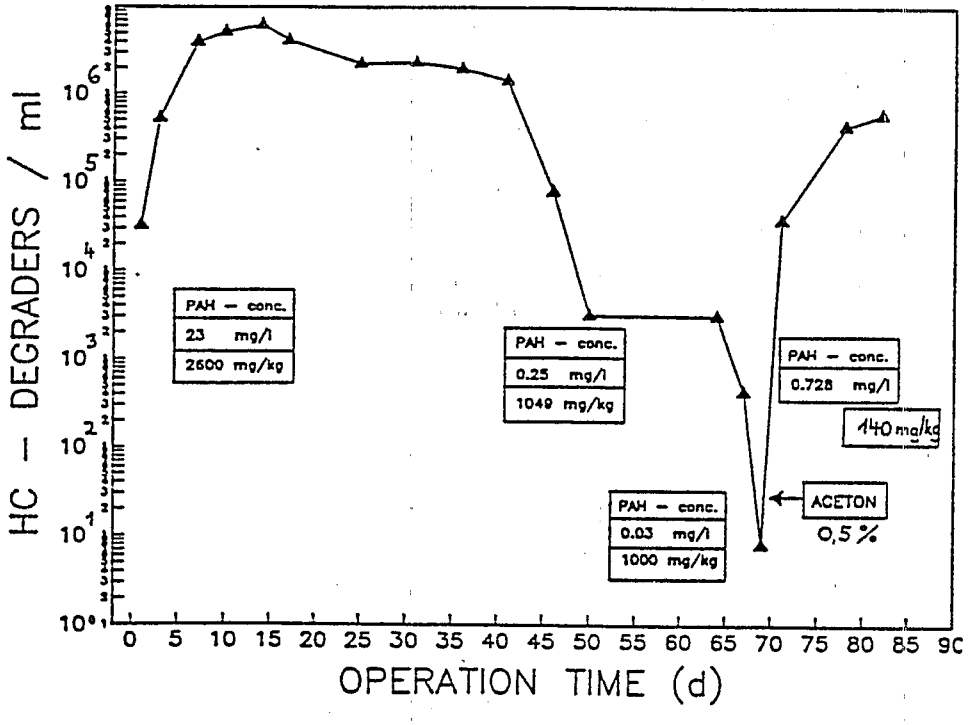

Figure 2: Hydrocarbondegraders with respect to the operation time in a laboratory experiment, showing the mineralisation of PAH's

(In a parallel experiment, in which $HgCl_2$ was used to kill the bacteria, only a slight decrease of PAH's could be found due to stipping effects [8]).

From these data we can conclude that the solubility of PAH's is the growth limiting factor.

The elution of pollutants from different soils is very unlike from the geological point of view and can be shown in an experiment demonstrated in Table 4.

In both soils (sand and clay) from different contaminated coalgasification plants in Germany there is almost the same concentration of the consortium of PAH's (about 2,1/kg soil dry weight). An aqueous elution of 100 g soil in 1 l of water in the result is almost undetectable in the case of clay while it is about 10 mg/l in the case of sand. For that reason, we have to look for a method to increase the release of pollutants from a clay material.

Table 4: Aqueous elution of PAH's out of sand and clay from contaminated sites

	CLAY concentration		SAND concentration	
	in the soil (mg/kg)	in the supernatant (mg/l)	in the soil (mg/kg)	in the supernatant (mg/l)
Indene	3,0	>0,01	2,5	0,10
Indan	6,2	>0,01	4,0	0,20
Naphthalene	70	0,04	105	6,00
1-Methylnaphthalene	82	0,04	65	0,80
2-Methylnaphthalene	110	0,07	210	1,00
Acenaphthene	210	>0,01	140	0,90
Acenaphthylene	20	>0,01	60	0,10
1,1-Biphenyl	25	0,02	60	0,20
Fluorene	265	0,02	400	0,15
Anthracene	130	>0,01	250	0,08
Penanthrene	240	>0,01	310	0,15
Pyrene	285	>0,01	220	0,09
Fluoranthene	400	>0,01	160	0,05
Crysene	110	>0,01	90	0,01
Benz(a)anthracene	165	>0,01	110	0,02
Sum	~ 2100	~ 0,2	~ 2200	~ 10

Prof. Paul Roberts and Dr. Lewis Semprini from Stanford University deal with similar problems concerning bioavailability of contaminants in the subsurface. They measure the effect of sorption on the rate of biodegradation [3]. This group puts the main focus on the biodegradation of chlorinated hydrocarbons. Another research group at Rice University in Houston carries out special experiments with the biodegradation of hydrocarbons in clay materials (Prof. Dr. Herb Ward). Thanks to the NATO/CCMS fellowship programme granted to me, I was able to contact both groups which deal with these problems. The close exchange of information still continues and another visit to Stanford University is planned with the support of the fellowships's financial remains.

The problem we have to tackle is the release of organics bound to the soil in order to increase the solubility and therefore to enable biodegradability in the first place.

The disadvantages of the use of organic surfactants are summarized in [1] and [9] and are not explained in detail here. I just want to mention the increase of biomass and gasproduction which decreases the hydraulic permeability to zero. Moreover, toxic surfactants can principally not be used.

The requirements a surfactant has to meet are:

- neither to prohibit nor to enhance biomass production
- no prohibiting effect on the biodegradation of the pollutants themselves
- no influence on the environment.

We were able to find out that pyrophosphates fullfil the preconditions, at least on a laboratory scale.

The exàmple of the experiment shows the effect of Na-Pyrophosphate on the release of PAH's attached to sand. The efficiency for the two consortia of PAH's is given in the figure of Table 3. The experimental conditions are described at the top of the figure. The best efficiency of pyrophosphates to increase the PAH content in the supernatant is in the concentration range of 0.1 %. Using 0.5 %, a decrease can already be observed which can be explained

by sedimentation processes. The sedimentation time in the case presented was 10 minutes.

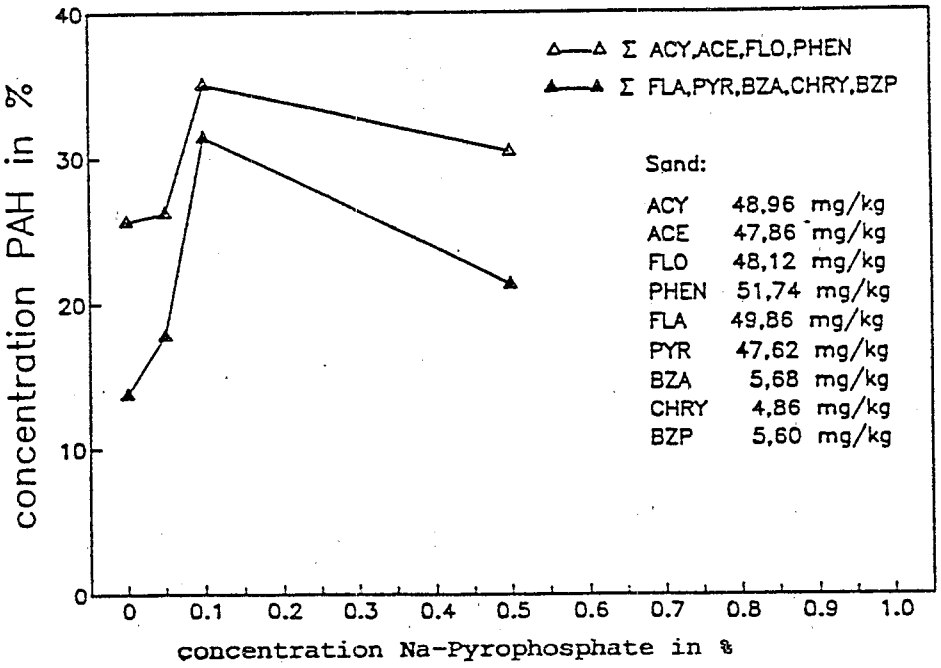

Figure 3: Effect of pyrophosphates on the release of PAH's attached to sand

The effect of pyrophoshates on the release of contaminants is even higher but on the other hand it results in a complete destruction of the soil structure itself. So far, we were not able to find any toxic or enhancing effect on the biodegradation of the pollutants themselves. In the frame of research programmes we follow the target to increase the concentration of pollutants in the aqueous phase by releasing them from the soil. Besides pyrophosphates, a consortium of other surfactants with similar effects is applied. An intensive exchange of information on this important question with the purpose to solve environmental problems by biodegradation will be continued in future.

2) Question of oxygen sources

Normally, the biodegradation of hydrocarbons optimally occurs under aerobic conditions. The solubility of oxygen in water, however, is limited to approximately 9-10 mg/l water at 10-15°C, which is the temperature of groundwater in Central Europe. Because of the high amounts and concentrations of pollutants normally found in the spill, the growth limiting factor is the available oxygen. As a rule, approximately 3 mg oxygen are consumed for the oxydation of 1 mg hydrocarbons. There are some indications that aromatic hydrocarbons can be biodegraded under methanogenic conditions but the kinetics of these processes are too slow to be used as a remediation method [10].

One way to increase the oxygen concentration is to use technical oxygen which will help to raise the values by the factor of 4 to 5. Another way is to work alternatively with other additional oxygen sources such as nitrates. For the complete mineralization of 1 mg hydrocarbons about 3,5-4 mg nitrates are consumed. Theoretically, the concentration of nitrates can be raised almost without limit. From this point of view, nitrate would be an excellent electronacceptor for the biodegradation of contaminants because the optimum final products are carbondioxide, water, and free nitrogen.

But unfortunately not all contaminants can be biodegraded in the presence of nitrates. It is evident that free oxygen must be available for the first oxidation step [5]. This is the case at least with aliphatic hydrocarbons. On the other hand, only very little is known about the mineralization of aromatic hydrocarbons under denitrification conditions. It seems as if some of them are inserted directly in denitrification processes [11, 12]. The problems concerning the biochemical pathways in these biodegradation processes have been discussed with M. Hutchins and J. Wilson from the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. The exchange of information will be continued because this research group is still focussing, like we do, on these interesting phenomena. The knowledge on the beneficial use of nitrate for the remediation of contaminated sites is still very poor. On the one hand, a lot of fundamental work in the laboratory has to be done, as it is described in [12]. On the other hand, it is already necessary to do practical field

work. Our institute is involved in two field projects in which nitrates are used as additional oxygen sources. The results will be published in 1990 and are to be presented at the next TNO/BMFT Congress in Karlsruhe in 1990.

Problems with the usage of nitrates mainly occur, besides in the selectivity of the substrate spectrum, in the production of the unwanted nitrite, which develops under so far undefined conditions.

Another possibility to bring additional oxygen into biological systems consists in using hydrogenperoxide. There are no problems with the disinfecting properties of this agent, as has been expected by microbiologists. In our own experiments concentrations up to 2000 mg/l of H_2O_2 could be used without killing the bacterial population. These results are confirmed by the experiences of Doug Downey [13]. Intensive discussions on the problems and an exchange of experiences have taken place and are also planned for the future. Own experiences were made in a field experiment comparing the use of nitrate and H_2O_2 in two similar sites. The results will be presented at the Conference on Subsurface Contamination by Immiscible Fluids in Calgary, Canada, in April 1990 [14].

The advantage of the usage of hydrogenperoxyde is that it works as electronacceptor for oxygen and that it can be diluted in water in high concentrations. The disadvantage lies in the fact that the agent disintegrates very rapidly to water and free oxygen which forms bubbles in the water.

Therefore, it is difficult to transport hydrogenperoxyde in the subsurface into areas where it is needed. The question of stabilizing this substances is not yet answered. On the other side, due to the production of gas bubbles in the aquifer, the hydraulic permeability decreases rapidly.

Conclusions and future plans for the fellowship programme

The objective of the fellowship programme was to elucidate problems in the frame of remediation measures of contaminated sites using microbial activites. Due to the financial support by NATO/CCMS I had the chance to exchange informations with other research groups. The focus of my work lay on two main topics concerning microbial remediation: the bioavailability of contaminants on the one side and the question of additional oxygen sources on the other.

The first step for a successful biological degradation is to bring bacteria and contaminants into close contact. Some methods to increase the concentration of the pollutants in the aqueous phase are described above. It is only in solution that optimum biodegradation conditions can be installed and above all maintained. Only when this problem has been solved, the question of additional and/or alternative oxygendonors can be taken into view. The application of nitrates and hydrogenperoxide is discussed in the report.

The NATO/CCMS fellowship programme allowed me to get into contact with different research groups treating similar topics as I deal with. All these groups are still working in order to find solutions for the problems, to get a better understanding of the limiting factors, and to overcome the difficulties. This will enable a more successful application in future of microbial methods for the remediation of contaminated sites.

In order to keep in good touch with these people, I plan to participate in the above mentioned conference in Canada where I will have the oportunity to present results of our own experiences.

The expenses of these travel activities can certainly not be covered with the second part of the NATO/CCMS grant alone. But nevertheless I intend to participate in the conference and to visit at least one university in order to stay in close contact and to be able to exchange experiences personally, which seems to be the best way. For that reason, I do not spare the rest of the travel expenses to be covered privately.

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Report on activities in the frame of the
NATO/CCMS Fellowship Programme

Title:

Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

To be presented at the 4th International NATO/CCMS Conference
at Angers (France) November, 5 - 9, 1990

1. Introduction

The paper presented here is the continuation of my report already printed and documented in the Summary of the "Third International NATO/CCMS Conference on Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater" in Montreal, Canada, November, 6 - 9, 1989.

The task of my fellowship programme is not to repeat things and facts which were already described in different journals or presented at different congresses. Nor is it good to believe anything announced in advertising brochures of firms which already offer biological remediation commercially.

As a microbiologist, I want to focus especially on problems that still exist in the field of biological processes used for remediation of contaminated sites. This will help us to get a better understanding for the ongoing processes. Moreover, it is necessary to regard biological processes on a realistic base. It is not worth exaggerating these methods not knowing enough about the background. The knowledge on biodegradation itself must be increased before the methods can be applied realistically. We must be aware of the problems and must admit that we do not know enough about them. Otherwise we might be blamed later for having dealt amateurishly with difficult question such as the remediation of contaminated sites. Certainly, it is very useful to apply biological methods where they really seem appropriate. But it is impossible to solve all problems with microbiology. The aim must always be a combination of different methods.

In my report mentioned above, I put the main interest on the two problems which inhibit biodegradation processes:

1) bioavailability of the contaminants
2) question of oxygen source.

The conclusions of the former presentation are not to be repeated here, but the aim of this paper should be the experiences made when biological methods are applied for the remediation of contaminated sites. Therefore, I want to compare different methods already used worldwide and to describe their applicability with all the advantages and disadvantages. Moreover, contaminants other than hydrocarbons are to be discussed here.

In addition to the institutions already mentioned in the first report, I contacted the following firms:

TNO, Delft (NL)
Umweltschutz Nord, Ganderkesee (D)

which have many experiences in the use of microbial biodegradation processes.

2. Contaminants

A lot of concern is concentrated on the biodegradation of the following substances, that can be found in contaminated sites. The table below contains the biodegradability itself and the applicability in practice.

Table 1: Contaminants of Special Interest

Contaminants	Biodegradability Proved in Laboratory	Biodegradability Proved at the Site	Applicability Proved in Remediation Measures
Aliphatic Contaminants	+	+	+
Aromatic Contaminants	+	+	+
Polyaromatic Hydrocarbons	±	±	-
Volatile Chlorinated Hydrocarbons	+	+	-
Phenols	+	+	+
Non-volatile Chlorinated Hydrocarbons	±	-	-
PCBs, Dioxins, Furans	-	-	-
Cyanides	±	±	±
Heavy Metals	-	-	-

With respect to aliphatic hydrocarbons it can be concluded that alcanes (C_5 - C_{16}) are fairly well biodegradable. Isoalcanes and alkenes are less biodegradable. Cycloalcanes are almost resistant. From this point of view it is of special interest to analyze in advance the combination of pollutants at a contaminated site in order to decide about the most suitable remediation method. Due to the great amount of contaminants normally found on spills with alipha-

tic hydrocarbons, the question of the additional oxygen source is important. Figure 1 shows the biodegradation pathway of aliphatic hydrocarbons which leads to the conclusion that nitrogen can only be applied in combination with oxygen as primary oxidant.

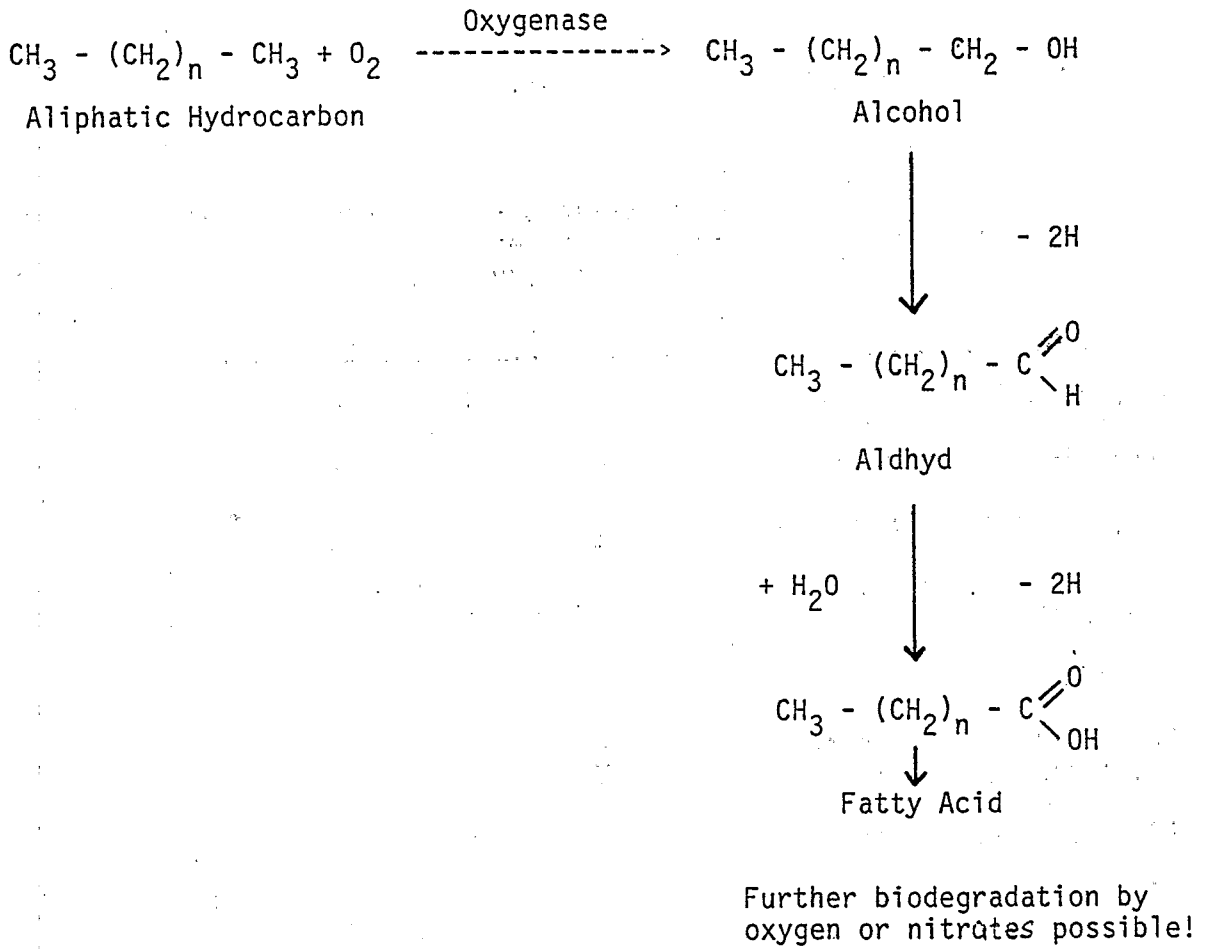

Figure 1: Biodegradation Pathways of Aliphatic Hydrocarbons with Respect to the Use of Nitrates

Phenols and most of the aromatic hydrocarbons can be biodegraded fairly well, reason why bioremediation of these contaminants is already used worldwide. The concentration of these substances is crucial for the success.

Polyaromatic hydrocarbons are especially important in Germany since its reunification because of the large number of abandoned coke-oven and coal-gasification plants, where these pollutants are predominant. In principle, biodegradation is possible. The problems of its applicability in practice are already described in detail in my first report and should not be repeated here.

The biodegradation of cyanides is also of special interest in the areas mentioned above. Non-complexed cyanides are well biodegradable in concentrations up to about 15 mg/l, although it is one of the most toxic inorganic substances known. The experiences show that cyanide in abandoned industrial areas is complexed and therefore not or only less toxic and less soluble. On the other side, it is almost not biodegradable in this form. Table 2 shows the occurence of cyanides and their toxic properties. As a rule, Prussian blue can be found predominantly in abandoned coal-gasification plants.

Table 2: Occurence and Behaviour of Cyanides

Form	Solubility	Toxicity	Biodegradability
"Non-complexed"			
KCN, NaCN, NH_4CN Cyanides	high	high	+
KOCN, NaOCN, NH_4OCN Cyanates	high	not toxic	+
KSCN, NaSCN, NH_4SCN Thiocyanates	high	low	+
$Zn(CN)_2$	low	fairly toxic	?
"Complexed"			
$K_3(Fe(CN)_6)$ red	high	low	-
$K_4(Fe(CN)_6)$ yellow	high	not toxic	-
$KFe(Fe(CN)_6)$ soluble Prussian blue	low	not toxic	-
$Fe_4(Fe(CN)_6)_3$ non-soluble Prussian blue*	not soluble	not toxic	-

* predominant in abandoned coal-gasification plants

Volatile chlorinated hydrocarbons are fairly well biodegradable under different environmental conditions. A lot of work was done in this field in the last few years. The experiences concerning this subject were summarized in 1989 by Werner and Ritter in a literature review called "Abbau- und Biotransformation von leichtflüchtigen Halogenkohlenwasserstoffen in der Umwelt unter besonderer Berücksichtigung der Vorgänge im Untergrund". The study can be ordered at the Landesanstalt für Umweltschutz im Karlsruhe (Germany). Due to the complexity of biodegradation pathways, no case of remediation based on microbial processes is known so far.

Only some of the non-volatile chlorinated hydrocarbons could be biodegraded under optimum conditions on laboratory scale. An applicability of microbial mineralization of these compounds is not known. PCBs, dioxins, and furans are tested for their biodegradability in laboratory set-ups. The results are only of scientific interest and cannot be transferred to bioremediation measures.

Heavy metals cannot be eliminated microbially. Only indirect mobilization by leaching processes are known.

3. Procedure in the Application of Bioremediation

The procedure to check the applicability of biological methods for the remediation of contaminated sites using in-situ or on-site measures is shown in Figure 2. The complexity of the scheme indicates that the decision whether these methods can be applied is time-consuming. Although some of the tests can be carried out parallely, the procedure takes a long time due to the complexity of the contaminations. The experience shows that in the case of hydrocarbons at least 4 - 6 months are necessary.

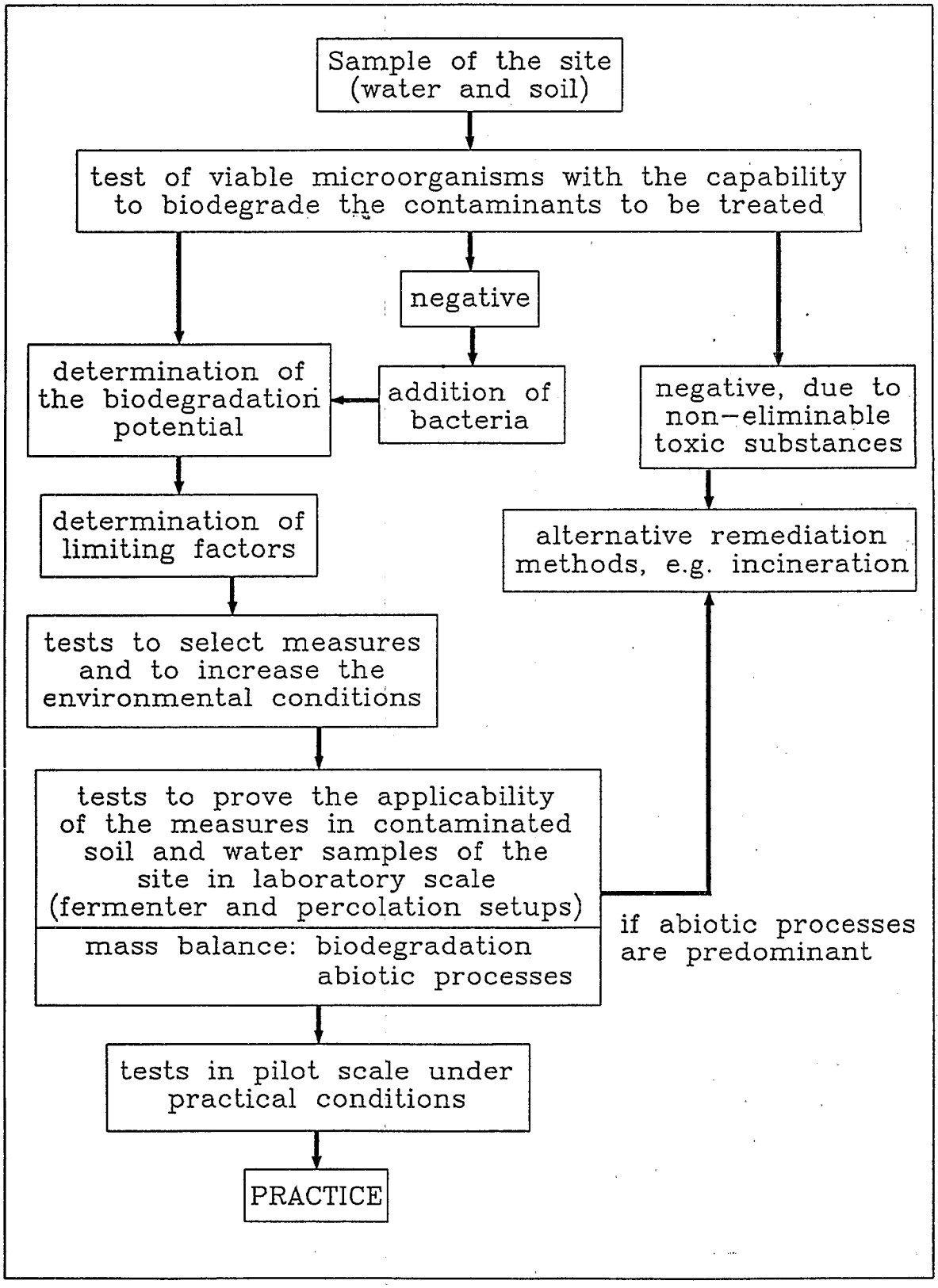

Figure 2: Procedure in the Application of Bioremediation

4. Mixed Contaminations

Contaminations are generally named after the main substance polluting the site (e. g. contamination with chlorinated hydrocarbons etc.). Most contaminations, however, are caused by a mixture of pollutants, i. e. soil and groundwater are contaminated to a different degree with a variety of chemical substances. The occurrence of a single substance is an exception which is usually confined to contaminations after transportation accidents. Single substances, however, can be dealt more easily than a mixture of substances.

Typical examples of a mixed contamination can be found in abandoned gas works. Analyses of soil and seepage water samples often show high amounts of pollutants, as the maximum concentrations given in Table 3 prove. The high contamination with aromatic hydrocarbons, such as benzene, toluene, xylene, as well as polycyclic aromatic hydrocarbons (PAH) is well demonstrated. Furthermore, high values of cyanide and ammonium are to be found. The water partly shows high concentrations of heavy metals and sulphates.

Table 3: Concentrations of Pollutants in Soil and Seepage Water of Abandoned Coke-oven and Gas Work Plants (Maximum Concentrations found so far)

Soil	Benzol	ca. 5000 mg/kg
	Toluol	ca. 5000 mg/kg
	Xylol	ca. 5000 mg/kg
	Naphtalene	ca. 5000 mg/kg
	Phenanthrene	ca. 5000 mg/kg
	PAH (Sum)	ca. 1000 mg/kg
	Cyanides (complexed)	ca. 1000 mg/kg
	Phenols	ca. 1000 mg/kg
Water	Aromats According to Maximum Solubility	
	Sulphate	ca. 3000 mg/l
	Nitrate	0 mg/l
	Oxygen	0 mg/l
	Ammonium	ca. 20 mg/l
	Iron	ca. 20 mg/l
	Manganese	ca. 10 mg/l

This example illustrates the mutual influences of the pollutants on microbial

degradation.

Substances such as ammonium, which in the first place is no pollutant, can impede the mineralization of hydrocarbons. Nitrification processes, i. e. the oxidation of ammonium to nitrite or nitrate, consume oxygen, which is then no more available for the oxidation of the pollutants themselves. This is also true for readily degradable organic substances which compete with the contaminants for the oxygen.

Oxidation of 1 mg ammonium or degradable DOC requires 3 - 4 mg oxygen. Compared to this, the oxygen consumption for oxidation of iron or manganese can be neglected.

Hydrocarbons often show a competitive degradation. BTX-aromats, mineral oils, and PAH probably do not mineralize at the same degradation rate. Better soluble components are in general more readily degraded. According to laboratory and field experiences m- and p-xylene are usually biodegraded a lot slower than other BTX-aromats. In some cases, biodegradation of m- and p-xylene does not start until the concentration of the other contaminants have sunk to a minimum.

High concentrations of heavy metals can have a negative effect on bacterial growth. Contaminations with lead and/or mercury, which often occur in abandoned gas works, are of special importance. Here, a microbiological remediation is out of the question. Even if bacterial strains that resist to heavy metals and mineralize hydrocarbons are increased, soil and groundwater cannot be considered as remediated due to the remaining heavy metals. Presently, there is no biological procedure for the elimination of heavy metals.

Another problem are the cyanides which are found as complexed cyanides in gas works, mostly in the shape of the non-toxic "Prussian blue". Although they do not impede the degradation of pollutants at all, they cannot be mineralized themselves. In contrast, the degradation of free cyanides is known and applied in sewage plants of coke oven works for the elimination of this substance. Chemical analysis for the detection of complexed cyanides is only possible

after special pre-treatment, so that often no difference can be noticed between free and complexed cyanide.

Mixed contaminations, however, also show a mutual influence in a positive way. Aliphatic chlorinated hydrocarbons (e. g. trichlorethene) are aerobically degradable in the presence of BTX-aromats. This mechanism is based on co-metabolism which certainly plays an important role in the degradation of contaminants. The knowledge about these processes, however, is still very little, so that the corresponding procedures can not yet be applied on a large scale. A mixed contamination with pollutants of high and low solubility in water (e. g. BTX-aromats and PAH) can sometimes bring about a process in which the component with low solubility is mobilized by the well soluble one. This might increase the availability of the components with low solubility to the microorganisms and thus fasten degradation.

Co-metabolic processes might also be significant in this case. The importance of the mentioned processes for natural degradation and the question whether these processes can be used for remediation measures cannot be assessed with the present state of knowledge. As a conclusion, the following can be stated:

From the analytical data of a water and soil contamination a possible microbial remediation procedure can be concluded. Degradability of a substance alone does not make sure that it is in fact eliminated in a remediation process. In an in-situ as well as an on- and off-site procedure all biological, chemical, and geohydrological factors have to be considered, most of which are not even known. When bioremediation measures are planned, small scale experiments in the shape of controllable on-site and in-situ fields are necessary in the first place. Their size is determined by the distribution of the pollutants and the geohydrological conditions.

All contaminants are individually composed and therefore require individual treatment. The type and size of contaminations in connection with geohydrological conditions can only be hints to the different possibilities of remediation.

5. Toxicity and Mutagenicity

Not only toxicity and mutagenicity of the initial substances are decisive for the risk assessment with relation to the environment, but also the development of these parameters during a remediation measure. Experiments in our own laboratory as well as of other research groups have shown that the toxicity of metabolic products is often higher than of the initial pollutants.

An example for this are the results of an own degradation experiment, given in Figure 3 a and 3 b.

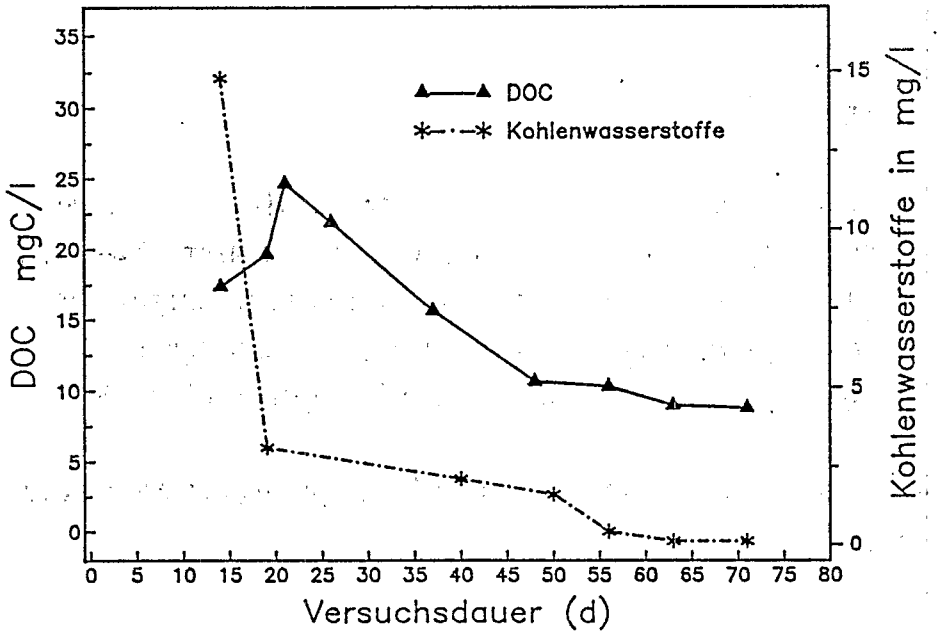

Figure 3 a: Degradation of a Mixture of Gaswork-specific Contaminants (Decane, Hexadecane, Pristane, Naphthalene)
- Development of DOC

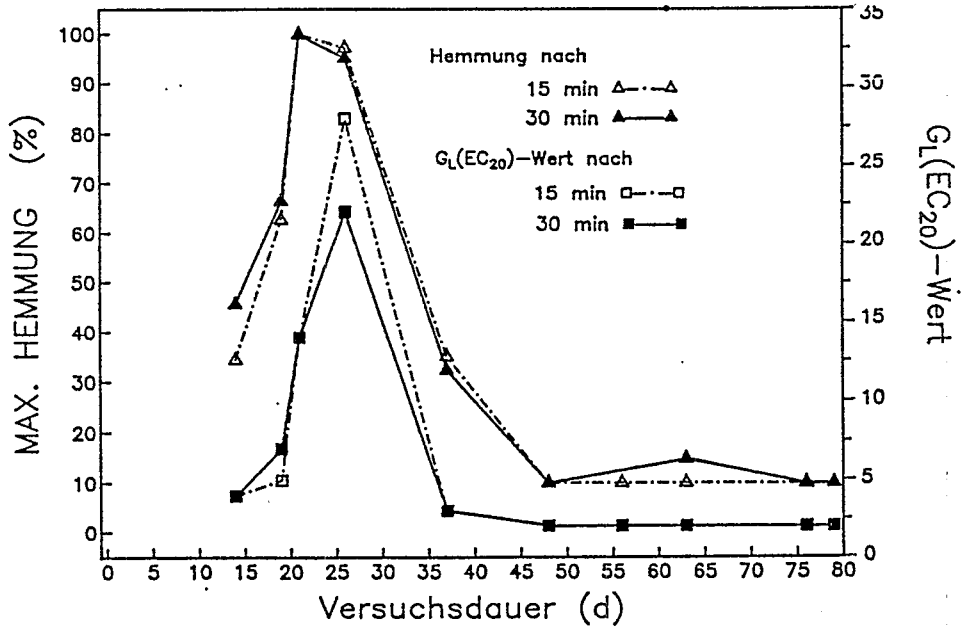

Figure 3 b: Degradation of a Mixture of Gaswork-specific Contaminants (Decane, Hexadecane, Pristane, Naphthalene)
- Development of Toxicity (Microtox)

The problem arising in this context is the fact that the metabolites in general are soluble in water and can therefore - without adequate safety measures - drain off into the groundwater.

If these substances are more toxic or mutagenic than the less mobile initial products, the risk of a negative impact on the environment through remediation is rather high. So far, there are only few data about the behaviour of metabolic products, which are generally difficult to detect.

In the procedure to test the applicability of biological measures described in chapter 3 the registration of the metabolites and their toxicological importance should especially be taken into consideration.

6. General Conclusions

The NATO/CCMS fellowship programme allowed me to get into contact with different research groups dealing with similar topics than I do. All these groups are still working on solutions for the problems in order to get a better understanding of the limiting factors and to overcome the difficulties mentioned above. This will, in future, allow a more successful application of microbial methods in the remediation of contaminated sites.

Although biological treatment of contaminated soil and groundwater is already in use worldwide even on a large scale, there are still a lot of questions to be answered about the success and further optimization of the processes. The facts and data of the different measures applied in special cases are published in detail esewhere. In order to improve the systems, it is of great interest and importance to know more about the problems we have to tackle and which occur during remediation measures based on biodegradation.

One of the main problems we have to overcome is the bioavailability of the contaminants for the bacteria. The limiting factors are both solubility of the pollutants (biodegradation only occurs in the aqueous phase) and spatial separation mainly due to geological conditions.

Furthermore, the question of additional and/or alternative electronacceptors has to be taken into consideration. A lot of research has to be done to decide which contaminants can be biodegraded with different oxygen sources.

One of the main problems in the frame of biodegradation is based on the mixture of several different pollutants contaminating a site. A lot of work has to be done to be able to mineralize all pollutants in an acceptable time and with acceptable efforts. It is not reasonable to eliminate just one substance out of a whole consortium. Therefore, the application of different methods, of which microbial degradation is one, is advisable.

Last but not least, there is the problem of metabolites which has to be solved. If metabolites are not avoidable the risk assessment of them has to be determined and taken into consideration when bioremediation is applied.

From this point of view, future research should mainly be focussed on the questions mentioned above, which have to be considered with respect to the application of microbial methods.

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Sunlight-Induced Inactivation of Halogenated Aromatics in Aqueous Media: Photodegradation Study of a Benzotrifluoride and an Evaluation of Some Industrial Methods

SUNLIGHT-INDUCED INACTIVATION OF HALOGENATED AROMATICS IN AQUEOUS MEDIA: PHOTODEGRADATION STUDY OF A BENZOTRIFLUORIDE AND AN EVALUATION OF SOME INDUSTRIAL METHODS

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ABSTRACT

Aqueous solutions of 4-chloro-3-nitrobenzotrifluoride (NCTT) were irradiated with a high intensity solar reactor. No NCTT disappearance was observed in pure water, or in the presence of 2 % cetylpyridinium chloride alone or mixed with 2 % cetylpyridinium chloroiodide. However, photodegradation was observed by adding the semiconductor TiO_2 (anatase powder). NCTT concentration diminished by 50 % within the first 45—60 min of irradiation, but the disappearance rate decreased with increasing length of irradiation. The experimental data were fitted with mathematical models; the linear combination of a simple exponential with a linear function provided the best fit.

In addition to the experimental activity carried out in our laboratory, this paper briefly describes photochemistry and photolysis equipment and application for industrial purposes. Two examples of photolytic processes utilized for detoxification operations are also reported.

Keywords: aqueous photodegradation, benzotrifluorides, photodegradation modelling, environmental reclamation, waste detoxification.

Note The present article was prepared for the Fifth International Conference of the NATO/CCMS Pilot Study on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater" (Washington, DC, November 18-21, 1991). The article is part and a continuation of the experimental project "Sunlight-Induced Inactivation of Halogenated Aromatics in Aqueous Media", which was presented by A. di Domenico in the November 1988 Bilthoven meeting of the same Pilot Study and is currently in progress in our laboratories. The former presentation should be referred to as a background for most of the information omitted here.

INTRODUCTION

In recent years the role of semiconductors in environmental and man-induced photodegradation of halogenated organic compounds has stirred much interest [Oliver et al., 1979]. In fact, it has been shown that aqueous suspensions of finely powdered semiconductors such as TiO_2, SnO_2, and ZnO—naturally occurring constituents of sediments and clays—can catalyze photochemical processes in chemicals otherwise not light-labile [Pelizzetti et al., 1985; Barbeni et al., 1985, 1986].

The range of the economically important applications of photochemistry—and photocatalysis—is very wide [Bard, 1979; Bloomfield and Owsley, 1982; Pelizzetti, 1986; Glatzmaier et al., 1990a,b]. Among these applications, we highlight: production of fuels from inexpensive raw materials, activation of selective pathways in the field of organic synthesis (e.g. catalysts determining special steric configuration and high chirality), inactivation of hazardous waste or toxic chemicals (e.g. dechlorination and mineralization of chlorosubstituted heteroaromatics), and sunlight-induced transformations (including natural degradation processes) of environmental contaminants.

The present article has been developed as a continuation of a former study [see footnote on page 1] and is composed of two distinct sections. In the first, preliminary results of a pilot investigation on chemical photodegradation carried out in our laboratory are reported. The second section deals specifically with examples of industrial technology in photochemistry and two cases of light-induced processes to inactivate toxic chemicals in diverse matrices.

LABORATORY INVESTIGATION

In the past, 4-chloro-3-nitrobenzotrifluoride (NCTT; Figure 1) and some other benzotrifluorides were detected in a groundwater system used for private and agricultural supplies in northern Italy. Contamination had been provoked by improper disposal of a chemical waste coming from a local factory producing intermediates for pharmaceutical products and agrochemicals [Carli et al., 1983].

Since we are currently investigating sunlight-based photochemical techniques for detoxification of environmentally important halogenated aromatics, we thought it of interest to use NCTT in a pilot study in order to define specific experimental methods and criteria, as well as a possible approach to select mathematical models suitable for describing photodegradation patterns.

EXPERIMENTAL

4-Chloro-3-nitrobenzotrifluoride NCTT is a stable chemical exhibiting the following chemico-physical properties: molecular weight, 225.6 amu; density, 1.542 g/mL; melting point, -7.5 °C; boiling point, 222 °C [Carli et al., 1983]. NCTT has a moderate acute toxicity in laboratory animals and a mutagenic potential (UDS test) [Benigni et al., 1982].

The UV spectra of NCTT (Figure 1) were recorded in high purity water and in n-hexane using a standard quartz cell. The absorbance reading for both solvents was negligible over the full spectral range. Only absorption bands below 400 nm were visible, with the following maxima: (a) in water, $\varepsilon = 1.48 \times 10^4$ and 3.71×10^3 L/(mol x cm) at $\lambda = 215 \pm 1$ and 252 ± 1 nm, respectively; (b) in n-hexane, $\varepsilon = 1.86 \times 10^4$ and 2.29×10^3 L/(mol x cm) at $\lambda = 213 \pm 1$ and 284 ± 1 nm, respectively [De Felip et al., 1990, 1991].

In order to assess the water solubility of NCTT, a saturated solution was prepared by adding an excess amount of the chemical to 0.5—1 L high purity water in a 1 L glass-stoppered Erlenmeyer flask. The mixture was protected from light and stirred continuously for 24 h, and then allowed to rest for the next 24 h prior to sampling. The latter was carried out by immerging the tip of a pipette into the saturated solution body, well beneath the surface but away from the undissolved chemical on the flask bottom; the pipette was retrieved and wiped externally before releasing the volume collected. For each solubility trial, 1.00 ± 0.01 mL of the saturated solution was sampled and combined with n-hexane (50.0 ± 0.1 mL) in a 100 mL glass-stoppered Erlenmeyer flask; a mild stirring was begun, and then 5 g of a 1:4 $NaCl$-Na_2SO_4 mixture were slowly added. The organic phase was left to dry overnight. Determination of the NCTT level in the n-hexane matrix was performed by gas chromatography. NCTT was found to be soluble at a level of 174 ± 12 mg/L (N = 12) at 20 °C [De Felip et al., 1990, 1991].

An NCTT mother solution was obtained by transferring an aliquot (1/3 to 1/2 of a liter) of the saturated solution to a 1 L (tolerance, ± 0.4 mL) glass-stoppered volumetric flask, followed by taking the volume up with high purity water. For photodegradation trials, an amount of this solution was added with TiO_2 (2.0 ± 0.1 g/L), or any one of the other reagents. All standard matrices were screened from light with aluminum foil and stirred continuously. NCTT, from Rimar Engineering (Trissino (Vicenza), Italy), was >95 % pure, as confirmed by NMR (main impurity: 4-chloro-3-nitrotoluene).

High purity water High purity water was obtained by first refluxing alkalinized distilled water in the presence of $KMnO_4$ for several hours in a glass apparatus. Refluxed water was then distilled off and collected. Water purity was checked spectrophotometrically [De Felip et al., 1990, 1991].

Chemicals Analytical grade n-hexane was obtained from Carlo Erba (Milan, Italy) and used after distillation in a glass apparatus. Carlo Erba also provided analytical grade anhydrous NaCl, NaOH, Na_2SO_4, and $KMnO_4$. High purity TiO_2 (anatase) powder, for use as a semiconductive catalytic support for NCTT [Barbeni et al., 1985, 1986], was from Aldrich Chimica (Milan, Italy). Cetylpyridinium chloride was furnished by Chemical Market Research Service (Eschen, FRG); cetylpyridinium chloroiodide was made in the laboratory [Botré et al., 1979].

Glassware Pyrex glassware was used throughout. Items were carefully cleansed with detergent and water, rinsed with distilled water, and kept at 250 °C overnight prior to use.

The cells for irradiation (Figure 2) were dark flat-bottomed cylinders (o.d., 3.0 cm; volume, 20 mL) with an open flanged top to accomodate a transparent quartz disk (o.d., 4.0 cm; thickness, 2.0 $\pm$ 0.1 mm), later sealed with high vacuum sealant to prevent volatilization losses [De Felip et al., 1990, 1991].

Apparatus A Hewlett-Packard (Palo Alto, California) Model 5710 gas chromatograph, equipped with an electron capture detector (GC/ECD) and an HP-5 10 m long 0.53 mm i.d. fused silica column, was used for analytical assessment. GC conditions were: (a) injection block, 200 °C; (b) oven, 130 °C; (c) detector, 300 °C; (d) carrier and makeup (for both, argon-10 % methane mixture) flow rates, 2.0 and 25 mL/min, respectively.

A "Solarbox" photoreactor (Figure 2) was purchased from CO.FO.ME.GRA. (Milan, Italy). Samples, placed in the center of the metal holder and irradiated singly, were kept at 15 °C by partially immerging the cells in water cooled by a Haake (Karlsruhe, FRG) Model F3 heat exchanger [De Felip et al., 1990, 1991].

NCTT assessment In general, a portion (0.50 or 1.00 mL) of the aqueous matrix containing NCTT was pipetted out and mixed with 50 mL n-hexane in a 100 mL glass-stoppered Erlenmeyer flask. While stirring mildly, the organic mixture was combined with a 5 g NaCl-Na_2SO_4 (1:4) mixture and allowed to dry overnight. For quantification, a 0.50 mL volume of the dry solution was transferred to a 10 mL cone-shaped bottom vial and diluted to 5.00 mL with n-hexane; then, a $\leq$2 µL aliquot was injected into the gas chromatograph. Generally, vials were kept sealed with Teflon-lined screw caps. GC/ECD determination was carried out with the external standard technique [De Felip et al., 1990, 1991].

RESULTS AND DISCUSSION

The results of this photodegradation study have been described elsewhere by De Felip et al. (1990, 1991) and are hereafter summarized.

NCTT volatilization loss from TiO_2-added aqueous media was checked by irradiating samples in cells which were completely covered with aluminum foil. Irradiation conditions and lengths (up to 240 min) in the different checks were the same as those later adopted in photodegradation trials. Since the NCTT concentration in unexposed samples (60.1 ± 3.2 mg/L; N = 10) was undistinguishable from the check samples (59.7 ± 3.4 mg/L; N = 10) (Table 1), the cells proved to be satisfactorily vapor-tight.

During photodegradation trials, which took several days, the stability of illumination energy was spot-checked at different irradiation times (from 0 to 240 min) by placing the gauge head at a fixed position next to the sample where illumination was optimized. When all readings were compared, it was found that the energy had remained constant (28.1 ± 0.7 W/m^2; N = 20) throughout the study (Table 1).

Experimental conditions were as described above; independent trials were repeated three to ten times and provided the outcomes of Table 2. For each time, data expressed in mg/L (measured concentrations) were averaged and then normalized against the mean concentration value of unexposed (t = 0) samples; standard deviation of normalized values was estimated via the error propagation method [Kolthoff et al., 1969]. Before normalization, single data were checked so as not to bring any biases into the final data set.

Normalized data appear also in Figure 3, where three regression curves are shown. It may be observed that 50 % of the initial NCTT disappeared within the first 45—60 min; however, the disappearance rate became less with increasing irradiation time. The following four mathematical models were used to fit the data: (a) an exponential function [I], and the linear combinations of (b) I and a steady state function [II], (c) I and a linear function [III], and (d) two Is [IV]. Aside from the latter, which did not provide a converging regression, the other models reached convergence yielding significant fittings (Table 3; Chi-square test) [Hoel, 1971]. Fittings were performed with the derivative-free nonlinear regression BMDP-AR Program (BMDP Statistical Software, Inc., 1987, Los Angeles, California). From Figure 3, it is evident that only III fits the experimental points closely, while the other models do not, especially for the longer irradiation times. The regression equation of Model III is:

$$F(t) = (0.543 \pm 0.059)\exp[-(0.0350 \pm 0.0067)t] + - (0.00100 \pm 0.00034)t + (0.464 \pm 0.060)$$

Mathematical modelling may have several utilizations. For instance, III reflects two distinct analytical trends: therefore, it may be presumed that—under the experimental conditions adopted in this investigation—NCTT photodegradation is associated with at least two processes with different (virtual) kinetics. However, as no data were

taken for irradiation times >240 min, it cannot be excluded that other kinetic trends, if any, went undetected: that is, the modelling may be considered reliable only over the range of the available experimental data and additional data should be gathered to improve the predictive quality of the model for longer exposures. As shown in the caption of Figure 3, a specific use of the regression equation may be that of predicting how long it takes for given amounts of NCTT to disappear. Clearly, once the photochemical system has been characterized according to the interactive components, the modelling approach might turn out to be a useful tool for describing and predicting the photochemical behavior of a compound in both a natural and a man-controlled environment.

NCTT photochemical behavior was studied also in different media. As could be predicted on the basis of its spectral features, no NCTT loss was observed in pure water. Similarly, losses were not observed when TiO_2 was replaced with 2 % cetylpyridinium chloride or with a mixture of 2 % cetylpyridinium chloride and 2 % cetylpyridinium chloroiodide [Botré et al., 1979], both producing micellar matrices. As to the latter, this finding was expected.

INDUSTRIAL PHOTOCHEMISTRY

It has been reported [see footnote on page 1] that photochemical energy generally causes reactions from the potential energy surfaces of electronically excited states: because of that, these reactions may be highly selective and very useful in organic synthesis. The electronically excited molecules may react by fragmenting into neutral molecules or free radicals, by electron transfer, by isomerization, or by addition to some other molecule. Complicated molecules may be obtained through one or a few steps directly from relatively inexpensive raw materials and at low temperatures. In fact, temperatures near absolute zero appear to have been used, although the majority of industrial photoreactions occurs in the range 0—125 ^{o}C [Bloomfield and Owsley, 1982].

LIGHT SOURCES

To be of interest for industrial uses, a light source must have the following characteristics: high intensity in the desired spectral region (for inactivation processes, generally between 250 and 400 nm), long life, emission stability, ease of operation, appropriate physical dimensions, and minimum amount of necessary auxiliary equipment. Man-made light sources have generally been developed for production purposes; however, as will be shown later, they may also be used for inactivation of hazardous materials.

Mercury arc lamps There are several lamps available on the market, but in general mercury arc lamps meet all the above requirements [Koller, 1965; Bloomfield and Owsley, 1982]. Mercury is rather inert, does not react with the glass and the electrode materials, and produces an emission spectrum which is rich in the UV light component (Table 4). The characteristics of the lamp (bulb shape and material, electrodes, mercury vapor pressure, and starter) are chosen to meet the overall features of the photochemical reactor and its specific uses.

The mercury emission spectrum contains a very large number of lines, whose relative intensities depend upon vapor pressure (high, medium, or low) of the metal, arc tube diameter, and applied current. At medium operating pressures (<2 atm; 1 atm = 0.1 MPa), all emission lines of greater interest—at 253.7 (mercury resonance line), 265.2, 280.4, 296.7, 302.2, 313.1, 365.4, 404.7, 435.8, 546.1, and 578.0 nm—appear distinctly over the dim continuous background radiation. However, the lines broaden and the background brightness increases with increasing pressure, until the spectral distribution approaches that of a continuum (approximately at 285 atm), where all traces of the line character of the spectrum disappear. As pressure increases, the 253.7 nm line intensity diminishes due to self-quenching: low pressure (<0.001 atm) lamps emit this radiation almost exclusively.

In industry, many photochemical reactions are carried out by employing high pressure mercury arcs operating in the range 2—110 atm. These lamps may have a high input wattage (up to several or tens of kW) and require an efficient cooling system to dissipate the heat. For lamps running at lower pressures (powers of up to 30 W), air cooling may be sufficient as heat evolution during operation is low. Medium pressure mercury arcs are used to simulate the UV component of sunlight (especially the B-section) by filtering out any radiations <280 nm. Low pressure lamps are mostly employed in sterilization operations.

Electrodeless mercury arc lamps These light sources emit as a result of the metal being subjected to 2450 MHz microwave irradiation [Bloomfield and Owsley, 1982]. As compared with conventional mercury arcs, they have the advantages of longer lifetimes, better safety, air-cooled operation, and shorter startup time. In addition, like the conventional ones, their spectral energy distribution may be changed by using additives (e.g. xenon).

Xenon arc lamps For many years mercury arcs have been the most widely used high energy light sources. However, during the last three or four decades there has been a notably increasing tendency to utilize high pressure xenon arcs, particularly in industry and technology.

Between 10 and 40 atm, xenon arcs are efficient sources of intense visible and UV radiation with a brightness comparable to that of a

carbon arc. Although in the 800—1100 nm region some strong lines are visible, at these pressures the xenon spectrum is substantially a continuum extending into the UV and IR regions. The lower emission limit of a lamp is normally set at around 170 nm due to the fused quartz envelope. Lamps with input power between 0.15 and 20 kW are commonly marketed. Mixed atmospheres of mercury and xenon produce arc spectra in which the mercury lines, although preponderant, are integrated with the IR components of xenon spectrum [Koller, 1965].

Sunlight As was reported previously [see footnote on page 1], the sun may be presumed to be a convenient light source in some chemical syntheses and possibly a useful tool in environmental and man-piloted degradation processes. The wavelength distribution reaching the earth's surface extends from approximately 300 nm to the far infrared. The minor fraction of this distribution at wavelengths <400 nm has great importance in photochemistry because of the high energy associated with it. A few facts about sunlight features and availability are recalled in the following.

The earth's atmosphere practically absorbs all of the radiation of wavelenths <295 nm which, however, is available in space (Table 5). Indeed, the solar UV intensity at the earth's surface very strongly depends on a number of factors including: time of day, time of year, latitude, elevation above sea level, atmospheric turbidity, and thickness of the ozone layer. The parameter named "air mass", M, is a common denominator for the first four factors as it provides a measure for the thickness of the layer of atmosphere the solar radiation traverses to hit the earth's surface in a given area: the larger M, the larger the amount of energy of the incident light absorbed by the atmosphere. When the sun is directly overhead (in the zenith), the length of the path of the radiation through the atmosphere is at its minimum: at sea level, M is set equal to 1 and is >1 for any other position of the sun. Outside the earth's atmosphere, M is 0 [Koller, 1965].

While traversing the atmosphere, sunlight undergoes considerable scattering. As a result, a significant amount of UV radiation reaches the earth's surface from the sky as well as directly from the sun (Table 5). Depending on the hour of the day, the magnitude of one component may be greater or smaller than the other's. However, over an entire day the two magnitudes are comparable.

On the whole, it may be envisaged that for an eventual year-round use in photochemistry, sunlight would be most effective in dry tropical areas elevated as much as possible above sea level and characterized by a high incidence of clear days. Of course, a hole in the overhead ozone layer would also be of help!

For specific uses (e.g. laboratory studies, solaria), sunlight may be simulated with man-made light sources. It is relatively simple to

match any limited region of the solar spectrum, but the exact duplication in its entirety is a more difficult problem. For instance, mercury arcs are deficient in the red and infrared regions (Table 4), whereas xenon arcs require correction at both ends of the spectrum. In general, sunlight is duplicated with a degree of approximation which is good for many purposes by using a combination of arcs, incandescent lamps, and filters.

REACTORS

Basically there are two different types of setups for photochemical processes. In one case, the light source is a long cylinder surrounded by a cooling jacket and immersed in the reaction medium (generally, in a liquid form). In the other case, the reaction medium is irradiated by a lamp placed outside, whose light is focused on the medium by means of an appropriate reflector to avoid excessive loss of radiated energy. Further, the reaction can be either batch or continuously operated.

Although developed especially for production purposes [Bloomfield and Owsley, 1982], it is appropriate to provide a short description of the main types of photochemical reactors and of their possible use in the light-induced inactivation or trasformation processes of chemicals. Figures 4—6 have been redrawn from the originals (cited authors) and somewhat simplified.

Batch reactor A typical apparatus (Figure 4) is made of a large container equipped with one or several light sources isolated from the atmosphere and ventilated by a nitrogen flow. However, a larger amount of heat is generally removed by flowing water between the quartz inner wall and the quartz or filter glass outer wall which make up, together, the lamp jacket. The cooling water may be replaced by a solution optically active as to modify the overall spectral quality of lamp emission. The container can also dissipate excess heat through a heat-exchange outer jacket. The batch chemicals are stirred mechanically and, if necessary, kept under an inert gas. On the other hand, a gaseous reactant may be insufflated into the chemical mixture through the same gas inlet.

As the light output of a lamp is associated with several prominent emission lines or bands, different concurrent photochemical reactions—requiring energy in each wavelength region—could be performed at the same time by creating appropriate concentric optical niches surrounding the lamp. However, even when the energy radiated by the lamp is exploited at best, some 50—65 % of the electric energy supplied to the lamp is lost as heat (to be removed by a cooling system).

Flow reactor Continuous reactors (Figure 5) are used in reactions characterized by high quantum yields. They can also be used in the batch mode and—because of their flexibility—are very useful in studies at pilot plant level.

Elliptical reflector photochemical reactor In this type of reactor the light source is placed outside of the reaction mixture (Figure 6). This reactor's design is very simple and, because of that, lends itself successfully to laboratory uses and preliminary investigations on photochemical processes despite the fact that the radiated energy cannot be used as efficiently as in other reactors.

INACTIVATION OF TOXIC WASTE

A number of studies have shown that hazardous chlorinated dibenzodioxins (PCDDs) are rapidly degraded by the UV radiation present in sunlight or from an artificial source [see footnote on page 1]. For the process to take place, PCDD molecules must be exposed to light in the presence of a substance acting as a hydrogen-donor. What follows provides examples of photolytic processes applied to the inactivation of two specific PCDD members—the nontoxic 1,2,3,4- and the highly toxic 2,3,7,8-tetrachloroidibenzodioxins (also known as TCDD or "dioxin")—in waste and chemical sludge. Indeed, aside from incineration, the only PCDD destruction method to be employed on a reasonably large scale has been photolysis.

Solar detoxification In recent years, the US Department of Energy has undertaken the development of solar detoxification technologies as part of a unified project managed by the Solar Energy Research Institute (SERI) in Golden, Colorado, in conjunction with Sandia National Laboratories. The SERI Project Manager, John V. Anderson, has provided the following synopsis of the overall objectives of the project (see footnote on page 11): "to identify and advance new applications for early utilization of solar technologies, and to address a growing national and international need for advanced, innovative technologies aimed at environmental cleanup". The above technologies are concerned with (a) treatment of hazardous chemicals in aqueous media and (b) destruction of chemicals in the gas phase. Development of commercialized solar detoxification technology is expected by the mid-1990s.

The cited activities would probably deserve a larger space in this presentation. However, owing to the vastness of the matter and especially the fact that the SERI endeavor is still relatively young, we will postpone the matter to another occasion and mention exclusively an example which also has relevance with the issues of our own project, the "Photox" detoxification system applied to the tracer 1,2,3,4-tetra-

chlorodibenzodioxin [Glatzmaier et al., 1990a,b]. The objective of the work, conducted in both laboratory and field tests, was to demonstrate that concentrated solar energy can be used for destruction of hazardous chemicals with a very high efficiency (99.9999 %) due to the combined effect of heat and light.

For the study—which has so far proven successful—a photochemical reactor was built and utilized. The vaporized chemical, in the presence of air, was subjected to temperatures between 750 and 1000 ^{o}C and flux levels of concentrated sunlight in the range 500—1000 kW/m^2, an energy level approximately three orders of magnitude greater than normal sunlight. The sample size of the tracer was chosen to generate a dilute solution in air which is typical of processes for decontaminating TCDD-laden soils. Tests also proved that the energy in the 300—400 nm wavelength region of the solar spectrum—although approximately only 2 % of the total energy of the incoming flux—determined a significant enhancement of the destruction reaction rate.

TCDD photolysis at Syntex In 1969, Syntex Agribusiness, Inc. (Springfield, Missouri) bought a chemical plant in Verona, Missouri, to manufacture animal feed additives. Part of the plant and property had been leased by the previous owner to another company which produced trichlorophenol and hexachlorophene. In 1971 this company went out of business and abandoned the plant. Only in 1974 did Syntex find out that the company had also abandoned on the property a large steel tank containing over 16 m^3 (approximately 21 t) of a dark chemical sludge laden with some 300—400 mg/kg (ppm) of deadly TCDD (on the whole, approximately 7.3 kg). After a cost-to-benefit evaluation, Syntex decided it would be best if they disposed of the waste and TCDD in the safest manner. The whole project lasted six years and entailed many different operations which included: assuring the security and safety of the storage tank until a decision could be made on how to handle the matter, choice of disposal method, and development and application of the photodegradation process [Anonymous, 1980; Worthy, 1983].

Syntex soon realized that, for various reasons, they could not ship the contaminated waste elsewhere for treatment (e.g. incineration), and started exploring the possibilities of on-site destruction. They engaged a company known to be experienced in environmental problems and management of hazardous waste. A committee of experts was formed to obtain independent judgement and guidance. The US Environmental Protection Agency as well as other US and Missouri state health and safety agencies were also involved throughout the phases of the project. After extensive evaluation, the photolytic method was chosen—not only as economically feasible to Syntex at a cost of US$

Note From the article by J.V. Anderson, H. Link, M. Bohn, and B. Gupta "Development of US Solar Detoxification Technology: An Introduction".

500,000 for equipment and installation, but especially because it seemed to guarantee the highest level of safety for personnel, public health, and the environment. In fact, it was a low pressure, low temperature, fully closed system presenting minimal human exposure and minimal release into the environment. In addition, several special safety procedures were incorporated into the system.

The approach required that TCDD first be separated from the waste by hexane extraction of 600 L sludge batches. For this step, some 5.8 m^3 of solvent were employed. After the mixture was stirred for several hours, the heavy residue was allowed to settle and the TCDD-containing organic layer was drawn off. The hexane extract was then exposed to high intensity UV light generated by an array of eight 10 kW mercury arc lamps. TCDD was photolytically broken down and the solvent distilled for recycling within the process. The sludge and aqueous waste left from the extraction process had only very minor amounts of TCDD (overall removal efficiency, >99.9 %) and were disposed of accordingly. The photodegradation efficiency was estimated at >99.97 %. The entire disposal process lasted approximately 11 weeks.

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Figure captions

Figure 1 UV spectra of NCTT (15.0 ± 0.1 mg/L; 20 °C) in high purity water (a) and n-hexane (b) were recorded with a Hewlett-Packard (Palo Alto, California, USA) Model 8452A diode-array spectrophotometer and a standard 1 cm lightpath cell. Instrumental conditions for spectra acquisition were: spectral bandwidth, 2 nm; wavelength accuracy, ±1 nm; full spectrum (190—820 nm) scan time, 0.1 s. Absorbance of both solvents was negligible over the full spectral range. NCTT appears to exhibit absorption bands below 400 nm only.

Figure 2 "Solarbox" photoreactor. The apparatus was equipped with a 1.5 kW xenon lamp and a filter system to cut off light <300 nm. Illumination energy was monitored with a gauge (from CO.FO.ME.GRA.) responding to 295—400 nm light. When the lamp was on, the irradiation chamber was ventilated to disperse the heat. For photodegradation experiments, samples in irradiation cells were placed one at the time in the center of the holding plate. This setup may be reasonably compared to that shown in Figure 6.

Figure 3 Photodegradation induced by simulated sunlight of aqueous NCTT in the presence of suspended TiO_2. Normalized experimental data and regression curves of Models I, II, and III are shown. With reference to Model III (mean estimates), it might be predicted that NCTT photodegrades by 90, 99, or 99.9 % after 360, 450, or 460 min irradiation times, respectively. For such estimates, it was arbitrarily assumed that there was no change in the kinetic trend for irradiation times >240 min.

Figure 4 Batch photochemical reactor. Higher wattage lamps are more efficient in producing a useful light emission up to approximately an input power of 10 kW. At that point, a decrease in UV emission efficiency (einsteins/(kW x hour)) is observed. Therefore, if the reactor is designed to exceed a 10 kW input power, an array of lamps is normally arranged. Lamps immersed in the reaction medium improve quantum efficiency by avoiding excessive scattering, reflection, or dispersion of light. In the picture, both lamps and reaction medium are cooled to avoid overheating.

Figure 5 Flow photochemical reactor. Continuous reactors are used in high quantum yield reactions for vapor, liquid, or mixed media. Contact times are short and high reaction rates are achieved. The heat generated by the light source is carried away by appropriate cooling, in the case shown, by ventilating the lamp well with air or nitrogen. Owing to the continuous flowing of the chemical medium, cooling is generally required solely to remove heat from the light source.

Figure 6 Elliptical reflector photochemical reactor. This is a system in which the light source is outside the reaction medium. To maximize utilization of the emitted light energy, radiation is focused upon the reaction vessel by an enveloping elliptical, highly reflective casing, lamp and vessel being placed at the focuses of the ellipse. Although heat is removed from the casing inside by efficient ventilation, the temperature of the reactant mixture can also be kept under control through an additional cooling system.

Figure 7 Syntex Agribusiness, Inc. (Springfield, Missouri), used photolysis to destroy highly toxic TCDD in chemical sludge waste contaminated at levels between 300 and 400 mg/kg (ppm). For the operation, over 16 m^3 of sludge were extracted batchwise with hexane, a common organic solvent. The organic layer was then irradiated with high intensity UV light to break down TCDD. From the process, an overall photo-induced reduction efficiency of >99.9 % was attained; the detoxified solvent was distilled for recycling. The aqueous layer (TCDD < 0.002 mg/kg) and the extracted sludge (TCDD < 0.5 mg/kg) were later disposed of.

Table 1 Stability tests. The left half of the table shows benzotrifluoride concentrations in samples wrapped with aluminum foil before (t=0) and after (t>0) irradiation. The right half shows readings of incident light intensity where this was most intense on the irradiation plate (middle point)

TRIAL	*IRRADIATION TIME (min)*											
	0.0	*30*	*60*	*90*	*120*	*240*	*0.0*	*30*	*60*	*90*	*120*	*240*
	Reactant concentration (mg/L)						*Incident light intensity (W/m^2)*					
1	65.1		63.1				27.9		27.8			
2	59.0				59.0		28.3				28.5	
3	62.3				63.5		29.2				28.9	
4	55.2					53.3	27.5					27.3
5	55.0					56.1	28.6					28.0
6	60.2	61.1					28.9	29.2				
7	62.0	62.9					27.3	27.3				
8	62.3			62.0			27.7			27.6		
9	60.1		58.0				29.0		28.3			
10	59.7					57.8	27.6					27.4
	Means and standard deviations											
t=0 N=10	60.1 ± 3.2 *mg/L*						28.2 ± 0.7 *W/m^2*					
t>0 N=10	59.7 ± 3.4						28.0 ± 0.7					
t≥0 N=20	59.9 ± 3.2						28.1 ± 0.7					

Table 2 Photodegradation induced by simulated sunlight of the benzotrifluoride in aqueous solution in the presence of TiO_2

TRIAL	*IRRADIATION TIME (min)*								
	0.0	*15*	*30*	*45*	*60*	*90*	*120*	*180*	*240*
	Reactant concentration (mg/L)								
1	65.1	48.3	37.5		27.9		21.2		11.3
2	59.0	50.1	37.8		27.0		21.1		14.0
3	62.3	50.0	42.0		31.3		23.3		13.2
4	55.2	50.0	38.4		27.1		21.0		11.9
5	55.0	48.0	38.9		29.4		23.0		12.0
6	60.2	47.5		32.0		26.1		18.7	
7	62.0	45.3		27.4		25.2		18.0	
8	62.3	45.0		29.5		25.0		16.4	
9	60.1	45.0	38.4		24.0		23.4		7.91[a]
10	59.7	46.5	34.0		27.2		22.0		7.80[a]
Mean (mg/L)	60.1	47.6	38.1	29.6	27.7	25.4	22.1	17.7	12.5
SD[b] (mg/L)	3.2	2.1	2.4	2.3	2.3	0.6	1.1	1.2	1.1
VC[c] (%)	5.25	4.34	6.17	7.77	8.16	2.30	4.86	6.66	8.77
N	10	10	7	3	7	3	7	3	5
Normalized mean	1.000	0.792	0.634	0.493	0.461	0.423	0.368	0.295	0.208
SD	0.074	0.054	0.051	0.046	0.045	0.024	0.026	0.025	0.020
VC (%)	7.42	6.81	8.10	9.38	9.70	5.73	7.15	8.48	10.6

(a) Outliers as per Chauvenet's rule
(b) Standard deviation
(c) Variation coefficient

Table 3 Regression analysis data of TiO_2-catalyzed photodegradation kinetics of 4-chloro-3-nitrobenzotrifluoride exposed to simulated sunlight in aqueous medium

MODEL I	*REGRESSION CONVERGENCE CRITERION:*		SATISFIED	
	RESIDUAL SUM OF SQUARES:		2.17E-03	
	CHI-SQUARE OF REGRESSION:		3.69E-01	(DOF=6)
	MEAN SQUARE ERROR:		3.10E-04	
	PARAMETER	*STANDARD DEVIATION*	*COEFFICIENT OF VARIATION*	
	y1 0.932419	0.052596	0.056408	
	k3 0.009980	0.001619	0.162265	
MODEL II	*REGRESSION CONVERGENCE CRITERION:*		SATISFIED	
	RESIDUAL SUM OF SQUARES:		3.17E-04	
	CHI-SQUARE OF REGRESSION:		3.67E-02	(DOF=5)
	MEAN SQUARE ERROR:		5.28E-05	
	PARAMETER	*STANDARD DEVIATION*	*COEFFICIENT OF VARIATION*	
	y1 0.721305	0.036920	0.051185	
	y2 0.276397	0.031402	0.113613	
	k3 0.023138	0.002830	0.122330	
MODEL III	*REGRESSION CONVERGENCE CRITERION:*		SATISFIED	
	RESIDUAL SUM OF SQUARES:		1.37E-04	
	CHI-SQUARE OF REGRESSION:		7.68E-03	(DOF=4)
	MEAN SQUARE ERROR:		2.74E-05	
	PARAMETER	*STANDARD DEVIATION*	*COEFFICIENT OF VARIATION*	
	y1 0.542964	0.059433	0.109459	
	y2 0.463933	0.059677	0.128633	
	k3 0.035038	0.006729	0.192062	
	k4 0.001001	0.000339	0.338789	

Table 4 Energy radiated by spectral region from an unfiltered medium pressure mercury lamp (of the General Electric Uviarc® type)

LAMP FEATURES

Arc current	*3.1 A*
Arc power	*0.25 kW*
Arc length	*8.4 cm*
Lamp length	*18.7 cm*
Lamp envelope material	*Quartz*

Wavelength band (nm)	*Principal lines (nm)*	*Radiated energy (W)*	*Wavelength band (nm)*	*Principal lines (nm)*	*Radiated energy (W)*
220-230		0.45	340-360		0.37
230-240		0.55	360-370	365.4	7.05
240-250		1.20	370-380		0.20
250-260	253.7	3.00	380-400		0.28
260-270	265.2	1.99	400-410	404.7	1.74
270-280		0.37	410-430		0.26
280-290	280.4	1.82	430-440	435.8	4.18
290-300	296.7	1.28	440-540		0.64
300-310	302.2	2.28	540-550	546.1	4.65
310-320	313.1	4.43	550-570		0.29
320-330		0.28	570-580	578.0	5.05
330-340		0.61	580-760		1.09

Total energy radiated in the 220-400 nm region, 26.2 W or 10.5% of input power (over 80% of UV energy carried by the seven strong lines singled out)

Total energy radiated in the 400-760 nm region, 17.9 W or 7.2% of input power

Table 5 Results of solar energy measurements performed at two geographical sites in the US during midday on clear days in midsummer

Solar energy (W/m^2) distribution[a] at Tucson, Arizona; sun in zenith (A) and without atmospheric absorption (B)[b]

λ (nm)	A	B	λ (nm)	A	B	λ (nm)	A	B
292	0.03	1.1	330	3.8	8.7	400	10.9	16
295	0.08	2.4	340	4.2	8.6	420	11.7	16.4
300	0.29	4.1	350	4.6	8.5	450	14.7	20
305	0.71	4.1	360	5.5	9.6	500	15.2	19.9
310	1.1	4.5	370	5.9	9.7	550	14.2	18.2
315	1.8	6.1	380	5.9	9.2	600	12.4	15.7
320	2.4	6.8	390	7.3	11.1	700	8.3	10.5
325	3.5	8.9						

(a) For 10 nm spectral bands centered on the wavelengths indicated

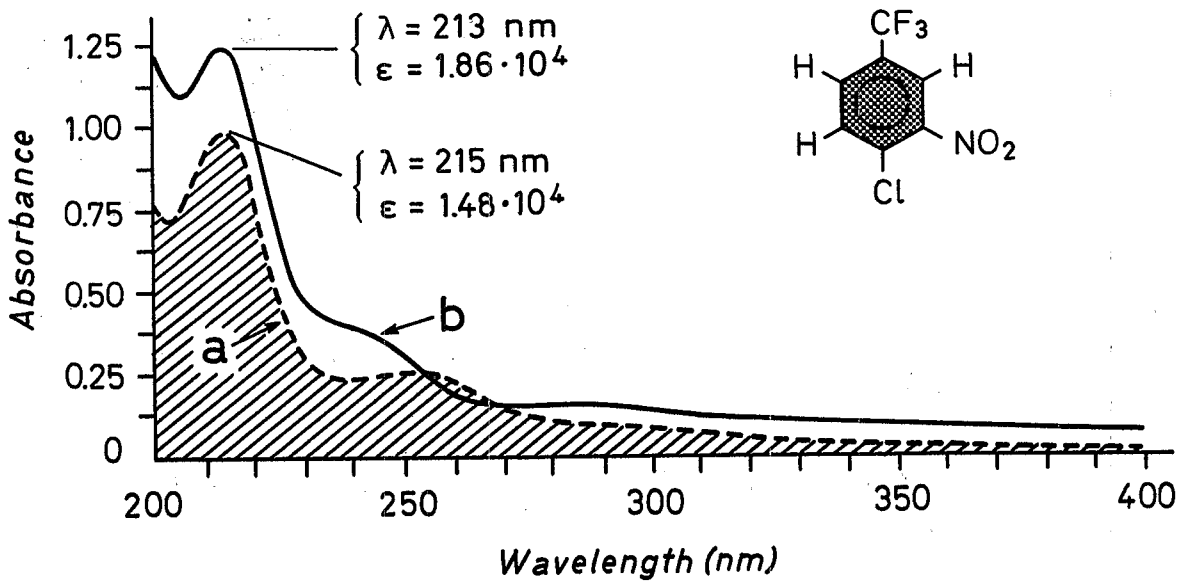
(b) The effect of the atmosphere is most visible toward the shorter wavelengths

Distribution[c] of total solar energy (A) at Cleveland, Ohio, broken down into direct sunlight (B) and sky light[d] (C). Energy in W/m^2

λ (nm)	A	B	C	λ (nm)	A	B	C	λ (nm)	A	B	C
300	0.052	0.026	0.026	450	6.69	4.53	2.16	580	6.46	5.14	1.32
310	0.475	0.24	0.235	460	7.26	4.92	2.34	590	6.32	5.08	1.24
320	1.25	0.65	0.60	470	7.43	5.14	2.29	600	6.21	5.03	1.18
330	2.04	1.08	0.96	480	7.43	5.25	2.18	610	6.05	4.92	1.13
340	2.33	1.26	1.07	490	7.32	5.25	2.07	620	5.96	4.86	1.10
355	2.59	1.44	1.15	500	7.18	5.25	1.93	630	5.82	4.75	1.07
370	3.25	1.86	1.39	510	6.92	5.08	1.84	640	5.66	4.64	1.02
385	3.33	1.92	1.36	520	6.60	4.92	1.68	650	5.56	4.59	0.97
400	4.33	2.68	1.65	530	6.76	5.14	1.62	660	5.46	4.53	0.93
410	5.48	3.39	2.09	540	7.93	5.35	1.58	670	5.51	4.59	0.92
420	6.00	3.77	2.23	550	6.89	5.35	1.54	680	5.72	4.81	0.91
430	6.17	4.04	2.13	560	6.71	5.25	1.46	690	5.64	4.75	0.89
440	6.27	4.26	2.01	570	6.63	5.25	1.38	700	5.49	4.64	0.85

(c) For 5 nm spectral bands centered on the wavelengths indicated

(d) Scattered sunlight radiation. Scattering is greater at shorter wavelengths



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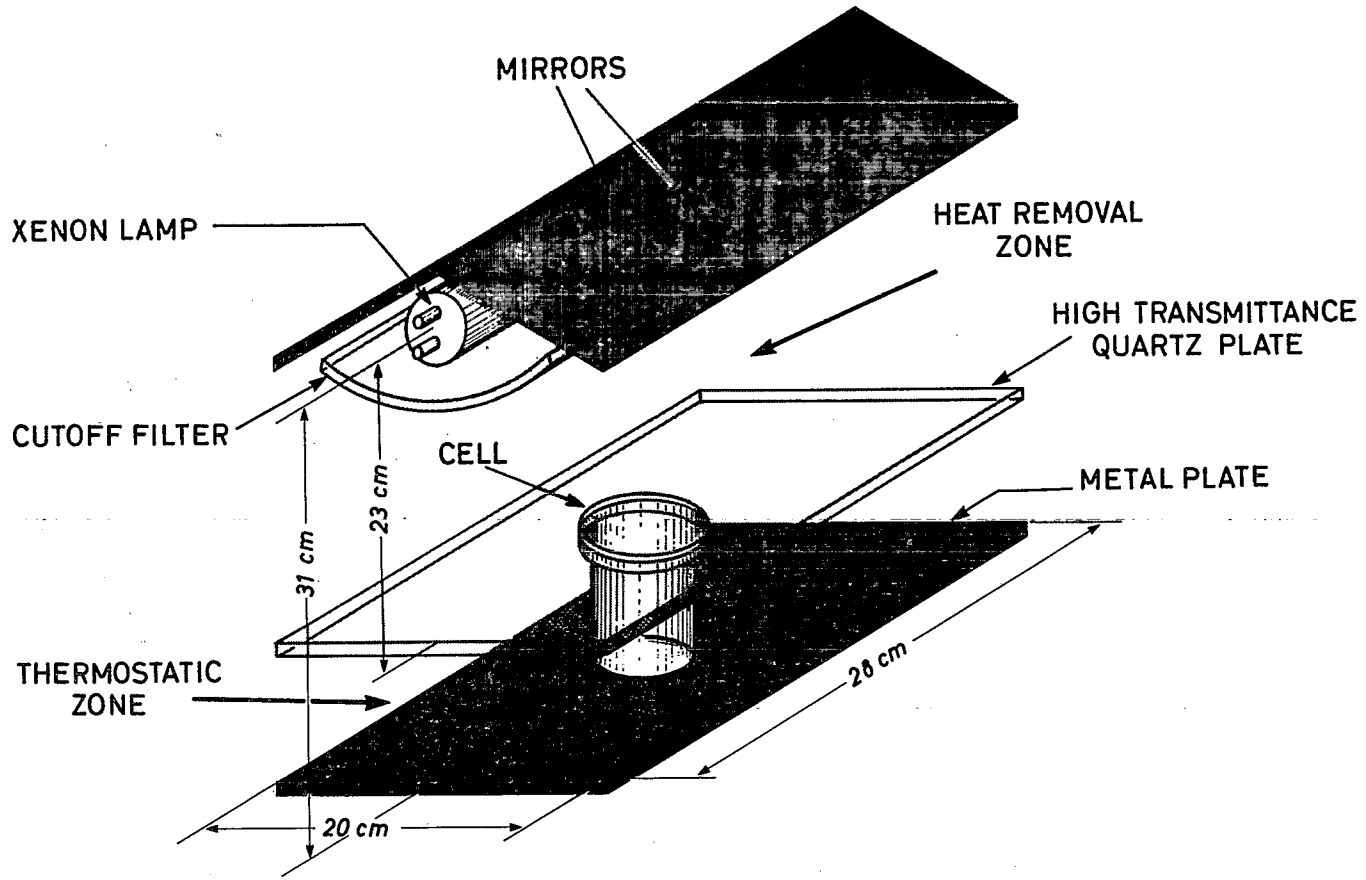

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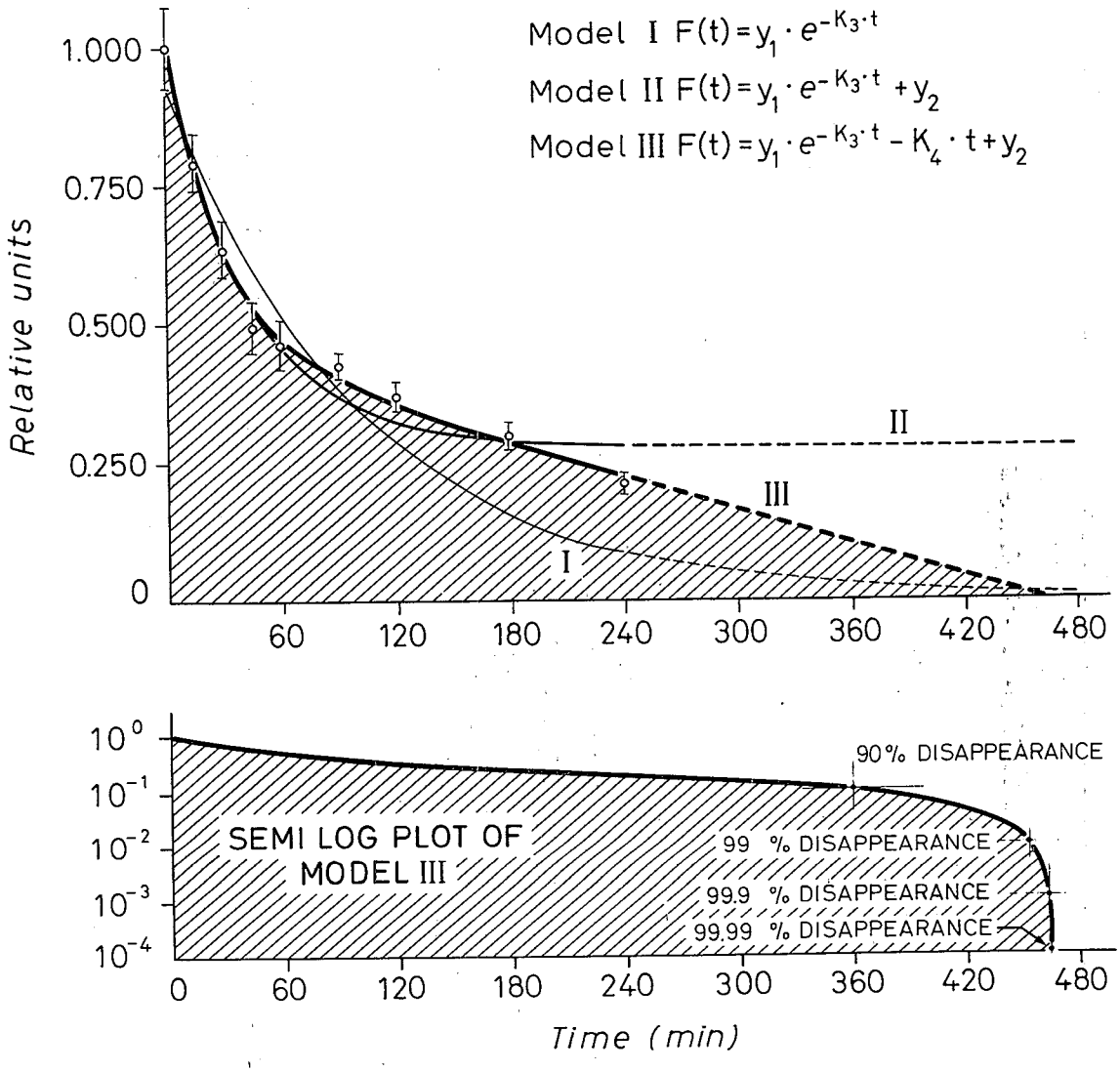

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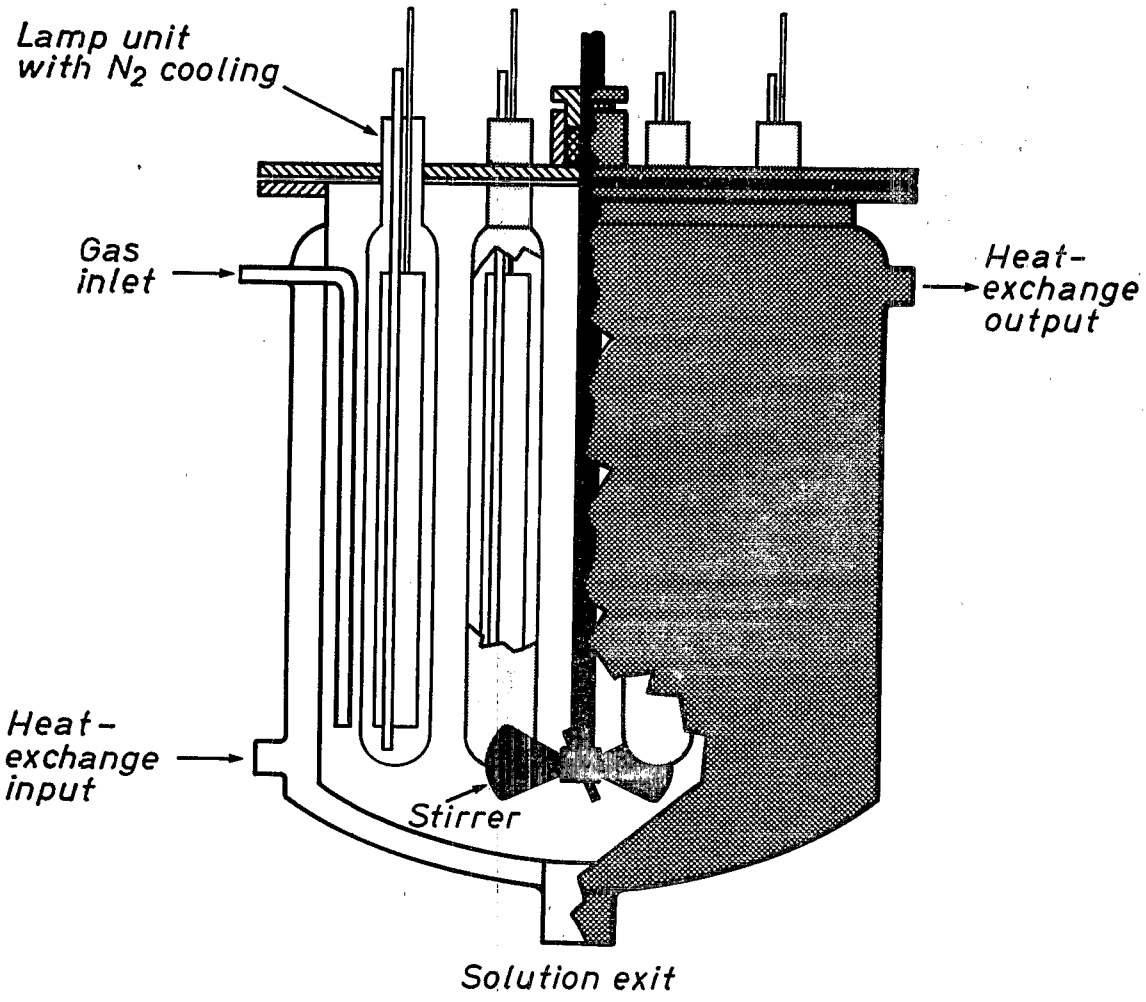
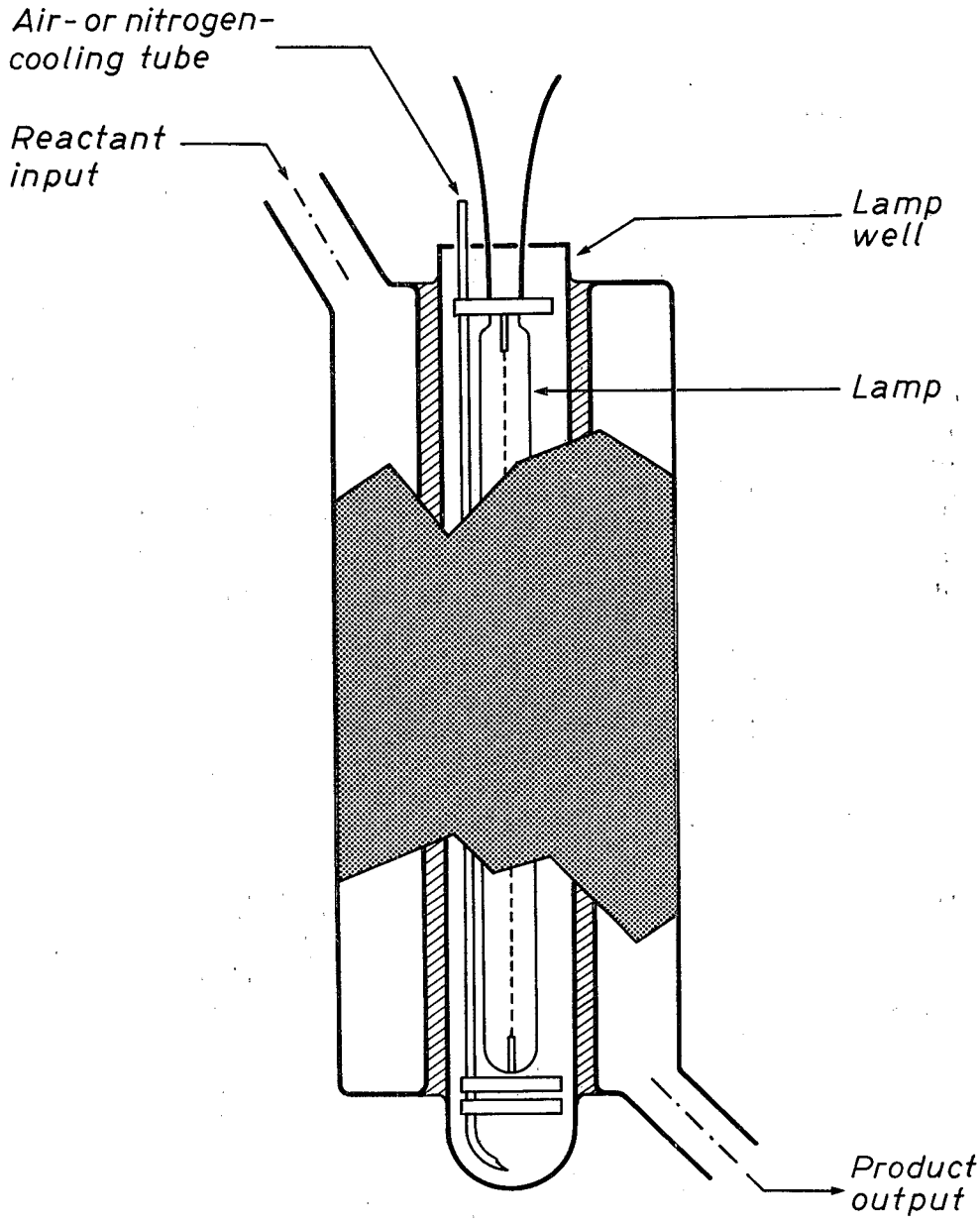


Figure 4 Batch photochemical reactor. Higher wattage lamps are more efficient in producing a useful light emission up to approximately an input power of 10 kW. At that point, a decrease in UV emission efficiency (einsteins x kW^{-1} x $hour^{-1}$) is observed. Therefore, if the reactor is designed to exceed a 10 kW input power, an array of lamps is normally arranged. Lamps immersed in the reaction medium improve quantum efficiency by avoiding excessive scattering, reflection, or dispersion of light. In the picture, both lamps and reaction medium are cooled to avoid overheating.



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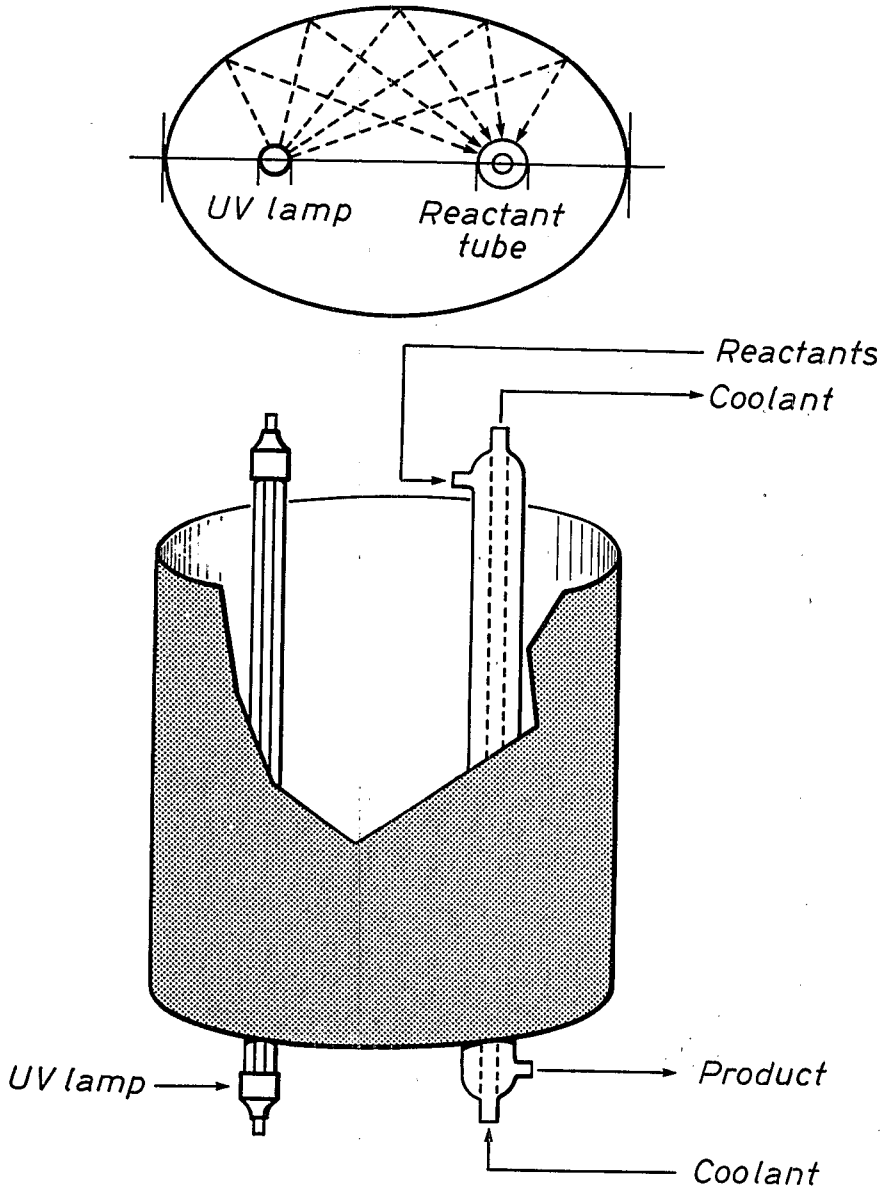

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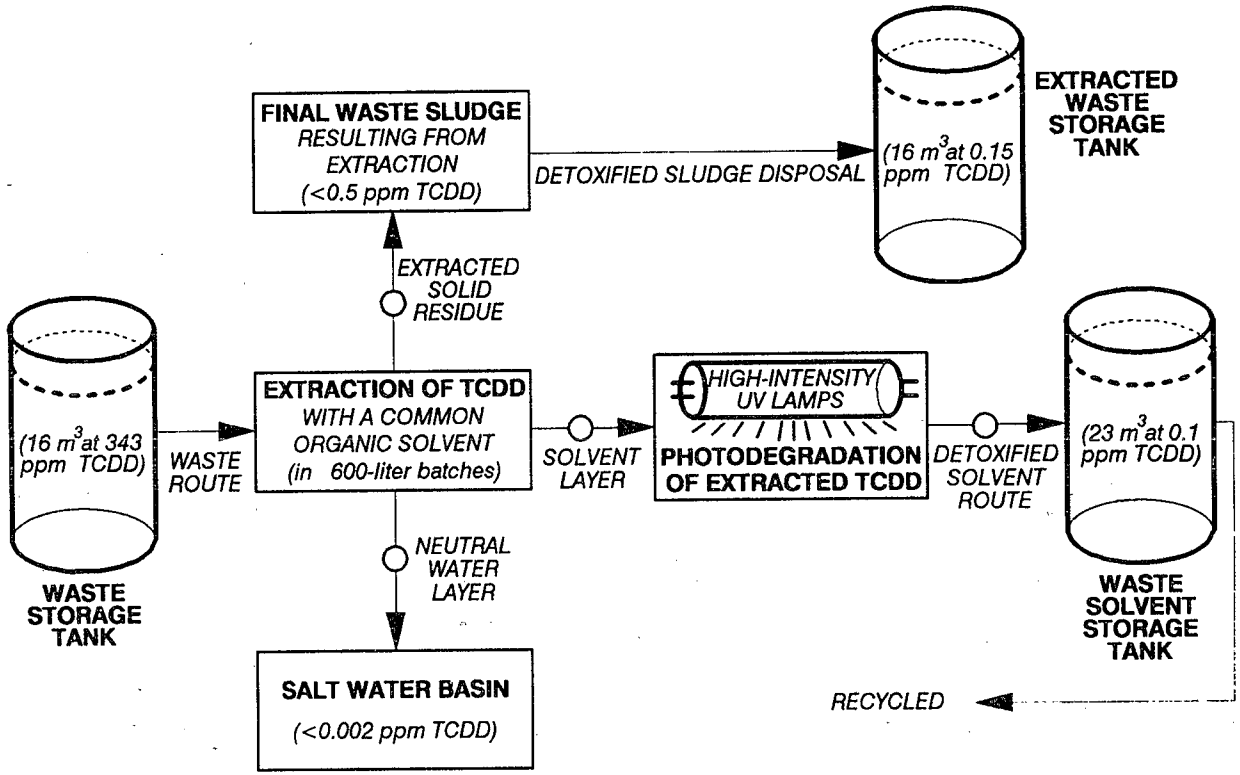

Figure 7 Syntex Agribusiness, Inc. (Springfield, Missouri), used photolysis to destroy highly toxic TCDD in chemical sludge waste contaminated at levels between 300 and 400 mg x kg^{-1} (ppm). For the operation, over 16 m^3 of sludge were extracted batchwise with hexane, a common organic solvent. The organic layer was then irradiated with high intensity UV light to break down TCDD. From the process, an overall photo-induced reduction efficiency of >99.9 % was attained. The detoxified solvent was distilled for recycling. The aqueous layer (TCDD < 0.002 mg x kg^{-1}) and the extracted sludge (TCDD < 0.5 mg x kg^{-1}) were later disposed of.

NATO/CCMS Fellow:

Sjef Staps, The Netherlands

International Evaluation of *In Situ* Bioremediation of Contaminated Soil and Groundwater

INTERNATIONAL EVALUATION OF IN-SITU BIORESTORATION OF CONTAMINATED SOIL AND GROUNDWATER.

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Final Fellowship report for the Third International Meeting of the NATO/CCMS pilot study on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater". Montreal, Canada, November 6-9, 1989.

ABSTRACT

This paper is the result of the RIVM-project "International evaluation of in-situ[1] biorestoration of contaminated soil and groundwater". As a fellowship project, it was associated with the international NATO/CCMS pilot project on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater".
The philosophy of in-situ biorestoration is to stimulate the indigenous soil microorganisms to degrade contaminants by improving the environmental conditions in the soil using a water recirculation system.
The objective of the project is to show the possibilities for application of the technique in relation with contaminants, soil conditions and other site-specific circumstances by means of integration and evaluation of results of in-situ biorestoration projects.
The project is limited to the Netherlands, West Germany and the USA. It was implemented by visiting 23 relevant projects in these three countries, which play a leading role in the development of remediation techniques for contaminated soil and groundwater.

In-situ biorestoration is a relatively young, developing technology. It has been used at several locations, mainly in the USA. It can be used especially for locations at which both the unsaturated zone and the groundwater are contaminated with hydrocarbons. A precondition is a good permeability of the soil.
Experience has especially been gained with in-situ biorestoration at hydrocarbon-contaminated petrol stations and industrial sites. The system generally consists of a water recirculation system, aboveground water treatment and conditioning of the infiltrating water with nutrients and an oxygen source. However, there is no one-and-only application method for in-situ biorestoration. The remediation, which can last from approximately six months to several years, can reach residual concentrations below the B-value of the Netherlands examination framework (see table 4). If applicable, in-situ biorestoration is generally more cost-effective than other remediation techniques; costs are approximately between 40-80 US $/m^3.
Recommendations from this evaluation include a further stimulation of the development of this technology, improvement of the preliminary research, expansion of the applicability to more recalcitrant contaminants, research on bio-availability and research into oxygen supply and distribution in the subsoil.

INTRODUCTION.

In behalf of the Dutch clean-up operation for contaminated soil, development of adequate clean-up methods is considered to be of prime importance. Besides thermal and extraction techniques, which still account for the greater part of the clean-up operation, biological techniques have been developed in the Netherlands. Landfarming, a biological treatment technology for excavated contaminated soil, is now being used on a practical scale (Soczó and Staps, 1988). However, in many cases it is impossible or too expensive to excavate

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1 in (its original) place

the soil. In-situ techniques are then the most appropriate methods, and can be employed for treating both the soil and the groundwater.
In the Netherlands, application of in-situ techniques by companies nowadays focusses on washing, circulating and cleaning of the groundwater (the former pump-and-treat method). Especially in recent years, increasing interest is also being shown in actual biorestoration in the soil. The environmental conditions in the subsoil are optimized by supplying oxygen and nutrients and circulating the water.

The first Dutch research into in-situ biorestoration was a feasibility study, carried out by Delft Geotechnics, to evaluate the scope of an in-situ soil-venting technique (van Eyk and Vreeken, 1988). The RIVM and the TNO (Netherlands Organization for Applied Scientific Research) are preparing a full-scale clean-up by means of a literature study and extensive experiments on laboratory-scale since 1985 (Verheul et.al., 1988). However, a clear need for information from full-scale clean-up projects and from foreign experience was still felt. From literature and international contacts is was known, that especially in the USA experience with this technology had been gained. Besides, developments were also under way in West Germany (Nagel et.al., 1982 and others).
While the problem of soil and water contamination also became evident in other countries, interest in remediation techniques, and especially in-situ technologies, increased. This emerged at the first international workshop of the NATO/CCMS pilot project on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater" in spring 1987. Several western countries, including the Netherlands and the USA are participating in this pilot project.
This was sufficient reason for the RIVM to start this evaluation in late 1987. The author was awarded a fellowship of the NATO/CCMS project. Because of its relevance to the development of remediation techniques in the Netherlands, the study is partly financed by The Netherlands Integrated Soil Research program.

The project is limited to the Netherlands, West Germany and the USA. The fellowship project was implemented by visiting 23 projects in this field in these three countries, which play a leading role in the development of remediation techniques for contaminated soil and groundwater. An overview of the projects is given in the appendix.
Information, results and data are directly obtained from the experts involved. Total information is arranged, and conclusions are drawn in this final paper. A more comprehensive report, including detailed information from the visited projects, is in print (Staps, 1989[b]). Information concerning analytical procedures is also included in this report.

EVALUATION OF IN-SITU BIORESTORATION PROJECTS

Introduction

Although not all organizations dealing with in-situ biorestoration are included, the 23 projects chosen do provide a good idea of the feasibility of this technology. The concerning group of 23 organizations consisted of fifteen private companies, three institutes, two universities, one co-operation of an institute, a university and a coast guard, and one air force.
A schematical overview of the projects, including several characteristics, is given in the appendix. Projects U8 and U9 cannot really be regarded as in-situ

biorestoration projects, because in both cases biorestoration does not take place in the original location. The clean-up site in project U8 is a lagoon, and in the case of U9, the clean-up consists of on-site landfarming. These two projects are not included in this chapter, but, because of the direct relationship to the other projects, they are included in the general overview. Other divergent projects are N5 and U5; both are research projects, where the contamination has been caused deliberately. Moreover, project N5 is deviating because the biostimulation is performed only by venting of the soil, and thus is limited to the unsaturated zone.
Projects D5 and D6 differ from the other ones in that they are still in the conceptual phase, and data from demonstration scale test are as yet not available.
A substantial proportion of the remaining group of "real" in-situ biorestoration projects is characterized by research aspects, with the majority having been set-up as a research project (N1, D2, U3, U5, U6).

Background of the sites at which in-situ biorestoration has been or is being applied

The locations at which in-situ biorestoration has been or is being applied can be divided into two main groups:
- filling stations (service stations, airforce bases, marshaling yards, bus stations) with leaking pipelines or storage tanks,
- chemical industry sites, mainly (former) refineries.

All locations were contaminated with hydrocarbons, for the most part defined as petrol and/or diesel. At airforce bases, also kerosene or JP-4 contaminations occur. One-fifth of the projects concerned chlorinated hydrocarbons. The smallest group of locations was contaminated with PAHs or a mixture of chlorinated hydrocarbons, mineral oil and PAHs. The latter has not yet been demonstrated.

Preliminary site characterization

The surface area of the sites at which in-situ biorestoration was applied, varies largely; from 20 to 75,000 m^2. Within this variety, two clear groups can be distinguished. The first group is formed by filling stations; the surface area is mainly 400 - 1,000 m^2. The second group consists of large chemical industry and (former) refinery sites, and here, the area is varying between 20,000 and 75,000 m^2. The depth upto which the contamination is dispersed is generally between 3 and 10 meters below surface level.
It was striking that the discovery of a second contamination during the cleanup-process occurred at several projects.

In relation with soil structure and geology, nearly all locations can be defined as sandy. At several places, clay layers are present. Only in an exceptional case, in-situ biorestoration is applied at a site with overburden clay and fractured bedrock.
Concerning geology, permeability is a very important parameter for in-situ biorestoration. For the projects reviewed, the K_f-value varied between 10^{-2} and 10^{-8} m/s, mainly having 10^{-3} -10^{-5} as order of magnitude. Generally, a K_f-value of 10^{-5} is regarded as being the minimum permeability for successful application of in-situ biorestoration.

Preliminary biodegradation research

In order to decide whether in-situ biorestoration can be applied at a contaminated site, microbiological, hydrogeological and chemical aspects must be regarded. Hydrogeological conditions include permeability, dispersion of contaminants, groundwater level and flow. The parameters which might be considered before chosing or designing in-situ biorestoration are:
- Microbial parameters (total cell count, nitrifiers, denitrifiers, hydrocarbon degraders)
- Oxygen demand
- Nutrient demand
- Contaminant degradation rate
- Bio-availability.

Total cell count forms the base for research on populations of microorganisms. Parameters in relation with biological activity are an important part of microbial research. For in-situ biorestoration, the number of metabolic active organisms and enzyme samples are important as an indicator for biodegradation in the subsurface. As regards hydrocarbon contamination, determination of the percentage of hydrocarbon degraders is an important monitoring aspect too.
Besides, there is a large group of relevant physical and chemical parameters, including permeability, pH, oxygen, redox conditions, temperature, TOC, DOC, BOD, Fe-concentration, Mn-concentration, concentration of (heavy) metals, N_{total}, ammonium-concentration, nitrate-concentration, nitrite-concentration and phosphate-concentration.

A high permeability is one of the conditions for a successful in-situ biorestoration.
Soil pH may affect sorption of ionizable compounds in addition to limiting the types of microorganisms in the subsurface. Methanogenes, which have been implicated in mineralization of some aromatic hydrocarbons, are inhibited at pH values below 6 (Lee et.al., 1988).
Biodegradation of many organic pollutants in the subsurface may be limited by insufficient concentrations of oxygen or unfavourable redox conditions.
Also temperature influences microbial metabolism of subsurface pollutants. The temperature of the upper 10 m of the subsurface may vary seasonably. However, in the Netherlands, it will not deviate much from 10°C. Also below 10 m, temperature will be about this value. It is important to keep this in mind when comparing results from projects in for example Florida (U6) or California (U5) where much higher temperatures (20-25°C) are measured with projects from other regions.
Total organic carbon (TOC), dissolved organic carbon (DOC), chemical oxygen demand (COD) and biological oxygen demand (BOD) are sum parameters. TOC and DOC are direct parameters for the carbon concentration of organic compounds. Decreasing concentrations of TOC and BOD values indicate mineralization of the organic contaminants.
Determination of Fe and Mn concentrations is important because high concentrations of these metals can cause precipitation under aerobic conditions, caused by the infiltration of oxygen during the biorestoration process.
Other heavy metals can be important, especially at contaminated sites, because at toxic levels, they can inhibit the activity of microorganisms.
Inorganic nutrients like nitrogen and phosphorus may be limiting when the carbon/nitrogen/phosphorus (C:N:P) ratio is unfavourable. Determination of

ammonium, nitrate and nitrite gives insight in the stage of the conditions in the subsoil.

After the characterization of the site regarding microbiological, hydrogeological and chemical/physical parameters, a first decision can be taken whether in-situ biorestoration is applicable at a specific site. However, there is no one-and-only application method for in-situ biorestoration. If the option of in-situ biorestoration is chosen, nearly all visited organizations perform preliminary biotreatment studies on laboratory scale to get insight in the optimal stimulatory actions for a biodegradation process at the site and to choose the right combination of microbial, hydrogeological and physical/chemical actions. Only organizations with very broad experience in the field of pump-and-treat and in-situ biorestoration design a site-specific in-situ biorestoration system almost directly based on the site characteristics (U1, U7). A large majority of the projects included preliminary laboratory research, both small-scale tests and percolation studies in columns. In a few cases, field experiments in a small area representative of the contaminated site have also been performed.

System design

Description of the installation

In-situ biorestoration involves the stimulation of the biodegradation of contaminants at contaminated sites without excavation of the soil. In this process, the soil of the contaminated location is used as a bioreactor (see figure 1).

The specifications of the "bioreactor" in the subsoil are based on the characteristics of the contaminated site, and the objectives and requirements of the clean-up. They include for example the type and distribution of the contaminants in the subsoil, the soil geology and hydrology and the need for isolation of the location.
In most cases a semi-closed configuration is used in such a way, that the contaminated location is isolated and controlled; uncontaminated groundwater can enter the contaminated site, but contaminated groundwater cannot move to uncontaminated areas.
The site can be isolated using hydrological intervention technologies or civil engineering operations. In general, a hydrological system is designed, in which the groundwater is centrally withdrawn, and after above-ground treatment, reinfiltrated at several points on the periphery of the location. The groundwater is withdrawn at a higher rate than it is infiltrated, the surplus generally being discharged into a sewer.
To support degradation in the subsurface, an above-ground treatment system is used to degrade the contaminants in the withdrawn groundwater, and to condition the water before re-infiltration.
Biodegradation relies entirely on the contact between the contaminants (in the water phase) and the microorganisms. In the case of highly volatile compounds as contaminants, clean-up can partly be achieved by vaporization of the unsaturated zone using a soil venting system, as is shown in project N4. The contaminated exhaust air can be treated above ground by adsorbtion (e.g. activated carbon) or oxidation in a biological, thermal or catalytic manner. Research project N5 describes the design of an in-situ soil venting system, used both as a physical (evaporation) and a biological process

(biodegradations). This system can be used for contaminations in the unsaturated zone.

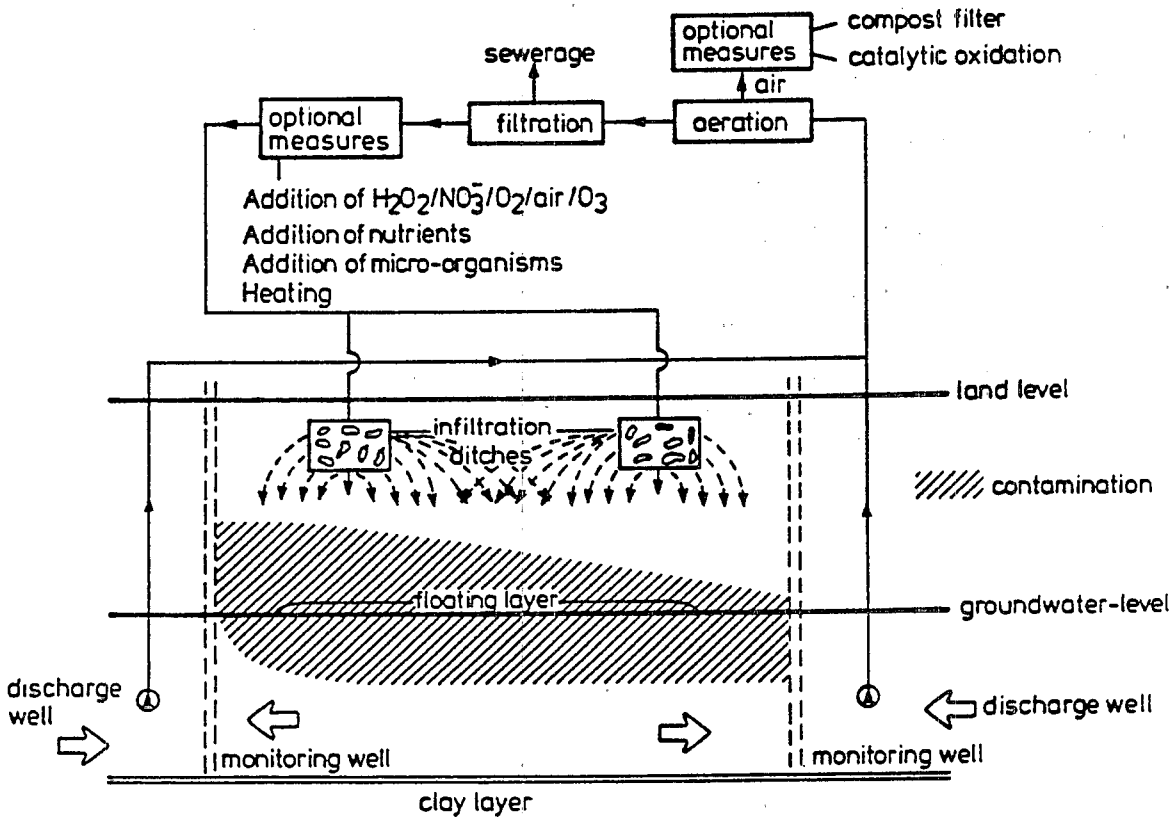

Figure 1. General scheme of in-situ biorestoration.

There are several options for reinfiltration:
- injection wells
- infiltration galleries
- surface application.

Infiltration into the saturated zone through injection wells is the most direct method, but also has disadvantages: oxygen and nutrients are only poorly delivered to the unsaturated zone and the wells have small surface areas. Therefore, they can prone to clogging. The installation cost decreases in the order: injection wells, infiltration galleries and surface application. When visiting the projects, it appeared that infiltration galleries were used nearly twice as often as injection wells. Surface application is only rarely used.
At one research project (U6, Downey 1988), the three options were used simultaneously in order to gain insight in their applicability.

As regards the above-ground treatment, the first part is generally a sandbox. Undissolved contaminants are removed in an oil/water separator. An air stripper is used to remove volatile contaminants. In a few projects, biological systems, such as a trickling filter, were used for degrading dissolved compounds.

When required by the legislator, the contaminated air from the air stripper is oxidized in order to bring about degradation of the contamination instead of moving the contaminants from one compartment (groundwater) to another (air). In the Netherlands, this is performed using a biological compost filter, in which adapted microorganisms degrade the contaminants. In the USA, catalytic oxidation systems are employed.

Hydrological aspects

In general, in-situ biorestoration is performed by means of saturating the subsoil. The main hydrological steps taken consist of central withdrawal of the groundwater and reinfiltration at several injection points on the periphery of the location. Groundwater is withdrawn at a higher rate than it is infiltrated. This occurred at about 95% of the locations.

At two projects, in-situ biorestoration was performed without water saturation (D2 and D4). However, saturating the soil makes it easier to optimize the environmental conditions in the soil with respect to other parameters like pH, oxygen content, nutrients, etc. It depends on the site-specific situation whether saturation and other optimizations will be chosen, or no saturation and fewer other optimizations. However, in most cases, saturation is the preferred method.

Oxygen supply

As far as is known, in-situ biorestoration has only been applied to hydrocarbon-contaminated sites. In order to initiate hydrocarbon oxidation, microbial populations utilize oxygen:

$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O \quad \text{(for benzene)}.$$

As a result of the contamination, the subsoil of contaminated sites is anaerobic, or contains very low concentrations of oxygen. Therefore, oxygen has to be supplied for in-situ biorestoration. Sources of oxygen include air, pure oxygen and hydrogen peroxide. Subsequent oxidation can also be sustained by alternative electron acceptors, for example nitrate.
Lack of oxygen or necessary redox conditions will limit in-situ biorestoration of contaminated soil and groundwater. When applying in-situ biorestoration in practice, oxygen is usually the limiting factor.
The alternatives to oxygen supply used in the projects visited were:

- air
- pure oxygen
- hydrogen peroxide
- nitrate
- nitrate / ozone
- methane / oxygen

Oxygen sources

The simplest method of supplying oxygen is aeration. However, the amount of oxygen that can be added with air is strongly limited: only 8 mg/l under normal groundwater conditions (table 1). As a result, very large volumes of oxygenated water may have to be infiltrated at the contaminated site, and

because of permeability constraints, the remediation time is then relatively long.

Table 1. Available quantities of oxygen from different sources.

	air-saturated water	O_2-saturated water	H_2O_2 200 mg/l	NO_3 200 mg/l
available oxygen (mg/l at 10°C)	10	40	94	168

As shown in table 1, this problem can be overcome in part by using pure oxygen (40 mg O_2/l) or hydrogen peroxide (100 mg O_2/l from 200 ppm H_2O_2):

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

Hydrogen peroxide is toxic at higher concentrations and can therefore only be used up to a limited concentration. In the case of H_2O_2, the bioremediation is usually started with low concentrations (40-50 mg H_2O_2/l), or even with pure oxygen. The objective of this measure is to let the indigenous population of microorganisms acclimate to the oxygenated environment. Once the population is acclimated, the peroxide concentrations can be increased in increments of approximately 50 to 250 ppm in intervals increasing from approximately one week to one month (U3), to achieve an increased infiltration of oxygen. Such a gradual increase of peroxide concentrations can be continued up to a concentration of about 1000 ppm H_2O_2.

In the initial phase of biorestoration, the oxygen supplied is utilized by the microorganisms in the vicinity of the infiltration point. When contaminants in this area have been degraded, the oxygen can be transported over larger distances, and biodegradation will then occur in an area, further away from the infiltration point. This process continues until oxygen breakthrough at the withdrawal wells.

An important aspect with respect to peroxide is its stability. As remediation of the site progresses, the H_2O_2 must be carried increasingly longer distances. This means that H_2O_2 must be stable in order to deliver the oxygen to the area where it is needed. The decomposition of peroxide is catalyzed by metals, such as iron and manganese. H_2O_2 can also be degraded by the bacterial cell, with the enzyme catalase serving as the catalyst. On the other hand, phosphate can stabilize hydrogen peroxide (Britton, 1985). This is actually performed at demonstration projects. The form of phosphate is mostly monophosphate. To reduce phosphate adsorbtion to the soil, a combination of simple and complex polyphosphate salts can be used (Brown et.al., 1986). The use of phosphate solutions is twofold: as a nutrient, it also has a positive influence on the biodegradation when the original concentration of phosphate is too low.

Nitrate as electron acceptor

Nitrate can serve as an electron acceptor. Comprehensive fundamental research regarding the use of nitrate has been performed in West Germany (Riss et.al., 1987). Here, laboratory research showed that nitrate can only be utilized when a first phase with elementary oxygen has passed, and when

the nitrate is present under anaerobic conditions. There has not always been given satisfaction to these preconditions when applying nitrate for in-situ biorestoration (see e.g. projects N1 and N4).
As is shown in table 1, one part of nitrate is equivalent to 0.84 parts of oxygen. Take, for example, the oxidation of methanol:

$$1.5\ O_2 + CH_3OH \rightarrow CO_2 + 2\ H_2O$$

$$NO_3^- + 1.08\ CH_3OH + H^+ \rightarrow 0.065\ C_5H_7NO_2 + 0.47\ N_2 + 0.76\ CO_2 + 2.44\ H_2O$$

(Brown, 1989).
Until now, application of nitrate has only occurred in a few German states and only incidentally in other countries. Application might encounter licensing problems. In project N4, nitrate is added to the oxygenated infiltrating water. Nitrate will also be used at project U3 as part of a research program. Utilization of nitrate could not be determined in research project N1 (Verheul et.al., 1988).
In project D9, a combination of ozone and nitrate has been used: ozone above ground, to treat the water and oxygenate the organic contaminants; nitrate in-situ, in the subsoil, to serve as an electron acceptor for subsequent biodegradation by the microorganisms.

Co-metabolism

At one research project (U5), biodegradation of chlorinated compounds by methane-oxidizing bacteria (methanotrophs) involves stimulating the population with methane- and oxygen-containing water. Methanotrophs obtain energy from the oxidation of methane. They synthesize the enzyme methane monooxygenase, which catalyzes the first step in the oxidation of methane, which they use for energy and growth. Monooxygenase oxidizes a range of hydrocarbons, and appears to bring about the epoxidation of chlorinated alkenes (co-metabolism):

$$CHCl{=}CHCl + H_2O \rightarrow CHClOCHCl + 2H^+ + 2e^-$$

These epoxides are unstable in water and hydrolyze to a variety of products which can be oxidized readily by other heterotrophic bacteria to inorganic end products (McCarty et.al., 1989, Janssen et.al., 1987).

Comparison of oxygen sources

Table 2 shows a comparison for various oxygen systems for a severely contaminated site.

It can be concluded, that there is a wide range in both cost effectiveness and in treatment effectiveness. For example, venting can only be applied in the vadose zone. In terms of cost effectiveness, the order is:

venting >> peroxide > nitrate > air sparger > water injection

while in order of treatment effectiveness, the order is

peroxide = nitrate > water injection > venting > air sparging.

Table 2. Cost/performance comparison for various oxygen systems; high degree of contamination.

System	Costs ($) Capital	Operation	Maintenance	Performance kg/Day Oxygen	% Site Treated	Utilization Efficiency %	Time of Treatment	$/kg oxygen Used
Air Sparging	35,000	800/month	1200/month	3	41	70	858 days	57.-
Water Injection	77,000	1200/month	1000/month	4	75	50	1580 days	62.-
Venting System	88,500	1500/month	1000/month	1810	60	5	132 days	8.-
Peroxide System	60,000	10,000/month	1500/month	86	100	15	330 days	41.-
Nitrate System	120,000	6500/month	1000/month	96	100	12.5	335 days	49.-

(Brown, 1989)

The choice of an oxygen supply is most dependent on the contaminant load, the mass transfer and the ease of transport and utilization. At low concentrations, simple systems, such as air sparging, become more cost effective.

Nutrient supply

The biodegradation rate will be limited when inorganic nutrients, such as nitrogen and phosphorus, are present in limiting concentrations or mutual ratio's. Regarding contaminated sites, the presence of nitrogen and phosphorus should be viewed in relation with the carbon concentration from the contaminants. In soil, a C:N:P ratio of 250:10:3 is considered to be optimal for biodegradation. Also other C:N:P-ratios, e.g. of 100:10:2 have been chosen.
The need for nutrients is dependent on the site characteristics. At certain sites, nutrient addition can be unnecessary. In other cases, increasing the inorganic concentrations at one time can be sufficient. If nutrient supply is needed during the clean-up, nearly always batch-mode addition has been chosen.
In order to satisfy nutrient requirements, a wide range of components can be added. This includes compounds like NH_4NO_3, Na- and K-orthophosphate and trace elements.
In a few projects, such as N1, addition of an easy degradable carbon source (NaAc) enhanced the initial degradation of hydrocarbons during laboratory experiments. However, the significance for demonstration scale seems to be limited.

Addition of microbial populations

Besides stimulating the indigenous microbial population to degrade organic compounds in the subsurface, another option is to add microorganisms with specific metabolic capabilities to the subsurface. This is demonstrated in projects D3, D4 and D7. Soil samples are taken from the contaminated site at spots where microorganisms occur, for example at the edge of the contamination. The microorganisms which are present at those spots, will be adapted to the contamination in the soil, and will be able to degrade the contaminants. The samples are taken to the laboratory, where selection occurs by enrichment culturing, until a suspension is obtained which contains the selected microorganisms in high density. This suspension of

microorganisms is then injected with the infiltrating water at the contaminated site. The objective of this inoculation is to increase the number of adapted microorganisms at the site, in order to accelerate biodegradation.
Another method to add microorganisms to the subsoil is applied when a biological groundwater treatment plant is applied above ground (N2 and N4). The effluent of such an installation will contain large amounts of adapted hydrocarbon degrading microorganisms which are injected in the soil. In a research project, also inoculation by effluent water of a wastewater treatment plant was used (project N5).
However, there is much uncertainty about the efficacy of the addition of microorganisms to the subsoil and the possibilities of transporting bacteria through the soil, in order to get them at the spots where they are needed. Generally, 95% of the soil population tends to adsorb on soil particles, whereas only 5% can be transported.

Results of the in-situ biorestoration projects

The projects visited differ widely in the clean-up results to be obtained. For example, some projects do not aim to achieve a given concentration; on the basis of the clean-up progress, it is decided what the residual concentrations of contaminants should be.
There are much differences; in the Netherlands, the objectives set by the legislator are generally 50 μg mineral oil per liter (groundwater) and 50 mg/kg in the soil. In a few cases, this level can be 200 μg/l and 1000 mg/kg d.w. in the soil.
In relation with the residual concentrations, it is important to notice that different objectives have been used; in several projects, the goal was to reach low concentrations in the groundwater, whereas in other projects low concentrations in the soil were decisive.

In the USA and West Germany, the reported objectives varied between undetectable levels (mineral oil) in the groundwater and less than 5000 mg/kg in the soil.

As regards results of in-situ biorestoration, the visited projects can be divided into three groups:

a) demonstration projects that have been finished (N3, N5, D4, D7, D8, D9, U1, U6)
b) demonstration projects that are under way (N2, N4, D1, D2, U2, U3, U4, U5, U7)
c) projects which are in the stage of preparation of a field demonstration (N1, D5, D6).

This paragraph is limited to projects of groups a) and b). Table 3 shows the results of the finished projects.

About half of the in-situ biorestoration projects reviewed in this study have been finished.

The significance of the results appears from relating the residual concentrations, which have been reached in the projects finished, to the

corresponding concentrations of the Netherlands examination framework for soil pollutants.

Table 4 shows the relevant values of this framework.

Table 3. Residual concentrations and remediation time for a few in-situ biorestoration projects finished.

Code	Contaminant	Residual concentration	Compartment	Remediation time (months)
N3	aromatics	< 30 µg/l	water	6
	mineral oil	< 200 µg/l	water	
N5	BTX	< 5 mg/kg	soil	12
	diesel oil	150 mg/kg	soil	18
D4	diesel oil	4600 mg/kg	soil	12
D7	fuel oil	< 100 mg/kg	soil	9
D8	diesel/arom.	30 mg/kg	soil	3 [1]
D9	aromatics oil	non-detectable levels	water	10 [1]
U1	gasoline	< 10 mg/kg	soil	48
U2	4-chloro-2-methylphenol	> 80% of area cleaned-up	water	24
U6	JP 4	550 kg hc removed	--	12

[1]) non-detectable levels reached for part of the contaminated area; clean-up was continued for gaining complete clean-up of the site.

Table 4. Relevant part of the Netherlands examination framework for soil pollutants.

Indicative values: A - reference value
B - indicative value for further investigation
C - indicative value for cleaning-up

Presence in:	soil(mg/kg dry weight)			groundwater (µg/l)		
	A	B	C	A	B	C
aromatic compounds						
benzene	0.05(d)	0.5	5	0.2(d)	1	5
ethylbenzene	0.05(d)	5	50	0.2(d)	20	60
toluene	0.05(d)	3	30	0.2(d)	15	50
xylene	0.05(d)	5	50	0.2(d)	20	60
phenols	0.05(d)	1	10	0.2(d)	15	50
aromatics (total)	-	7	70	-	30	100
polycyclic aromatic hydrocarbons (PAHs)						
total PAHs	1	20	200	-	10	40
chlorinated organic compounds						
aliphatic chlor. comp. (total)	-	7	70	-	15	70
chlorophenols (total)	-	1	10	-	0.5	2
mineral oil	*	1000	5000	50(d)	200	600

* = reference value soil quality
d = detection limit

As regards the Netherlands examination framework for soil pollutants, residual concentrations below B-level, or even undetectable levels of contaminants have been reached in the finished projects. Five out of nine projects reach the A-level, thus meeting the standards used in the Netherlands. Venting (N5) was successful as regards volatile components (petrol), but not for PAHs.

The results of the projects which are underway are generally promising.

Comparison of the results of the different in-situ biorestoration projects is very tricky. This is mainly caused by the application of different methods, used in the course of the in-situ biorestoration projects:
- methods of soil and groundwater sampling and analysis,
- determination of physical and chemical site parameters.
Occasionally, there are also gaps in the total overview of the restoration course.

The total overview of the in-situ biorestoration projects, as presented in the appendix, also shows the results in relation with other aspects, such as soil structure, oxygen source, applied system and nutrients used.

The remediation time varied between 90 days and 4 years, and is largely dependent on the site characterization (soil structure) and the kind of contaminants.

Costs for in-situ biorestoration

A wide range of site- and system characteristics and objectives influences total costs for in-situ biorestoration projects. These include:
- geology and soil structure
- type and concentrations of contamination
- distribution of contaminants in the subsoil
- total surface and volume of the contaminated area
- system characteristics: recirculation, water and gas treatment a.o.
Because these aspects can vary significantly, the costs for completing the projects can vary considerably.
It must be stressed that these figures should always be seen in relation to other treatment techniques for a certain contaminated location, including cost for excavation and transport.

The projects can be divided into two main groups:
- petrol stations (approximately 400 - 1,000 m^3 ; 1,000 - 5,000 m^3)
- refinery- and industrial sites (approximately 20,000 - 75,000 m^3 ; 30,000 - 400,000 m^3).

Petrol stations

Costs for in-situ biorestoration at contaminated petrol stations varied between 62,000 and 750,000 US $ (40- 250 US $/$m^3$). Included are relatively cheap projects of approximately 60 US $/$m^3$ which could be performed without abovegroundwater treatment (U1) or without water recirculation (D4).

A comprehensive itemization of the different costs for using in-situ biorestoration to treat a specific petrol station is shown in table 5 (Fournier, 1988).

It should be noted that, dependent on the situation, the contribution of hydrogen peroxide to the total cost of the operation can be substantially higher; contributions of 90% have occurred.

Table 5. Estimated costs for in-situ biorestoration of a petrol station (Fournier, 1988).

		$	%
Capital costs			
Groundwater monitoring wells	5,000		
Reinjection well		2,300	
Nutrient and peroxide addition equipment		5,000	
Recirculation equipment		5,000	
Equipment total		17,300	12
Preliminary site assessment costs			
Laboratory tests		16,300	
Field tests		5,000	
Reports		2,000	
Total preliminary testing		23,300	16
Total initial expenditures		40,600	
Annual operating and maintenance costs			
Groundwater monitoring		8,200	
Reinjection well maintenance		14,200	
Chemical costs		12,000	
Total annual costs		34,400	72
Present worth factor for 3 years		x 2.402	
Present worth of O&M costs		82,630	
Present worth of ISB option		123,230	
Total costs over 3 years		$143,800	100

Refinery- and industrial sites

Cost for in-situ biorestoration at refinery- and industrial sites varied between 330,000 and 16 million US $. Again, especially system design determines total cost: 7.- US $/m³ if a relatively simple in-situ type of landfarming is used (D2) up to approximately 150.- US $/m³ for a more complex system design.

From the information from the projects it can be concluded that operating and maintenance costs account for about 2/3 of the total costs. Generally, 1/3 of the costs is due to preliminary research and installation costs, in about equal amounts.

In many cases in-situ biorestoration will be more cost-effective than other techniques, such as incineration and soil washing of the excavated soil, possibly combined with groundwater treatment (approximately 70-170 $/m³ excluding excavation and transport costs (Staps, 1989[a])).

CONCLUSIONS

Application

- The locations at which in-situ biorestoration has been used can be divided into two main groups:
  * filling stations (service stations, airforce bases, marshalling yards, bus stations) with leaking pipelines or storage tanks (400 - 1,000 m^2),
  * chemical industry sites, mainly (former) refineries (20,000-75,000 m^2).

- With respect to soil structure and geology, nearly all locations can be defined as sandy. Clay layers are present in several areas. Only in an exceptional case in-situ biorestoration is used at a site with overburden clay and fractured bedrock.

- Regarding hydrology, permeability is a very important parameter for in-situ biorestoration. In the projects reviewed, the K_f-values varied between 10^{-2} and 10^{-5} m/s, but was mostly of the order of 10^{-3} -10^{-5} m/s. In general, a K_f-value of 10^{-3} m/s is regarded as being the minimum permeability required for successful application of in-situ biorestoration.

- All locations were contaminated with hydrocarbons. Most contaminations are defined as petrol and/or diesel. A few locations were contaminated with PAHs or a mixture of chlorinated hydrocarbons, mineral oil and PAHs. The frequent discovery of secondary sources of contamination points out that the characterization is not always sufficiently carried out.

Design

- The approach of in-situ biorestoration at the visited projects could be characterized by either a hydrological or a microbiological background. Only rarely, a good integration of both disciplines could be seen.

- The decision for application of in-situ biorestoration can only be taken after a comprehensive site-characterization. The specific characterization of the contaminated site and preliminary biotreatment laboratory studies (if possible followed by field studies) should be performed to determine optimal stimulation actions and thus the different forms in which the technology can be applied.

- As regards hydrological measures, generally a system is designed, in which the groundwater is centrally withdrawn and, after aboveground treatment, is reinfiltrated at several spots at the outer border of the location. In order to support the degradation in the subsurface, an aboveground treatment system is used to degrade the contaminants in the groundwater which is pumped-up, and to condition the water before reinfiltration.

- As regards the aboveground treatment, the first part is generally a sandbox. Undissolved contaminants are removed in an oil/water separator. An air stripper is applied for removal of volatile contaminants. At a few projects, biological systems, such as a trickling filter, were used for degradation of dissolved compounds.

- Recirculation of the pumped-up groundwater has positive effects on the biodegradation in the soil. This may be due to the infiltration of degradation products, which are relatively easy to break down and which stimulate the activity of the microorganisms in the subsoil.

- The contaminating vapours in the air from the air stripper can be oxidated by means of a biological compost filter or a catalytic oxidizing system in order to acquire degradation of the contamination instead of moving the contaminants from one compartment (groundwater) to another (air).

- On demonstration scale, most of the time the limiting factor is lack of oxygen or necessary redox conditions. Hydrogen peroxide is most popular as oxygen source. However, for certain applications it can be relatively expensive. Other sources are air, pure oxygen and nitrate (as electron acceptor). The choice for a system is based on cost-efficiency, contaminant load and the ease of transport and utilization.

- Necessary nutrient addition is fully dependent on the original available nutrients in the soil and the uptake by the microorganisms. Usually, addition of nitrogen and phosphorus is necessary. In a few cases, also trace elements have been supplied. Other projects could be biorestorated without any artificial supply of nutrients.

- The effect of the adding detergents is still questionable. Fundamental research and most practical experience indicate that the effect on degradation is negative. Clogging of the soil can occur when detergents are supplied, probably due to an interaction between the oil, water, detergent and solid phase.

- Addition of microorganisms to the subsoil, with the aim of enhancing the biodegradation, is being used by a few companies. Although such supply will always have some beneficial effect, until now, this has not been proved. Cost-benefit calculations are also lacking. A major objection here is, that soil microorganisms tend to adsorb onto (soil) particles, and consequently cannot be transported over long distances in the subsoil. This implies that the effect of the inoculation is very limited.

White spots

- Bottle-necks in relation with in-situ biorestoration can be:
  * insufficient infiltration rates, mostly caused by clogging,
  * insufficient hydrological isolation,
  * relatively long remediation period, needed for reaching low concentrations of contaminants,

- When using in-situ biorestoration, the precise fate of degraded hydrocarbons, such as gasoline, is not yet known. A proportion is transformed to leachable DOC, another part to DIC, but a large part is still unaccounted for.

- With the exception of project N1, research on in-situ biorestoration has not provided knowledge about mass balances. When degradation occurred in project N1, the percentages of leached and degraded aromatics were about

the same. The aliphatics were removed by degradation only, and then almost completely.

Results and significance

- As regards feasibility, in-situ biorestoration can technologically compete with other technologies when it is applied at a suitable location, and the process is well run. As regards the Netherlands examination framework for soil pollutants, residual concentrations below B-level, or even undetectable levels of contaminants have been reached in most of the finished projects. Contaminants are mainly hydrocarbons (gasoline, diesel, mineral oil).
  The remediation time varies roughly between 3 months and 4 years, largely depending on the initial concentrations, the kind of contaminants, the soil structure and the requirements which are set. Concerning practical projects without research aspects, costs can vary between approximately 40-80 $/m^3. This means that in many cases in-situ biorestoration will also be more cost-effective than other techniques (approximately 70-170 $/m^3 excluding excavation and transport costs (Staps, 1989[a])).

RECOMMENDATIONS

General policy

- This evaluation included the visit of 17 contaminated sites, and concludes that in-situ biorestoration is a promising technology for a selection of contaminated sites. However, it is important to notice that most spills, and thus damage to the environment and the spending of large amounts of money for remediation, could have been prevented by good house-keeping. Therefore, at locations where spills might occur, prevention is recommended in the first place.

- The most fundamental recommendation that can be made from this study, is to stimulate the development of in-situ biorestoration. This study shows that the technology has a large potential. At present, it is important to collect reliable (demonstration) data, which can be used in the following areas:
  * optimization of the technology, mainly regarding oxygen transport and utilization, peroxide transport and stability and removal of contaminant residuals from soils (bio-availability).
  * extending the technology's range of applications, especially to more recalcitrant contaminants.
  * development of models of (in-situ) biorestoration.

- In-situ biorestoration is expected to be a promising technology, especially for application at contaminated industrial sites. This is mainly because of the minimal physical impact on the environment, caused by the process; industrial activities can be continued during the clean-up.

- When demanding certain residual concentration levels, regulators should not only consider concentrations in the groundwater, but also in the soil. It should be prevented that an in-situ biorestoration project is finished because the contamination levels in the groundwater are

sufficiently low, while significant concentrations are still present in the unsaturated zone of the soil. Percolating water from precipitation will transport (a part of) residual contaminants and contaminate the clean groundwater again, making a second clean-up operation necessary.

- The approach taken by the experts involved in several of the projects visited can be characterized by either a hydrological or a microbiological background. However, in-situ biorestoration is not only pure biotechnology, but is indeed an integration of biotechnology and hydrology. Integration of a number of disciplines is indispensable.

- Because of the general complexity of soils, the course of the degradation process can never be predicted completely. Therefore, preliminary research, both in the laboratory and in field tests will always be necessary. The field tests should include oxygen utilization rates, possible in-situ peroxide stability and potential clogging problems. Laboratory methods for predicting the course of the in-situ biodegradation should all be improved.

- There is a need for more sharing of meaningful site data by those experiencing in this technology. This is especially needed as regards data on peroxide stability and transport, oxygen utilization and the removal of fuel residuals from soils. Therefore, projects like N1, U3 and U6 are very useful. An open policy of organizations with experience of the technology can expose bottlenecks concerning both practice and demonstration, thereby directing the research of universities and institutes and making this research more valuable.

- Knowledge about modelling of transport behavior in the soil seems to be sufficient. Modelling of biodegradation processes in the soil however, is still a difficult problem and requires further attention. A precondition for further development however is the availability of representative data, which should be published by the experts involved in in-situ biorestoration projects.

System design

- Venting of volatile contaminating compounds in the unsaturated zone and treatment of these components above ground (possibly combined with recirculation and biorestoration in the saturated zone) seems to be a promising and cost-effective method calling for further attention.

- A combination of chemical treatment above ground and biological treatment in the subsoil can possibly expand the application of in-situ biorestoration, especially to compounds which are more difficult to break down biologically (such as PAHs) and more readily biodegraded once a first oxidation step has taken place. Further research in this field can be recommended.

- Stimulation of the biological activity by heating the infiltrating groundwater was used at one project only (D5). Here, it was not conclusively shown that this was a cost-effective method. Measurements in test plots should be conducted to demonstrate whether and when the heating effect is economical.

- There is much uncertainty about the efficacy of the supply and distribution of oxygen (-sources) in the subsoil. Research on alternative oxygen sources (O_2, H_2O_2) and electron acceptors (NO_3^-) is useful. Hydrogen peroxide is a relatively expensive oxygen source, the more so because only a very limited part of it can actively be used for the biodegradation of the contaminants; this is estimated to be approximately 15% (Brown, 1989).

- In-situ peroxide stability must be greatly improved to provide adequate oxygen downgradient of injection points.

- As regards inoculation, the selection by enrichment culturing is especially performed by compounds of the contamination. A very interesting possibility would be to expand this technique to a selection for the tendency of microorganisms to adsorb onto soil particles. The small percentage of the population that does not tend to sorb, could thus be selected, possibly resulting in improved biodegradation in situ because these organisms can be carried a longer distance in the subsoil. This aspect needs further attention.

- Co-metabolism, such as the biodegradation by methanotrophes, deserves more attention because it may broaden the applicability of biorestoration.

- Detergents could be useful with respect to the following aspects:
  * limitations caused by the low availability of contaminants to the microorganisms,
  * extension of the applicability of in-situ biorestoration for compounds with a low solubility.

  In order to open up possibilities for these aspects, fundamental research into the use of detergents in this field is necessary. Not only artificial supply of detergents in the in-situ biorestoration system should be considered, but also the possible use of surfactants produced by microorganisms in the soil.

Mass balances

- There is a strong need for mass balances on both laboratory and pilot plant scale. Mass balances will improve the insight in the contribution of different processes in the total biodegradation process.

- The limited possibilities to monitor biological activities in the soil is partly responsible for the lack of knowledge about the process of in-situ biorestoration. The development of methods, which can be used for monitoring the biological processes in the soil, would greatly contribute to a better understanding of the processes, and thereby, to a more selective and economical supply of for example oxygen and nutrients.

- In order to gain a better insight into the contribution of biodegradation to the total degradation process in the laboratory, a satisfactory method for sterile experiments should be developed. The methods currently available are insufficient.

- The precise fate of degradation products is not yet known. A proportion is converted to leachable DOC, another part to DIC, but a large part is still unaccounted for. Insight into the quantity, quality and significance of degraded hydrocarbons, such as gasoline, is needed, especially as regards the question of "how clean is clean?".

Specific problems

- More attention should be paid to the problem of clogging in the subsoil, resulting in disappointing infiltration rates. This problem can be related to different factors, such as geology (permeability), excessive growth of microorganisms, or high concentrations of iron or manganese.

- Once relatively low residual (threshold) concentrations with in-situ biorestoration have been reached, the limiting factor usually becomes the availability of contaminants to the microorganisms. This is in the region of, for example, less than 250 mg/kg of dry soil in the case of mineral oil. When cleaning up soil contaminated by mineral oil in the Netherlands, residual concentrations must always be less than 50 mg/kg. This makes the limiting factor in this case, principally availability, even more important. Further fundamental research in this area is recommended.

Overview

An overview of the most important recommendations is given in table 6.

Table 6. General overview of recommendations.

Policy	System design	Research
* stimulation of experience and sharing of information	* combination of biorestoration and venting	* oxygen:
* integration of microbiology, hydrology and (soil-) chemistry	* problem of clogging	- supply and distribution
* preliminary research including heating and mass balances		- alternative oxygen sources
* consideration of both soil and groundwater		- peroxide stability
		* monitoring possibilities
		* extension to broader application
		* threshold concentrations
		* co-metabolism
		* addition of micro-organisms
		* addition of detergents
		* sterile experiments
		* modelling of biorestoration
		* combination of chemical and biological treatment

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Code	Organization	Location	Soil structure	Contamination	Oxygen source	System	Nutrients	Costs	Results	Remediation time	Problems
N1	RIVM / TNO	Filling station	sand	petrol	hydrogen peroxide	recirculation	NH4NO3 KH2PO4/Na2HPO4	$ 325,000 $ 125/ton		Exp: 6-12 months	
N2	HTTS	Filling station	sandy	petrol / diesel	air	recirculation	COD:N:P=100:5:2		46-99.6% removed in 6 months		-infiltration -control system
N3	DRM	Contaminated soil beneath building	sand and loamy sand layers 10e-5 / 6x10e-4	domestic fuel oil	air	recirculation	KNO3 C:N:P=100:10:1		B-value for aliphatics and mineral oil	half year	infiltration in loamy layers
N4	NAM	Gas exploration site	sandy with clayy layers	condensate; volatile arom.	air nitrate	recirculation	NO3 K2O	$ 350,000			pumped up conc.>than expected
N5	Delft Geotechnics	Field test	sand 4x10e-4<K<10e-4	petrol and diesel	air	venting inoculation	C:N:P=100:10:2		p:96% removed d:33% removed	12 months	
D1	Messer-Griesheim	Chemical industry site	gravel / sand	hydrocarbons	Pure oxygen	Recirculation	Na3PO4	< 41 $/m3	COD 175->30 in 1 year		hydrologic. isolation
D2	Institut fuer Mikrobiologie	Solution industry site	sandy with clay	chlorinated hydrocarbons	nitrate	unsaturated	nitrate fertilizer	330,000 $; 6-8 $/m3	120->60 mg/l in 14 months		
D3	AnaKat	Bus station		hydrocarbons	hydrogen peroxide	inoculation					
D4	Argus	Filling station	coarse sand	diesel oil	air	unsaturated / inoculation	phosphate ammonium manganese	62 $/m3	<4600 mg/kg	12 months	
D5	TGU	Refinery	sand / gravel	PAH's	nitrate	recirculation / heating	(NH4)3PO4			Exp: 5 years	
D6	Baugrund Institut	Former refinery	clay layers and gravel sands	chlorinated hydrocarbons / mineral oil PAH's	nitrate	will result from research	id				

D7	IMA GmbH	Industry site	sandy 10e-2 / 10e-3.5	fuel oil	hydrogen peroxide	unsaturated / inoculation	(NH4)3PO4 + trace elements	41-80 $/m3	6000-><100 mg/kg	9 months	
D8	Kloeckner Oecotec	Refinery		diesel petrol aromatics		saturated / recirculation	not specified		175->25 mg/kg	15 weeks	
D9	Engler-Bunte Institut	Marshalling yard	coarse sand and gravel 2.1x10e-3	oil aromatics	nitrate / ozone	saturated / recirculation / heating			undetectable levels	300 days	
U1	DuPont Biosystems	Filling station		gasoline	hydrogen peroxide	saturated / recirculation	C:N:P=6:1:1	$ 750,000 $9/kg hc	<10 mg/kg	4 years	
U2	ECOVA	Pesticide production	sandy till	4-chloro-2-methylphenol	air	saturated / recirculation	no addition	$300,000		5 years (planned)	
U3	RS Kerr Env. Lab US Coast Guard Rice University	Air station, leaking storage tank	sand and gravel highly permeable	BTEX	hydrogen peroxide	no recirculation	NH4Cl KH2PO4 Na2HPO4		7.2x10e-4 mg/l in 250 days	> 6 months	
U4	John Mathes & Ass., Inc.	Leaking pipeline assembling plant	overburden clay 10e-5 m/s	gasoline	hydrogen peroxide	recirculation and venting	Restore 375R		undetectable (80% of area)	2 years	NO3 formation
U5	Stanford University	Research project	sand / gravel 10e-3 m/s	DCE, TCE	methane / oxygen	recirculation		--	50% TCE, 90% t-1,2-DCE and VC removed	8 days	
U6	USAF Eng. and Serv. Center	Airforce Base Leaking pipeline	coastal sand 7x10e-4 m/s	JP 4	hydrogen peroxide	infiltr. gallery injection wells spray irrigation	Restore 375R	> $ 1.4 mln	550 kg hc removed	12 months	peroxide destabilization
U7	Groundwater Technology	Industrial facility	glacial till	BTEX C4-C12	hydrogen peroxide	recirculation	Restore		undetectable levels (80%)	72 days	
U8	ENSR	Hazardous waste lagoon	lagoon	BTE, naphtalene chloroform a.o.	air sparging	aerating / mixing	no addition	Exp:$90 mln	90% in 112 days		
U9	LSU	Abandoned refinery (research)	river silt / sandy clay	(polycyclic) aromatics, oil		landfarming		$ 6 mln	80-83% degrad. in 25 days		

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Heavy Metal and Pesticide Removal from Contaminated Ground Water by the Use of Metallurgical Solid Waste Solvents

HEAVY METAL AND PESTICIDE REMOVAL FROM CONTAMINATED GROUND WATER BY THE USE OF METALLURGICAL SOLID WASTE SORBENTS

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ABSTRACT

The prospects for heavy metal and pesticide removal from contaminated ground water by the use of waste metallurgical solid adsorbents such as bauxite wastes of alumina manufacture (red muds), blast furnace slags and coal fly ashes are assessed. In this regard, the composition of solid waste sorbents (sws); individual adsorption capacities of constituents; metal speciation in regard to adsorption/desorption; design of composite sorbents; sorption performance of sws for metals, phosphate and chlorinated pesticides; pretreatment of sws; mobilization and ground water transport of metals; solidification of sorbents after loading with metals; leachability of metals from the solidified mass; technology selection and prospects for further studies are discussed.

The Composition of Solid Waste Sorbents

Red muds are the alkaline leaching solid wastes of bauxite in the Bayer Process of alumina production. The red muds (rm) had the following chemical composition: Fe_2O_3:37.26%, Al_2O_3:17.58%, SiO_2:16.94%, TiO_2:5.55%, Na_2O:8.31%, CaO:4.38%, loss on igntion:7.17%. Red muds, being multicomponent systems, are composed of sodium aluminosilicates, kaolinite, chamosite, iron oxides (hematite) and hydroxides. Basically iron is in the form of hematite, titanium is in the form of iron-Ti oxides, and Al in the form of aluminosilicates. 94% of rm-s have less than 10 microns grain size. They are supplied from the Seydişehir Aluminum Plant.

The blast furnace slags (bfs) were supplied from İskenderun iron and steel plant, and had the following composition: CaO:43.9%, SiO_2:36.3%, Al_2O_3:16.9%, MgO:1.6%, Fe_2O_3:0.3%, MnO:0.3%, S:0.7%.

Fly ash is the very fine ash produced by combustion of powdered coal with forced draft,and is often carried off with the flue gases.Recovered by electrostatic precipitators,fly ash is a mixture of alumina,silica,unburned carbon and various metallic oxides including TiO_2.

All these waste solids emerge as unwanted by-products of widespread metallurgical processes in bulk quantities. Before discussing the adsorptive performance of these metallurgical waste solids,one needs to know the individual adsorption capacities of their constituents.

Individual Adsorption Capacities of Constituents

The essential synthetic adsorbents used for metal removal -which also take place in the compositions of sws- are alumina,iron oxides (hematite and goethite),SiO_2,hydrous oxides of Ti and Mn(IV),and carbon.

Activated carbon and carbonaceous materials:

These are capable of adsorbing a great number of metal cations and anions.Their highest performance is observed with soft metal compounds(Hg,Cd,Pb,etc.) and organics.Activated C shows an affinity for Cr(VI);adsorption conforms to a Freundlich isotherm (Watanabe,1982).Powdered actvd.C was more effective in adsorbing Cd(II) from electroplating effluents than granulated actvd. C.The rate of Cd removal at pH 7 was proportional to Cd concn.,the C dosage and the available surface sites.The used C may be regenerated with strong acids (Huang,1982).Cd adsorption conformed to the Langmuir isotherm (Shirakashi,1984).The activated C species (powder,granular and felt) as well as C black,graphitized C,graphite, glassy C and anthracite were useful for Hg adsorption in the range pH 1-14.The lower valence of Hg is favoured in adsorption (Koshima,1982).

Activated alumina:

As(V) is effectively removed from water by adsorption onto activated alumina.Adsorption isotherms can be developed by batch tests of 7 days (or more) duration (Rosenblum,1983). Alumina is an excellent adsorbent for phosphate (which may cause eutrophication in lakes and water bodies),arsenate and a number of metals.

Hydrous manganese(IV)oxide:

Adsorption of Zn(II) occurs at the neutral-type surface sites which are predominant at pH 3-7 (Tamura,1984).Maximum retention by hydrous MnO_2 of As(III) occurs at pH<5,declining at higher pH to almost half of the total As at pH 10.The adsorption capacity of pyrolusite at pH 6.5 for As(V) species is 10 mmol/kg.The saturation level by $MnO_2.xH_2O$ was 10 mmol/kg at an As(V) concn.of $5-8x10^{-6}$M;but the uptake steadily increased with concn. up to 68 mmol/kg with an As(V) concn.of $2x10^{-5}$M.Added As(III) was oxidized rapidly and most of the product was retained at pH 3.As release from the sorbent occurs upon exposure to reducing and complexing agents (Thanabalasingam,1986).

Hg adsorption on MnO_2 is dependent on electrolyte concn.; all cations and anions like thiosulfate,thiocyanate,iodide suppress adsorption.The greater the ionic potential of Hg, the weaker the Hg adsorption.A Freundlich type isotherm is observed over a wide Hg concn. range (Hasany,1986).

Hydrous Titanium dioxide:

Traces of Fe,Cu,Co,Ni,Mn,Cr and V ions are adsorbed on hydroxylated TiO_2 from carbonate solutions (Koryukova,1984). Hydrous TiO_2 is an excellent adsorbent for U(VI) even in HCO_3^- media;this makes TiO_2 an efficient sorbent for U recovery from sea water.(See Fig.1)Although the isoelectric point of TiO_2 is at pH 5.5 (Tewari,1975),U adsorption is still significant at higher pH showing that specific chemical (non-electrostatic) interaction may be responsible for the U uptake (Jaffrezic-Renault,1980).

Goethite (α-FeOOH):

Metal adsorption on goethite strongly increases with pH in the interval pH 4-8.The $pH_{.50}$ values (corresponding to 50% adsorption) are 4.9,5.6 and 5.8 for Zn(II),Ni(II) and Cd(II),respectively.The differences between the $pH_{.50}$ values agree with the differences between the pK values of the 1st. hydrolysis constants of these cations.Trace metal adsorption by the hydroxylated Fe-oxide surface is strongly affected

by hydroxo-complex formation of these metals.Besides adsorption,some metal sorption occurs within the goethite lattice as occlusion,and the latter resists to desorption even in acid leaching (Gerth,1983).

Hingston et al.(Hingston,1967) observed a linear decrease in the apparent maximum sorption capacity of goethite for phosphate as pH increased,with a change in slope occurring at pK_a values of orthophosphoric acid (pK_2:7.2 and pK_3:12.3). He suggested that the net surface charge and phosphate speciation determined the max. sorption capacity of goethite as a function of pH;the high capacity above pH 7 was thought to be caused by a higher affinity of goethite for $H_2PO_4^-$ than for HPO_4^{2-} (Mayer,1986).

Hydrated iron(III)oxide:

Transition metals bind strongly to both iron and manganese oxides (Murray,1978).The relative adsorption rate constants for metals on iron oxide follow the order Pb > Cu > Cd,as in the case of their thermodynamic equilibrium constants of hydrolysis (Zhuang,1984).Surface complexation constants for cations on hydrous Fe(III)oxide follows the same order of their first hydrolysis constants (β_{11}) as Pb > Cu > Cd (Smith,1991).

In a recent study,Cd sorption on $Fe_2O_3.H_2O$ (am) in the presence of alkaline-earth cations was investigated with emphasis on the Cd-Ca binary system.Competition was observed primarily in Cd-Ca binary mixtures.Solubility limitations in soil and ground water systems will prevent Sr and Ba from reaching concentrations high enough to allow them to compete with Cd on iron oxides.However competitive adsorption of Cd with Ca can be important in soil or ground water.The extent of competition increased with increasing Ca concn., and may inhibit Cd adsorption up to 20 % or more depending upon pH and concn.In single-element experiments,changes in ionic strength(between 0.005 and 0.5 M) did not influence Cd sorption but did affect Ca sorption,implying that a portion of the Ca surface complexes were outer sphere (Cowan,1991). In single-element adsorption studies,the fractional adsorption

of Cd (10^{-6} and 10^{-7}M) increased from 0 to 100% over the pH range from 5.0 to 8.5 (Farley,1985).The $pH_{.50}$ was 6.4 for 10^{-7}M Cd and 6.7 for 10^{-6}M Cd.As is typical of cation adsorption,the pH of 50% adsorption increased as the concn. of the Cd and thus the ratio of adsorbate (Cd) to adsorbent ($Fe_2O_3.H_2O$(am)) increased (Benjamin,1981).

Adsorption of uranyl(VI) on hematite vs.equilibrium concn.of U in solution at various pH values is shown in Fig.2.The characteristics of the adsorbent hematite sol are: particle size:0.12 microns,specific surface area:34 m^2/g, α-Fe_2O_3 content:>98%,and isoelectric point:pH 7.6 (Ho,1985).

In general,surface complexation constants of various metals on hydrated Fe and Mn oxides may be calculated by the aid of the triple-layer model of the oxide/water interface (Smith,1991).These constants help to estimate specific metal adsorption on hydrous oxide surfaces.

Metal Speciation in regard to Adsorption/Desorption

One or more metal species may be involved in adsorption which occurs as a result of specific interaction between the adsorbent and the adsorbate.Therefore the distribution of metal species with respect to water conditions such as pH, Eh,free ligand concn.etc. may be important for adsorption/ desorption.This will be exemplified with U uptake from water by iron oxides.

In the case of uranyl(VI),all the Fe-oxide materials (well-characterized goethite,amorphous FeOOH,and hematite sols) strongly adsorb dissolved uranyl species at pH>5-6 (with adsorption greatest onto amorphous FeOOH and least onto well-crystallized specular hematite).The presence of Ca and Mg at the 10^{-3}M level does not significantly affect U adsorption.However uranyl carbonate and hydroxy-carbonate complexing severely inhibits adsorption (desorption is favoured).Monodentate UO_2OH^+ and mono- to tri-dentate $(UO_2)_3(OH)_5^+$ surface complexation are assumed to compensate for the observed specific adsorption (Hsi,1985).Thus it may be deduced that U(VI) speciation,i.e.,the relative abundance of certain hydrolyzed species in solution,is of utmost importance in determining the adsorption of U on hydrous oxides,e.g., hematite sol.

The sudden increase in U(VI) adsorption onto hematite around pH 5 may be attributed to increased relative abundance of $(UO_2)_3(OH)_5^+$ among the hydrolytic uranyl(VI) cations.This idea is also supported by IR data.(Ho,1985) Fig.3 compares the pH dependence of uranyl adsorption on hematite with the percentage of major hydrolysis products of U(VI).Since the major species responsible for U(VI) adsorption is $(UO_2)_3(OH)_5^+$ which is specifically adsorbed,desorption is not feasible at pH 6.2.Because iron (III)orthohydroxide"$Fe(OH)_3.xH_2O$" has multiple sites for adsorption,some weakly adsorbed uranyl species at high adsorption density may be desorbed.However U is basically strongly retained at low adsorption density indicating irreversible adsorption as long as the pH is kept around 6. At pH$\leq$4,the adsorbate dissociates to UO_2^{2+} which is released from the oxide surface.In other words,the equilibrium

$$(UO_2)_3(OH)_5^+ \rightleftharpoons 3\ UO_2^{2+} + 5\ OH^-$$

shifts to the right.

U(VI) speciation as given in Fig.4 is based on the assumption of dissolution of atmospheric CO_2 in aqueous solution at the indicated pH.(See Fig.4 for observing the percentage of U(VI) hydrolytic species and percentage adsorption with respect to pH at a total U concn. of 10^{-5}M) Thus the relative abundance of a given species is recorded vs. pH.Actually relative abundance needs also be shown vs. $p[CO_3^{2-}] = -\text{Log}[CO_3^{2-}]$ so as to discuss adsorption/desorption behaviour in carbonate and bicarbonate media of a given strength (HCO_3^- is abundant in Turkish ground waters).(See Appendix 1:"The distribution of species in uranyl-carbonate-hydroxide complex equilibria",Apak et al., 1990)

An appreciable concn. of U is still adsorbed by hematite in bicarbonate solutions.IR data demonstrate that the adsorbed uranyl(VI) species contain carbonate(Ho,1986). Comparison of the pH dependence of adsorption of uranyl species on hematite with the relative abundance of uranyl species in solution containing 10^{-3}M total HCO_3^- suggests that $(UO_2)_2CO_3(OH)_3^-$ may be the active species responsible for adsorption (See Fig.5)The uptake of U decreases with

increasing solution pH; the decrease coincides with a decrease in the proportion of $(UO_2)_2CO_3(OH)_3^-$ present (Ho,1986). A specific chemical interaction between the adsorbent and the adsorbate is again indicated. Below isoelectric pH of hematite (pH 7.6), positively charged hematite particles adsorb negatively charged U(VI) species. Above pH 7.6, the particles are negatively charged, and adsorption of uranyl-carbonate species makes them more negative. Especially above pH 8.5, $UO_2(CO_3)_3^{4-}$ becomes predominant, enhancing desorption of U from hematite. However the adsorption below 7.6 is not simply of electrostatic origin, as TiO_2 (isoelectric pH 5.5) shows partial adsorption at pH 7.6 (See Fig. 1- Adsorption of U(VI) on TiO_2 hydrate in 10^{-3}M HCO_3^- solution as a function of pH). The adsorption of U is irreversible on hematite as long as the pH is maintained (at 8.1). However fast desorption occurs at pH 9, the final amount of U retained being equal to the equilibrium adsorption of U at pH 9.0. Thus adsorption is reversible wrt. pH in this range.

The addition of humic acid to a hematite sol alters the uhtake of U by the hematite particles. The magnitude of this alteration varies with the solution pH and with the amount of humic acid added. Changes in U speciation as well as the blockage of the active surface sites, and the extent of U-humic acid interactions are the dominant factors. IR spectroscopic analysis suggests that new bond formation may be involved in the uptake of humic acid/U by hematite (Ho and Miller,1985). Humic acid enhances U(VI) uptake at low pH and humic acid concn. Once humic acid species cover the hematite surface, the adsorption pattern between pH 4.4 and 6.4 is reversed, which is reflected in an abrupt decrease in U uptake in the presence of small amounts of humic acid. In this case, surface blockage and complex formation between unbound humic acid in solution and the U ions tend to keep the U from being adsorbed.

The fact that the relative adsorption rate constants (Zhuang,1984), surface complexation constants (Smith,1991)

and the pH values for 50% adsorption ($pH_{.50}$) of a number of divalent heavy metals(Gerth,1983) agree with the first hydrolysis constants of these metal cations reflects the key role of metal-hydroxo complexes in specific metal adsorption on the hydrous oxide surfaces (e.g.,iron(III) oxides).The same trend is observed with red muds (Pb > Cu > Cd) when the corresponding slopes of their adsorption isotherms are compared.Thus the importance of species distribution in aqueous solution wrt. polynuclear hydroxo-metal complexes is indicated.The fact that water-soluble complexing ligands closely control Cu speciation is reflected in the observed decrease of Cu adsorption onto Na-montmorillonite with increased pH in the presence of organics-rich soil extract (Gupta,1983).

Design of Composite Sorbents

Design of composite sorbents for the purpose of combining the advantages of individual sorbents is an important part of sorption studies.Such a task may also serve to manufacture cost-effective sorbents which can remove a variety of contaminants in specific pollution problems.Some examples are cited below:

A combined adsorbent showing a high sorption capacity for phosphate can be synthesized by coprecipitation of Na-silicate and $Al_2(SO_4)_3$ solutions resulting in an aluminosilicate structure (Yagodin,1982).A porous sorbent prepared from α-Al_2O_3 and containing 15% C may be made by using (0-30%) of montmorillonite binder (Komarov,1983). Thus the properties of clay-like adsorbents are combined with those of oxide-like adsorbents.A composite sorbent Containing TiO_2 and activated C may be used for U recovery from sea water (Sakane,1982).A triple combination of an inorganic residue,an organic residue,and a dehydrating agent (salt,acid etc.) is mixed and heat-treated to yield a hydrophobic adsorbent.Such adsorbents are made from fly ash,spent sulfite liquor,modified bitumen,etc. (Kinder,1984).Adsorbents may be prepared from TiO_2,Al_2O_3 and their mixtures as porous support materials,and chemically treated by freshly precipitating ferric hydroxide

onto their surfaces.Column experiments with the synthesized adsorbents yielded breakthrough capacities ranging between 3.2-8.7 mg As/g-adsorbent working with 0.05 mg/L arsenic concentrations(Hlavay,1984).TiO_2-Al_2O_3 adsorbents prepared from the hydrolytic precipitation of Ti(IV) and Al-hydroxides show a high surface area and Co sorption capacity after calcination (Fujita,1985).Carbonaceous sorbent materials may be prepared by using a mixture of peat with industrial wastes (Ogurtsov,1985).

A detailed list of unconventional coagulants and sorbents used for heavy metal removal from water (with references) was presented in the first report(Apak,1988).

The basic advantage of rm-s and bfs-s is their versatility.Since they are comprised of a number of adsorbents and flocculants-all of which are specific for certain treatment procedures-these muds and slags are applicable in diverse applications.Fo example,in the case of As removal,Fe(III) compounds are especially important,and the combined effects of ferric and Al compounds are stronger than that of unassisted alum.Lime should be used in combination with alum and polybasic aluminium chloride for turbidity removal (Csanady,1982).From the perspective of coagulation to remove particulates,orthophosphorus exerts a coagulant demand for Al and Fe(III).$Ca(OH)_2$ precipitates orthophosphates better,while aluminum sulfate shows higher efficiency for polyphosphates removal.Fly ash,when combined with alumina,is a more suitable adsorbent for P removal than alumina alone,The combined usage of Fe(III) and Al sulfates provides a more satisfactory removal of U from drinking water (Lee,1983).Alum coagulants of improved efficiency are produced by adding small amounts of Ti(IV)sulfate to Al-sulfate coagulants, accelerating the hydrolysis of Al-sulfate even at low temperature,and improving the growth of the flocs. (Fukumori,1974).

On the other hand,mineral acid-activated red muds (rm) contain soluble Al,Fe(III) and titanyl(IV) sulfates (or chlorides)which present a valuable combined coagulant,

while Ca and Na-aluminosilicates of varying composition in red muds and slags contribute a mixture of adsorbents for different effluent treatments.Thus the beneficial properties of oxide-like and clay-like minerals in soils are combined in a single sorbent which makes use of both non-electrostatic specific chemical interaction and ion-exchange interaction between the adsorbent and the adsorbate.In the interim report (Apak,1989) the preparation of a composite sorbent of bfs and rm in 2:1 ratio was reported.The heat-treated (at 1100^{o} for 1/2 h) adsorbent was useful for heavy metal removal.The manufactured adsorbent could be used for the treatment of pumped ground water which might have been contaminated,e.g.,by seepage containing metal plating and metal finishing wastewater at a pH above 5.5.After the relatively easy separation of sludge with or without the use of diatomaceous earth or perlite as filtering aid,the treated ground water may be used for irrigation or dilution of contaminated ground water (Apak,1989).

Sorption Performance of Waste Solid Sorbents for Metals, Phosphates and Chlorinated Pesticides

Red muds and blast furnace slags have been utilized in the removals of heavy metals,radionuclides,inorganic and organic materials,suspended solids,colour,biological and chemical oxygen demand from water streams as cheap adsorbents and flocculants (Sho,1973 and 1980).These metallurgical solid wastes,especially red muds in natural form,have a high neutralization capacity of acidic waters due to their high alkali content.Thus they are good precipitating agents for heavy metals via hydrolytic precipitation reactions.

Alumized red mud solids (ARMS) obtained by sulfuric acid treatment of red muds contain the double salts of Na-Al-sulfates as the major constituents,with significant amounts of $CaSO_4$,$Na_2O.Al_2O_3.2SiO_2.2H_2O$,$FeSO_4$,$SiO_2$,$TiO_2$, $Fe_2(SO_4)_3$ and Fe_2O_3 (Bayer,1972 and 1974).The indicated composition may serve to act both as a flocculant and adsorbent for water and waste water.An ARMS plant for P

removal has been shown to be at least 50% cheaper in operation costs than a conventional plant working with alum (Shannon,1975).

The basic materials subject to this research,i.e., activated or natural rm-s,bfs-s and fly ashes act in a four step mechanism: (i) Gel precipitation (sweep flocculation), (ii) Flocculation by adsorption of hydrolytic products, (iii) Conventional adsorption, (iv) Ion exchange.

Gel precipitation is the most important contribution to mineral acid-activated rm in water treatment,and most heavy metals are removed via coprecipitation (Gregory,1978). Due to the presence of strongly hydrolyzable species of Al(III),Fe(III) and Ti(IV),the primary effect of ARMS in particulate removal results from the hydroxide precipitate initially in the form of a fine colloidal dispersion.The particles then aggregate to form hydroxide flocs which enmesh the originally existing colloids.The entire process is referred to as 'sweep flocculation'.

Besides sweep flocculation,ferric and Al salts in ARMS can cause flocculation by specific adsorption of hydrolytic products.The multinuclear hydrolysis products, formed as kinetic intermediates,including $Fe_2(OH)_4^{2+}$, $Fe_3(OH)_4^{5+}$,$Al_4(OH)_8^{4+}$ and $Al_8(OH)_{20}^{4+}$ are even more effective flocculants than their parent ions due to their higher charge and strong specific adsorptivities.

Conventional adsorption is also a mechanism of pollutant removal for metallurgical solid wastes.Natural waste adsorbents have physical (conforming to adsorption isotherms) and semi-chemical adsorption as their primary mode of action,while after acid treatment,gel-precipitation may become the dominant mechanism.(Apak,1989)

Especially granulated bf-slags and fly ashes can function as synthetic cation exchangers.The cation exchangers produced from these waste solids after acid treatment have porous silicagel-H^+ macromolecular structure in which the chief constituents,Na- and Ca-aluminosilicates, act as zeolites.

The lab experiments with solid waste sorbents (sws) will be presented in terms of the metal removed. First some terms need to be defined.

A Freundlich isotherm for adsorption is in the form

$m = k\ C_s^{(1/n)}$ or $\text{Log } m = \text{Log } k + (1/n)\ \text{Log } C_s$

where

m: equil. amt. of solute in the solid phase per unit wt. of adsorbent (µg/g)

C_s: solution concn. of pollutant remaining at equil. (µg/mL)

k and (1/n): Freundlich parameters which relate to specific equilibrium capacity and intensity, respectively.

R_d is a measure of metal sorption efficiency of adsorbent (i.e., metal distribution coefficient)

R_d = metal(bound)/metal(free)

R_d = µg metal removed per g sorbent/µg metal remaining per mL of solution

Lead:

Precipitation and adsorption procedures were compared for Pb(II) at various pH values. For pptn. experiments, 50 mL of 300 ppm Pb soln-as $Pb(NO_3)_2$- was equilibrated at the desired pH by the addition of appropriate quantities of 1 M HCl and 0.1 M NaOH solns. For adsorption experiments, 2.0 g of dried red mud (prewashed with H_2O, -100 mesh) was equilibrated with 60 mL of 250 ppm Pb soln. at the specified pH. The results are shown in Table 1.

Table 1- Comparison of pptn. and adsorption for Pb(II)

Soln. pH	Pptn. removal, %	Adsorption removal, % (a)
4.9	7.3	98.6
6.4	...	99.5
6.7	25.6	99.8
8.0	48.0	...
8.2	...	>99.9
10.3	99.6	>99.9

(a) Less than 0.1% can be desorbed after drying with a 6:1 water-solid ratio at pH 5.0 after 4 d.

The chemisorption type of interaction of Pb with the -OH groups of the hydroxylated rm surface minimizes the leachability of Pb from these surfaces as shown by desorption tests.

Fig.6 shows R_d vs. C_o curves of 90 mL $Pb(NO_3)_2$ influent solution contacted with A):1 g rm B):2 g rm C):2 g bfs at pH 4 for 6 h (room temp.).The rm-s were acid-treated and bfs-s were washed,as described before.The Freundlich parameters were:

Case	Log k	(1/n)
(A)	2.923	0.125
(B)	2.894	0.093
(C)	2.677	0.320

Sorption of Pb with synthetically prepared hydrous MnO_2 conformed to a Langmuir isotherm of the type:

$1/m = 1.514 \times 10^{-4}(1/C_s)$ for $10 \leq C_s \leq 310$

$pH_{.50}$:2 and removal is essentially complete above pH 4.

Copper:

Fig.7 shows R_d vs. C_o curves of 100 mL Cu(II) soln. contacted with (A):1 g rm (B): 1 g bfs at pH 4.5 for 5 h. The corresponding Freundlich parameters are:

Case	Log k	(1/n)
(A)	3.694	0.116
(B)	3.383	0.154

Actvd. rm is generally more effective for Cu(II) removal than bfs.

For Cu(II) adsorption with a synthetic $Fe(OH)_3$ suspension in 1 M NH_3 soln.,Log k and (1/n) are 4.135 and 0.130, respectively for the interval $250 \leq C_s \leq 6000$ µg/mL.

Cadmium:

Fig.8 shows R_d vs C_o variation of Cd(II) contacted with 1 g of activated rm at pH 4.5.Log k and(1/n)are 3.508 and 0.101,respectively.

Mercury(II):

The fly ashes had quartz and silica,alumina,loss on ignition(mainly amorphous carbon) and ferric oxide as the major constituents,SiO_2 having the highest proportion.The variable composition of fly ash depended upon the origin of coal and the combustion process.The fly as was washed with dil.HNO_3,then with H_2O,dried and sieved through 100 mesh-sieve.2 h equilibration of fly ash with the specified

$Hg(NO_3)_2$ concn. was carried out at room temp.The Hg adsorption conformed to a Freundlich eqn..The optimal pH interval was $3.5 \leq pH \leq 4.5$.10 ppm or less concentrations of Hg showed 100% adsorption by using 2 g of fly ash per 100 mL of solution.The adsorption isotherms at different pH were (m is in mg/g and C_s is in mg/L) :

Soln.pH	k	(1/n)
2.1	1.01	0.05
3.2	1.08	0.34
4.2	1.30	0.36

Although the Freundlich capacity factor (k) of fly ash for Hg was lower than that of activated C,the intensity factor (1/n) was comparable at optimal pH.

Uranium(VI) removal:

Basaltic ground water,having a higher pH and carbonate/bicarbonate content than granitic ground water,has the ability to leach out uranium possibly as the tricarbonate complex;this may be important for the mobilization of U from uranium mill and mine dumps and vitrified fission products of nuclear reactors.Aquifers surrounding the U,ore zone and related ground waters have been reported to show uranium contamination incidents at 'in situ leach mining' sites (Vandell,1982).

R_d vs. C_o curves of uranyl(VI) with rm and bfs are given in Fig. 9 and Fig.10 ,resp.,100 mL of uranyl nitrate soln.of a particular pH being equilibrated with 1 g of adsorbent in each case.The corresponding Freundlich parameters with red mud (rm) were:

Soln.pH	Log k	(1/n)
3.0	1.864	0.899
4.5	3.605	0.217
7.0	3.265	0.383

m:µg/g and C:µg/mL

The parameters with blast furnace slag (bfs) were:

Soln pH	Log k	(1/n)
4.5	3.722	0.051
7.0	1.098	1.326

Rm is a much better adsorbent for uranyl than bfs.The higher sorption of uranyl on rm at pH 4.5-when compared

to that of pH 7.0 may be attributed to specific adsorption of the hydrous oxide surface, since the former pH is much lower than the point of zero charge of most oxides constituting the rm. (The PZC of the used rm was found to lie between 7.5 and 8.5, as observed from acidimetric titration curves-See Fig.11). On the other hand, the basic mechanism of removal near hydrolytic pptn. pH values seems to be gel precipitation.

At pH 4.5, an uranium loading of 10 mg/g on treated red muds has been observed in batch equilibration tests Apak, V., 1987).

Phosphorus:

In batch tests, phosphorus removal by activated rm was observed to proceed rapidly at first, then relatively slower, about 70% of the total P being removed in the initial stage. Heat treatment of rm prior to P removal resulted in dehydration and loss of hydroxyl group components which occurred to the detriment of phosphate adsorption. The P removal mechanism comprises adsorptive flocculation and partly ion-exchange resulting in the adsorption of $Al(OH)_2H_2PO_4$ on the rm surface (Apak, V., 1987).

In conventional treatment techniques, phosphate removal is maximum at pH 4 with Fe(III) and at pH 6 with Al salts as coagulants (Recht, 1970). For waters of higher alkalinity, economics usually dictate the use of additional metal salt rather than pH adjustment. Theoretically the min. solubility of $AlPO_4$ occurs at pH 6.3, and that of $FePO_4$ at pH 5.3 (Apak, 1989).

Column experiments were performed by using a NaH_2PO_4 solution; Fig.12 shows the experimental set-up for obtaining the breakthrough and elution curves of phosphate from the rm column. The rate of influent percolation through the adsorbent was 15 mL per 8 h, with the purpose of simulating ground water movement at a hydraulic loading rate of 1 ft/d. Fig.13 shows the breakthrough curve.

In ground water,hydrogen ions are produced in equilibrium reactions involving biooxidation of organic matter and ammonia,and through oxidative hydrolysis of Fe(II) and Mn(II).These H^+ ions react with HCO_3^- in natural waters to produce carbonic acid which lowers the pH.Thus elution possibilities of the retained phosphate with CO_2 saturated water (H_2CO_3) were investigated so as to assess the recontamination risks of the aquifer.A relatively low proportion of retained phosphate could be eluted from the rm column with CO_2-saturated water (Fig.14).

Arsenic:

Arsenic in an oxidative environment dissolves in ground water as arsenate(V),and in weakly reducing environments,the predominant species is arsenite(III).At low pE,As(III)sulfide is stable and As is well beyond the limits bet for drinking water.Since its main species are chargeless or negatively charged,As would not be expected to be retained by adsorption or ion-exchange during ground water flow.

Arsenate (AsO_4^{3-}) removal by coprecipitation was maximum between pH 6-7 on ferric hydroxide,and between pH 5 and 8 on Al-hydroxide.

Equilibrated beaker tests showed that 1 g activated rm almost completely removed 100 mL of 20 ppm As between pH 5 and 6.Arsenate taken up by the rm could be leached with alkaline solutions.

Arsenic adsorption on rm shows a slow kinetics,and sometimes equilibrium could not be attained in column tests.

Information regarding metal removal with rm and bfs may be summarized in Table 2.

Sorption of chlorinated pesticides on red mud is given in Appendix 2 (Apak,V.,1991).

Table 2- Metal removal with rm and bfs .

Metal removed	Initial metal concn.(ppm) used in sorption studies	Removal efficiency (4 h contact)
Pb(II)	5-30	450-1300µg /g-rm
Pb(II)	5-30	450-1250µg /g-bfs
Cu(II)	100-180	7260-8400µg /g-rm
Cu(II)	30-70	2700-3700µg /g-bfs
Cd(II)	30-100	2940-4600µg /g-rm
UO_2(II)	60-150 (pH3.0)	1570-3300µg /g-rm
UO_2(II)	60-200 (pH4.5)	5630-10980µg/g-rm
UO_2(II)	60-150 (pH7.0)	4800-9100µg /g-rm

Pretreatment of Waste Solid Sorbents and Possible Benefits

Even if no pretreatment of wss is carried out,a thorough washing is necessary (with H_2O) in order not to contaminate water any further.In the case of rm the alkaline filtrate of rm slurry may later be used for the fixation of heavy metals in the used sorbent-cement mixtures in the form of insoluble hydroxides prior to landfill or burial.

In experimental studies,100 g of rm was refluxed with 2 L of 20% HCl for 2 h according to the method of Shiao et al.(Shiao,1977).The acid-treated rm was filtered, washed with water until the washings were free of acid (or chloride),dried at 110°,and sieved through a 80-mesh sieve.Heat treatment may or may not follow acid treatment depending on the purpose.Although heat treatment can be performed at relatively high temperatures,a temperature higher than 200-300° is not recommendable for P removal. Heat treatment also makes column experiments easy as the physical properties of heat-treated red muds are generally improved.

Acid-activation increases the surface area of rm and related adsorbents up to a certain acid concn. Although all mineral acids may be used for that purpose, sulphuric acid is cheaper than HCl for treatment.A combination of 10% HCl-15% $FeCl_2$ may also be used to obtain water treatment coagulants (mixed oxides of Al,Fe,Ti) (Zakharova,1985).

The pulp obtained from HCl leaching of rm is a hydrophobic colloidal dispersion of thixotropic structure. The addition of an electrolyte, or an increased concn. of HCl causes the densification of the dispersion and aggregation of particles. The treated pulp may be dewatered by filtration and centrifugation (Zakharova, 1985). Acid-activation of rm generally enhances the sweep flocculation and gel precipitation mechanisms of metal adsorption.

An alternative acid treatment procedure for the neutralization of rm slurries may be the treatment with flue gases (NO_x and $SO_{2,3}$) to maintain a final pH of 6.5-8.5 (Versiani, 1983). If alkaline rm is let to be exposed to atmospheric weathering, CO_2 is absorbed. $CaCO_3$ may then be precipitated by the addition of gypsum, and a pH just above 8 may be attained. The resulting neutralized rm is a good adsorbent for Cd but a weak one for phosphate (Barrow, 1982).

Granulated bfs-s, whose active components are calcium aluminosilicates, were washed with water, dried at 110°, ground and sieved through a 80 mesh-sieve. When using the bfs as adsorbent, sulfide, an environmentally hazardous precipitating agent for Cu, As and most heavy metals, may be leached out at acidic pH from the adsorbent. Thus the sulfide problem, which may bring further environmental risks, may be overcome. On the other hand, the presence of S^{2-} may be advantageous in the immobilization of heavy metals in the form of their insoluble sulfides in cement matrixes before landfill. Sulfide is also beneficial in reducing the toxic hexavalent chromium of leather tanning effluents by the reaction

$$Cr_2O_7^{2-} + 2\ FeS + 7H_2O \longrightarrow 2Fe(OH)_3 + 2Cr(OH)_3 + 2S + 2\ OH^-$$

In any case, sulfide in water must be carefully monitored (Freeman, 1988).

Polymer binding of rm may be recommended for converting it into adsorbent particles or pellets of improved physical properties. When a water-soluble polymer (e.g., Na-alginate) is dissolved in a rm slurry and sprayed as droplets

into a solution containing a hardener(e.g.,$CaCl_2$ soln.), insoluble pellets are formed which may be separated from solution,cleaned and fired at 200-850° to form the red mud adsorbent particles of increased surface area and favourable usage (Seto,1986).

In the interim report (Apak,1989),the formulation of a calcined composite sorbent for water purification was given.The bfs and rm of identical grain size (-80 mesh) were mixed in 2:1 ratio and calcined at 1100° for 1/2 h. The calcined material was denser than water,and gave definite alkaline reaction in aqueous suspension.A max.amt. of 0.5% S compounds as "S" was tolerated in the resulting material (S coming from bfs).This material successfully removed the divalent metal cations of Pb,Cd,Cu and uranyl from their 10 ppm solutions with an adsorbent dosage of 1 g per 100 mL.The metals taken up by the calcined sorbent did not leach out at a pH of 5.4 (EPA test).However as the pH was lowered,the silicate structure of the calcined material would be affected by acidity and desorption of metals would start to occur.

MOBILIZATION AND GROUND WATER TRANSPORT OF METALS

In general,carbonates and bicarbonates and humic acids mobilize the sorbed U(VI) from hydrous oxides and oxide-type mineral soils.As the soln. pH and humic acid concn. increase,a surface blocking effect and a complex formation with the free humic acid tend to keep uranium from being adsorbed onto hematite;desorption is favoured (Ho and Miller,1985).Adsorption of U on hematite in HCO_3^- medium is irreversible as long as the pH is maintained at 8.1;however fast desorption occurs at pH 9 due to carbonate complexation,the final amt. of U retained on hematite being equal to the equilibrium adsorption of U at pH 9.Thus adsorption is reversible with pH for this range (Ho and Miller,1986).Uranyl-carbonate and hydroxo-carbonate complexation severely inhibited U(VI) adsorption on ferric oxyhydroxides,U adsorption being highest

onto amorphous FeOOH and least onto well-crystallized specular hematite.Presence of Ca or Mg -abundant in ground waters- at the 10^{-3}M level did not significantly affect U sorption (Hsi,1985).U(VI) penetration in tuff between pH 3 and 4 was not sufficiently reversible but was a competitive process consisting of diffusion and adsorption.However the penetration depth was thin above pH 6 due to high adsorption coefficient and rate.(Sato,1986)

The Eh and pH conditions of soil and ground water significantly affect As speciation and mobilization from the adsorbed phase.Greatest mobility of As in arsenical waters codisposed with domestic solid wastes occurs under mildly reducing conditions at pH 5-9,conditions typical of the initial stages of leaching of domestic solid wastes.Under strongly reducing,e.g.,H_2S,environments, precipitation of As as As_2S_3 (or copptn. with FeS) maintained a leachate concn.of less than 10 mg/L for all wastes (Blakey,1984).pH and Eh conditions,presence of other major elements,specific surface area and electric properties of colloidal soil particles,As valence and speciation all affect the desorption and mobility of As to differing extents (Hu,1985).

pH and complexing agents control Cu mobilization. Specific adsorption of Cu(II) on goethite is accompanied by 1-2 moles of proton release per mole of cation adsorbed. Desorption experiments revealed two adsorption sites for Cu of weak and strong binding,corresponding to the readily and less-readily desorbed Cu fractions.The two kinds of binding are associated with the cation being coordinated to 1- and 2- surface-OH moieties,respectively.The gradual interchange of some readily desorbed Cu(II) into a category that is not readily desorbed after an initial time-lag between adsorption and desorption is attributed to possible time-dependent isomorphous substitution of Fe(III) and Cu(II) in the goethite lattice.(Padmanapham, 1983).The ratio of the moles of charge of Cu(II) adsorbed to that of the released protons from synthetic MnO_2

surface indicated that specific interaction of adsorbent and adsorbate takes place in addition to electrostatic forces at a pH less than PZC of MnO_2 (Kanungo,1984).Humic acid concn. up to 1 ppm in soln. caused a sharp decrease in Cu adsorption on kaolin (Gupta,1982).Cu desorption occurred from Na-montmorillonite with increased pH in the presence of organics-rich soil extract while Cd adsorption was only slightly affected (Gupta,1983). Among the metals of Cd,Cu,Ni and Zn;Cu moved least readily through mineral soil columns.All metals showed least mobility in a mineral soil with a relatively high pH, cation exchanging capacity,and exchangeable base content. The order of mobility of metals was $Cu \ll Zn \leq Ni \leq Cd$.These metals were almost completely extractable from a limed and unlimed acid soil by 0.1 M HCl soln.,but were less extractable from a non-acid mineral soil and an organic soil. This behaviour is attributed partly to irreversible binding of the metals in organic matter,a phenomenon inhibited by the presence of Al on organic complexation sites (Tyler,1982).Zn and Cu supply parameters increased when carbonates were removed from a sandy clay soil(Raikhy,1983). Desorption of divalent metals from goethite is a function of pH such that the 50% adsorption pH($pH_{.50}$) order of metals,i.e.,$Zn < Ni < Cd$ as $4.9 < 5.6 < 5.8$,respectively, agrees with the pK values of the 1st.hydrolysis constants of these metals (Gerth,1983).Therefore desorption follows the dissociation of hydroxo-metal complexes.Organic substances in soil (esp. in smaller sized soil particles) enhances the reduction of Cr(VI) to Cr(III) and subsequently causes an increase in Cr(III) adsorption (Zhu, 1985).Electrolytes such as KCl increased and fertilizers decreased Hg leaching from Hg-loaded peaty soil (Lodenius,1983).

In general,prediction of heavy metal behaviour and mobility in mineral soils is difficult because (i) surface of crystn. clay minerals is usually coated with amorphous

clay minerals (ii) existence of clay mineral-organic matter complexes in soil make this behaviour more complicated (Yamamoto,1985).

Solidification of Sorbents after Loading with Metals

The best alternative for the disposal of a heavy metal (and/or pesticide)-loaded waste solid sorbent is the stabilization/solidification treatment by mixing with cement and Ca/silica containing hardener,and curing the resulting mass to increase the compressive strength and decrease chemical leachability.Some examples are cited:

A plating waste containing Cr(VI) and CN^- was mixed with 30% calcined dolomite and 30% portland cement to prepare a sandy product which leached out 0.3 mg Cr(VI) per L and 0.1 mg CN^-/L (Onoda Cement Co.,1982).A slag solidification agent contained alumina and portland cement, CaO,gypsum and soda ash (Mitsuboshi Kagaku,1983).Coal fly ash was mixed with 16% cement and 35% water,cast and cured for 4 h at 80^o for solidification (Mitsubishi Heavy Ind.,1982).100 pts of rm containing 60% H_2O was mixed with 8 pts of portland cement and 0.6 pt.hardening promoter to solidify the mud.A sludge solidifying agent (100 pts) may be synthesized from 30-60 pts of pulverized bfs,20-45 pts of gypsum and 15-40 pts of quicklime dust.100 pts of industrial sludge may be solidified with 7 pts of this agent to yield a solid mass of 1 Kg/cm^2 after 3 d of curing (Sumitomo Metal,1985).The compressive strength may be doubled within 1 month.Another sludge solidifying agent was synthesized from fly ash-quicklime--aluminium sulfate in 70/20/10 proportions.This agent may be added at 10% ratio to the sludge to be solidified (Autoset,1985).Portland cement was used for stabilizing hazardous waste containing Cd,Pb,aldrin and chlordane. When the water/cement ratio was 0.5,the amt. of leached waste was minimum and the sample had max. compressive strength.

In general, a mixture of industrial sludge (or consumed waste solid sorbent), portland cement, and a silica-rich material (e.g., bfs) can be solidified into a mass which does not leach out the retained metals and can be safely disposed of. A compressive stregth at the order of a few t/ft^2 may be achieved within 1 month curing. In order to aid stabilization, metals may be immobilized via pptn. as their insoluble hydroxides or sulfides prior to mixing with cement so that the resulting solid mass has better leaching resistance. A concentrate of alkaline washings of the rm-s and the sulfide from bfs may be used for this purpose.

Some wastes (such as As, which slows the curing of cement) can cause problems with the cement-based grout. In that case an initial precipitation with $Ca(OH)_2$-or with rm slurries- may be necessary (Hass, 1984).

Leachability of Metals from the Solidified Mass

Since the cement grouts have a basic pH ensuring the formation of insoluble metal hydroxides, most toxic heavy metals are immobilized as hydroxides or sulfides in consumed sorbent-cement mixtures. Also normally leachable radioactive cations, e.g., of the IA and IIA elements, are converted to insoluble forms. By using the proper cement and hardener compositions, metal leach rates as low as 10^{-9}-10^{-8} $g/cm^2.d$ may be achieved (Forsberg, 1984). These wastes may be processed into a granular form, transported in bulk to a regional disposal site, mixed with special cement-based grouts, and pumped as a wet, waste-cement mixture into underground caverns of a selected disposal site (Forsberg, 1984). This is recommendable esp. in the case of most toxic heavy metals, e.g., Pb, Hg and Cd. Solid masses containing less toxic metals may be used in landfill procedures.

Technology Selection and EPA's Recommendation

EPA's Technology Screening Guide* recommends in situ chemical remediation for heavy metal-contaminated soils and sludges, the potential applications of which include treatment of metals and radionuclides (mining mill tailings) by neutralization, precipitation, and solidification/stabilization; and treatment of hydrocarbons, metals and radionuclides by oxidation/reduction. The methods worked out up to this point for simulated purification of heavy metal-contaminated ground waters mainly focus on the volume reduction technologies of neutralization/precipitation and adsorption/flocculation with industrial waste sorbents. Solidification with cement-based grouts is recommended for ultimate disposal.

Evaluation and Prospects

The proposed technology for ground water decontamination is constructed from a chemist's view point. This work must be supported with the proper engineering design and pilot projects in order to take the form of an applicable technology for ground water treatment. Thus the cost-efective solid waste sorbents will have taken over the conventional synthetic sorbents, and a cost minimization will be achieved.

Although the presented activity does not introduce a novel technology of treatment, it may bring a novel approach in respect to the materials suggested for use in the treatment of ground water.

*EPA "Technology Screening Guide for Treatment of CERCLA Soils and Sludges", EPA/540/2-88/004, Superfund, Sept., 1988.

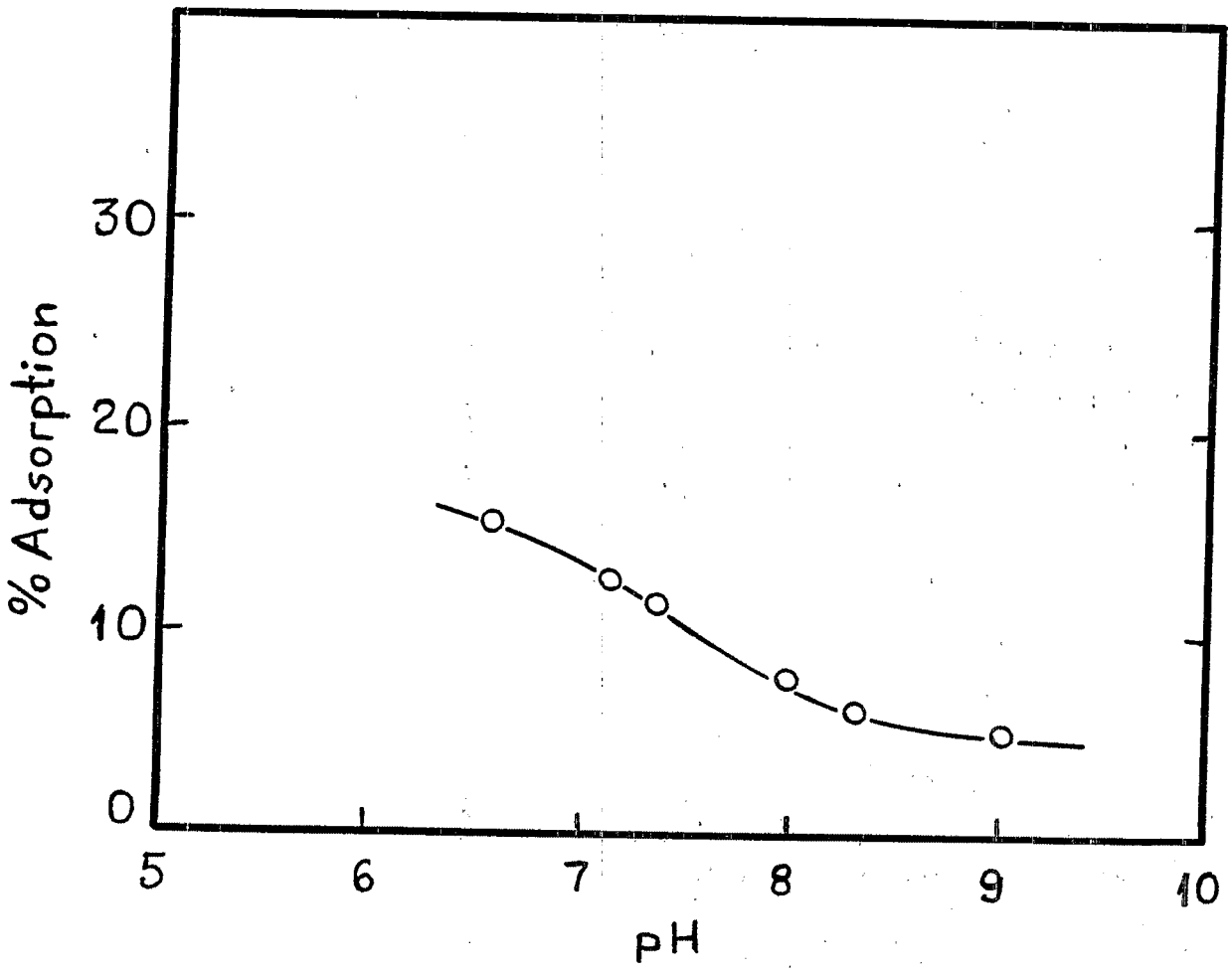
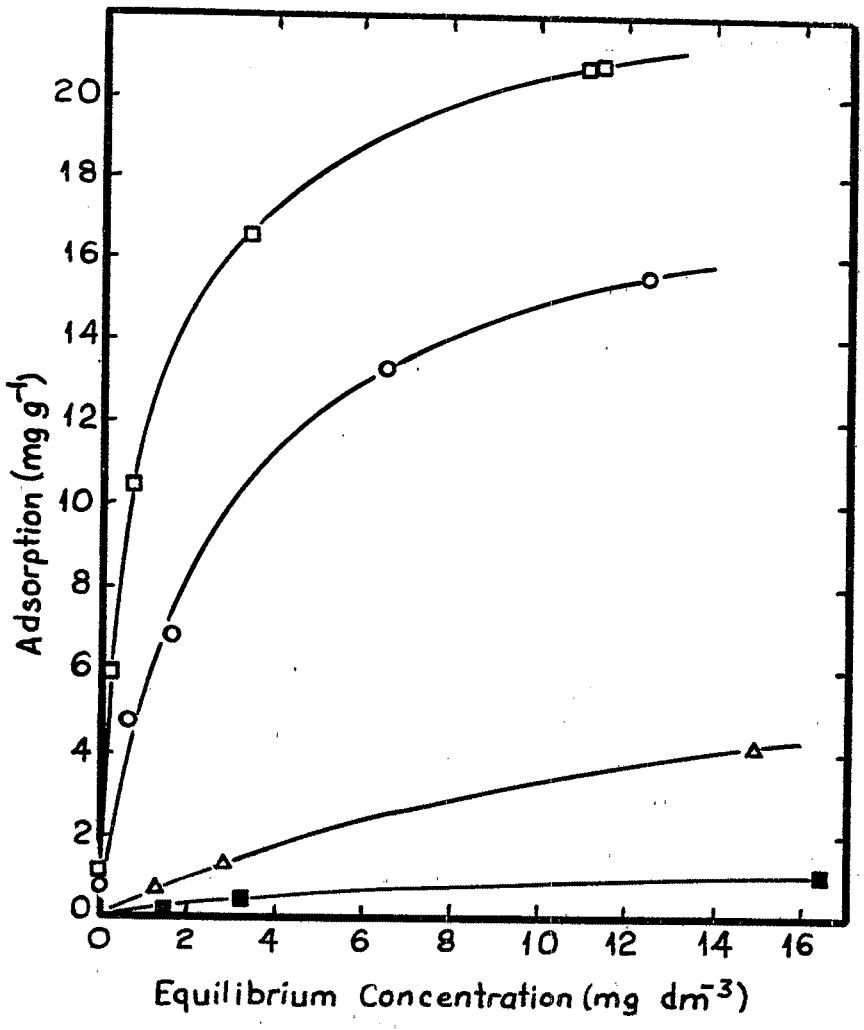


Fig.1- U(VI) uptake by hydrated TiO_2 wrt. pH
Concn. of hematite sol= 0.2 g/L , HCO_3^- concn.=1.x10^{-3}M



□ : pH 5.95 – 6.19 ; ○ : pH 5.26 – 5.45 ;

△ : pH 4.51 – 4.58 ; ■ : pH 3.04 – 3.06

Fig.2-Adsorption of uranyl(VI) on hematite vs. equilibrium U concn. in solution at various pH values
Hematite sol concn.=0.2 g/L, contact time=16 h, t=25°
Ionic strength maintained with $5.\times10^{-4}$M NaCl

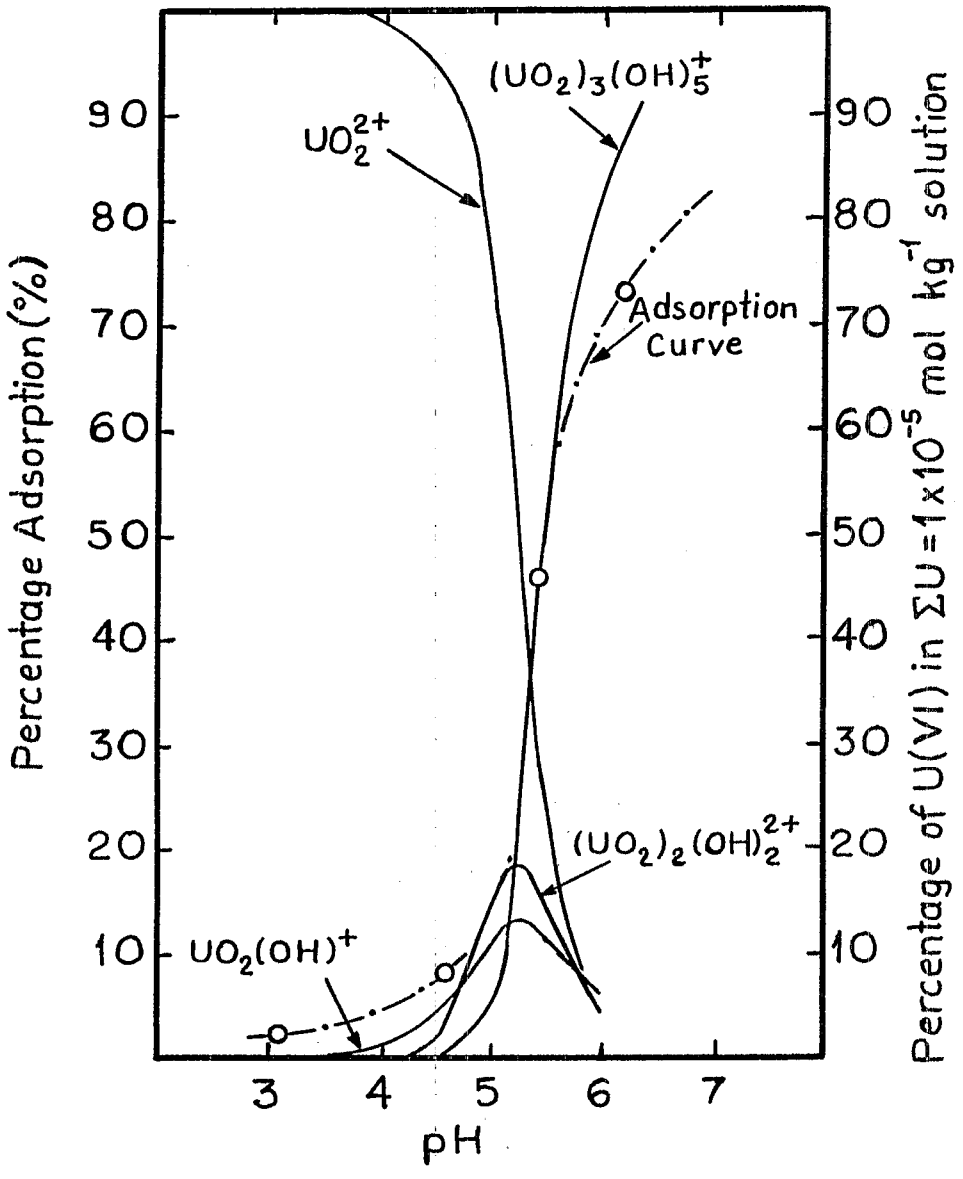


Fig.3- Comparison of the pH dependence of uranyl adsorption on hematite with the percentage of major hydrolysis products of U(VI).
Total U(VI) concn.=1.x10^{-5}mol/L; concn.of hematite sol is 0.2 g/L.

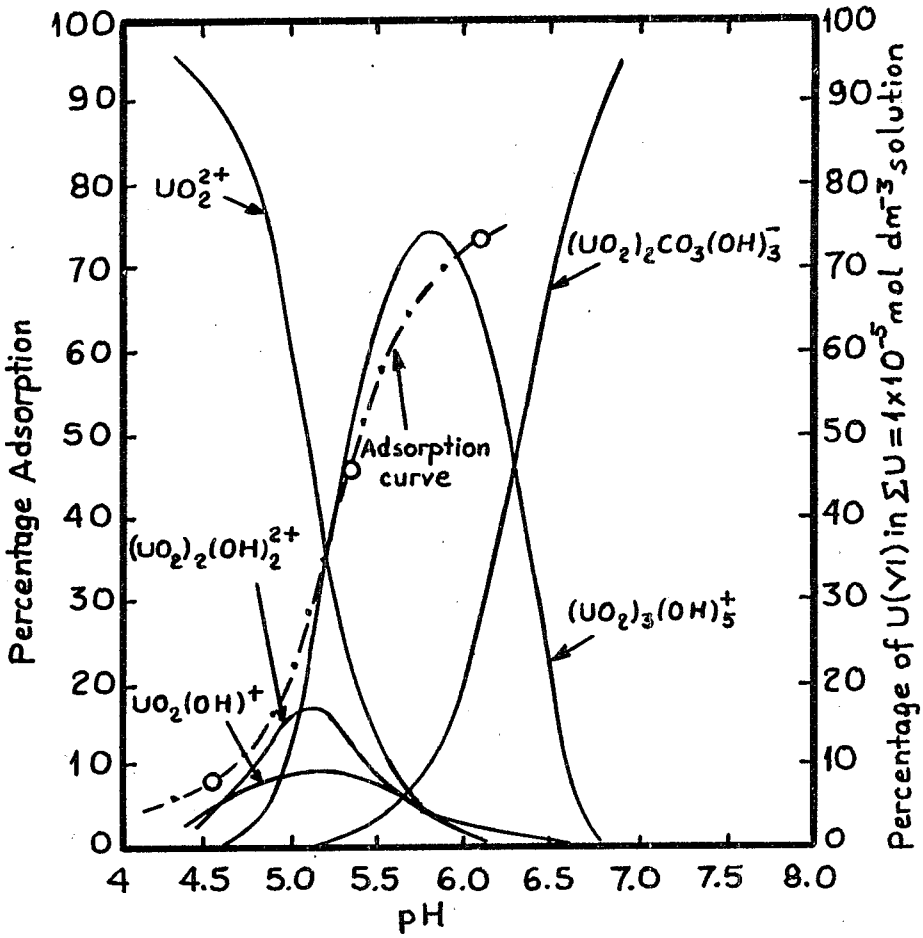


Fig.4- The percentage of U(VI) hydrolytic species and percentage adsorption wrt. pH at a total U concn. of $1.x10^{-5}$mol/L. Carbonate in solution is assumed to be formed from dissolved atmospheric CO_2 .

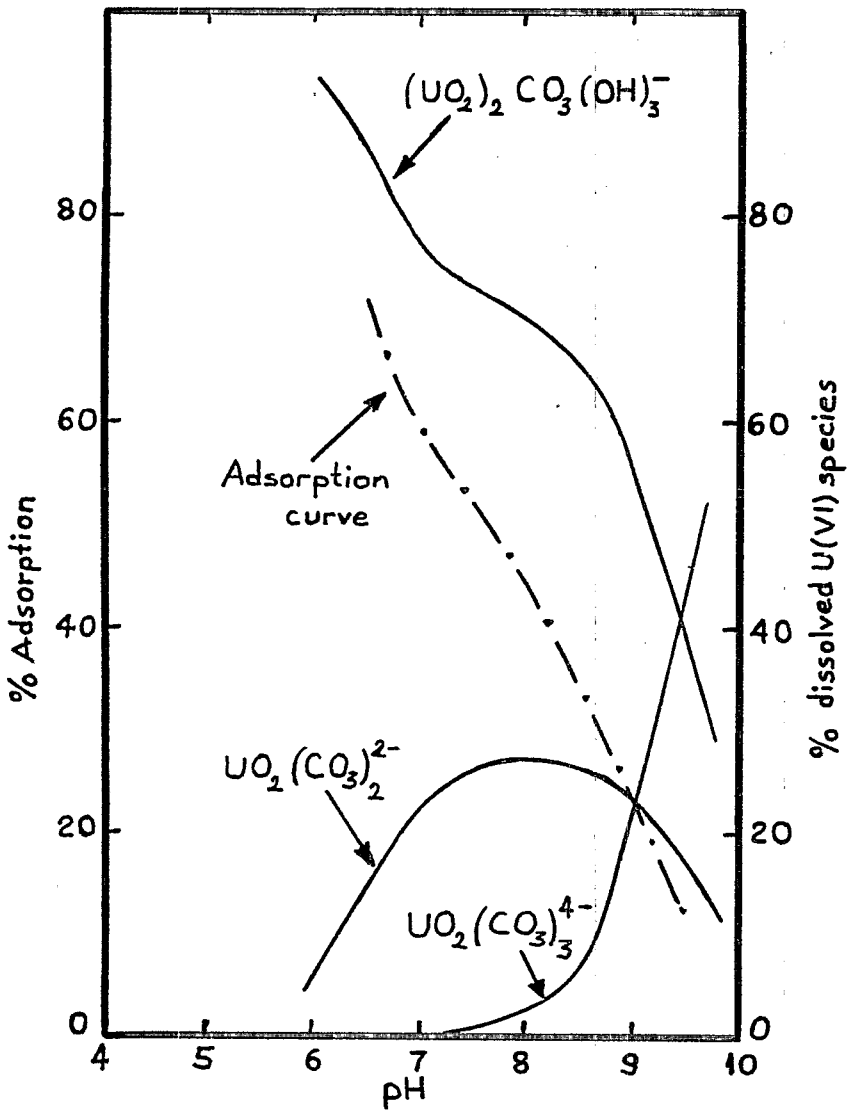


Fig.5- Comparison of the pH dependence of U(VI) adsorption on hematite with the percentage of dissolved U(VI) species present in 10^{-3} M total HCO_3^- soln. Concn.of hematite sol=0.2 g/L ,Tot.U(VI) concn.=$1.x10^{-5}$M

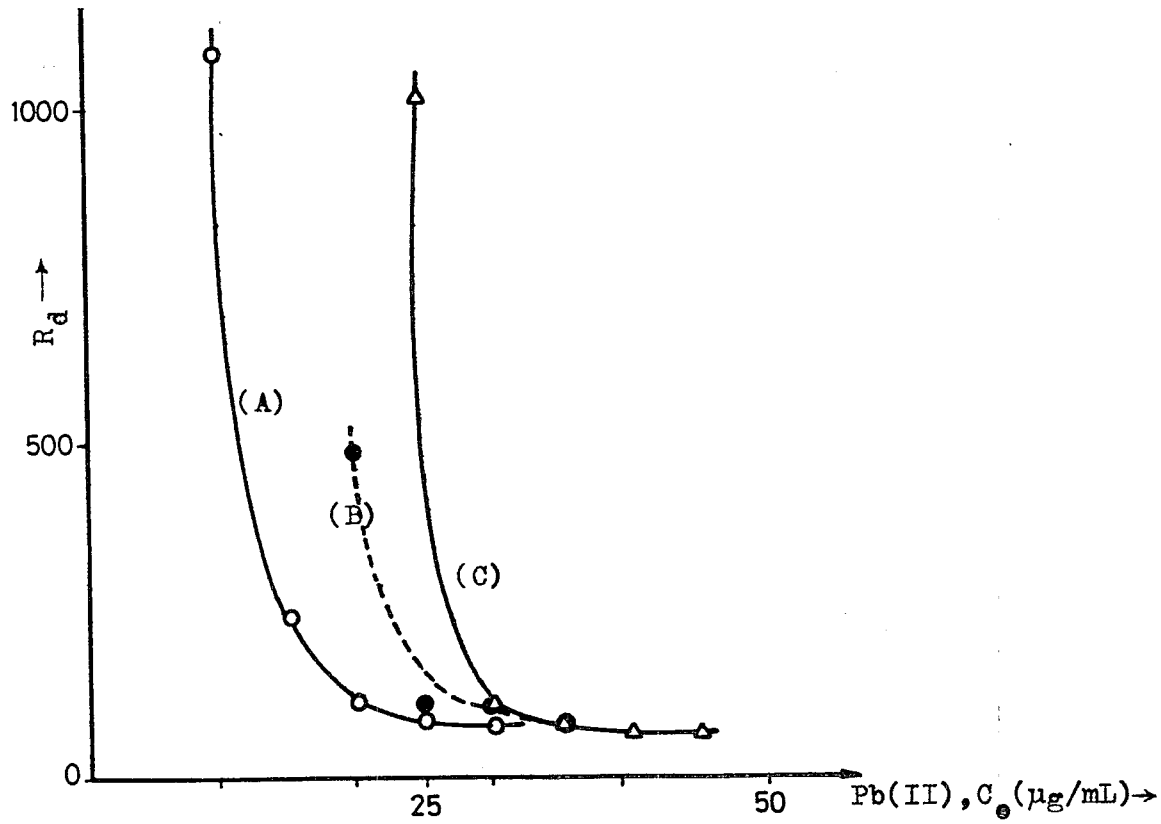


Fig.6- R_d vs. C_o curves of lead(II) with (A):1 g r.m.(B):2 g r.m. (C):2 g b.f.s.

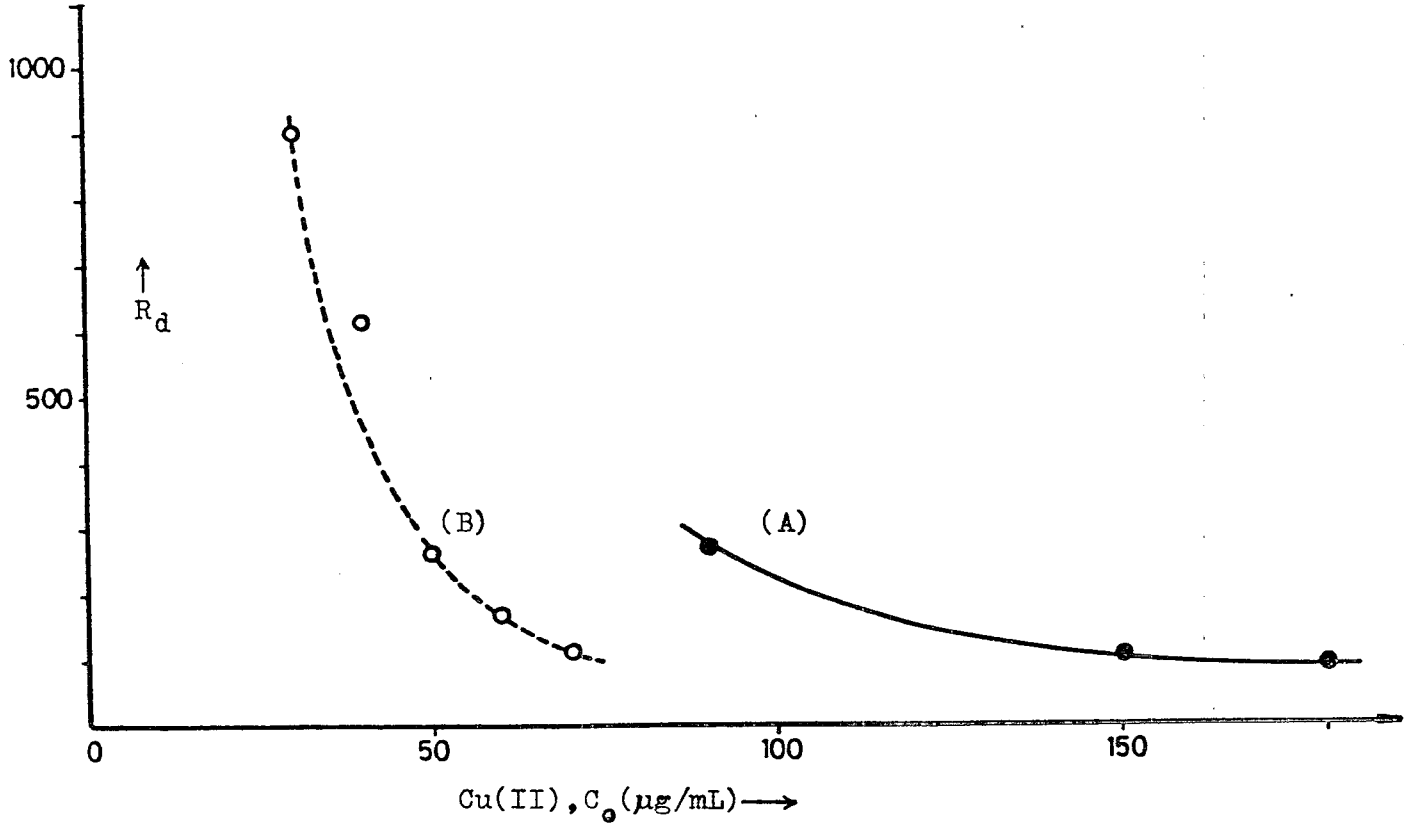


Fig.7- R_d vs. C_o graph fer Cu(II) with (A): 1 g r.m.(B):1 g bfs.

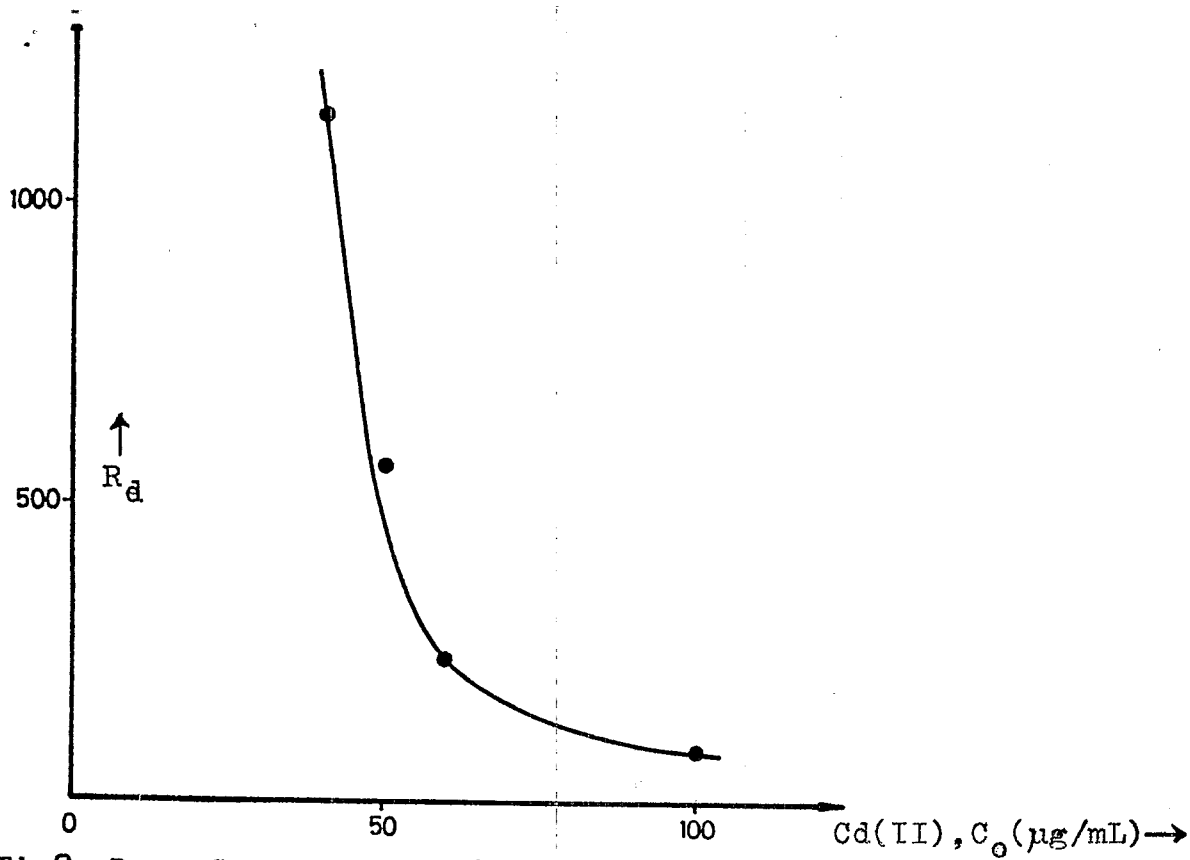


Fig.3- R_d vs. C_e curve for Cd(II) with 1 g r.m.

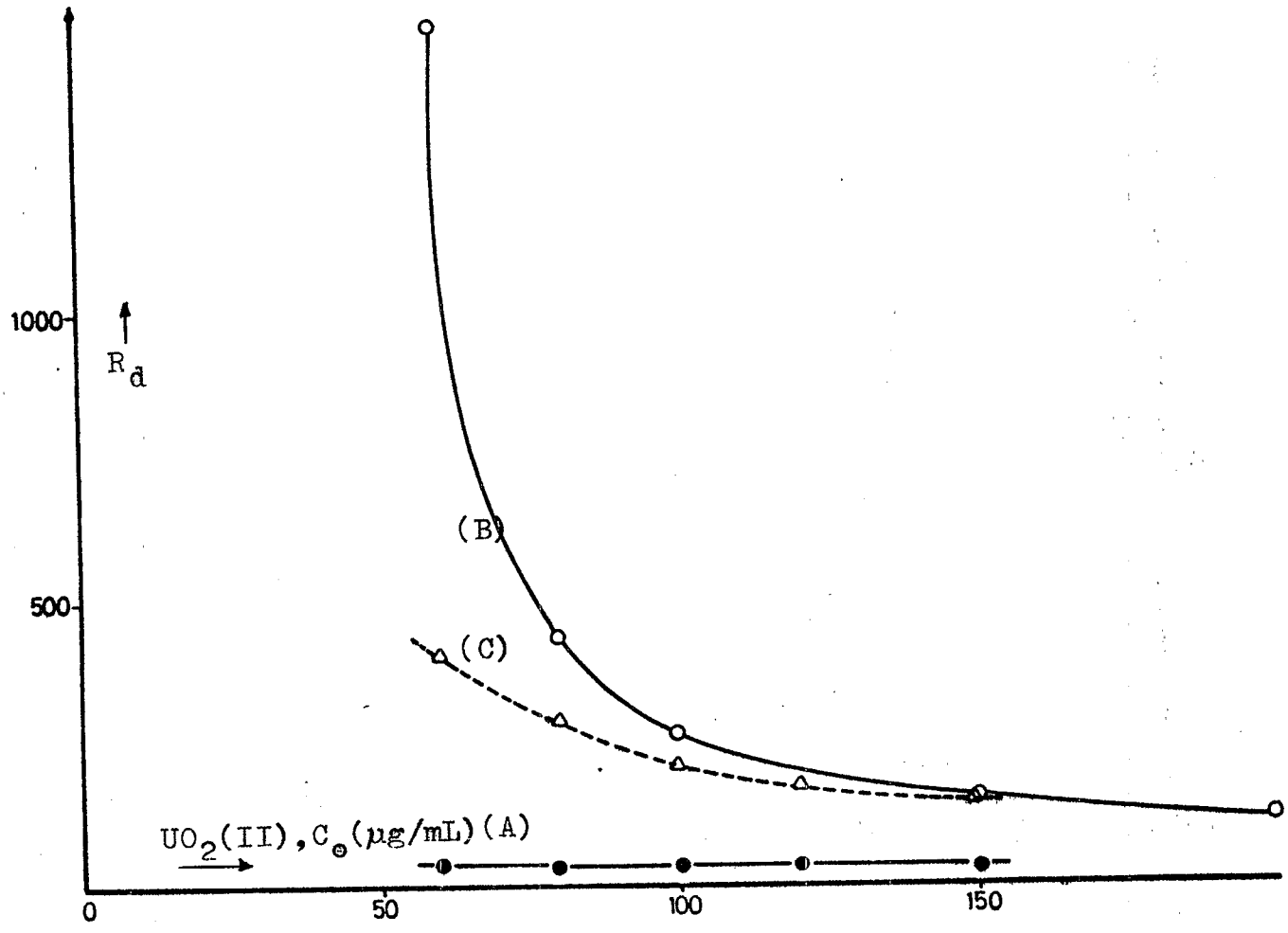


Fig.9 -R_d vs. C_e curves for UO_2(II) with 1 g r.m.(A)pH 3.0 (B)pH4.5 (C)pH7.0

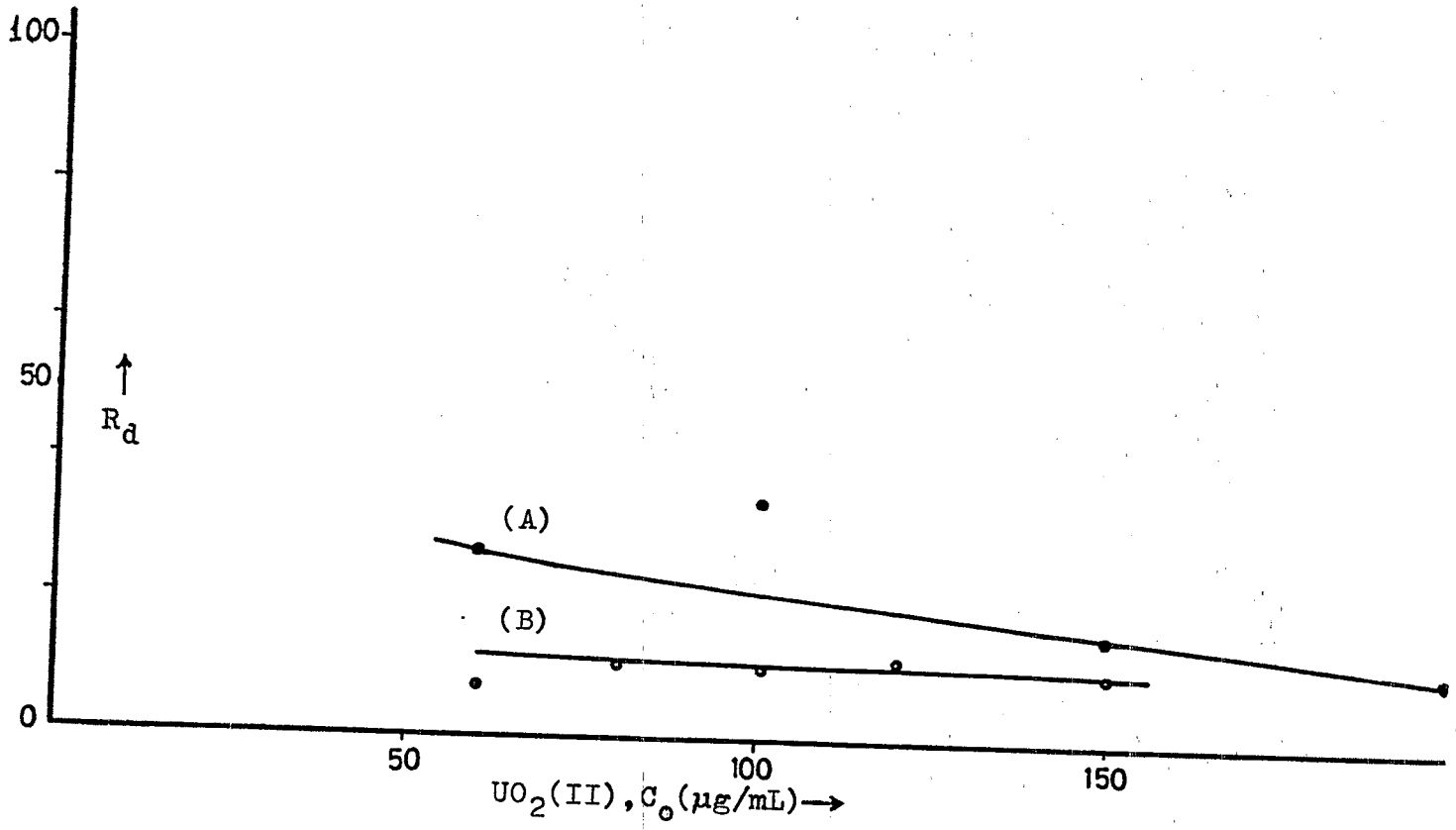


Fig.10 -R_d vs.C_o for UO_2(II) with bfs. (A)pH:4.5 (B)pH:7.0

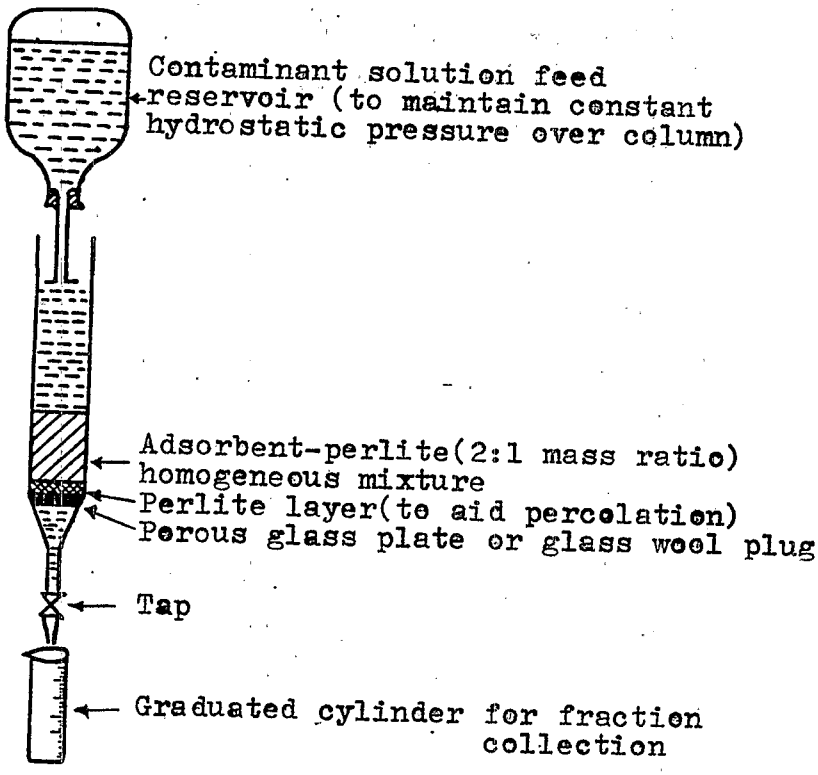


Fig.12-Experimental set-up for obtaining breakthrough and elution curves

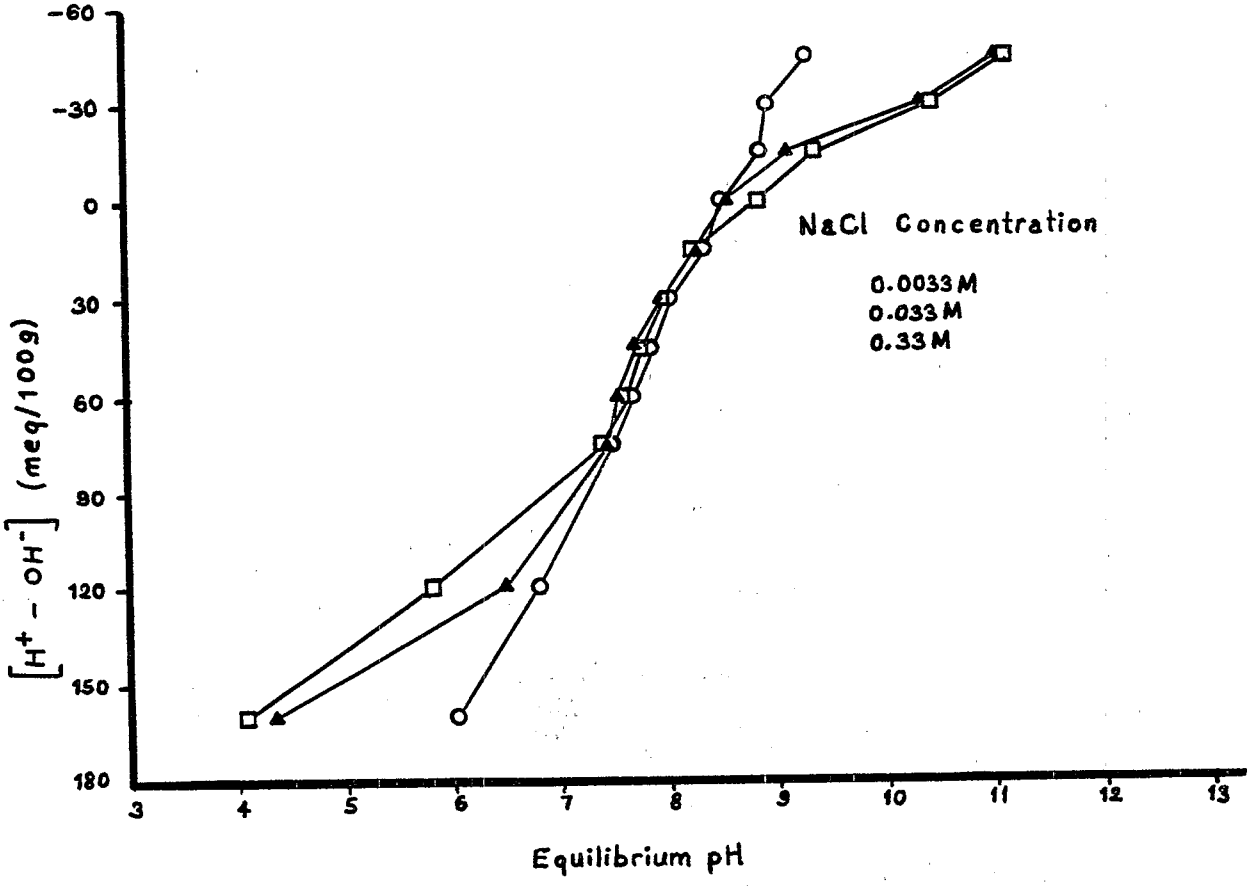


Fig.11- The determination of point of zero charge (PZC) of red mud as observed from acidimetric titration at different electrolyte concentrations.

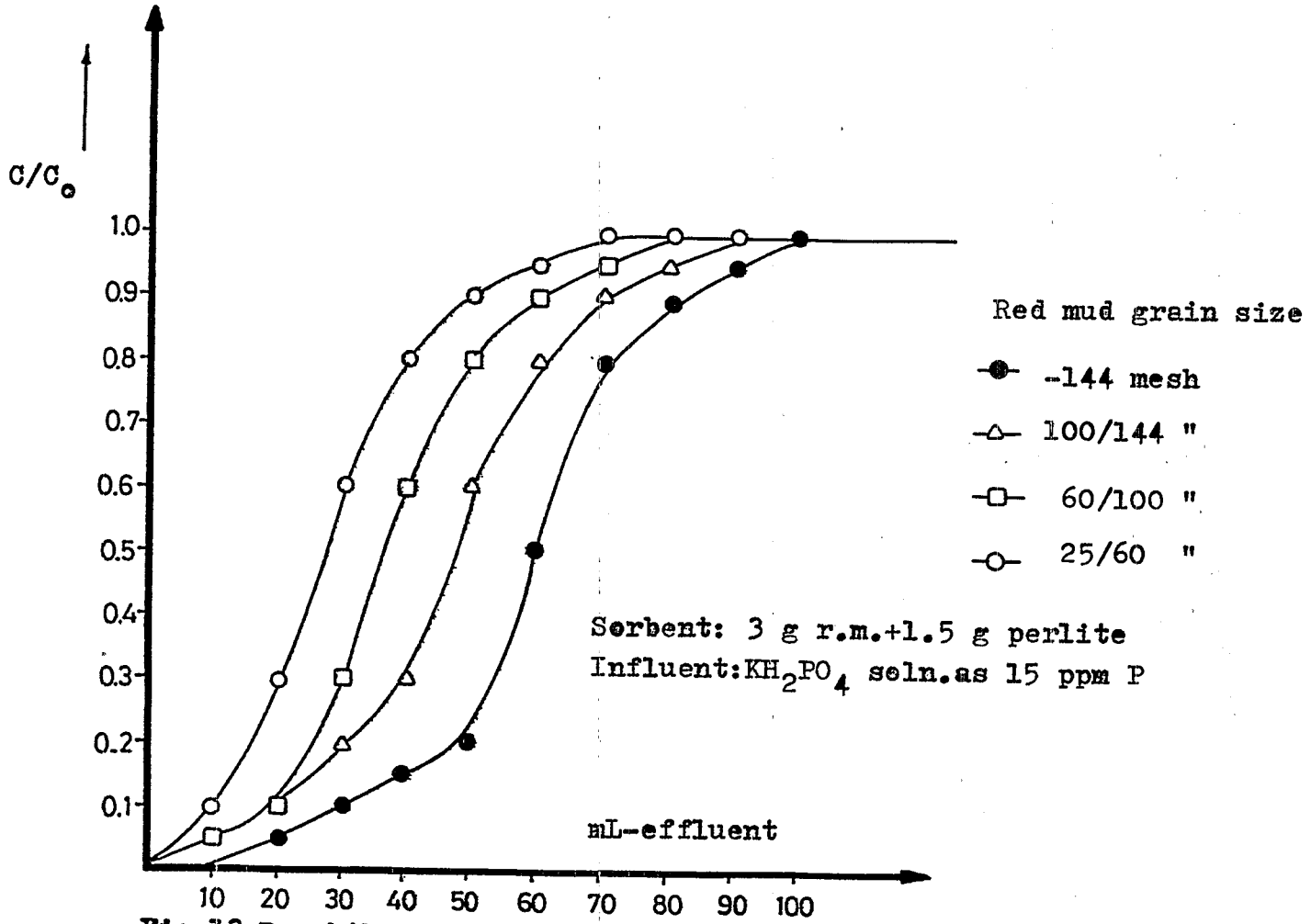


Fig.13-Breakthrough curves for phosphorus adsorption on r.m.

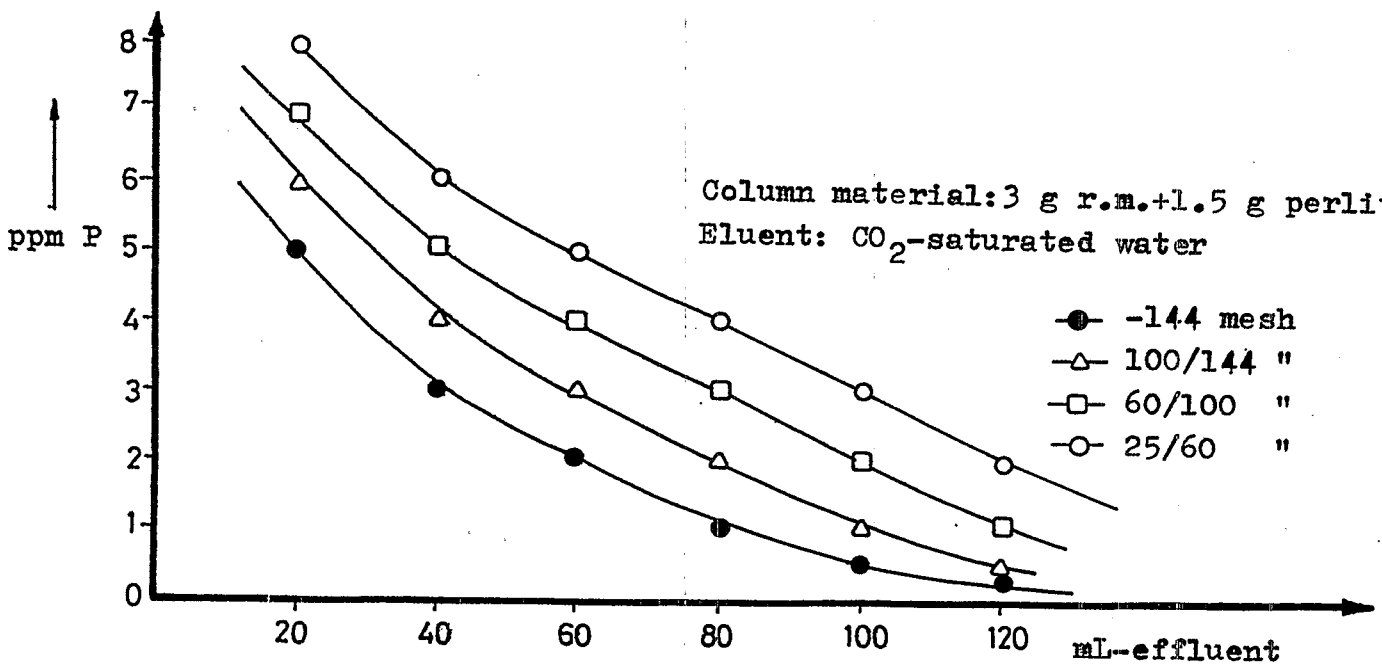


Fig.14-Elution of phosphorus from r.m. by CO_2saturated water

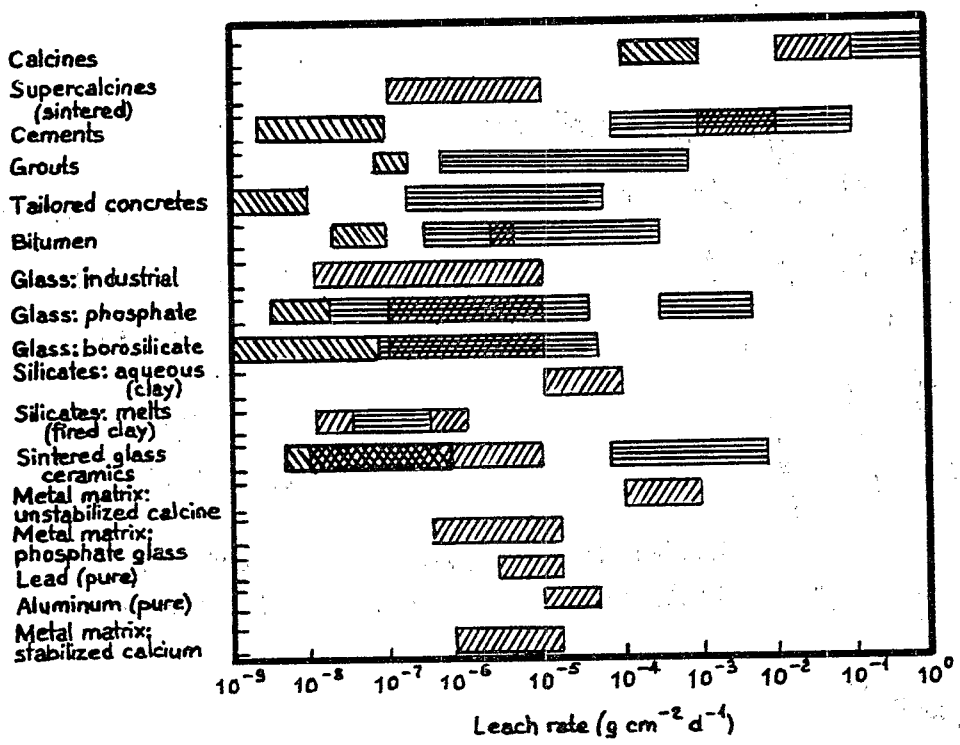


Fig.15-Leach rates for some radionuclides in several matrix materials (taken from Forsberg,C.W., Environmental Science and Technology,18(1984)56A).

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A P P E N D I X - (1)

THE DISTRIBUTION OF SPECIES IN URANYL-CARBONATE-HYDROXIDE COMPLEX EQUILIBRIA

E.Tütem,M.H.Turgut,R.Apak and V.Apak
Third International KfK/TNO Conference on Contaminated Soil,10-14 Dec.,1990,Karlsruhe,BDR
"Poster presentation"

Hexavalent uranium-UO_2(VI)-as a contaminant may be fixed with strong-to-moderate forces from uranium mill effluents and leachates of dumping areas.When ground water conditions change as a result of natural carbonatation processes and pH variance,remobilization may take place in the form of anionic carbonate- or cationic hydroxo-complexes of uranyl.Alkaline soils will also yield aqueous leachates containing carbonate and bicarbonate.Carbonate may also be added deliberately as a complexing agent for mobilizing the fixed uranium which has got bound to silt- and clay-type soils with high affinity.

Since carbonatation produces a second ligand,i.e., hydroxide,by virtue of the hydrolysis reactions;

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$ and $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

a complex mixture of uranyl species is formed,each of which will be adsorbed onto solid mineral phases to different extents depending on their charges and specific adsodbabilities.Cationic poly-nuclear hydroxo complexes are held strongly on hydrous oxide constituents of soils by specific adsorption or chemisorption,and anionic carbonate complexes are either physically adsorbed or ion-exchanged by mineral surfaces.

If the total uranyl(VI) and carbonate concentrations in the aqueous phase are known,the distribution of dissolved species can be found by analysis of simultaneous complex equilibria.The calculations reveal the equilibrium concn.of each species,which is crucial in estimating the remobilization possibilities of U(VI)

without considering the adsorption/desorption kinetics.

There are two ways of dealing with this problem:
(i) If M denotes UO_2(VI) and L denotes CO_3^{2-}, then simple modelling predicts the presence of M, MOH, $M_2(OH)_2$, $M_3(OH)_5$, L, HL, H_2L, ML, ML_2, ML_3, Na^+, H^+, NO_3^- and OH^- in aqueous mixtures of uranyl nitrate and sodium carbonate. If the total metal concn. is M_t, and total ligand (free+bound) concn. is L_t, then the pair of equations holds for clear mixtures:

$$M_t = [M] + \beta_1[M][L] + \beta_2[M][L]^2 + \beta_3[M][L]^3 + K_{11}[M]10^{(pH-14)} + \ldots$$
$$\ldots + 2K_{22}[M]^2\,10^{(2pH-28)} + 3\,K_{35}[M]^3\,10^{(5pH-70)} \quad \ldots(1)$$

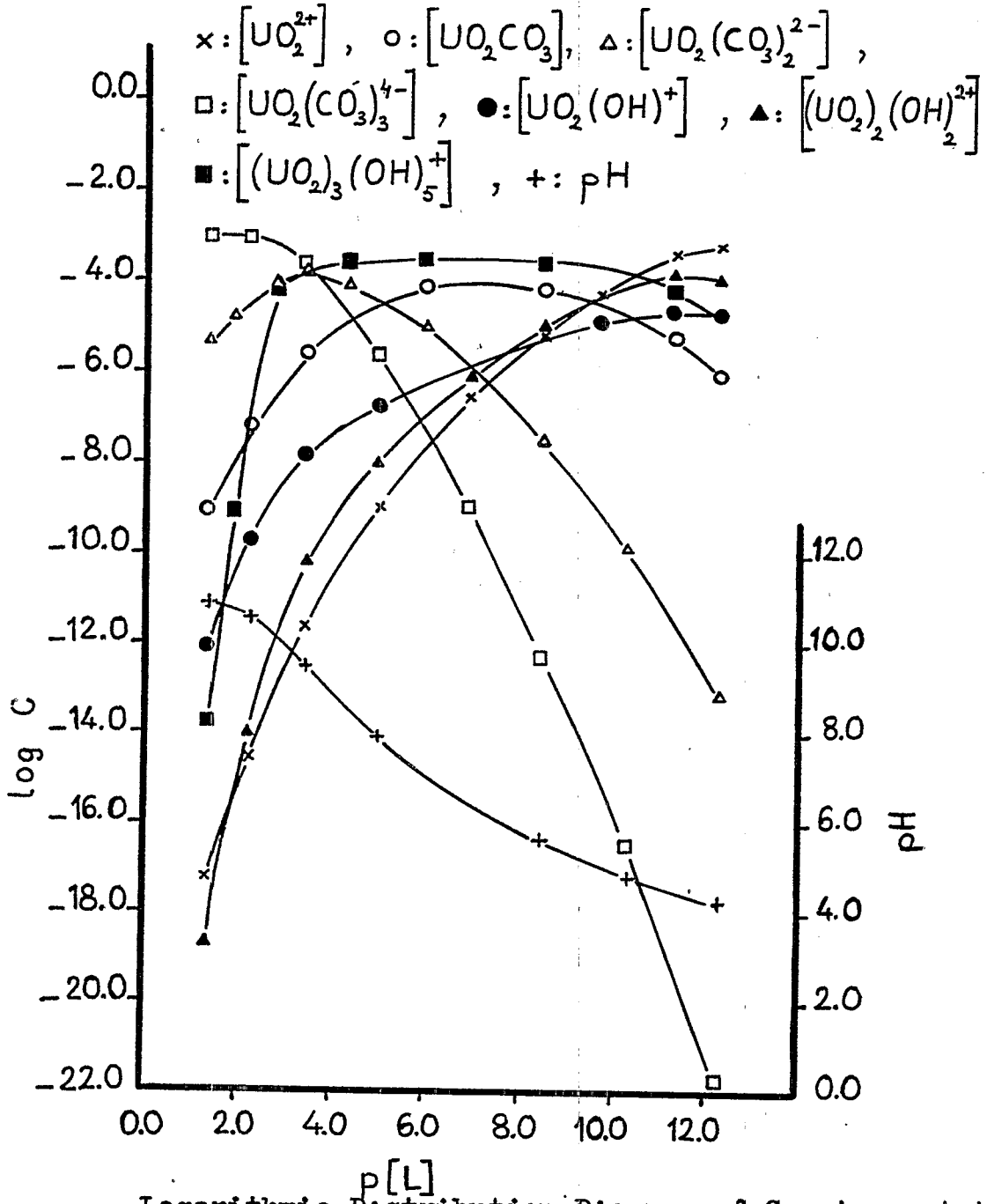
$$L_t = [L] + 10^{-pH}K_{a2}^{-1}[L] + 10^{-2pH}(K_{a1}K_{a2})^{-1}[L] + \beta_1[M][L] + \ldots$$
$$\ldots + 2\beta_2[M][L]^2 + 3\beta_3[M][L]^3 \quad \ldots(2)$$

where the cumulative stability constants of uranyl carbonate and uranyl hydroxide complexes are represented by β_i and K_{ij}, respectively, and K_{a1} and K_{a2} are the consecutive acidity constants of carbonic acid. Equations (1) and (2) may be solved simultaneously for $[M]$ and $[L]$ if the equilibrium pH of mixtures are measured. Subsequently, the concn. of each species may be found, giving rise to the logarithmic distribution diagram.

(ii) If the electroneutrality principle (stating the equivalence of total charges of positive and negative species) is introduced, equations (1) and (2) may be solved simultaneously by the aid of a computer program* without necessitating pH measurement of mixtures. This gives rise to an identical diagram as above (i).

The possible presence of other species is not included in the model, the variance of pH with ionic strength, and the slow kinetics of uranyl solutions to attain equilibrium may account for the small discrepancies between the theoretical and practical U(VI) speciation.

*The details of the computer program may be obtained from the authors upon request.



Logarithmic Distribution Diagram of Species wrt. the Free Ligand Concentration and pH (experimental and computational curves)

(M_t=1.017x10^{-3} mol/L; Log C=logarithm of the molar concn. of the indicated species; pH=-log a_{H^+} ; p[L]=-log(free ligand) concn.

L symbolizes carbonate.

A P P E N D I X (2)

SORPTION OF CHLORINATED PESTICIDES ON RED MUD

V. APAK, A.Y.ERKOL and S.BAYULKEN

Introduction

Chlorinated pesticides, being persistent pollutants in the environment, are of major concern with respect to toxicity to humans. Chlorinated hydrocarbons constitute 70-85% of the residual pesticides transferred to men through the food chain.

Chlorinated pesticides (CP's) have limited aqueous solubility; they are mostly associated with suspended matter such as organic substances, sediments and planktons. The pesticide enrichment in planktons compared to surrounding waters (bioaccumulation) assumes the form of biomagnification toward the higher members of the predator chain whereas enrichment factors as high as 10^4 may be observed in certain fish.

Pesticides, although diluted to insignificant concentrations in sea water, are mostly concentrated in ground water.

Possible sorbents for CP's

A cold trap filled with activated alumina traps all hydrocarbons except methane from a dry gas mixture stripped from a water sample with Ar bubbling[1]. Higher molecular weight hydrocarbons than C_4-fractions are retained on a stationary phase consisting of 20% silicone oil on Chromosorb. Murray and Riley (1973) have stripped very low concentrations of chlorinated hydrocarbons from the water with a stream of nitrogen, and adsorbed them in a cold trap packed with silicone oil on Chromosorb-W prior to analysis with GC equipped with an electron capture detector[1].

Traces of organic substances in water may be sorbed on an activated carbon filter and recovered by extracting the carbon with chloroform[2]. Other interfering pollutants accompanying chlorinated pesticides may be removed by chromatography on alumina, and the recovered insecticide may be analyzed by IR spectroscopy[3] besides GC.

Red muds and other unconventional adsorbents, as received or pretreated, have been shown to be effective sorbents for heavy metals and anions such as phosphate and arsenate[4].

In this work, they are tested for their efficiency in CP removal so as to develop multipurpose sorbents for retaining a combination of heavy metal ions and CP's.

EXPERIMENTAL

Instrumentation

Gas chromatograph: Perkin-Elmer 8500
Detector: Electron-capture detector
Column: 1.5%OV-17, 1.95% OV 210 on Chromosorb W.HP 100-120 mesh packed column (GLT, diameter: 1/8inch, length: 2 m).
Column tube temperature: 200°C
Injector temp.: 275°C
Detector temp.: 350°C
Composition of carrier gas: 95% Ar+5% methane
Rate of flow of carrier gas: 60 mL/min.

Materials

Red muds (major constituents being sodium aluminosilicates, kaolinite, chamosite, iron oxides and oxy-hydrates) were received from Seydişehir Aluminium Plant. Their composition was: Fe_2O_3: 37.26%, Al_2O_3: 17.58%, SiO_2: 16.94%, TiO_2: 5.55%, Na_2O: 8.31%, CaO: 4.38%, loss on ignition: 7.17% .

Although red muds may be heat- or acid-treated for raising their sorption capacity, they were used as received for the sake of procedure simplicity and economy. They were washed throughly with water until the leachate was no longer alkaline, dried in an oven at 110°C, ground and sieved through a 100 mesh sieve. Perlite was mixed with red mud to prevent column blockage by adhering particles. n-Hexane, acetone and sodium sulfate were obtained from E.Merck, and were of extra pure grade. The CP's, namely aldrin, γ-BHC, endrin, dieldrin, p,p'-DDE, p,p'-DDT, were received from EPA.

Methods

Since common chlorinated pesticides were basically insoluble in water, their concentrated solutions in acetone were diluted to relatively higher volumes with water to yield final solutions up to 30 ppm of pesticide.

Column experiments: 3 g of red mud were mixed with 1 g of perlite, and the column was filled with this mixture as the stationary phase. 1 ppm of p,p'-DDT solution was passed through, and the concn. of the eluate was continuously controlled in 5 mL portions. The pesticide was recovered from the eluate by extracting with an equal volume of hexane (5ml per 5 mL), dessicated through a Na_2SO_4 column and analyzed by GC. p,p'-DDT was retained by the red mud in the column up to a quantity of 8600 µg (The value for activated carbon is 10,000 µg per 3 g). Since the column experiments were lengthy, the experiments were continued by agitating the red mud with the pesticide solution.

Aldrin, γ-BHC, endrin, dieldrin and p,p'-DDE were tested under similar conditions. 100 mL of the pesticide solution of concn. 10, 15, 20, 25 and 30 ppm were agitated with 0.500 g of red mud for 1 hr. 2 mL portions of the original and agitated solutions were extracted with 8 mL of hexane, dessicated in Na_2SO_4 column and analyzed by GC. The results are depicted in Table 1.

RESULTS

All chlorinated pesticides, excluding γ-BHC, are retained by the red mud column at several 10^3 µg/g levels. For retaining the latter, red mud-activated carbon filter combinations may be required.

Thus red muds may be used to remove CP's from ground water. In this respect, they may be used for preconcentration of CP's prior to GC analyses as well as for pollutant removal from natural waters. This finding is in accord with a literature observation that the pesticide 2,4-D is held by iron oxides (goethite).[5]

In conclusion, red muds may serve as multi-purpose sorbents for a variety of pollutants including heavy metals and pesticides.

Table 1: Sorption of Chlorinated Pesticides on Red Mud

Initial concn.(ppm)	Name of pesticide: Aldrin	Endrin	Dieldrin	DDE	DDT	γ-BHC	
10	83	80	99	89	78	0	:Removal %
	(788)	(784)	(940)	(872)	(764)	-	: µg-removed
15	91	86	98	98	75	0	:Removal %
	(1296)	(1264)	(1405)	(1440)	(1102)	-	: µg-removed
20	95	88	98	99	75	0	:Removal %
	(1805)	(1725)	(1856)	(1940)	(1470)	-	: µg-removed
25	91	92	93	99	84	0	:Removal %
	(2161)	(2254)	(2218)	(2425)	(2058)	-	: µg-removed
30	88	94	79	99	90	0	:Removal %
	(2516)	(2763)	(2248)	(2910)	(2646)	-	: µg-removed

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100 mL of the indicated pesticide solution was agitated with 0.500 g of red mud for 1 hr.

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Cyanide Behaviour in Soil and Groundwater and Its Control

CYANIDE BEHAVIOUR IN SOIL AND GROUNDWATER AND ITS CONTROL

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INTRODUCTION

An important percentage of total water consumption in Turkey is supplied from groundwater (about 34 %). When only domestic water supply is considered (drinking + household use) about 40 % of water is supplied by dams and the remaining is supplied from groundwater and springs. Thus, the contribution of groundwater to the domestic water consumption is about 60 %. As this high value indicates groundwater pollution control is very important for Turkey.

Although the history of environmental pollution control studies do not go back very far in Turkey, the environmental problems are not yet at an unsolvable stage. At present, because of the infra-structure inadequacy problems in many places, there are local water, sea and soil pollution problems.

The causes of groundwater pollution in Turkey may be grouped as follows:

a. Pollution due to the domestic wastes: A considerable percentage of inhabited areas is unsewered and septic pools are used for wastewater disposal. The incidence of waterborne infection indicates evidence of wastewater infiltration into the groundwater. Also fecal coliform and total coliform analysis confirm the same result. In some areas sewerage systems is very old and leaking sewers result in groundwater contamination.

b. Fertilizer and pesticide application: Although industrialization is taking place at a rapid rate, Turkey still keeps her main characteristic of being an agricultural country. Since chlorinated hydrocarbons (including DDT), organophosphates, carbamates and many other types of pesticides have been used in Turkey, some studies reveal that groundwater contains some amounts of these chemicals, especially non biodegredable ones (Temizer, 1979).

c. Industrial pollution: Because many industries discharge their wastes which are not in compliance with the standards put forward by "Water Pollution Control Regulation", it is inevitable to have groundwater contamination by industrial source.

This study gives a case study of groundwater contamination by cyanides and reveals the rate of natural decay under different conditions and investigates its control.

A GROUNDWATER CONTAMINATION CASE

Kemalpaşa, one of the provinces that belong to Izmir, is established at the South East corner of the Kemalpaşa plain. Its surface area is 30 km² and height 200 m from the sea level (Figure 1). The settlement is 29 km away from Izmir and takes place between the mountains and the Kemalpaşa plain which is valuable and fertile. The plain is famous for its cherry trees. Transportation is easy with a main asphalt road.

Kemalpaşa has a relatively mild climate with cool temperatures and fairly heavy rainfall in winter and hot and dry summers. The deficency of water in summer is compensated by water resources in the area. Because the settlement is at the foot of the mountain, the summers are relatively cool and growing different kinds of crops are possible (Kalaycıoğlu, 1978).

The surface distribution of the geologic formation that underlie Kemalpaşa Plain area are shown on the hydrogeologic map (Figure 2). The area may be studied under two separete headings: metamorphic mountainous mass and alluvial plain that formed lately. The plain remains between Küçük Menderes River basin and İzmir basins.

Water resources in the area may be divided into two groups. The most important water source, Nif River is fed by many small creeks flowing from the Nif mountain. Some of these small creeks dries completely during the summer.

No sewerage system is present in the town. The cesspools are rather primitive and unhealthy. The immediate need for infrastructure is pointed out in reports. In 1948, water is brought from 1500 m away by a network. Because it is insufficient, groundwater and spring water are also used in the area. Some springs are abandoned due to the pollution.

The springs in the area issue through the layers of flysh (at the bottom), limestone (in between) and gravel and debris (at top). Rainfall infiltrates to the bottom along the cracks of limestone until the impermeable flysh layer is reached. Then it moves upward along the fault to the surface at two sides of the valley where the springs are located (Kalaycıoğlu, 1987). Hydrogeological survey in the area reveals the following:

1.The aquifer formation in the area are; limestone, alluvial deposits that consist of sand and gravel, and Neogen series which consist of sand, gravel and conglomerates.

2.Safe perennial yield of groundwater in the area is 25×10^6 m^3.

3.The wells in the area which is indicated as "Area appropriate for groundwater abstraction" in Figure 2, gives water from about 75-100 m deep, and the yield is about 20 l/s (DSI, 1979).

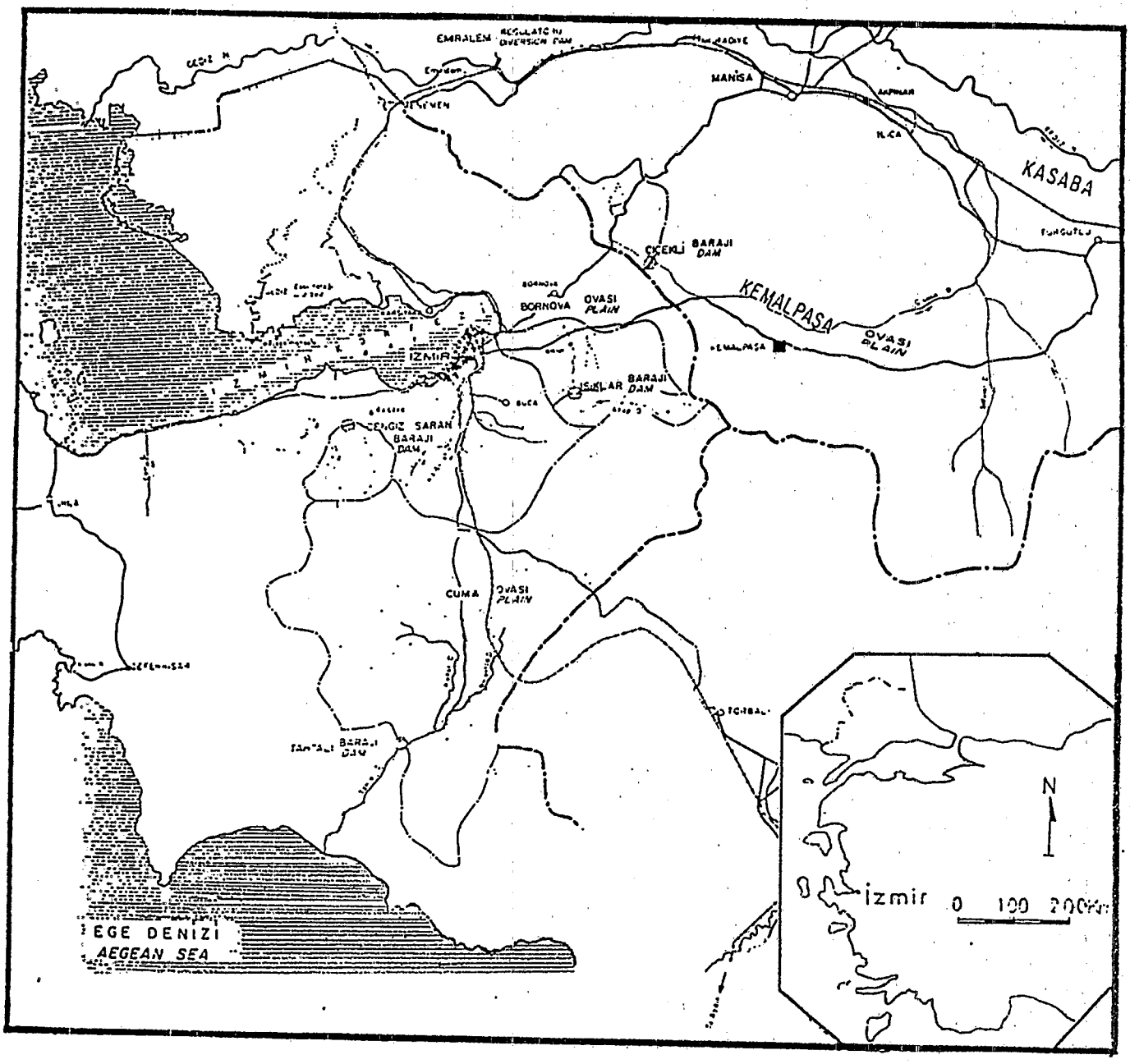


Figure 1: Project area location map

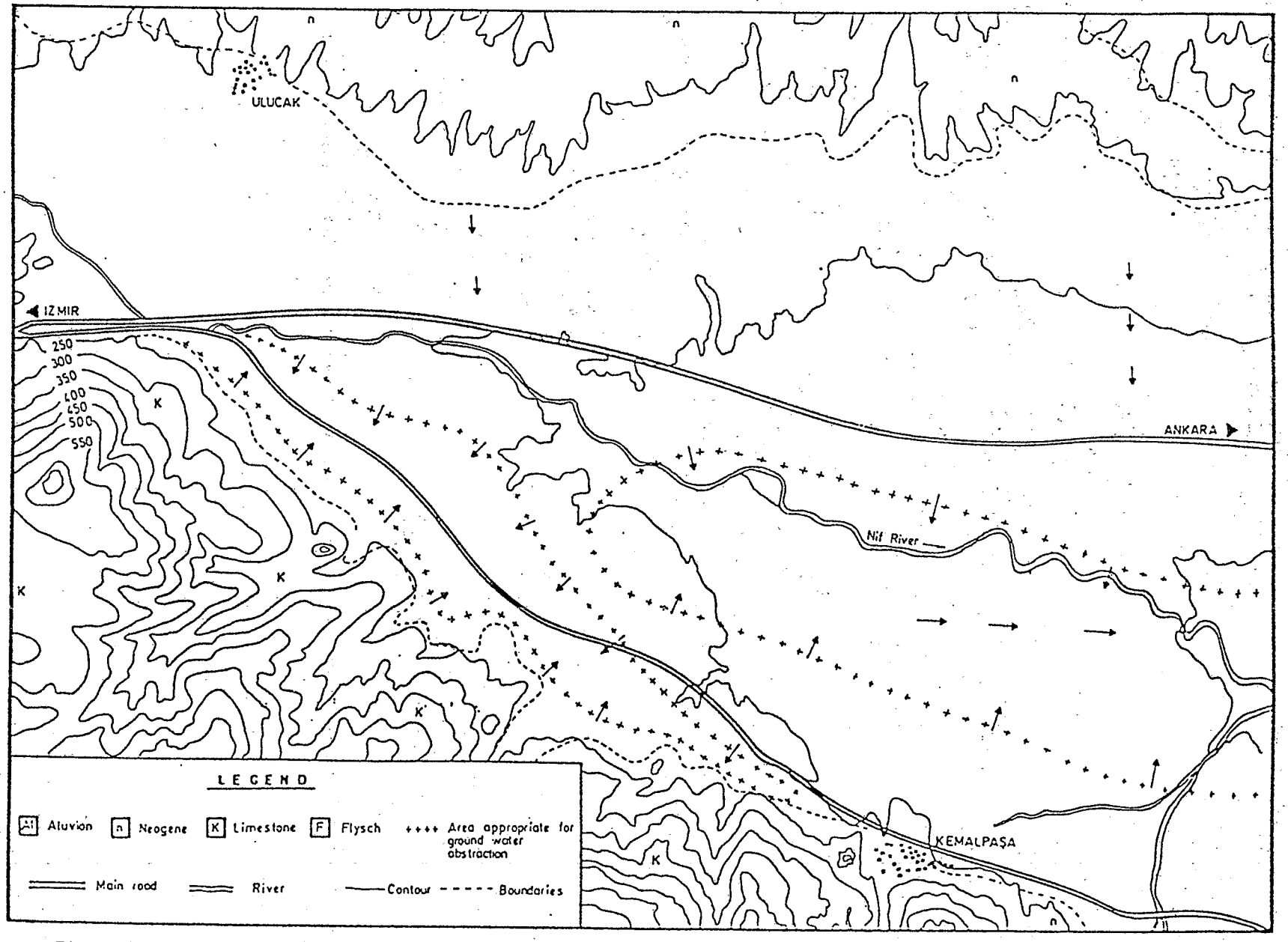


Figure 2: Hydrogeological map of the study area

More than 100 industrial organizations are located in Kemalpaşa. Some of them are shown in Figure 3. Cyanide contamination was detected as follows:

Kemalpaşa Municipality asks the industries to analyse their effluents in order to determine industrial wastewater pollution load in the area. The samples were brought to the Dokuz Eylül University laboratory and many environmental parameters were tested including cyanide. 0.16 mg CN^-/l was found at the effluent of a chemical industry (situated near no.14 in Figure 3) which mainly processes natural resin. The industry objected to the analytical result on the ground that they do not use any cyanide compound. When the wastewater analysis was repeated, the same result was obtained after which groundwater was suspected to contain the cyanide. In fact, groundwater sample analysis indicated the presence of 0.07 mg of CN^- per liter. The water was abandoned for use as drinking water. Now it is only used as process water.

When groundwater of the chemical industry was found to contain cyanide, other nearby industries using groundwater were also curious about their water quality. The analysis of groundwater samples in the area revealed that a cyanide contamination of about 0.04 mg/l of CN^- existed (Table 1).

Table 1: Cyanide concentrations of groundwater samples in the study area

Location of the well	Depth of the well	Date	cyanide concent. mg/l
Beverage Industry (10)		27.1.1988	0.04
Zipper Manufacture (4)		13.9.1988	0.02
Coca-Cola (5)	120 m	20.1.1988	0.04
	135 m	20.1.1988	0.04
Chemicals Industry II	60 m	14.1.1988	0.07
Food industry (9)		27.1.1988	0.03

CYANIDES IN WATER

Cyanide refers to all of the CN^- groups in cyanide compounds that can be determined as the cyanide ion. The cyanide compounds in which cyanide can be obtained as CN^- are classed as simple and complex cyanides.

In aqueous solutions of the simple alkali cyanides, the cyanide group is present as CN^- and molecular HCN, the ratio depending on pH. In most natural water HCN greatly predominates. In solutions of simple metal cyanides; the CN group may occur also in the form of complex metal-cyanide anions of varying stability. Many of the simple metal cyanides are sparingly soluble or almost insoluble, but they form a variety of highly soluble, complex metal cyanides in the presence of alkali cyanides.

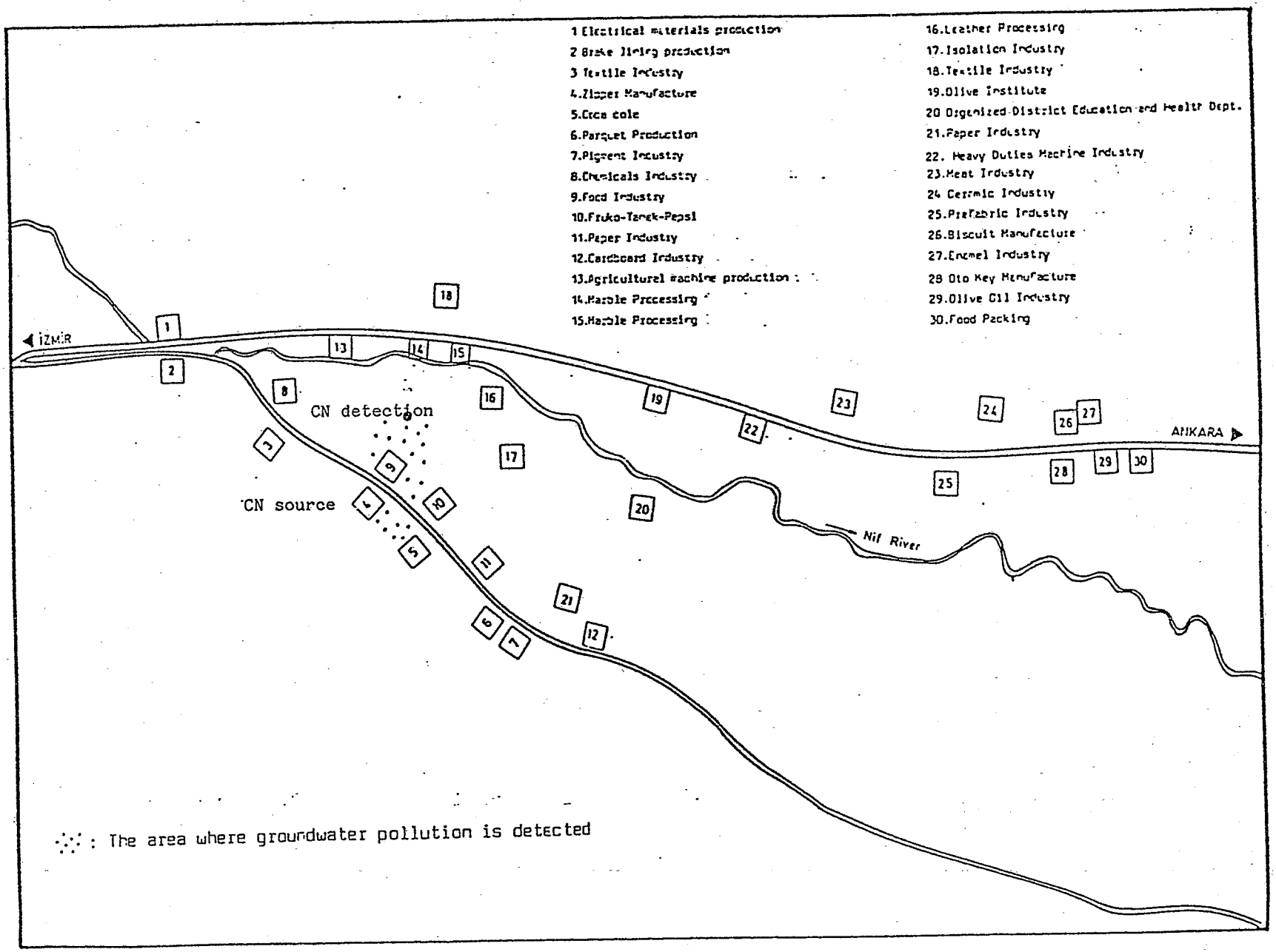


Figure 3: Location of industries in the project area

The complex cyanides have a variety of formula, but the alkali metalic cyanides normally can be represented by $A_yM(CN)_x$. In this formula, A represents the alkali present y times, M the heavy metal (ferrous and ferric ion, cadmium, copper, nickel, silver, zinc or others), and x the number of CN groups. The initial dissociation of each of these soluble, alkali-metalic complex cyanides yields an anion that is the radical $M(CN)_x^{y-}$. This may dissociate to some extend depending on several factors, with the liberation of CN^- ion and consequent formation of HCN (Standard Methods, 1981).

The great toxicity to aquatic life of molecular HCN, formed in solutions of cyanides by hydrolytic reaction of CN^- with water is well known. The toxicitiy of CN^- is less than that of molecular HCN and it usually is unimportant because most of the free cyanide (CN group present as CN^- or as HCN) exists as HCN.

HCN is largely undissociated at pH values of 8 and less. Hence when toxicities are expressed in terms of the cyanide ion it must be realized that most of the cyanide in water is in the form of HCN. It must also be recognized that toxicities may vary markedly with pH and that a given concentration that is innocuous at pH 8 may become detrimental if the pH is lowered to 6.

The degree of dissociation of the various metallocyanide complexes at equilibrium, which may not be attained for a long time, increases with decreased concentration and decreased pH, and is inversely related to their highly variable stability.

The ion-cyanide complex ions are very stable and not materially toxic in the dark. Acutely toxic level of HCN is attained only in solutions that are not very dilute and have been aged for a long time. However, these complexes are subject to intensive and rapid photolysis yielding toxic HCN, on exposure of dilute solution to direct sunlight. The photodecomposition is slow in deep, turbid and shaded receiving waters. Loss of HCN to the atmosphere and its bacterial and chemical destruction concurrent with its production tend to prevent increases of HCN concentrations to harmful levels (Standard Methods, 1981).

The WHO International and WHO European Drinking Water Standards both set a maximum allowable limit of 0.05 mg/l for cyanides as CN^- (Schipper, 1984). For the first time in 1962, the USPHS Drinking Water Standards set a recommended limit of 0.01 mg/l and a mandatory limit of 0.2 mg/l (McKee, 1978).

The biodegradability of cyanides has been studied by many investigators. The species or groups of organisms that have been reported to assimilate cyanide are listed in a study conducted by Zenon Environmentals (1985). It has been shown that microorganisms can convert cyanide to less toxic products (carbondioxide, ammonia, nitrite or nitrate). If free cyanides are the only soluble cyanide species of concern, the technology for the removal would be relatively straigtforward. However, in the presence of metallo-cyanides, the chemical attributes (e.g. decay rate) of complexed cyanide become very important. Both ferro and ferricyanide complexes

exibit slow exchange, but their exchange rate increases with exposure to UV irradiation (Simovic, 1984). Natural degredation of cyanides have been modelled for predicting degredation in gold mill effluents (Simovic, 1984). Cyanide degradation was found to follow a first order reaction with respect to free cyanide and metallo-cyanide complexes of Zn, Ni, Cu, and Fe (Simovic, 1985).

Cyanide is possible to destroy by oxidation. In case groundwater contamination by cyanides takes place, the water must be oxidized or passed through an ion exchanger. If oxidation is considered, chlorine, hydrogen peroxide or ozone may be used for this purpose. Ion exchange technique may also be used for removal.

Chlorination: The following reactions take place when chlorine is added to a cyanide containing water:

$$NaCN + Cl_2 \longrightarrow CNCl + NaCl \qquad (1)$$

$$CN^- + Cl_2 + 2OH^- \longrightarrow CNO^- + 2Cl^- + H_2O \qquad (2)$$

$$2CNO^- + 3Cl_2 + 4OH^- \longrightarrow 2CO_2 + N_2 + 6Cl^- + H_2O \qquad (3)$$

Although the first reaction take place at all pH values, the second reaction occurs at pH values greater than 8. Thus the medium is made alkaline with the addition of a base and the reaction is accelerated. Cyanide is destroyed completely as the third reaction indicates, but if the water is to be used for any purpose, pH correction is required.

Theoretically, the first reaction requires 2.7 mg chlorine for each mg of cyanide. For the second reaction, 1 mg cyanide requires 2.7 mg chlorine and 3.1 mg NaOH. As already known, the toxicity of cyanate is much lower than cyanide. But, if cyanide is to be destroyed completely, the third reaction should take place. Second step oxidation requires 2.5 mg of chlorine and 1.9 mg of NaOH for 1 mg of CNO^-. Totally, for 1 mg of cyanide, 6.8 mg Cl_2 is necessary for complete dectruction of cyanide. Generally, the required amounts of chemicals found by calculation is different than the practice. In this study, experiments were conducted to determine the cyanide destruction rates related to the chlorine dose in distilled and tap water.

THE EXPERIMENTAL STUDY

The study consisted of four parts:

1) The origin of cyanide in groundwater have ben investigated in the study area.
2) Cyanide containing groundwater samples have been chlorinated to determine the extend of cyanide removal by chemical oxidation.
3) A model study is conducted to determine the cyanide retention capacity of soil.
4) Natural degradation of cyanide have been observed in laboratory conditions to determine the reaction rate constant and time required for cyanide concentration to drop to a nonharmful level.

First series: In the area where cyanide pollution took place there are many industries that may discharge cyanide containing wastes. These are dye industries (3), leather industries (3), enamel industries (2), zipper industry (1), chemicals industries (3), metal industries (8) and textile industries (8).

In order to determine the industry or industries causing groundwater and wastewater samples are analysed for their cyanide content and shown in Table 2.

Table 2: Cyanide concentrations in groundwater and wastewater samples of some industries in the study area

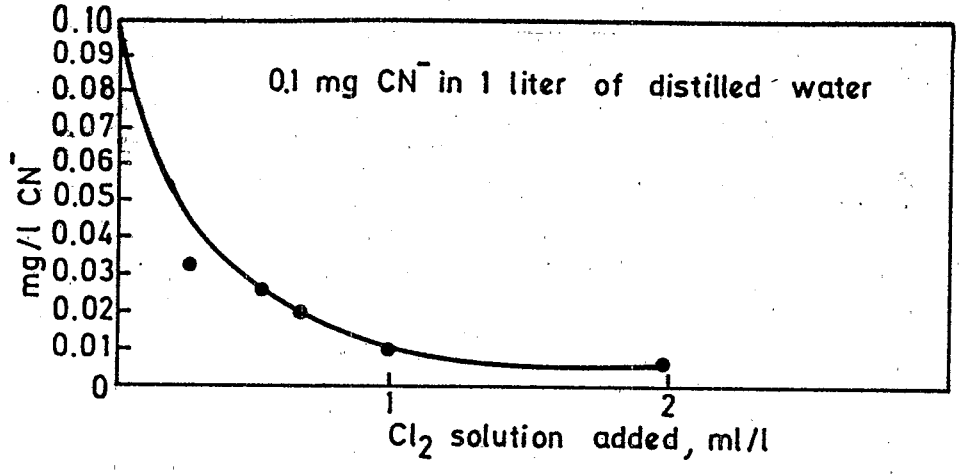
CN^- conc. mg/l	1988 WW	1988 GW	March 89 WW	March 89 GW	May 89 WW	May 89 GW
Textile ind.			0.01		0.09	
Ceramics ind.			0.45	0.02	0.05	trace
Metal pl.ind	.18	.03	0.02	0.01	0.19	0.18
Zipper ind.	.44	.02				
Chemicals Industry	.16	.07	0.16	0.03		
Nif River			0.54		0.03	

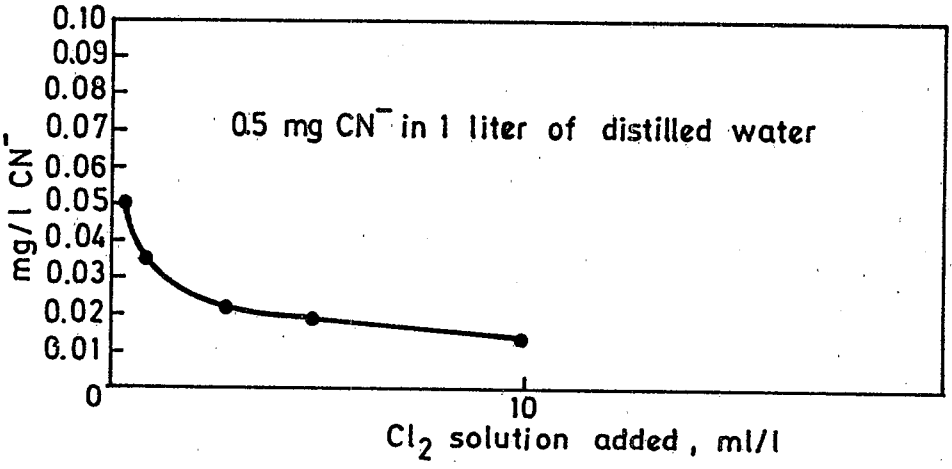
WW: Wastewater sample, GW: Groundwater Sample

Second series: In this part of the study the effect of chlorination on cyanide content has been determined. When groundwater is supplied by municipality, in general it is chlorinated prior to entering the distribution system. Thus, the cyanide is destroyed by chemical oxidation. Although the theoretical amount of chlorine required for cyanide oxidation can be found with the help of stoichiometry, because of the differences between the theoretical and practical values, a laboratory study is conducted. Known amounts of cyanides are added to distilled water and tap water and chlorination results are shown in Figures 4 and 5.

According to the experimental results of the study, complete destruction of 1 mg of cyanide requires 14.5-20 mg chlorine in distilled water and 18-30 mg in tap water. The study has been conducted at normal pH values.

Third series: The model shown in Figure 6 has been constructed to observe the cyanide retention capacity of soil. Cyanide containing water has been percolated through the soil and the amount of cyanide remaining in water has been measured. Since the soil composition effects the amount of cyanide retained by the soil, the experiment was repeated after the addition of iron salts to the soil. The experimental results are given in Table 3 for Kemalpaşa soil, Table 4 Bornova soil and Table 5 for Küçükdere soil.





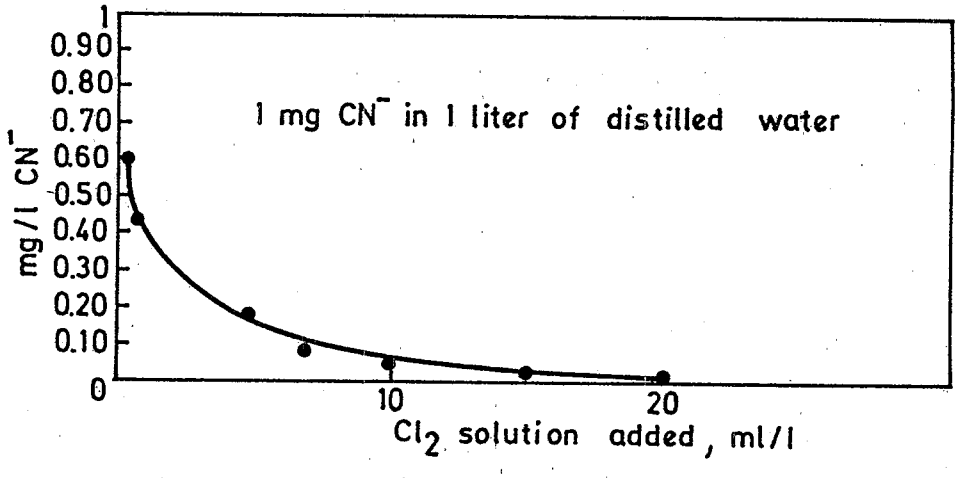
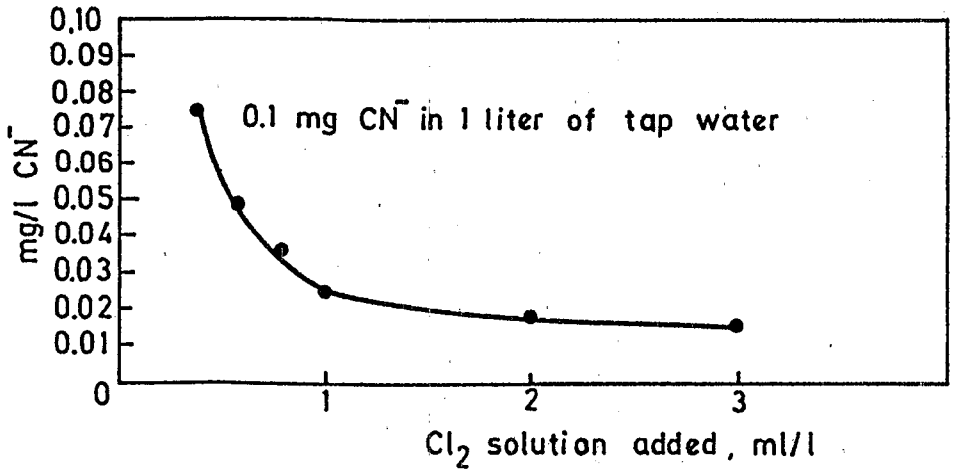
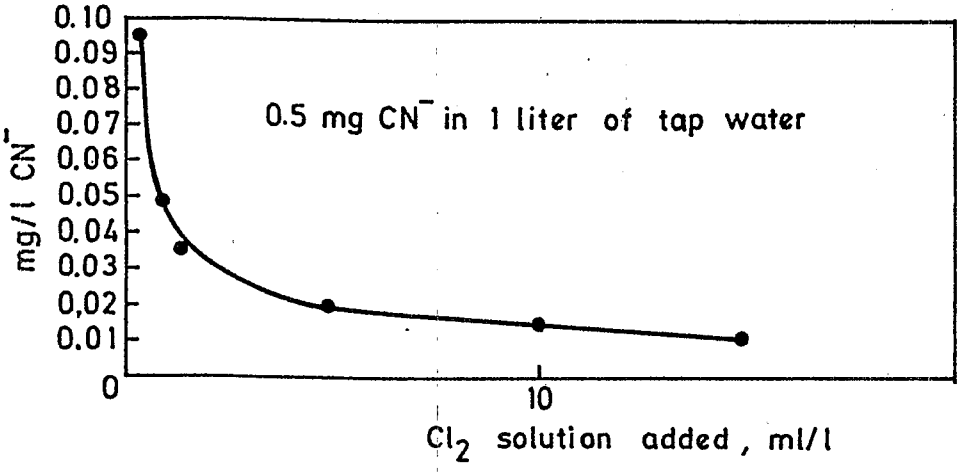


Figure 4: Chemical oxidation of cyanide with chorine in distilled water





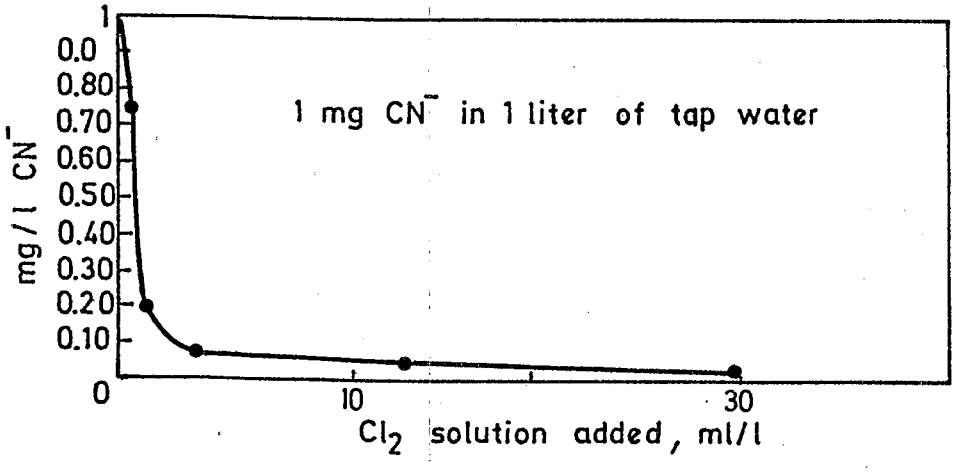


Figure 5: Chemical oxidation of cyanide with chlorine in tap water

Table 3: Cyanide Retention by Kemalpaşa Soil

Chemicals added	Influent cyanide concentration 1 mg/l	2 mg/l	5 mg/l	Average removal
Kemalpaşa Soil	0.37 mg/l (63 %)	0.78 mg/l (61 %)	1.9 mg/l (62 %)	62 %
Soil(3 kg)+3 mg $FeCl_3$/mg CN^-	0.30 mg/l (70 %)	0.68 mg/l (66 %)	1.70 mg/l (66 %)	67 %
Soil + 2.5 mg $FeSO_4$	0.52 mg/l (48 %)	1.1 mg/l (45%)	2.7 mg/l (46 %)	46 %
Soil + mixture of $FeSO_4$+$FeCl_3$ 2.8 mg/mg CN^-	0.67 mg/l (33 %)	1.38 mg/l (31 %)	3.4 mg/l (32 %)	32 %

Table 4: Cyanide retention by Bornova Soil

Chemicals added	Influent cyanide concentration 1 mg/l	2 mg/l	5 mg/l	Average removal
Bornova Soil	0.5 mg/l (50 %)	1.04 mg/l (48 %)	2.65 mg/l (47 %)	48 %
3 kg soil+3 mg $FeCl_3$/mg/CN^-	0.45 mg/l (55 %)	1.00 mg/l (50 %)	2.5 mg/l (50%)	52 %
Soil + 2.5 mg $FeSO_4$/mg CN^-	0.77 mg/l (23 %)	1.56 mg/l (22 %)	3.93 mg/l (21 %)	22%
Soil+mixture of $FeSO_4$+$FeCl_3$ 2.8 mg/mg CN^-	0.80 mg/l (20 %)	1.65 mg/l (18 %)	4.21 mg/l (16 %)	18 %

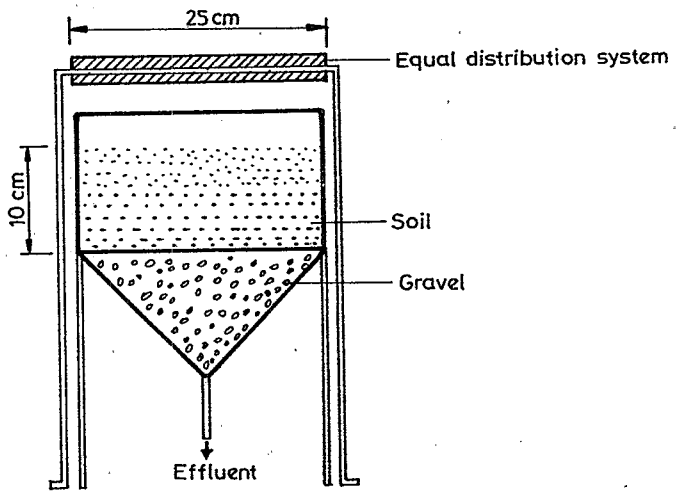


Figure 6. The model used to determine cyanide retention capacity of soil.

Table 5. Cyanide retention by Küçükdere soil.

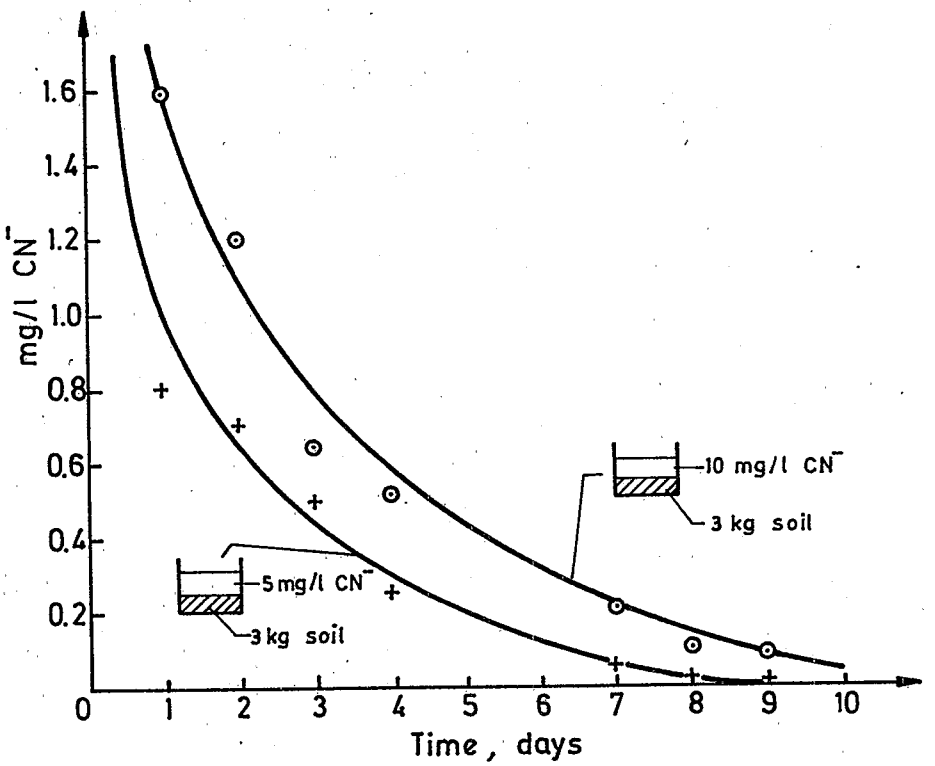
Chemicals added	Effluent cyanide concentration (Infl:5 mg/l)	Average removal,%
3 kg soil	2.8	44
3 kg soil + +150 mg $FeSO_4$	2.5	50
Soil+ 150 mg $FeCl_3$	2.6	48
Soil+ 150 mg $FeSO_4$ 150 mg $FeCl_3$	2.4	52
Soil+ 10 g $FeCl_3$	0.9	83
Soil+ 10 g $FeSO_4$	1.2	76
Soil+ 5 gr $FeSO_4$ +5 gr $FeCl_3$	2.0	60

Fourth Series: Since cyanides undergo biochemical degradation cyanide concentation in polluted groundwater decreases in time. When enough time is given cyanide concentation drops down to nonharmful levels. The cyanide reduction experiment was conducted in two runs. In the first run, three 10 liters plastic containers have been used. One of them contained 3 kg of soil + 6 liters of tap water containing 5 mg/l of CN, the third container contains tap water with 5 mg/l of CN. Experimental results are given in Table 6 and the data obtained are plotted in Figure 7.

In the second run 8 containers are filled with the following:

a) 10 mg/l cyanide solution (2 liters) + soil (0.5 kg) | under light conditions
b) 10 mg/l cyanide solution (2 liters) | under light conditions
c) 2 mg/l cyanide solution (2 liters) + soil (0.5 kg) | under light conditions
d) 2 mg/l cyanide solution (2 liters) | under light conditions
e) 10 mg/l cyanide solution (2 liters) + soil (0.5 kg) | under dark conditions
f) 10 mg/l cyanide solution (2 liters) | under dark conditions
g) 2 mg/l cyanide solution (2 liters) + soil (0.5 kg) | under dark conditions
h) 2 mg/l cyanide solution (2 liters) | under dark conditions

The decomposition results are given in Table 7 and the time concentration curves in dark and light conditions with and without the addition of soil are shown in Figures 8 and 9. All the cyanide concentrations were determined according to colorimetric method (Standard Methods, 1981). The decay rate constants obtained for various conditions are summarized in Table 8.



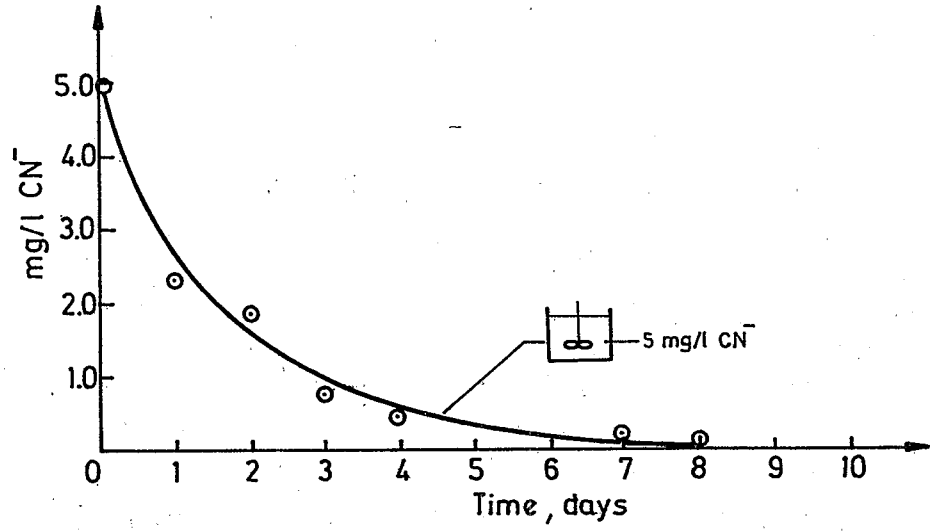


Figure 7: Decomposition of cyanide

Table 6. Decomposition of cyanide.

Time, days	Cyanide Concentration		
	5 mg/l, aerated	5 mg/l+soil	10 mg/l+soil
1	2.35	0.90	1.60
2	1.90	0.70	1.20
3	0.80	0.50	0.65
4	0.44	0.25	0.52
5			
6			
7	0.21	0.12	0.20
8	0.13	0.04	0.10
9	0.08	0.01	0.03
10	0.0	0.005	0.025

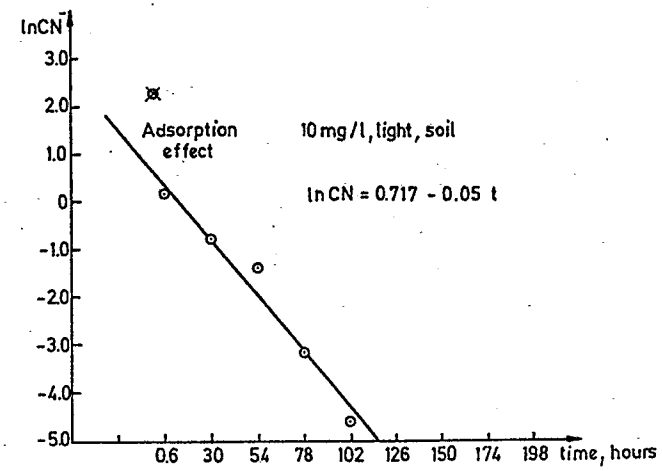
Table 7. Variation in cyanide concentration (mg/l) with time.

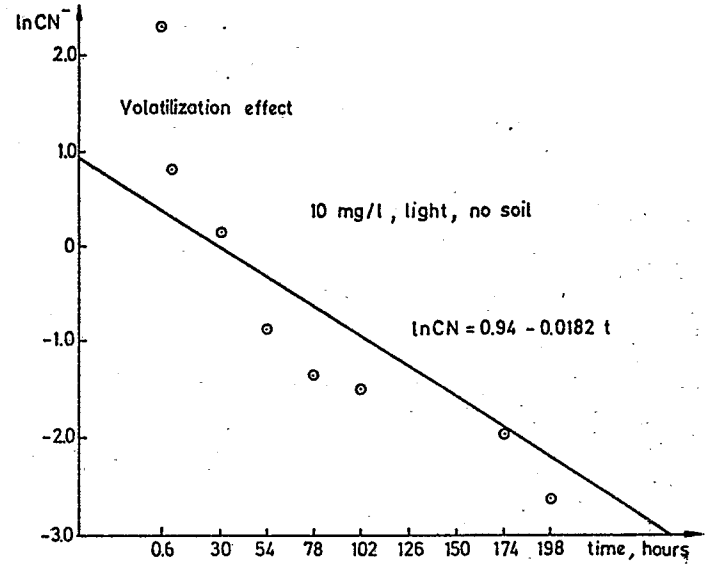
Hours	0	6	30	54	78	102	126	150	174	198
Light+S	10.0	1.18	0.45	0.24	0.04	0.01	-	-	0.0	0.0
Dark+S	10.0	1.38	0.79	0.41	0.14	0.04	-	-	0.0	0.0
Light No soil	10.0	2.23	1.18	0.55	0.26	0.23	-	-	0.0	0.0
Dark No soil	10.0	3.06	1.54	0.88	0.45	0.37	-	-	0.25	0.14
Light+S	2.0	0.68	0.31	0.15	0.03	0.01	-	-	0.0	0.0
Dark+S	2.0	0.69	0.40	0.25	0.10	0.05	-	-	0.0	0.0
Light No soil	2.0	0.78	0.48	0.27	0.16	0.08	-	-	0.02	0.01
Dark No soil	2.0	1.07	0.70	0.37	0.24	0.22	-	-	0.09	0.04

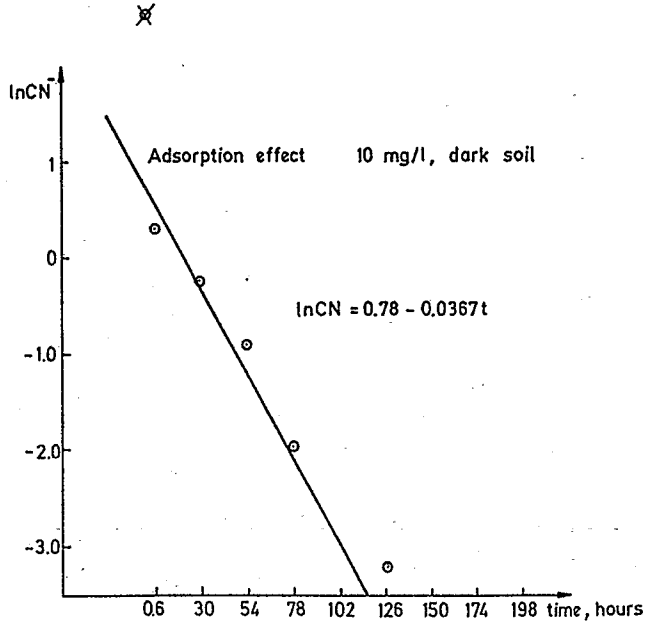
S indicates the presence of 0.5 kg of soil.

Table 8. Cyanide decay rate constants obtained under varying conditions ($hour^{-1}$).

Concentration	Ligth Condition		Soil	
	Light	Dark	Present	Absent
10 mg/l	0.0500	0.0367	×	
10 mg/l	0.0182	0.0176		×
2 mg/l	0.0440	0.0300	×	
2 mg/l	0.0242	0.0190		×







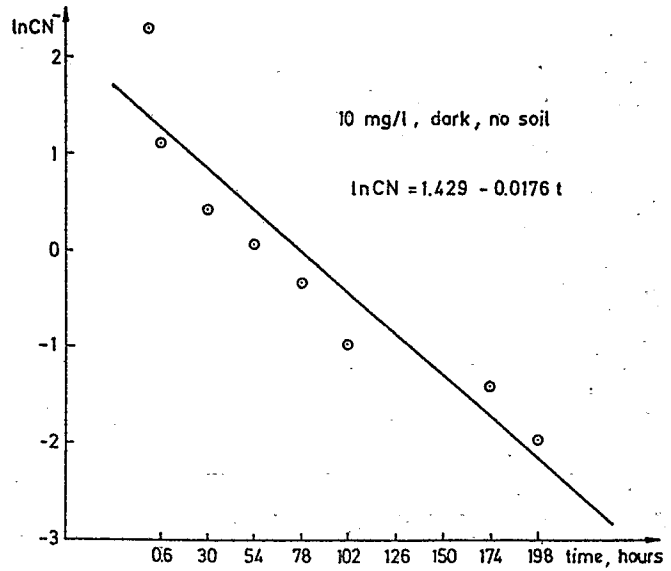
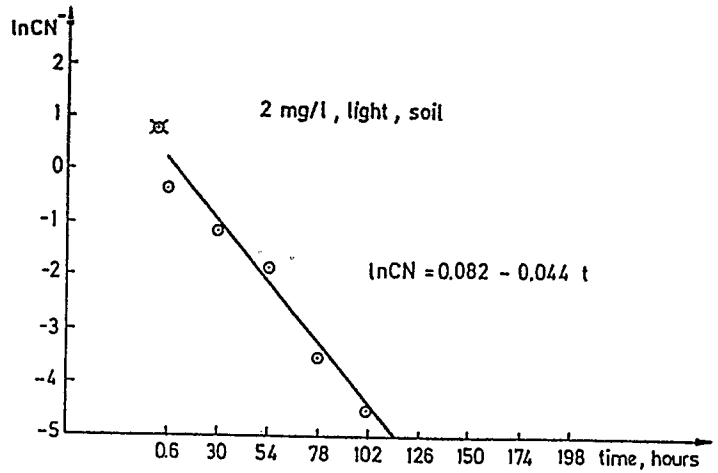
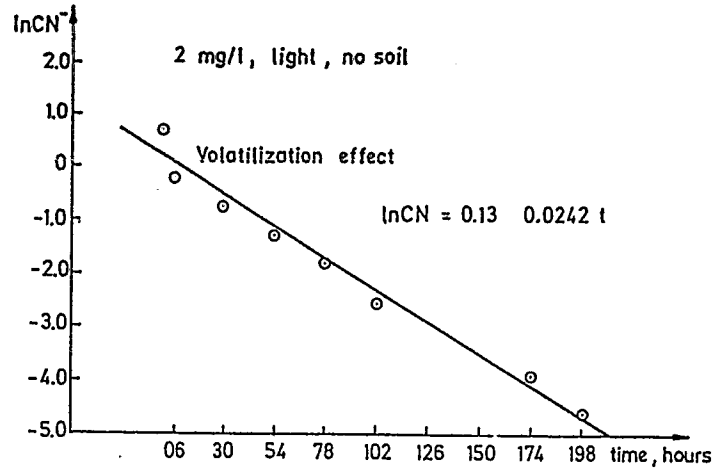
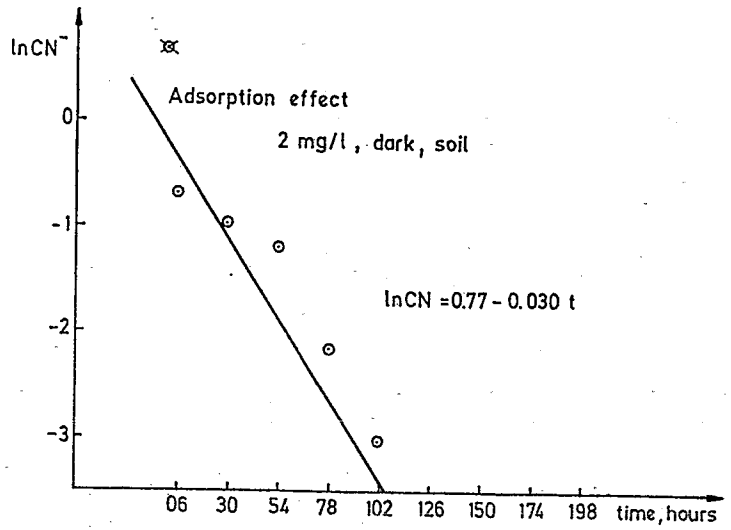


Figure 8: Decay of 10 mg/l cyanide under different conditions







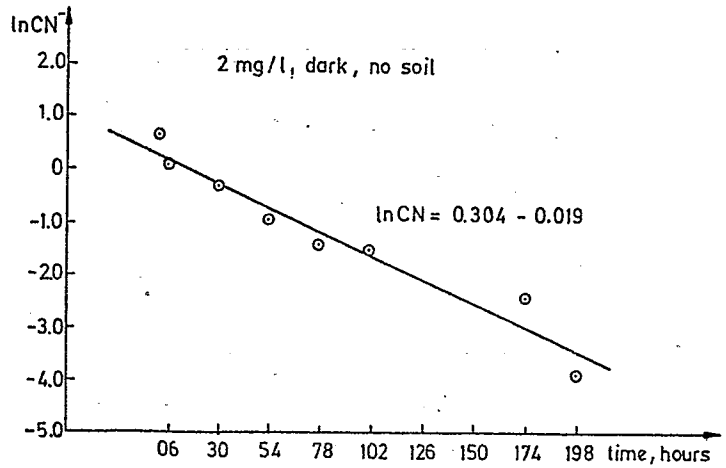


Figure 9: Decay of 2 mg/l cyanide under different conditions

BEHAVIOUR OF CYANIDES IN WATER

Although the groundwater contamination by cyanides is not very common, it may take place especially in areas where cesspools are used for industrial wastewater disposal. In Turkey, water pollution by cyanides is a very important problem. For example it has been reported that about 58 kg of cyanides are discharged to water bodies by industries in the city of Izmir (Şengül, 1987).

It is difficult to find the origin of cyanide when the concentrations are low and the source is more than one or diffuse as is the case in this study. Only experimental results did not give a straightforward result but when it is combined with site histories, it was possible to reach a conclusion.

That the groundwater contamination was caused by zipper industry was found as follows: Textile, metal plating and zipper industries were discharging their wastes to cesspools and the others to Nif river. Ceramics industry had its treatment plant. Nif River analysis indicate that the river receives same cyanide containing wastes, but it is diluted so much that the order of cyanides in Nif River is the same as in groundwater in the area. Thus the idea that cyanide containing wastes discharged to Nif River have percolated to groundwater has been rejected. It is possible that cyanide concentration in Nif River may reach to very high concentrations from time to time but it is carried away so rapidly that it is not very probable that it will cause a groundwater pollution of about 2 km diameter. Although there may be some contribution of cyanides from Nif River, it cannot be the only source. Wastewater analysis and discussion with the industries who discharge to cesspools revealed that the textile industy wastewaters did not contain more than 0.1 mg/l of cyanide and metal planting industry was collecting their cyanide wastes in metal containers. Zipper industry had the complete manufacturing units until about one year ago. Later on, they decided that the metal plating of zippers would be made in another place. Informal information obtained from the personnel revealed that they used to discharge zipper plating wastes to the cesspool. After the cyanide contamination was detected in groundwater within a circle of about 2 kilometer including the zipper industry, they found it more suitabe to move the cyanide baths to another branch they had in a small town. Although many experiments have been conducted to determine the cyanide source in the area, it was possible to determine the contaminating industry by communicating with the people, not by scientific judgement that arises by interpreting the experimental results.

Although chlorination of cyanide contaminated groundwater as a drinking water treatment is not recomendable due to the risks involved, the effect of chlorine on cyanide concentration have been investigated in this research in connection to the event occured in Izmir. In some areas, it is possible that the cyanide contamination may not be noticed if the water is chlorinated and cyanide concentration is not very high. As Figures 4 and 5 indicate the cyanide concentration diminish very fast with the application of chlorine. The chlorine solution used is available in the market and

contains 20 % chlorine. The solution is prepared in such a way that ml/l dose was equivalent to mg/l. The concentration of chlorine solution was determined before each run considering its decomposition reactions.

The rate of this reaction is pH dependent and at alkaline conditions the oxidation is accomplished most completely and rapidly. However, in the laboratory study conducted, water pH was not increased since the aim was not the optimize the removal conditions but to observe the change in cyanide concentration under natural conditions. Comparison of Figure 4 and 5 reveal that less cyanide was oxidized in the case of tap water. Although the theoretical amount of chlorine for cyanide oxidation was found to be 7 mg O_2/ mg of cyanide, in practice 15-20 mg Cl_2/mg CN^- is determined to be sufficientt. The difference may be attributed to the short time and pH conditions of the medium.

If cyanide contamination takes place as cyanide being the single pollutant, chlorination may be considered as a solution. But when industrial wastewater percolates to the groundwater, cyanide may be accompanied by other pollutants also. Therefore, chlorination is not recommended as a solution for cyanide contaminated groundwater.

When cyanide containing wastewater percolates thorough the soil, part of cyanide is retained in the soil and some reaches to the groundwater. The part that reaches to the groundwater is diluted and microbiologically degraded in the course of time. Thus the original cyanide containing water is much more concentrated than the contaminated groundwater.

The amount of cyanides that is retained by the ground depends on the type of soil medium and its organic matter content. Comparison of Tables 3, 4 and 5 indicates the effect of differences in soil type and iron content. Although all the soils from different regions contain clay, sand and gravel, their ratio of these substances and organic matter contents are different.

A 10 cm layer of soil can retain 55 % of cyanide in soil. Cyanides that are adsorbed on soil particules slowly decompose with help of microorganisms. The part that form complexes in water are much less toxic than HCN, but as decomposition takes place HCN is produced in groundwater, this reaction will be very slow because of the dark medium and it is not very probable to reach toxic concentrations unless the source is continuous.

Iron chloride addition causes a slight increase on cyanide retention capacity of soils. This may be explained by the strong interaction of Fe^{+3} ion with cyanide ions to for the ferricyanide ion $Fe(CN)_6$

$$Fe^{+3} + 6\ C{=}N \longrightarrow Fe(:C{=}N)_6$$

The ferricyanide ion formed is strongly adsorbed on soil particules, but addition of Fe^{++} salt or combination of Fe^{++} and Fe^{+++} salts diminished the retention.

As Table 5 indicates, at very high levels of iron addition the positive effect of ferrocyanide retention was pronounced.

Despite the repeated experimental studies conducted to determine the effect of presence of iron salts, the results were somewhat unclear. But in any case, it can be said that the presence of iron salts has a positive effect due to the decreased toxicity of cyanides.

When cyanide contaning water comes into contact with the soil, the cyanide concentration drops sharply at the beginning as shown in Figure 7. An 80 % reduction of cyanide in the first day is caused by adsorption by soil, later on adsorption and microbial degredation should have occured together. In about 10 days time cyanide concentration drops to nonharmful levels. But the concentration is expected to fluctuate later on due to the reactions like hydrolysis, disociation, etc. Although at a slower rate, the cyanide concentration in water drops in the course of time to nonhamful levels as shown in Figure 7.

In fact, the cyanide determination experiments conducted in contaminated wells in Kemalpaşa after six months indicated that cyanide has been removed completely from the water since the source has been removed from the area.

Reaction rate constants (microbial decay + volatilization) have been calculated by assuming that cyanide decomposition fits to first order kinetics (Figures 8 and 9). Thus, the k values have been found to be 0.039 for aerated samples (5 mg/l), and varying between 0.03 and 0.05 for soil containing samples; and between 0.018 and 0.024 for samples which do not contain any soil. This means that the presence of soil (i.e. adsoption as a dominant removal mechanism), is very effective in cyanide removal.

Table 7 which has been completed after 200 hours of experiment time, reveals the following:

1. Adsorption of cyanide by soil is very effective. That is why in case the soil is present, the first values are omitted in decay equation.

2. As can be seen from Table 8, decay rates were found to be highest in case of soil containing samples (0.05 and 0.04 for 10 mg/l and 0.04 and 0.03 for 2 mg/l). As these values indicate, the concentration does not have a significant effect. The reason fo this is due to the immediate adsorption, the simultaneous reduction of concentrations to 2.23 and 0.68. Thus the difference between the two concentrations is reduced to 1.5 mg/l from 5 mg/l. Consequently, not only the concentration, but also the toxicity is reduced. The effect of light conditions is considerably smaller than the effect of presence of soil. Soil is a very important factor on decay rate. This shows the presence of cyanide assimilating oganisms in soil and the dominant effect of adsorption on cyanide removal.

The volatilization rates have not been taken into account. But since the pH value has not been changed during the experiments, the

volatilization is assumed to take place to a certain extent. Thus, the actual decay rates must be smaller than the values obtained here. In fact higher decay rate at high concentration is an indication of high volatilization at high concentration.

Adsorption is dominant only at the beginning of the experiment and reaches to equilibrium. But volatilization is assumed to be taking place during the course of the experiment.

In order to eliminate the effect of adsorption on decay rate in cases the soil is present, the first values were ommitted and not taken into account in decay rate calculation. Besides that, zero values were also omitted also since it is not known exactly at what time the concentration has reached to zero mg/l.

The first order kinetics fit the experimental data very well the R^2 values being around 90 to 98 %. The cyanide concentrations decrease to levels much less than 1 mg/l in about 10 days time. These findings suggested that the natural degredation of cyanide is a potentially feasible option for environmental control unless the source is continous and the concentration is very high.

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Environmental Legislation in Europe

Environmental Legislation in Europe

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Legislation is the driving force behind much of the environmental activity in the UK and is becoming increasingly influenced by laws and directives coming from the European Economic Community. Indeed it is now almost impossible to understand national policy without first understanding the European policy into which it fits.

The European Economic Community (EC) was established by the Treaty of Rome in 1957. It now has some 12 member countries. The Single European Act of 1986 first added the word "environment" to European policy and gave explicit recognition to the preservation and protection of the environment. This is a powerful tool and all legislation of the EC now has to consider affects upon the environment.

Environmental Action Programmes are used by the EC as a policy framework to outline intentions and ideas for legislation and other activities in the year ahead. We are currently in the 4th Programme which runs until 1992.

Before the Single European Act of 1987, all EC legislation had to be adopted unanimously. Now it follows the "cooperation procedure" and can be approved by majority vote. EC legislation must be implemented in the member countries, through national legislation, typically between 18 months and three years of EC adoption. The range of EC legislation is now vast, and includes second generation traditional and new areas of law such as environmental auditing, environmental assessment and eco-labelling. Legislation items adopted per year has increased from 1 to 5 in the early 1970's, 10 to 15 in the early 1980's, to 29 in 1989.

The key areas of EC environmental legislation are relatively simple to understand. Briefly they are as follows:

Wastes

a) EC law establishes a framework for waste disposal
b) It requires toxic and dangerous waste to be disposed of without human health or environmental effects
c) It establishes a system for transfrontier shipments

Water

a) EC law sets quality criteria standards for 62 compounds
b) It prohibits and regulates discharges to groundwater of listed substances

c) It sets a framework to eliminate 17 compounds of inland, coastal and territorial waters

Air

a) EC law sets air quality limit values for SO_2, NO_2, lead and dust
b) It ensures BATNEEC (Best Available Technology Not Entailing Excessive Costs) for new industrial plants
c) It sets emission limits for combustion plants for SO_2, NOx and dust

Chemicals

a) EC law has limited the production of CFC's and other ozone depletors
b) It establishes a new system for testing, classifying and packaging new chemicals
c) It bans or restricts the use of PCB's, PCT's, benzene asbestos, lead and organotoxins.

There are many EC laws coming forward. Those agreed by the EC but not yet implemented in the UK include:

a) Procedures to be followed to allow the release of genetically modified organisms
b) A freedom of information act which allows the public to gain all environmental data
c) The establishment of a European Environmental Agency

Proposals currently being considered by the EC include:

a) Fixed vehicle emissions
b) Cadmium as a dangerous substance
c) New systems for introducing pesticides
d) Risk assessments for existing chemicals
e) A new definition for hazardous waste
f) Stopping waste shipments to Africa, Pacific and the Caribbean
g) Minimum standards for landfills
h) Secondary treatment for all sewage discharges.

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In-situ Vitrification

IN-SITU VITRIFICATION

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1. INTRODUCTION

In-situ vitrification (ISV) involves the in-situ melting of contaminated solids at temperatures typically in the range 1600 to 2000°C. The energy required is applied through electrodes inserted into the ground. Organic contaminants are destroyed by pyrolysis. Inorganic pollutants are immobilized in the solidified mass.

In the United States this technology is available (but see below) from only one commercial vendor (Geosafe Corporation) and has been under development by Battelle Memorial Institute since 1980.

This technology was to have been the subject of a separate chapter in the main report, however, for the reasons explained below, the US Environmental Protection Agency's SITE demonstration project on which it was to have been based did not go ahead. Although it was not possible to complete the chapter as planned it was decided to include an account of the technology, based on information available in the published literature, as an Appendix to the main report.

The SITE demonstration, and the main clean-up project that it was to complement, could not go ahead because the vendor of the technology withdrew it from the market.

In July 1991 Geosafe Corp. informed the US Environmental Protection Agency (EPA) that it would no longer being offering its in-situ vitrification technology. This decision was prompted by an accident that occurred in March 1991 during large scale testing which resulted in a fire and destruction of some equipment. The company took the view that although the accident "involved only non-hazardous materials, .. such an event could have unacceptable consequences if it were to happen at a hazardous waste site." The company did "not consider it prudent to proceed with commercial

large-scale operations if there is any reasonable chance of recurrence of this event.." Some work is continuing with the Department of Energy (Anon 1991).

Although the planned demonstration project was not completed, some background information on the site where it was to have been carried out has been included in this Appendix, as a indication of the type of site to which the technology might be applied, if the technical problems can be overcome.

2. SCIENTIFIC AND ENGINEERING BACKGROUND

2.1 The Process

The description below is based on a number of references (e.g. Geosafe 1989, Hansen & Fitzpatrick 1989, Hansen, EPA 1990) generally originating from the Geosafe Corporation.

An array of four electrodes is placed to the desired treatment depth in the volume to be treated. A conductive mixture of graphite and glass frit is placed on the surface between the electrodes to serve as an initial conductive path. As electric potential is applied between the electrodes, current flows through the starter path heating it and the adjacent soil to the melting temperature of the soil (typically 1600-2000°C). Once molten, typical soils become electrically conducting (conductivity tends to relate to the concentrations of monovalent alkali cations (Na, K etc) and in some circumstances these may need to be added). Thus the molten mass becomes the primary conductor and heat transfer medium allowing the process to continue. The molten mass grows downwards and horizontally as long as power is applied. The process of melt growth is illustrated in Fig. 1.

With present equipment a single "setting" treats a zone 8m (27ft) square by about 6m (20ft) deep (about 900 tonnes at a bulk density of 2,200kg/m^3) and takes 7 to 10 days to complete. The treated mass takes several months to a year or more to cool, although the collection hood can be removed after a few hours. Once one setting is completed, the equipment is moved to an adjacent area (this is claimed to take about 16hours). Neighbouring blocks fuse together.

The temperature needed to melt the soil or other materials to be treated will depend on their composition. Typically temperatures of 1600 to 2000°C are reached. High concentrations of alkalies or halides may be expected to act as fluxes resulting in lower melting temperatures.

As the high temperature melt expands by about 25-50mm/hr (3.6-5.5 tonnes/hour, 4-6 short tons/hour), a very steep thermal gradient (600 to 1000°C/100mm) precedes the melt. Within the melt a vigorous

chemically reducing environment is produced.

It is claimed that vapours migrate towards the melt zone. At appropriate temperature regimes within this zone and the melt itself, solids and contaminants undergo a change of physical state and decomposition/degradation reactions.

As a result of the ISV process individual contaminants may:

(a) undergo chemical and/or thermal destruction,

(b) enter the off-gases from which they can then be removed,

(c) be chemically or physically incorporated into the resultant solid product.

Typically, organic materials are destroyed by pyrolysis (thermal decomposition in the absence of oxygen to component elements), and inorganic contaminants are incorporated into the glassy or microcrystalline, monolithic residual product.

Organic products of incomplete pyrolysis are usually gaseous. These will move slowly through the highly viscous melt towards the surface. Some may dissolve in the melt, the remainder evolving from the surface are captured in a collection hood. In the presence of air those that are combustible will burn (this clearly has safety implications). Finally, evolved volatiles and the products of surface combustion are subjected to appropriate off-gas treatment processes.

Inorganic compounds may thermally decompose or otherwise be retained within the melt. For example, nitrates, carbonates and sulphates yield gaseous products which may dissolve in the melt or evolve through it to enter the off-gas collection hood.

As stated above, it is claimed that vapours will be drawn towards the melt. A theoretical explanation for this phenomenon has been provided (Geosafe 1989). However, what happens in practice must relate closely to the porosity/particle sizing of the soil as conflicting processes, capillary suction and vapour diffusion are involved which respond differently to these parameters. It is said that within the heating zone around the melt an equilibrium will be established between inward migration caused by capillary action (for example as fine soils dry out soil suction will increase) and outward migration of vapours (more rapid through permeable soils). Vapours will diffuse towards the melt and outwards towards cooler zones due to concentration and thermal gradients. However, those moving outwards will tend to condense being drawn once again towards the heated zone. Any that are adsorbed on the particle surfaces will be dealt with by other settings as processing moves across the site.

Within the dry zone movement will be aided by channelling and cracking, and possibly by the negative pressure sustained within the off-gas collection hood (see below).

Movement of organic vapours may also be assisted by the presence of relatively large quantities of water vapour - a process analogous to steam stripping may occur.

2.2 Applicability

The process may be applied to contaminated natural soils, but also to other naturally occurring soil-like materials and solid process wastes, including silts, sediments, sludges and tailings.

Most soil types can be treated provided there is sufficient silica and alumina present to form a melt at the temperatures achievable with the system. There need to be sufficient monovalent alkali cations (Na, K etc) present to provide the degree of electrical conductivity necessary for efficient operation. If necessary, alkali fluxing agents such as sodium carbonate may be added to the soil. In general alkalis and halides such as chlorides and fluorides will act as fluxing agents lowering the temperatures at which a melt will form.

While broadly applicable to a range of contaminants, present equipment is limited to maximum concentrations of organics in the 5 to 10 wt % range, depending on the compounds present; and to metal concentrations not exceeding 16 wt %. It is also limited by the presence of buried metals in excess of 5 wt % and the need to maintain a negative pressure within the off-gas collection hood.

The limitations on organics content arise from constraints imposed by the gas collection and treatment systems in terms of amounts of heat and gases that can be tolerated/handled.

If metal concentrations are too high, reduction to the metal may occur under the reducing conditions in the melt. Metals such as iron may then collect as a separate phase at the base of the melt. In contrast, low melting metals such as lead may partially volatilize and enter the off-gasses. It is to be expected that all mercury will be lost in this way.

The process is applicable to fully saturated soils, however it is limited to those situations in which recharge to the treatment zone is reasonable relative to the rate of growth of the molten zone (limiting permeability is put at 1×10^{-5}cm/sec). In these situations steps can be taken to limit the rate of recharge, for example, by lowering the water table by pumping. It takes about the same amount of electrical energy to remove a unit mass of water as it does to melt a similar mass of soil. There are thus obvious

advantages in controlling the water regime within the treatment area.

It is claimed (Geosafe 1989) that in tests at various scales the process is applicable to soils containing volatiles, semi-volatiles, and refractory (non-volatile) organic compounds and inorganics (heavy metals), a variety of radioactive materials, and a broad range of combustible, metallic, and inorganic scrap materials (e.g. paper, plastic, wood, drums, concrete, rock, asphalt). It is also claimed that drummed organic wastes can be treated.

The ISV process results in a 20 to 40% reduction in volume for typical soils. Once processing is completed clean backfill is placed over the residual monolith to restore site levels. As cooling continues additional subsidence may occur.

There are some topographic constraints to application of the process. The hood is fitted with a skirt capable of accepting variations in ground levels of about 0.15m (6in). The ground area supporting the hood should not slope by more than 5%. Care must be taken to prevent surface water from entering the treatment zone.

In general therefore, some prior preparation of the site to accommodate the equipment, may be required.

The process should be performed at sufficient distance from any structures to avoid damage. This might occur because of thermal effects or subsidence due to soil densification.

During cooling of the melt the thermal gradient will tend to spread out compared to that during the operating stage. For example, the 100°C isotherm may move from about 0.3m to as far as 1.5 to 2.1m (5-7ft) from the residual monolith. The rule of thumb advice from Geosafe is that no setting should be placed closer than about 4.6m (15ft) to any vulnerable structure of service run (utility run). Similarly potential subsidence effects should be taken into account and precautions taken if necessary.

There is no evidence (Geosafe 1989) that the process has induced stray electrical potential or currents in nearby structures, service lines or pipelines.

2.3 Residual Product

The residual product is typically about 10 times stronger than unreinforced concrete in both tension (27-55MPa, 4,000-8,000psi) and compression (206-276MPa, 30,000-40,000psi). It is not affected by either wet/dry or freeze/thaw cycling. It is free of organics and passes the US Environmental Protection Agency's EP-Tox and TCLP

leach testing criteria for priority pollutant metals. It also has acceptable biotoxicity relative to near surface life forms. It is projected that the residual product will withstand environmental exposure for geologic time periods.

Depending upon composition, silicoaluminate glasses, such as those produced in the ISV process, may be reactive with water, particularly in the presence of alkalies. An example of this reactivity is provided by vitrified blastfurnace slag which has been used for over one hundred years as a cementitious material with Portland cement or alkaline hydroxides as activators. However, because of the monolithic nature of the residual product, any reaction would be restricted to the immediate surface of the mass of material and is therefore very unlikely to lead to significant release of toxic materials even over very long periods of time. It should also be noted, that the slowly cooling parts of the mass may undergo some crystallization: i.e. it is unlikely that the final mass will be completely vitrified in the true sense of being a uniform glass.

Tests to assess the rate of hydration of the mass have been carried out (Geosafe 1989).

2.4 Equipment

The basic ISV equipment system is shown in Fig.2. The maximum distance between electrodes in the large-scale system is about 5.5m (18ft) allowing formation of a maximum treatment zone of about 8.2m (27ft) radius.

The major part of the ISV equipment system is the off-gas collection and treatment system. A 16.8m (55ft) diameter off-gas collection hood directs any evolved gas to the treatment system utilizing quenching, pH controlled venturi scrubbing, mist elimination (dewatering), humidity control, particulate filtration and carbon adsorption, to ensure clean air emissions. The quenching and scrubbing solution is cooled by a self-contained glycol cooling system eliminating the need for a continuous on-site water supply.

Flow of air through the hood is controlled to maintain a negative pressure (3.4-6.9Pa, 0.5-1.0in water gauge). An ample supply of air provides oxygen for combustion of pyrolysis products and volatile organic compounds (VOCs). Typically evolved gases amount to less than about 1% of the total volume of gas processed by the treatment system.

Contaminants collected in the scrubber solution, filters and or carbon adsorption beds may be disposed of by feeding them back into the treatment zone.

Electric power is typically taken from a public supply at either 12.5 or 13.8kV. The AC power is converted to 2-phase and transformed down to 4000 volts for initial processing. Voltage is then progressively reduced during an ISV "setting" to offset the increased conductivity of the growing melt. Typical soil applications require 0.8-0.9 kwh/kg (0.35-0.4 kwh/lb) of material treated. Such electrical services are usually available from public supplies but may also be provided by diesel generators when necessary.

Means are required to determine the extent of the molten zone (geophysical, optical and thermal methods may be employed) and for gas migration.

2.5 Health & Safety

The most direct hazards would appear to be the very high temperatures reached in the process and the large amounts of electricity that must be employed.

It seems likely that hazardous conditions could occur in the collection hood if significant quantities of volatile organic compounds are evolved, especially given the high temperatures involved.

2.6 Potential Environmental Impacts

Impacts on the environment and public health should be small given the in-situ nature of the process. Operation may, however, require some preliminary earth moving works to prepare the site within the constraints on site topography of the ISV system. Thus, should perimeter dust problems might arise.

The process requires 24hr operation so in populated areas there may be noise and other operating impacts.

3. THE PLANNED CASE STUDY

3.1 Introduction

Although the planned case study was not completed the background information on the proposed study has been included in this Appendix as an indication of the type of site it is believed that technology of this type might be applicable to.

3.2 The Case Study Site

Only one case study was to have been included in the NATO/CCMS STUDY: A US EPA SITE (Superfund Innovative Technology Evaluation) Demonstration was to have been carried out during 1991 at the Parsons Chemical site, Grand Ledge, Michigan, USA. The site is contaminated with mercury, arsenic, heavy metals, chlordane, DDT and TCCDs (2,3,7,8-tetrachloro-dibenzo-p-dioxins) from the formulation of pesticides. The process applied involved the excavation and staging of the contaminated materials for processing.

3.3 Background

Following a hydrogeological investigation of the Parsons Chemical/ ETM Enterprises (Parsons/ETM) site carried out for the present owners (ETM) in 1980 limited action was taken to remove a septic tank and "leach field."

The near surface geology (to about 5m) can be generally characterized as a glacial till deposit of stratified clay and loam with minor sand stringers. a thin loamy top soil ranging from 150 - 600mm in thickness covers the site. Below this is found either a brown loam or clay with variable amounts of granular material ranging in thickness from 2.1 to 3.5m. This material contains thin, saturated sand stringers. Overall moisture content varies from relatively dry, firm clay to soft loam to the saturated sand stringers. The underlying layer is a grey firm till clay which dips to the south.

The groundwater appears to be perched and occurs at variable depths across the site with only limited connections between the water bearing units.

Prior to ETM occupying the property, Parsons Chemical Works Inc. engaged in the mixing, manufacture and packaging of agricultural chemicals. Materials handled included pesticides, herbicides, solvents and mercury based compounds. Concern arose in 1979 and 1980 when the Michigan Department of Natural Resources (MDNR) collected sediments from a creek and ditch adjacent to the site. Elevated concentrations of lead, mercury, arsenic, and pesticides, including chlordane and DDT (dichloro-diphenyl-trichloroethane).

Dioxins were detected on the site in 1984 following a US EPA screening operation. In 1988 a MDNR survey revealed the presence of on the site of widespread contamination with mercury (up to 150mg/kg) and high pesticide concentrations including 4,4'-DDE, 4,4'-DDT, dieldrin, and chlordane.

ETM continued to operate on the site in 1990 but with the two areas contaminated with pesticides and TCDD fenced.

3.4 Treatability Study

Geosafe Corporation, in conjunction with Battelle Pacific Northwest, conducted a treatability test on soils from the Parsons/ETM site. Both contaminated and uncontaminated soils were shipped for testing.

Preliminary results available November 1989 (CCMS 1991) revealed destruction efficiencies (DE) for dioxins and furans ranging from 76.3 to 99.9%. DEs for pesticides ranged from 99.98 to 99.998%. When calculated with the efficiency of the off-gas treatment system, the demonstrated removal efficiency (DRE) was 99.9763 to 99.9999% for dioxins and furans and 99.99998 tO 99.999998% for pesticides. The calculation of DE was limited by analytical procedures and detection limits achievable for suspect compounds.

A DRE for mercury was not calculated. Mass balance calculations accounts for only 5.4% of the original mercury concentration: the assumption was that the greater part was retained in the melt (it seems odd that this was not determined analytically but it may simply be that such results were not available in November 1989).

4. PERFORMANCE

At the time of writing (December 1991) only data produced by Battelle/Geosafe were available.

In one test on soil containing 550 mg/kg PCBs the initial destruction efficiency (i.e. as a result of the heating associated with the melting) was 99.9%. However, the small amount of PCB that did escape thermal destruction was scrubbed from the off-gas to give an overall destruction and removal efficiency of 99.9999%. Other data can be found in the listed literature.

The vitrified waste has been subjected to a variety of leaching tests including the EPS-tox and TCLP. These tests show (Geosafe 1989) a uniformly low leach rate for heavy metals of about $5x10^{-7}$ $g/cm^2/day$ or lower, and the material appears to qualify for delisting under US regulations.

5. LIMITATIONS

As described in the introduction, there have been some major operational difficulties with the process and unless these can be overcome the technology is only likely to receive limited application.

There has been some controversy over the question of possible migration of vapours away from the hot zone, but the balance of opinion is that any outward migration would not be of great practical importance. It would be dealt with by neighbouring settings for example. However, it is clearly something that should be watched for in any practical application of the technology.

6. COSTS

ISV processing is claimed to be "quite energy efficient." Soil is a very good insulator and thus little heat is lost to soil around the heat zoning (and that which does effectively preheats the soil). The greatest heat loss occurs through the surface by radiation and release of hot off-gases.

ISV of typical soils requires 880-1100kwh/tonne (800-1000kwh/short ton) total energy input, most of which is accounted for the heat of fusion of the melt. This is in fact less than that required to incinerate soils in direct energy applied (but this does not account for energy losses during generation and transmission of electric power).

Treatability testing (by Geosafe) is said to cost US $35,000-40,000 provided there are no exceptional analytical requirements (e.g. for the presence of dioxins) and to take about 8 to 10 weeks.

Mobilization costs are about $50,000-60,000 plus $30-40 per kilometre from Geosafe's Richland, Washington base location.

Technical support is estimated to cost about $25,000-75,000.

Operational costs will be influenced by a number of site-specific factors including:

- the amount of site preparation required
- properties of the soil/waste to be treated (e.g. dry density, moisture content)
- volume of material to be processed
- depth of processing
- unit price of electricity
- season of the year

Depth of processing has an important impact because it affects the ratio between operational time and time devoted to moving the equipment between settings etc. The process economics are

consequently more favourable for greater treatment depths. For shallow contamination, say a metre or so, it is likely to be more economic to move the material (stage) to form deeper treatment beds.

Costs can vary by $55-77/tonne ($50-70/short ton) between dry soil and fully saturated soil. In some cases, e.g. wet sediments, pre-drying may be justified.

Electricity is assumed in the above costings to be available from public supplies for less than $0.07-0.08/kwh.

On-site processing costs are put at $275-385/tonne ($250-350 per short ton), including all elements of direct and indirect cost such as labour, materials, energy, equipment amortization, and contractor overhead and profit. The most significant variables affecting the cost include the price of electricity, amount of water to be removed during processing, and the amount of chemical analysis required associated with process control and disposal of wastes etc.

It is not completely clear whether these costs include any element of site preparation costs e.g. if the site needs to be regraded to meet the limitations of the equipment i.e. surface level variations not greater than 0.15m and slopes of no more than 5%.

7. PROGNOSIS FOR TECHNOLOGY

In view of the decision by Geosafe in July 1991 to cease to offer the technology the prospects appear poor for short-term application.

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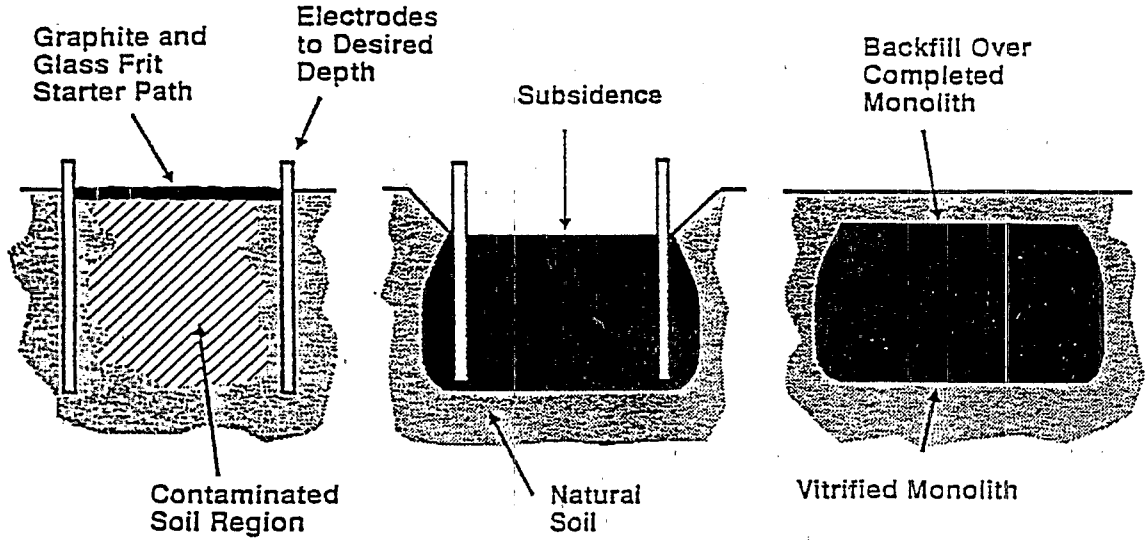


FIGURE 1. Stages of ISV Processing

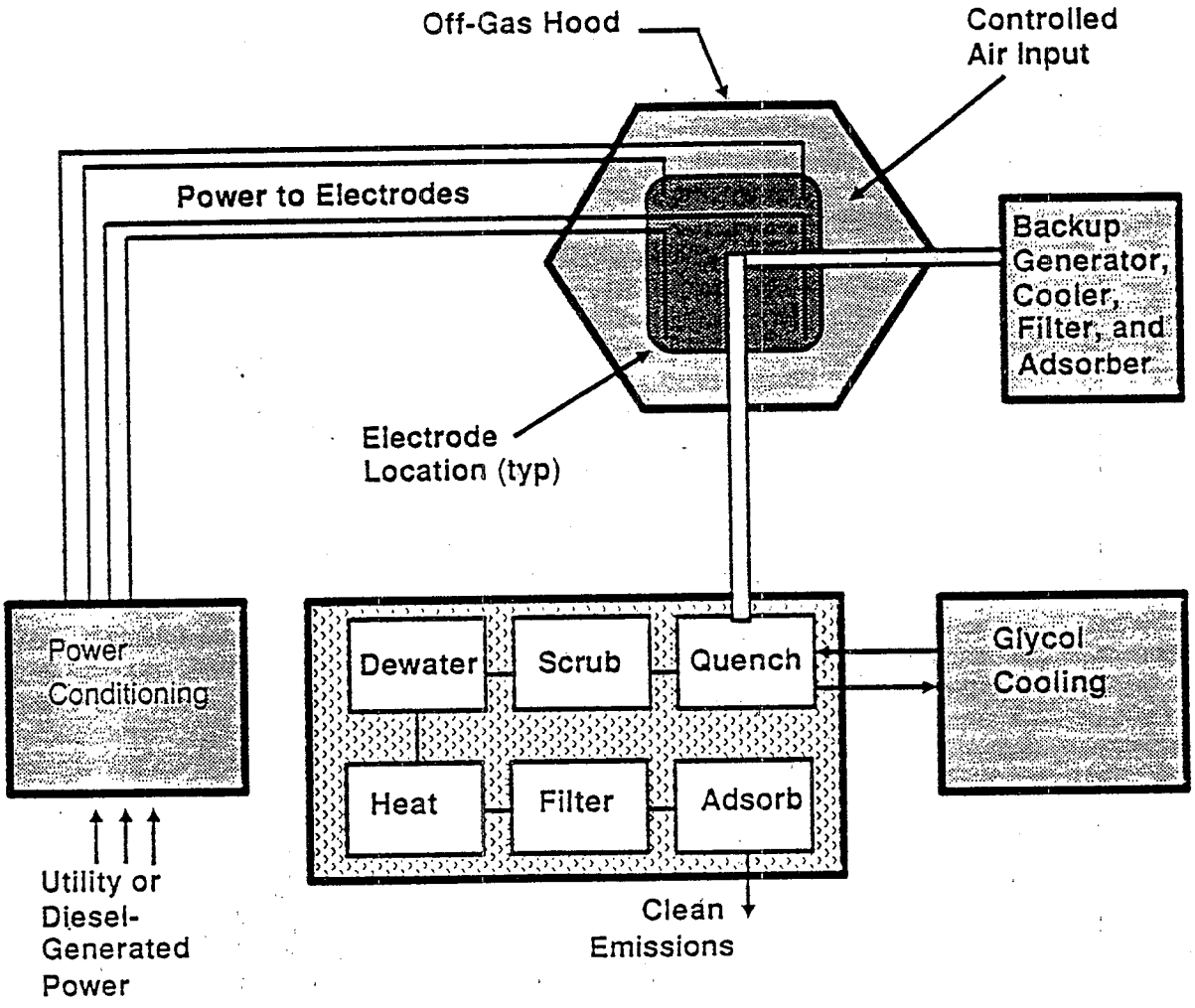
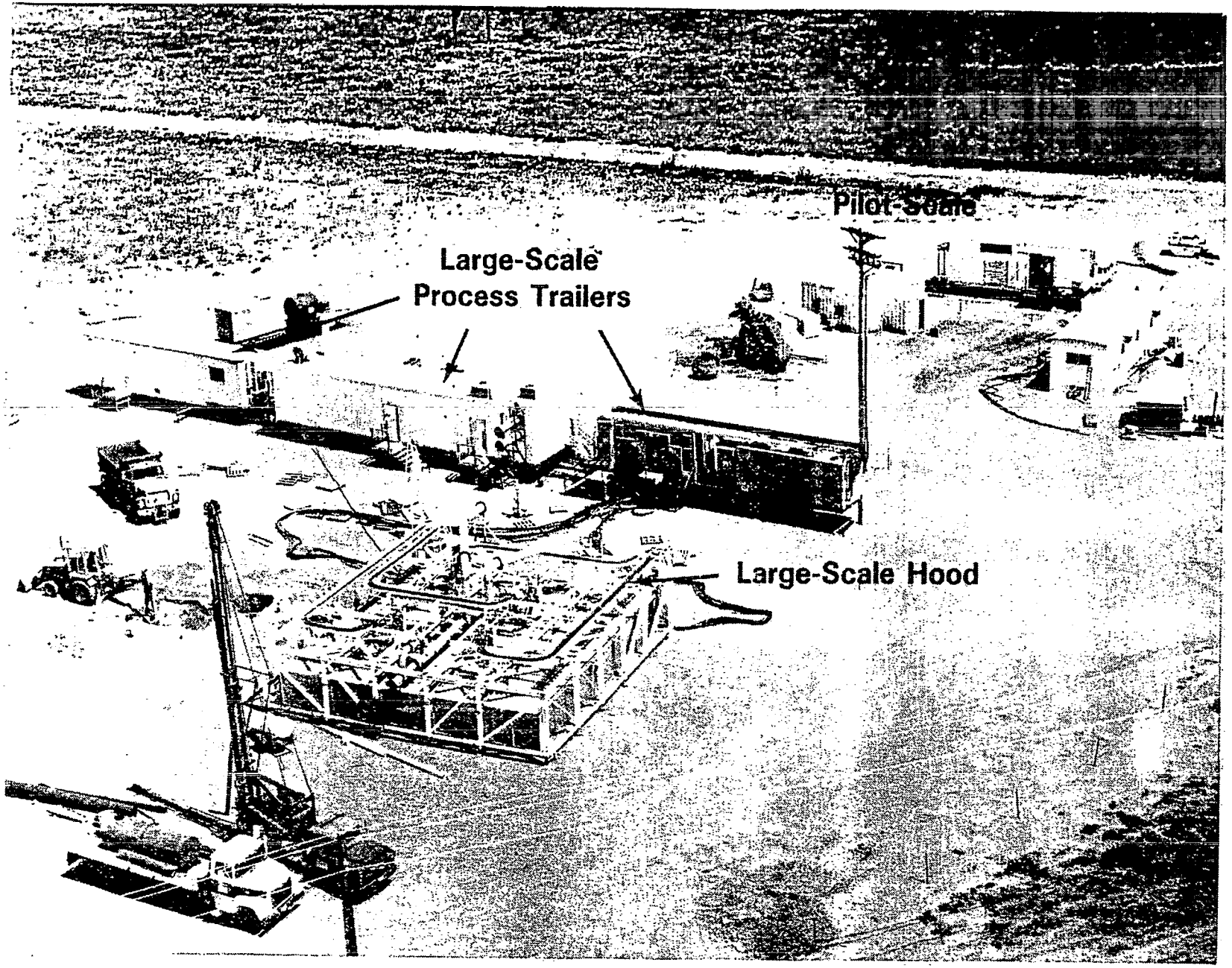


FIGURE 3.4 ISV Equipment System


Pilot-Scale
Large-Scale
Process Trailers
Large-Scale Hood

NATO/CCMS Fellow:

James M. Gossett, United States

Biodegradation of Dichloromethane Under Methanogenic Conditions

BIOTRANSFORMATION OF DICHLOROMETHANE IN METHANOGENIC SYSTEMS

by

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Remedial Action Technologies for Contaminated Land and Groundwater

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Montreal, Canada

I. INTRODUCTION

The research reported herein is part of a larger, USAF-sponsored effort to investigate the potential for biodegradation of four chlorinated solvents under methanogenic conditions: tetrachloroethylene (PCE), trichloroethylene (TCE), chloroform (CF), and dichloromethane (DCM). In this present paper, we focus on our investigations with DCM.

A. Objectives and Scope of Work

The broad goal of our research effort is to investigate the fundamental factors influencing the biodegradation of dichloromethane (DCM) by enrichment cultures grown under methanogenic conditions. Gaining a deeper understanding of how DCM is degraded under such conditions will markedly improve the chances of successfully employing bioremediation technologies.

More specifically, our research objectives are:

1. To determine if DCM can serve as a growth substrate.

2. To elucidate the pathways by which DCM is degraded under methanogenic conditions, including the construction of an oxidation/reduction balance.

3. To determine which class of organisms — methanogens or nonmethanogens — is responsible for mediating DCM degradation.

4. To develop a kinetic model of DCM degradation in mixed cultures.

5. To develop continuous-flow biological reactor systems for treatment of DCM-contaminated waters.

Surprisingly little information is available in the literature concerning the degradation of DCM under methanogenic conditions. The progress we have made thus far includes: development of a DCM-degrading enrichment culture; correlation of DCM degradation to methanogenesis; demonstration of the pivotal role played by acetogenic bacteria in DCM degradation; delineation of degradative pathways; determination that DCM can serve as a growth substrate; and successful operation of a fixed-film, continuous-flow reactor which degrades DCM to CH_4 and CO_2 at 20°C.

II. SUMMARY OF PROGRESS TO DATE

A. Experimental Strategy

The starting point for this research was the development of a mixed culture capable of degrading DCM under methanogenic conditions. This was accomplished using the mixed liquor from a laboratory digester. The digester had been started with sewage sludge from the Ithaca, NY

Wastewater Treatment Plant, then operated in a semicontinuous mode with a 10 g COD/L synthetic substrate, designed to maintain a diverse population of anaerobes. DCM degradation was achieved in a culture derived directly from the lab digester.

The DCM degrading mixed liquor was then used to inoculate a series of enrichment cultures. The purpose of the enrichments was to eliminate as many of the organisms as possible which weren't involved in DCM degradation, as well as to remove significant amounts of extraneous, undefined organic matter. Developing enrichment cultures has enabled progress in correlating DCM degradation to methanogenesis, and in analysis of the pathway(s) by which DCM has been degraded (Gossett and Freedman, 1988).

B. Materials and Methods

Chemicals and Radioisotopes. DCM was obtained in neat form (99 mol % pure; Fisher Scientific); Chloromethane (CM) was purchased dissolved in methanol (200 µg/mL, 1 mL ampule; Supelco, Inc.). [^{14}C]DCM (Sigma Radiochemical) was diluted in 150 mL distilled deionized water and stored in a 160 mL serum bottle, capped with a Teflon™ lined rubber septum. The [^{14}C]DCM stock solution contained 2.93 x 10^7 dpm/mL (4.68 µmoles DCM/mL); GC analysis of the [^{14}C]DCM stock bottle headspace indicated the presence of an unidentified contaminant, which was shown not to be radiolabeled. There was also no indication that this contaminant interfered (e.g., as an inhibitor) with the DCM degradation studies. ScintiVerse-E™ (Fisher Scientific) liquid-scintillation cocktail (LSC) was employed for [^{14}C] assays .

Cultures and Enrichment Procedures. With the exception of some continuous-flow, fixed-film reactor studies, all experiments were conducted at 35°C, under quiescent conditions, in 160-mL serum bottles to which 100 mL of liquid was added. The bottles were sealed with slotted grey butyl rubber septa and aluminum crimp caps (Wheaton Scientific). Virtually no loss of DCM was observed from water controls (WC) which used these septa; they were less permeable to oxygen than Teflon™-lined rubber septa, were easier to puncture, and maintained better flexibility following autoclaving. [They were not used in PCE/TCE studies because significant losses of these compounds (and their reductive dechlorination products) were noted in water controls.]

Autoclaved seed controls (ASC) were used to evaluate the degree of sorption and abiotic transformations of DCM. When these phenomena were consistently shown to be negligible, use of the ASCs was discontinued.

Semicontinuous operation of the enrichment cultures was often practiced with bottles which were actively degrading DCM. This entailed removal of a volume (usually 4.0 mL) of well-mixed liquid and its subsequent replacement by some combination of basal medium and DCM-saturated water to yield the desired DCM concentration. When semicontinuous operation was not practiced, the disappearance of DCM was followed by addition of only DCM-saturated water.

Analytical Methods. Analysis of volatile organics was performed by gas chromatographic (GC) analysis of a 0.5-mL headspace sample, using a flame-ionization detector

(FID) in conjunction with a 3.2-mm x 2.44-m stainless-steel column packed with 1% SP-1000 on 60/80 Carbopack-B, as previously described (Gossett, 1987; Freedman and Gossett, 1989).

Degradative pathways were examined through semi-continuous addition of radiolabeled [^{14}C]DCM to sixth-generation enrichment cultures. Following various periods of operation, distribution of ^{14}C among suspected DCM degradation products was determined as previously described (Gossett and Freedman, 1988; Freedman and Gossett, 1989).

HPLC analysis was employed to determine the concentrations of soluble, nonvolatile fermentation products, similar to the method described by Zinder and Koch (1984). A Hewlett Packard 1090 HPLC was used to pump 250-µL samples through a 300-mm HP X-87H ion exchange column (Bio-Rad Laboratories) and into an LC-25 refractive index detector (Perkin-Elmer). The mobile phase (13mM H_2SO_4) was delivered at 0.7 mL/min. By operating the ion exchange column at two temperatures (30 and 65°C) it was possible to resolve formate, formaldehyde, acetate, propionate, methanol, isobutyrate, butyrate, and ethanol. For example, although methanol and propionate coeluted at 30°C, they were well resolved at 65°C.

C. Results and Discussion

Pathways of DCM Metabolism. Figure 1 summarizes the pathways involved in biotransformation of DCM by a methanogenic mixed culture. The radiotracer studies which led us to this model were presented earlier (Gossett and Freedman, 1988) and will not be detailed here. In essence, the model is the result of studies with [^{14}C]DCM in which various levels of bromoethanesulfonate (BES), a selective inhibitor of methanogenesis, were employed to inhibit either acetoclastic methanogens (at low levels of BES) or all methanogens (at high levels of BES). Subsequent monitoring of [^{14}C] species and H_2 allowed deductive development of the model.

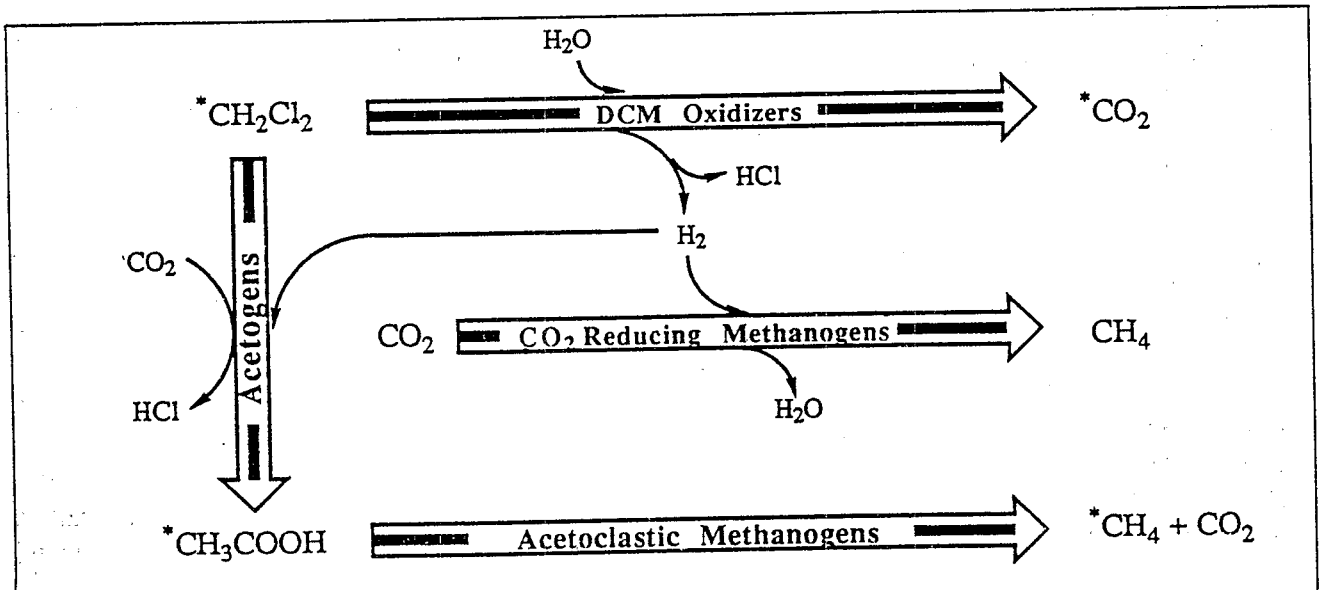


Figure 1. Proposed Model for Biodegradation of DCM by a Methanogenic Mixed Culture.

The accumulated evidence suggests that acetogenic bacteria mediate the degradation of DCM, not methanogens. This evidence includes the degradation of DCM in the complete absence of any methane formation (due to BES inhibition), and the formation of both acetic acid and hydrogen as products of DCM degradation.

Additional indirect evidence which implicates non-methanogens was obtained by examining DCM degradation in the presence of a potent antibiotic. Four bottles were set-up identically, continuously shaken, and incubated at 35°C. Over the first 29 days of operation, the ability of each bottle to repetitively degrade increasing levels of initial DCM doses was established. On day 29, two of the bottles received 10 mg of vancomycin (an inhibitor of cell wall synthesis in eubacteria), while the other two bottles continued to receive only DCM. As shown in Figure 2, the two bottles which did not receive vancomycin were able to repetitively degrade increasing levels of DCM (no effort was made to increase the initial DCM dose above approximately 120 μmoles/100 mL, though it certainly would have been possible). In the other bottles, DCM degradation was sustained for at least one spike after adding the vancomycin, but then DCM degradation began to fall off considerably. Assuming that the vancomycin dose used affected eubacteria and not methanogens (demonstrated by other investigators), these results add to the evidence indicating the central role played by non-methanogens in DCM degradation. Though we cannot be absolutely sure, we believe acetogens are the principal DCM oxidizers, as well as responsible for acetate production from DCM.

Figure 3 shows the pathways we have observed to be affected by vancomycin and BES additions.

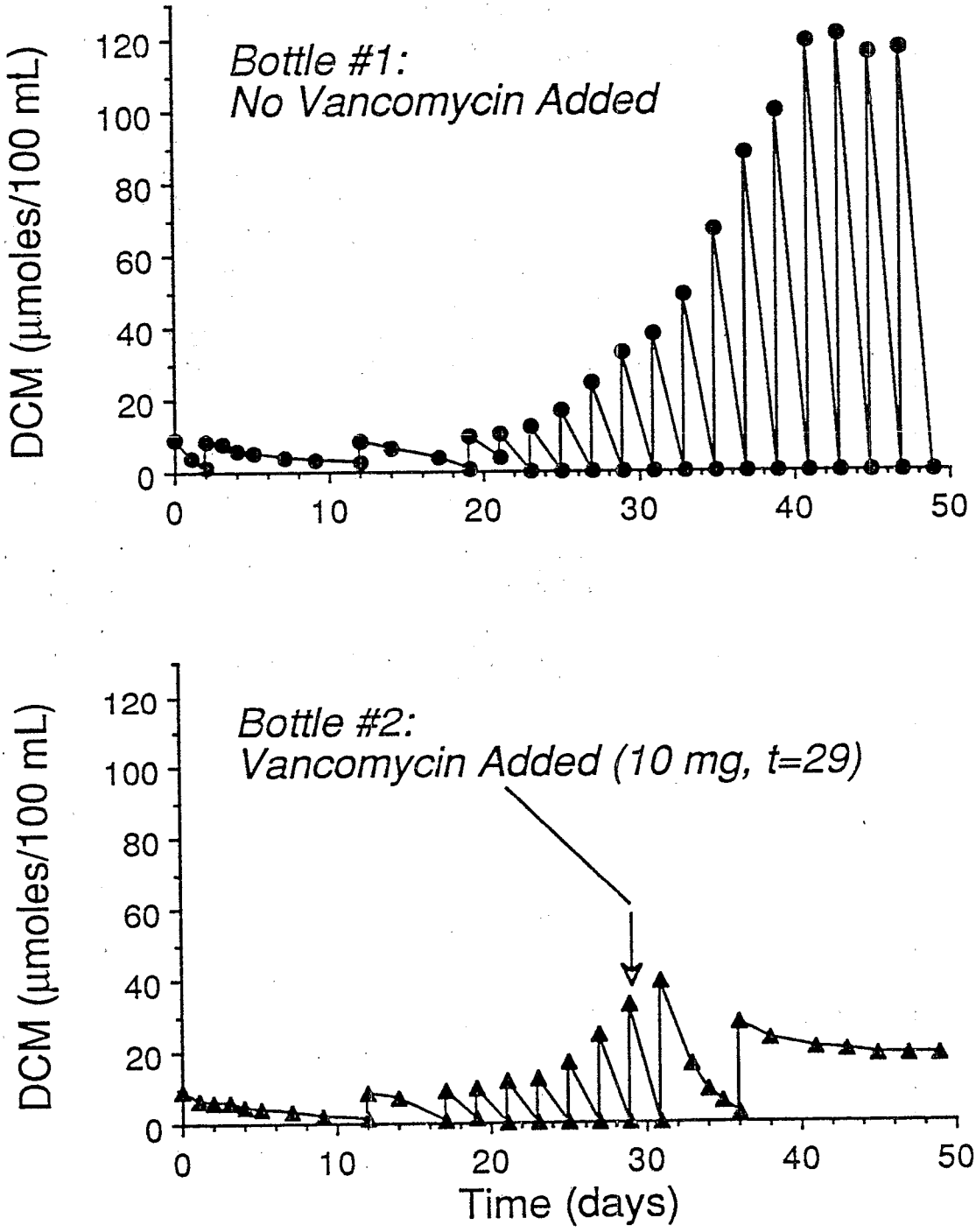


Figure 2. Effect of Vancomycin on DCM Degradation.

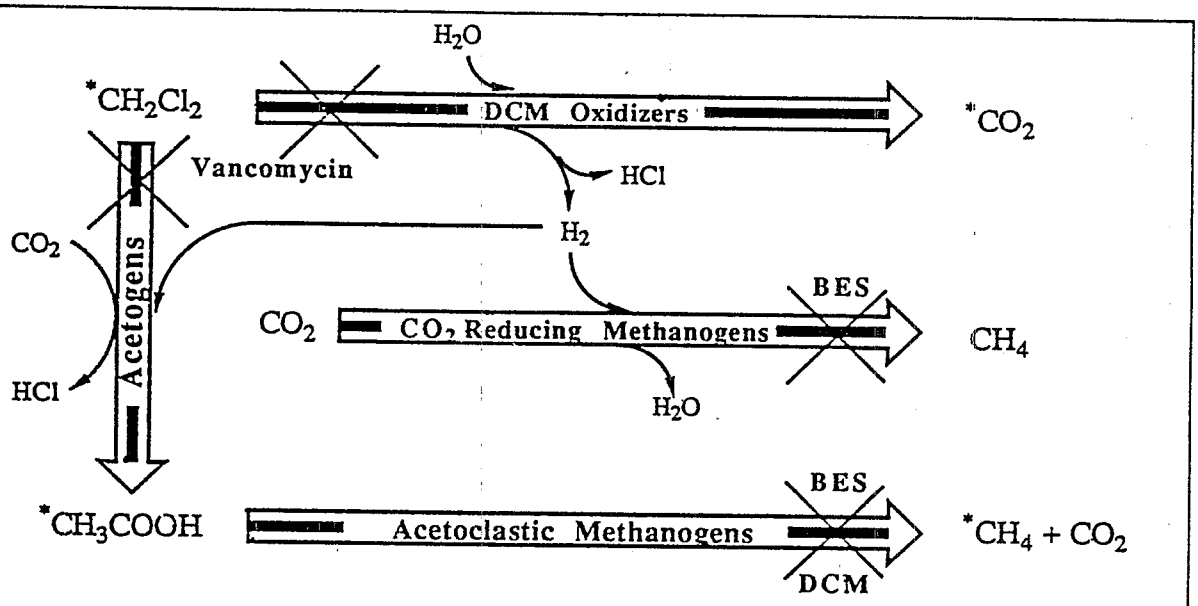
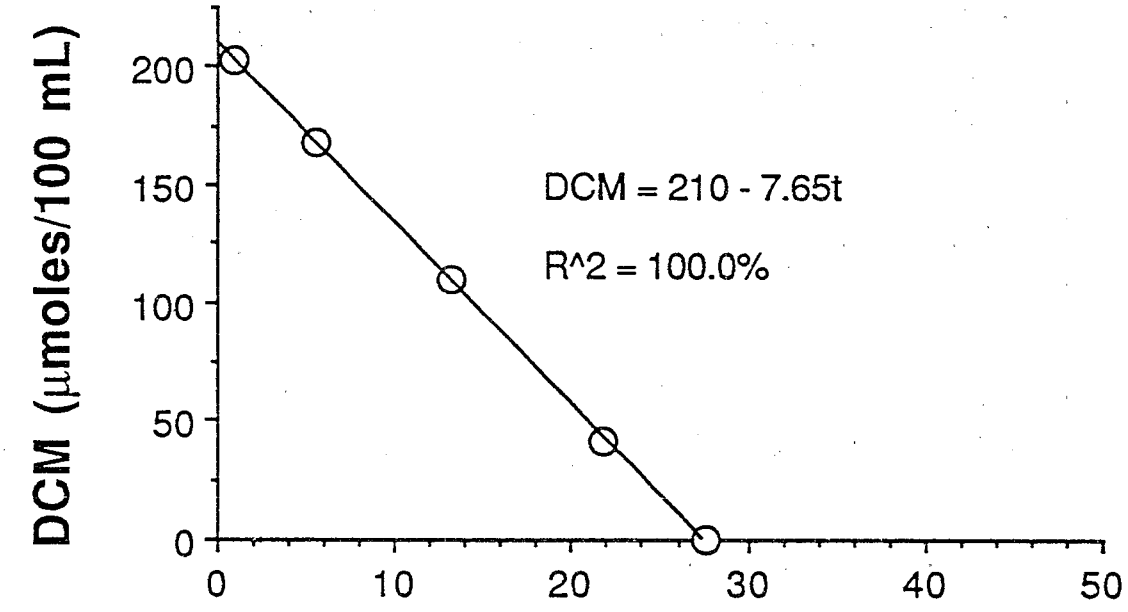


Figure 3. Pathways in the Proposed Model Which are Affected by BES and/or Vancomycin.

Kinetics of DCM Degradation. The rate of DCM degradation at 35°C was measured using batch-fed DCM enrichments to which an initial DCM concentration of 2 mM was added (170 mg/L). At such a high concentration, methanogenesis was inhibited and hydrogen accumulated (Figure 4); when DCM concentration was sufficiently reduced, methane production resumed. DCM degradation followed an apparently zero-order kinetic model (constant rate = 7.6 µmol DCM/hr). The quantity of methane which resulted (about 8 µmol) was far lower than the 100 µmol expected from degradation of 200 µmol of DCM. This suggests that most of the methane formed resulted from CO_2-reducing methanogens, not from acetoclastic methanogens. The latter organisms were likely more severely inhibited by the high initial levels of DCM employed.

DCM as Growth Substrate. Significant progress has been made in determining whether or not DCM can serve as a growth substrate, using the following experimental design. Four serum bottles were set-up. Each received 90 mL of basal medium (with 50 mg/L yeast extract as the only non-DCM carbon source) plus 10 mL of inoculum from cultures which were actively degrading DCM, and incubated in an orbital shaker bath maintained at 35°C. Two of the bottles ("with-DCM") received repetitive additions of DCM. Initially, these additions were approximately 10 µmoles/100 mL; over time they were increased to as high as 2.4 mM (204 mg/L). Two other bottles ("without-DCM") — serving as controls — were set-up identically but received no DCM.



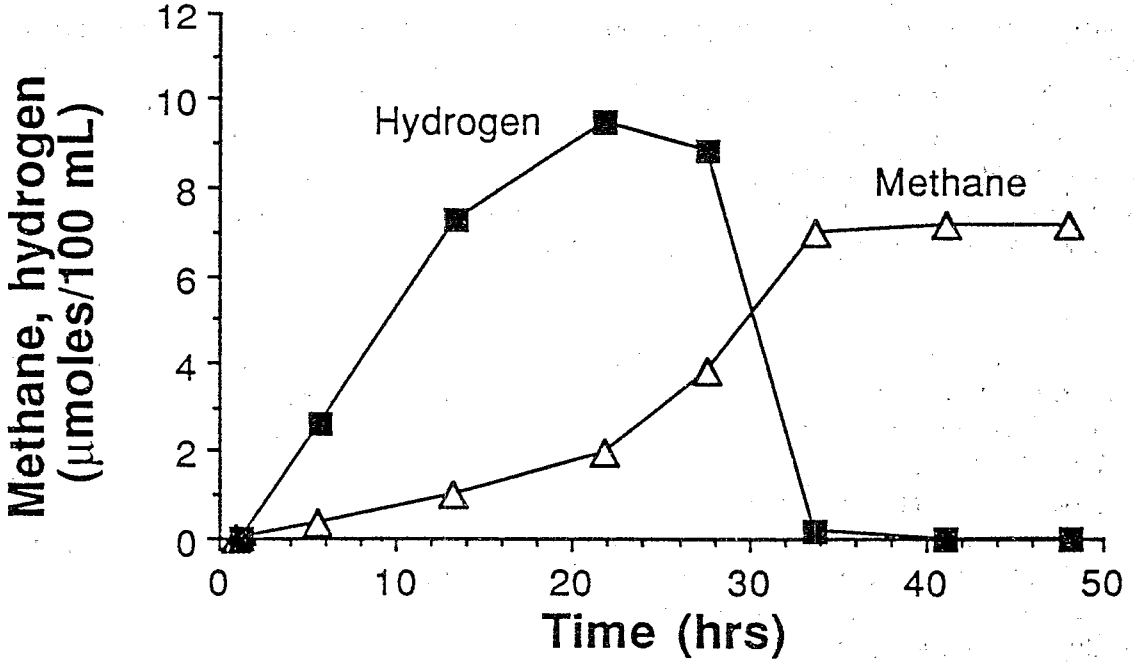


Figure 4. Kinetic Experiment, 35°C.

Suspended organic carbon (SOC) was used as the measure of growth. At approximately 14-day intervals, 5 mL was removed from each of the bottles, and replaced with 5 mL of basal medium containing yeast extract (50 mg/L). 2.3 mL of the sample was used to measure total organic carbon (TOC); 2.7 mL was filtered (0.45 μm) and used to measure dissolved organic carbon (DOC). The difference between TOC and DOC was SOC. Net growth on DCM was calculated by subtracting SOC in the "without-DCM" bottles from SOC in the "with-DCM" bottles.

Results after 133 days of operation are shown in Figure 5. SOC in the "with-DCM" bottles began to rise definitively above SOC in the "without-DCM" bottles on day 49, just as cumulative DCM consumption began to rise significantly. Concern still remained, however, that this growth may have been attributable — at least in part — to methanogens (through the use of DCM degradation products) and not to the organisms responsible for DCM degradation. Nevertheless, even though BES was not added to these bottles, methane output was well below the stoichiometric level expected (Figure 6), due to inhibition by high levels of DCM. This inhibition was evident initially, when methane output in the "with-DCM" bottles was slightly below that of the "without-DCM" bottles. Methane output in the "with-DCM" bottles did eventually surpass that in the "without-DCM" bottles, but it slowed and nearly stopped when DCM additions exceeded approximately 1.8 mM (around day 63). By day 77, average cumulative DCM degradation was 2565 μmoles; had methanogenesis not been inhibited, cumulative methane output would have been 1401 μmoles (1283 as a consequence of DCM degradation plus 118 from the yeast extract). Instead, only 357 μmoles were produced, indicating severe inhibition of methanogenesis.

Another, initially unexpected form of inhibition was encountered in these experiments — that due to low pH resulting from HCl production in biological dechlorination of DCM! Around day 75, DCM consumption stalled. Measurements on day 91 indicated that pH had dropped to 5.1 and 5.4 in the two bottles receiving DCM, whereas the two without DCM had pHs of 7.4 and 7.6. Addition of bicarbonate buffer, along with a 5% reinoculation from an active DCM-degrading enrichment, revived the culture, allowing renewed DCM consumption, followed by renewed biomass formation (as defined by SOC). Note, however, that after this period of upset, biomass formation lagged considerably behind DCM consumption.

Day-91 samples were also analyzed for HAc and MeOH concentration, using a HPLC with a refractive index detector. HAc concentrations were 6.77 mM and 6.94 mM in the two "with-DCM" bottles. MeOH was not detected in either of the samples. The bottles receiving no DCM had no detectable levels of HAc or MeOH.

The correlation between SOC formed and DCM degraded is quite good (Figure 7). SOC formation was calculated by subtracting average SOC in "without-DCM" bottles from the SOC in "with-DCM" bottles. These data indicate that approximately 8.5% of the DCM carbon degraded was converted to cell carbon, a yield within the range expected for anaerobic microorganisms. The accumulation of SOC in the "with-DCM" bottles was likely due to *organisms other than methanogens* — i.e., from degradation of DCM, rather than from acetate or H_2. To explain the observed synthesis as resulting solely from methanogenic activity on H_2 or acetate requires that unrealistically high yield coefficients be assumed. Thus, we conclude that DCM does indeed serve as a growth substrate.

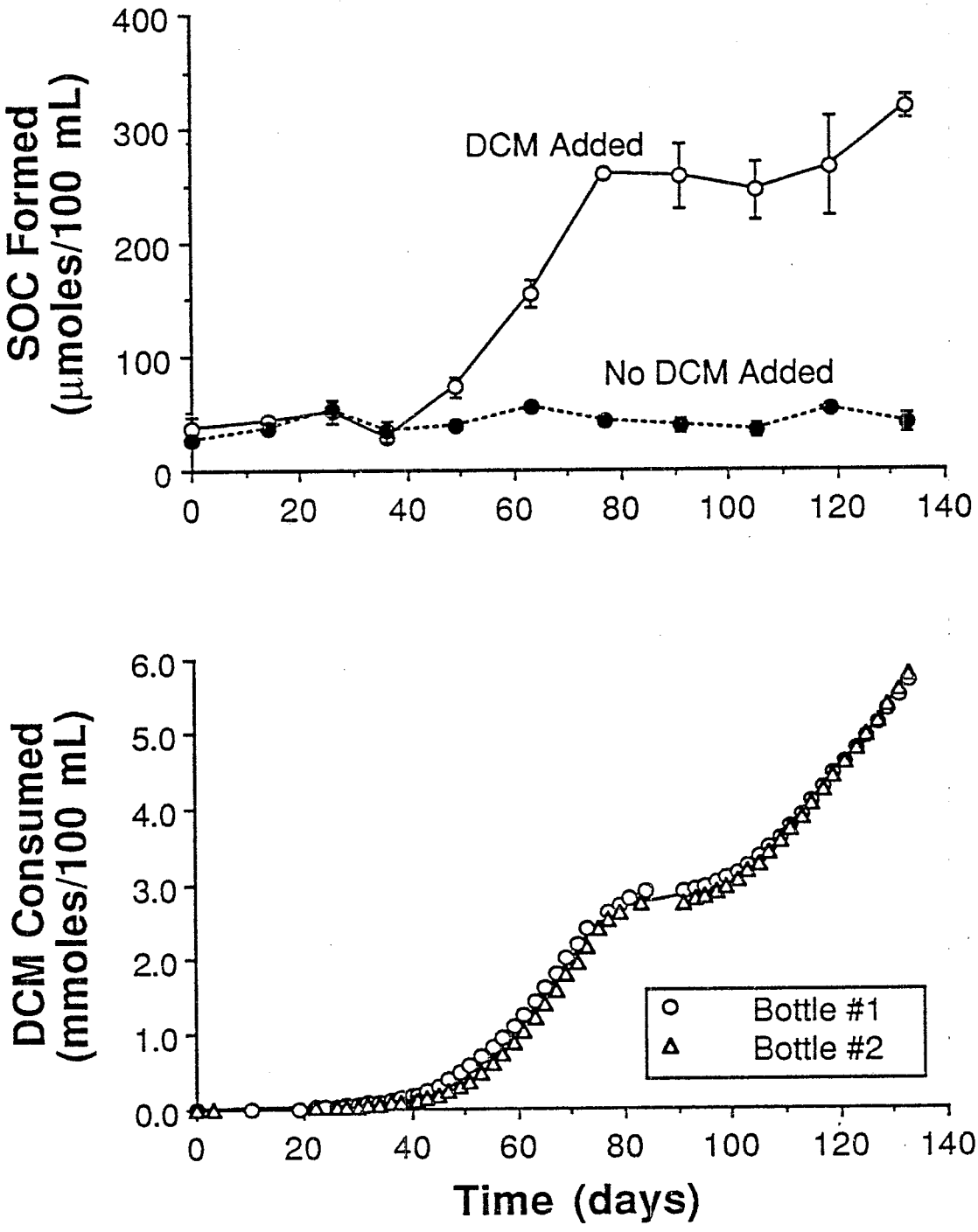


Figure 5. Growth on DCM.

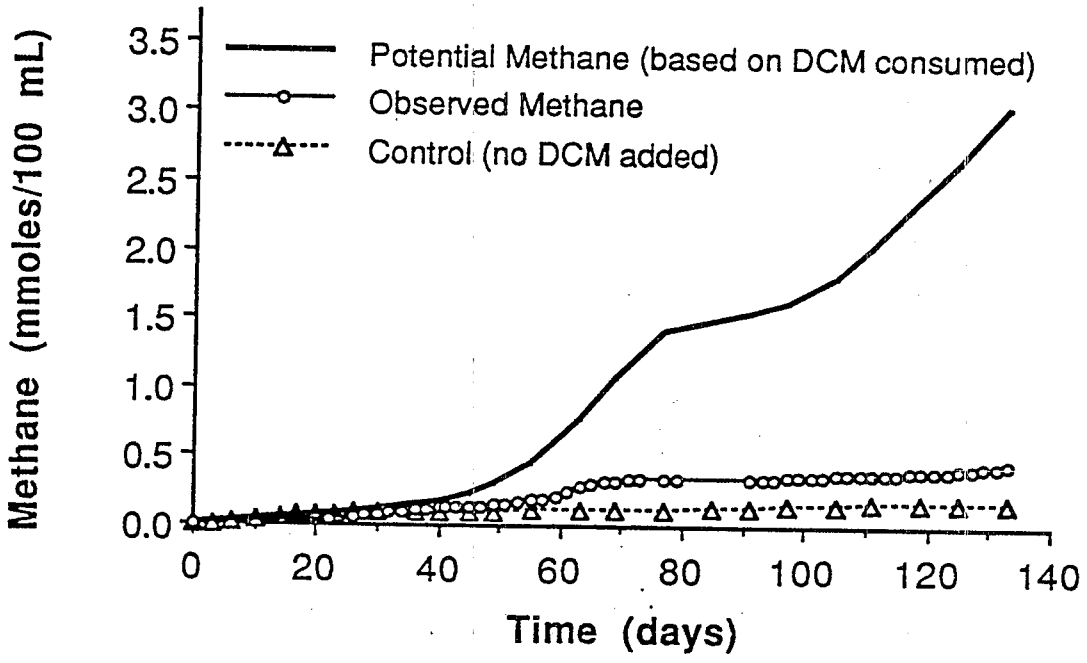


Figure 6. Methane Formation During the "Growth" Experiment Depicted in Figure 5.

Fixed-Film Reactor Studies. A fixed-film reactor is currently in operation to study biodegradation of DCM under continuous-flow conditions. Figure 8 is a schematic of the system, which consists of two glass columns, each 91-cm (3-ft) long x 5-cm (2-inch) diameter, filled with 6-mm glass beads (added as a medium for bacterial attachment). The columns are connected in series.

The first column contains a mixed culture of facultative and strict anaerobes and is intended solely to maintain anaerobiosis for the second column. A refrigerated basal salts medium containing acetate (100 mg/L) is provided by a peristaltic pump to the bottom of this "pre-column". Numerous HPLC analyses consistently indicate that all of the acetate is consumed in the pre-column. Since resazurin is included in the feed, it is evident that the culture in the pre-column is maintaining low redox conditions; the resazurin in the column remains clear even though the feed is blue (indicating high redox) or pink (indicating redox potential of > -50 mV). Effluent from the pre-column enters the "DCM column" at its bottom. DCM-saturated water is injected into the flow (using a syringe pump) prior to entering the DCM column.

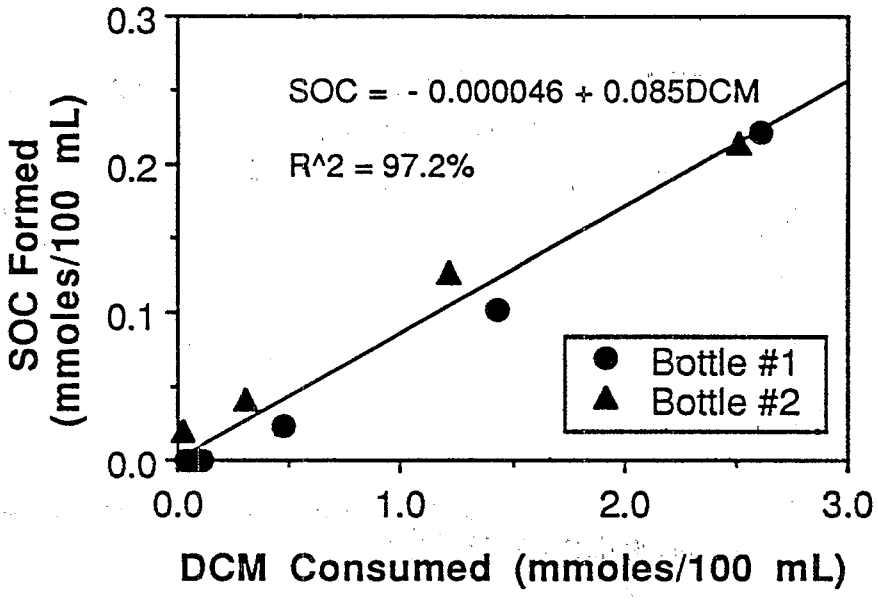


Figure 7. Biomass Formation from DCM Degradation — Day 26 through Day 77.

Sample ports are spaced at 15.24-cm (6-inch) intervals along the length of the DCM column. Sample ports are constructed of a hollow stainless-steel cylinder, machined to extend from the exterior of the sample port to near the column center. The steel is held firmly in place by a Teflon™ O-ring and bushing assembly. The exterior of the steel is covered with a Teflon™-lined rubber septum. The septum is held in place by an aluminum crimp cap.

The DCM column was inoculated with 2 liters of an active, DCM-degrading enrichment culture. The DCM column was first operated in recycle mode for 22 days (at 35°C) to facilitate microbial attachment. During this period, 0.1 mM DCM (8.5 mg/L) was added to the column, allowed to degrade (in 2-3 days), then added again. Following this recirculation period, the pre-column was connected in series and the system was operated in continuous-flow mode. The DCM column was initially operated at a 2-day hydraulic retention time (HRT) based on void volume, with a nominal DCM influent concentration of 0.1 mM. Eight days after commencing continuous operation, only traces of DCM (<1.2 μM) were detected at the first sample port within the column, and none at any higher location. Significant CH_4 levels were noted at higher points within the column, indicating biotransformation.

Samples are taken from the column routinely as follows: a 5-mL gas-tight syringe (Supelco, Inc.) fitted with a custom-made, 4-inch side-port needle (Dynatech Precision Instruments) is purged with 30%CO_2/70%N_2 and inserted in the effluent (top) sample port. A 4-mL liquid sample is drawn from the column and injected into a 14-mL vial sealed with a Teflon™-lined septum and aluminum crimp cap. The volume of sample delivered to the vial is determined

gravimetrically. Samples are taken in this manner from each sample port from top to bottom. Following equilibration at 35°C, a 0.5-mL headspace sample is analyzed by GC.

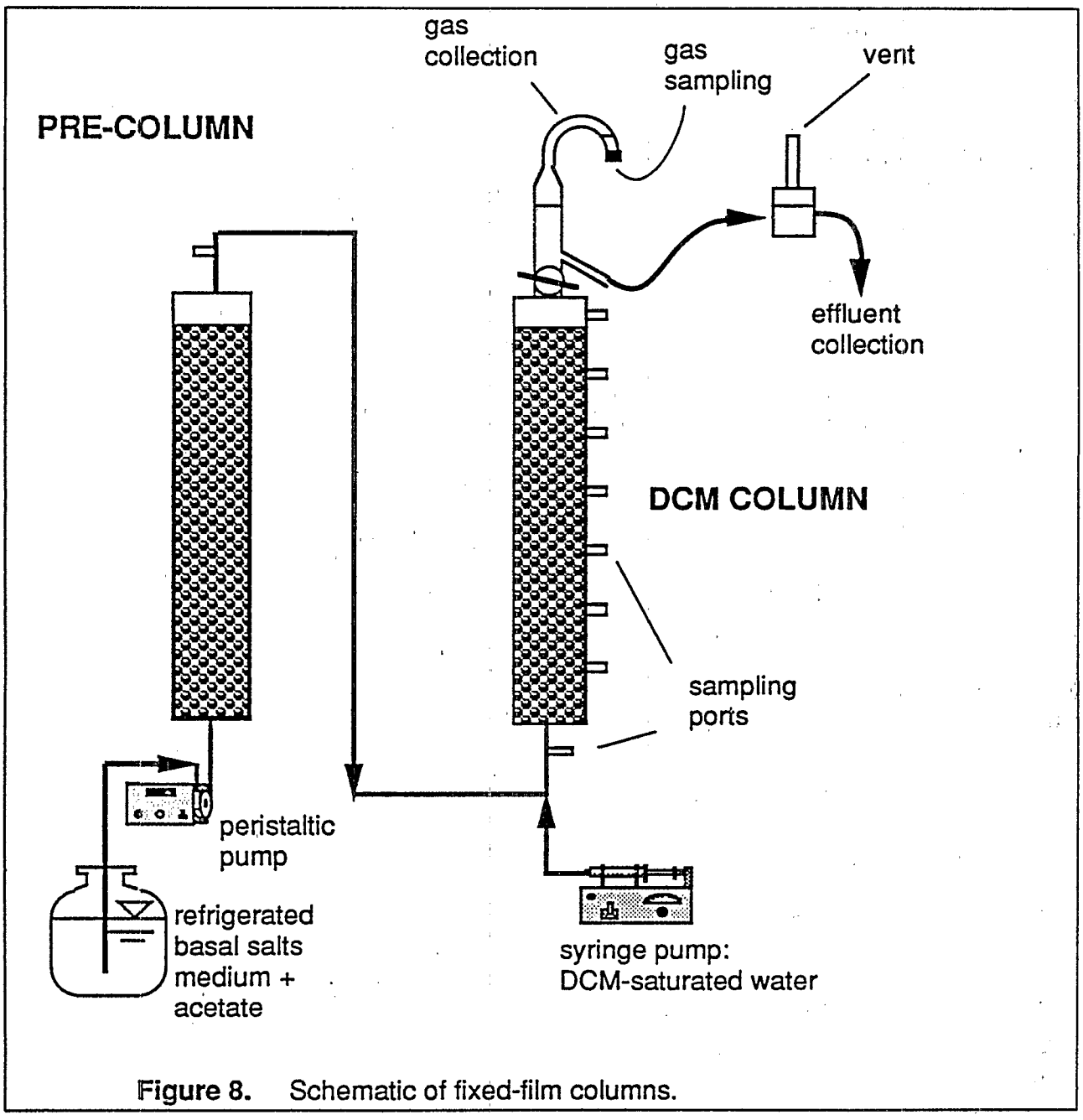


Figure 8. Schematic of fixed-film columns.

After one month of operation, we began lowering the column temperature — ultimately to 20°C, where it is now operating. Noting successful degradation at 20°C, we stepped up the influent concentration of DCM to 0.4 mM (34 mg/L). Figure 9 shows the column profile for such conditions. At such a high influent DCM concentration, inhibition of methanogenesis is expected; the displacement of methane production to higher points within the column suggests that

inhibition is indeed occurring. Due to the relative lack of sensitivity associated with our acetate method, we had not attempted measurements of acetate within the column. However, as influent DCM is increased, we expect to be able to detect acetate and H_2 at intermediate points of the column (positions "12" through "24").

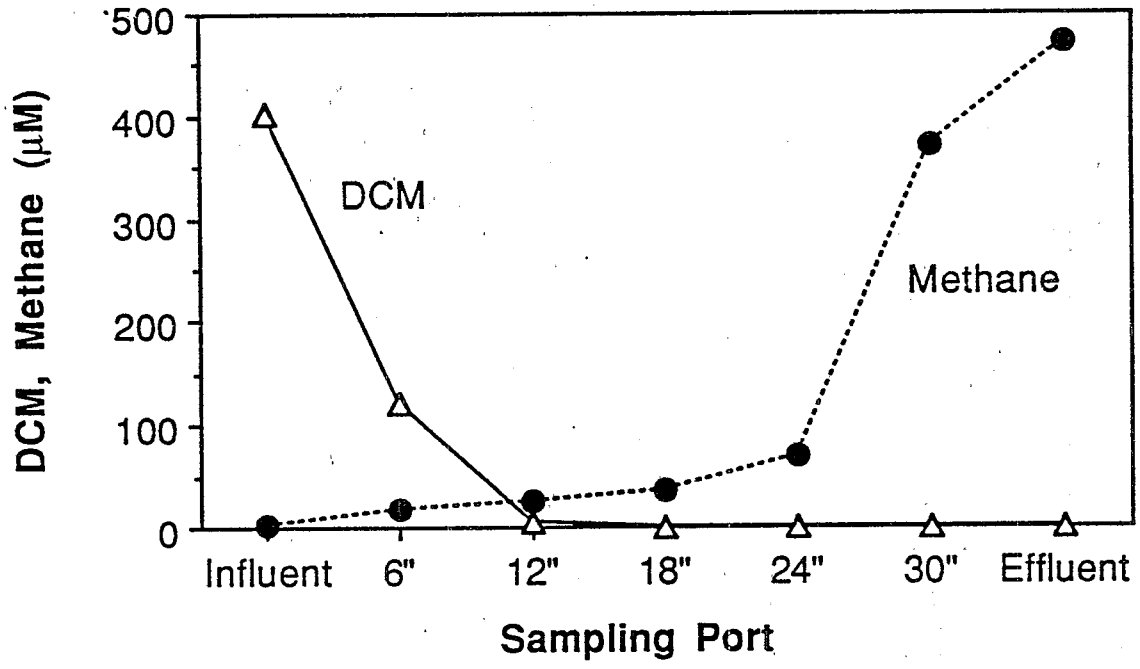


Figure 9. Profile of Fixed-Film, Continuous-Flow Column Receiving DCM at 400 µM Concentration. Conditions: T = 20°C; hydraulic retention time = 2 days; 0.5 mg/L yeast extract in feed.

III. FUTURE PLANS

In order to advance the prospect of using methanogenic systems for treatment of DCM contaminated water, further research is being carried out in both suspended-growth and immobilized-cell reactors. The suspended-growth studies will allow examination of more fundamental issues:

- *Isolation of the microorganisms responsible for DCM degradation;*
- *Characterization of the isolates* (including the ability to grow on a variety of non-chlorinated substrates, a property of significant practical importance in systems where the level of DCM may be too low to alone support growth);

- *Delineation of degradation pathways* (i.e., a more fundamental approach that previously employed; cell-free extracts from isolates will be purified with reversed-phase HPLC);

- *Determination of the ability of enrichments to degrade chlorinated compounds other than DCM.*

The fixed-film reactor studies are oriented more towards the practical issues of how best to accomplish treatment. Foremost in this regard is the capability of the DCM degrading organisms to attach to fixed-film media. Assuming this is possible, the reactors will be used to evaluate a variety of treatment conditions, including DCM concentration, variation in hydraulic residence time, and the effect of other chlorinated aliphatics — particularly CF — on the efficiency of DCM removal.

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Alternative Physico - Chemical and Thermal Cleaning Technologies for Contaminated Soil

Recent Developments in Extraction and Flotation Techniques for Contaminated Soils and Sediments

ALTERNATIVE PHYSICO-CHEMICAL AND THERMAL CLEANING TECHNOLOGIES FOR CONTAMINATED SOIL

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1. ABSTRACT

This study has been carried out within the framework of the Netherlands Integrated Soil Research Programme. Aim of the study is to make both a systematic evaluation as well as a selection of technologies currently developed world-wide which offer possibilities for the decontamination of soils. The study has been carried out in three phases. This paper describes the first phase: a survey of alternative techniques and a first selection of the most promising ones. In the second phase, a more detailed analysis and a further selection of technologies will be made, followed by a research programme for the selected techniques in the third phase.

2. INTRODUCTION

In the Netherlands some 15 physico-chemical and thermal cleaning installations are readily available. With the present technology a large part of the contaminated soils, however, is not or problematically cleanable. This is particularly true for soils that are contaminated with halogenated (aromatic) hydrocarbons and/or heavy metals, and soils containing a large fraction of fines (< 0.050 mm). Problems arising are, for example:

- emission of hazardous compounds (e.g. with thermal treatment);
- unacceptably high residual concentrations (as is often the case with extraction techniques); or
- production of a large amount of contaminated sludge (e.g. with cleaning of clay in extraction installations).

In addition to this, some of the techniques used at present, involve quite high cleaning costs. It is, therefore, essential to develop alternative techniques that either do not have the above mentioned disadvantages or lead to lower cleaning costs.

3. CONTAMINATED SOIL IN THE NETHERLANDS; SIZE OF THE PROBLEM

At present the soil remediation activities are carried out following two lines:
- Remediation within the framework of the Interim Law on Soil Remediation (IBS), the so-called IBS-sites (IBS = Interim wet Bodem Sanering); and
- Remediation carried out by private parties; the so-called non-IBS-sites.

In 1987, the total number of potential IBS-sites was approximately 7,500. At the time it was estimated that approximately 1,600 of them urgently needed remediation and should be remediated within the framework of the IBS. A new estimate of the total number of contaminated sites (including the non-IBS- sites) was made in 1988 [1]. A summary of the results of this estimate is given in Table 1.
In the governmental "Ten Year Scenario Soil Remediation" [1], it is planned that from the total number of sites (about 110,000) 6,000 very urgent cases will be remediated within the coming ten years, leading to expenses in the order of 5 milliard Dutch guilders (abt. 2.10^9 ECU).

TABLE 1: Number of sites needing remediation for five industrial sources.

Source	Number of sites	Number of sites needing remediation	Percentage needing remediation
Gaswork sites	234	234	100%
Dump sites	3,290	150	5%
Carwreck sites	2,100	1,200	60%
Former industrial sites	abt. 400,000	abt. 80,000	20%
Present industrial sites	abt. 120,000	abt. 25,000	20%
Total	abt. 530,000	abt. 110,000	20%

4. SHORTCOMINGS OF CLEANING TECHNOLOGIES IN THE NETHERLANDS

4.1. Features and shortcomings per technique

Thermal techniques
In the Netherlands rotary kiln ovens are used. The soil can be directly heated, indirectly heated or through combinations thereof. At the moment these techniques are only applicable for organic contaminants (including cyanides). Basically, thermal techniques can also be used for mercury contaminants. But this is not practised at present because of emission control problems. The energy need of these thermal techniques is rather high and emissions of hazardous contaminants are possible. In the

Netherlands it is not allowed to treat soil contaminated with chlorinated hydrocarbons in thermal soil cleaning installations for reasons of hazardous emissions.

Extraction and fractionation techniques
Most soluble components are easily removable by flushing the soil with an extractant. Unfortunately, contaminants are often preferentially sorbed to the fines in the soil. The extraction techniques available at present make use of this phenomenon by separating the heavily contaminated fines from the bulk of the soil. But a consequence hereof is that soils containing many fines cause an excessive sludge production. If, in some cases, the bulk of the contaminants is present in the coarser fraction, this fraction will be removed from the soil. At this moment, extraction techniques along with flotation techniques are the only techniques that can deal with heavy metals. There is very limited experience with in-situ extraction techniques.

Biological techniques (not subject of this study)
For these techniques only large-scale experience with alifatic and aromatic hydrocarbons is available. Presently, use of these techniques leads to long treatment periods (e.g. landfarming). Reduction of concentrations to acceptable levels (i.e. A-level) is very difficult. Chlorinated hydrocarbons are hardly biodegradable and heavy metals can hardly be removed. Apart from the already mentioned problems, clogging and channeling of the aquifer may occur when using in-situ techniques, leading to insufficient cleaning results.

4.2. Features and shortcomings per contaminant

Heavy metals
Can only be removed by extraction and flotation. There is no operational technique that can remove heavy metals from clay or sludges.

Cyanides
Can be removed from all types of soil by thermal treatment. Clay can pose some problems in the treatment of the off-gases. Sludges must have a dry-matter content of at least 50% to avoid handling problems. Cyanides can be removed by extraction as well as flotation unless the soil contains a large fraction of fines or organics (clay and peat). Biological techniques may be applicable.

Non-chlorinated alifatic components and simple aromatics
These compounds are easy to treat thermally. Extraction and flotation can be applied for these contaminants, unless they are present in clay or peat. These compounds are easily biodegradable and are not considered a major problem.

Polycyclic aromatic compounds
Can be easily treated thermally, resulting in low rest concentrations. Extraction and flotation are possible with varying results. Low polycyclic compounds (less than four rings) are good biodegradable. Biodegradability of higher polycyclic compounds is very low.

Non-volatile chlorinated hydrocarbons
In principle thermal treatment is suitable when dealing with these compounds. However, it is not allowed to use the presently available thermal soil cleaning techniques for these compounds in the Netherlands. The reason is that this treatment may cause hazardous emissions (e.g. dioxines). Extraction and the presently used flotation technique are applicable to these compounds only when they are present in sand or sandy soils (not peat or clay).

Volatile (chlorinated) hydrocarbons and pesticides
For the above-mentioned reasons, these compounds cannot be treated thermally in the Netherlands. Extraction and flotation are applicable in principle, but are quite expensive for these easily removable contaminants. A better way of treating these compounds is by stripping them from the soil. This technique, however, is not very well developed in the Netherlands. Because of their volatility, the handling of these contaminants needs additional safety precautions. Usually, very low rest concentrations are required.

5. OVERVIEW AND SELECTION OF ALTERNATIVE TECHNIQUES

An inventory of alternative techniques that offer possibilities for treating soil or sludge is listed in Table 2. These techniques can be either emerging techniques for soil, or existing techniques for other material (e.g. mining techniques).

TABLE 2: Overview of alternative techniques.

Techniques	Developer	Features
	EX-SITU TECHNIQUES	
Wet thermal techniques		
Supercritical oxidation 1	Modar	mixed and plugflow reactor in series
Supercritical oxidation 2	Oxidyne	vertical pipe reactor 3000 m
Wet oxidation 1	Zimpro; Kenneth	bubble column
Wet oxidation 2	Vertech	vertical pipe reactor 1600 m
Wet oxidation 3	RISO	horizontal pipe reactor
Dry thermal techniques		
Fluid bed oven 1	Waste Tech	stationairy bed
Fluid bed oven 2	Thyssen	not yet realized stationairy bed
Fluid bed oven 3	Ogden	circulating bed
Electrical infra-red oven 1	Shirco	tunnel oven
Electrical infra-red oven 2	Thagard	high temperature fluid wall
Plasma reactor	SKF	free plasma, abt. 2000 °C
Thermal immobilization techniques		
Ceramic application 1	University Utrecht	sediments for bricks

Table 2. Continued

Techniques	Developer	Features
Ceramic application 2	PBI	cement, fly ash
Vitrification 1	Vitrifix	asbest treatment
Vitrification 2	Westinghouse	electric pyrolyser
Vitrification 3	Retech	centrifugal reactor
Vitrification 4	Nuclear Research Centre	2500 °C, RAD-waste
Physico-chemical immobilization techniques		
Immobilization based on:		
- cement	Many developers	
- chalk and/or puzzolanes	Many developers	
- thermoplasts	Many developers	bitumen, parrafines, polyethylene
- organic polymers	Many developers	polyesters, epoxides
- waterglass	Many developers	
Dechlorination techniques		
Hydrothermal decomposition	Delft University of Techn.	hydrogen, 300 C, 18 MPa
Ultraviolet dechlorination	Atlantic Research Corp.	LARC system
Radiolytic dechlorination	Atomic Energy of Canada	propanol, gammaradiation
Chemical dechlorination	EPA	APEG
Sodium detoxification	Degussa	pure sodium
Particle separation techniques		
Heavy media separation	No developer for soil	based on density of particles
Heavy media cyclonation	No developer for soil	based on density of particles
Jig technique	No developer for soil	pulsating waterbed
Wet concentrating tables	No developer for soil	shaking tables
Humphrey spiral separation	No developer for soil	vertical spiral
Reichert cone separation	No developer for soil	perforated plate
Pinched sluice process	No developer for soil	conus-formed stream pipe
Revolving round table	No developer for soil	based on friction, inertia
Tilting frame separation	No developer for soil	based on sedimentation velocity
Vanner separation	No developer for soil	conveyor belt
Bartles-Mozley separation	No developer for soil	rotating tilting frame
Froth flotation	Mosmans	sorption on air bubbles
High gradient magnetic separation	No developer for soil	paramagnetic particles
Extraction techniques		
Extraction with		
- complexing agents	PBI	heap leaching
- crown ethers	No developer	
- acids	No developer	
- organic solvents	Smet Jet; Sanitex	Methylene chloride

Table 2. Continued

Techniques	Developer	Features
- aliphatic amines	Resources Conservation Co.	reverse solubility
- fluidized gases	CF Systems Corporation	propane, butane
Supercritical extraction	Critical Fluid Systems	CO_2 extraction
Other techniques		
Steam stripping	Heymans	stripping in asphalt mixer
Air stripping	Many developers	
Chemical and photochem. oxidation	Ultrox	H_2O_2, ozone and UV-light
	IN-SITU TECHNIQUES	
Stripping and extraction techniques		
Air stripping	Many developers	
Vacuum extraction	Many developers	
Compressed air injection	Many developers	
Steam stripping	Heymans	
Extraction with acids	Mourik Groot Ammers	extraction of cadmium
Immobilization techniques		
DCR-technology	Many developers	chalk
Silicagel injection	Many developers	
Vitrification	Batelle	electrodes in-situ
Other techniques		
Electroreclamation	Geokinetics	electrodes, circulation syst.
Adsorbtion by DCR or CAF	No developer	adsorption by chalk or foam
Hydrolysis	No developer	raising pH to abt. 11
Chemical dechlorination	EPA	APEG
High frequency heating	IIT Research Institute	electrodes in-situ

6. CRITERIA FOR A FIRST SELECTION OF ALTERNATIVE TECHNIQUES

Information on some alternative techniques is limited. Therefore, the possibilities of alternative techniques for cleaning soils can only be roughly estimated. It should be clearly understood: for new techniques of which there is only little or just commercial information available, the estimate of experienced scientists in the field is indispensable. In order to be able to make a reliable selection from the large amount of techniques, the knowledge of specialists should be used as coherent and objectively as possible. An important aid in this can be the use of a ranking system. Such a ranking system consists of: a set of criteria, a quantification of these criteria and a quantification of the relative importance of the criteria. Unfortunately, this paper does not allow a lengthy description of the ranking system used. Only the criteria

used and some main features of the ranking system are indicated below. In the study, a set of four criteria were chosen for a first selection of techniques:

A. *Applicability of the technique for different matrices and contaminants*
Techniques that are applicable to a broad range of matrices and contaminants, or combinations thereof, score high on applicability. The ranking system expresses the relative importance of the combination of organics and heavy metals in more than one soil type (sand, loamy sand, peaty sand and clay).

B. *Priority concerning matrix or contaminant*
In the ranking system, the relative priority of removing heavy metals from most matrices and polyaromatic hydrocarbons and non-volatile chlorinated hydrocarbons from clay and sludges is incorporated.

C. *Status of development*
The study was conducted in order to find alternative techniques that could be developed to a practical stage within the near future. For this reason (and some other reasons of minor importance not mentioned here) a higher development stage influences the score in a positive way.

D. *Market perspective and costs*
The scoring of market perspectives is merely a valuation in extremes. Most techniques score neutral on this criterium. Only if the techniques are excessively expensive, complicated, etc. or excessively cheap, simple, etc. they score lower or higher respectively.

The present ranking system is a quick and rough aid in method for selecting the most promising techniques. In some cases the indication given by the ranking system was overruled by additional reasons or information not incorporated in the ranking system.

7. SELECTION OF THE MOST PROMISING TECHNIQUES

A total of 63 alternative techniques are listed. By using the scoring system we were able to eliminate 31 techniques from this list. Furthermore, 11 techniques could be selected for further study on the basis of the scores. An intermediate group for which the scoring system was not decisive, contained 21 techniques. The size of this group is an indication for the difficulty of selecting alternative techniques for which information is either very limited or of low credibility. Below a short account of the selection of techniques is given.

Wet thermal techniques (ex-situ)
In this category, two alternative techniques were found promising: supercritical extraction of Modar and wet oxidation of Zimpro. Both techniques are comparable as to their applicability and problems. The major advantage of supercritical oxidation, compared to wet oxidation, is the possibility of treating chlorinated hydrocarbons. Supercritical oxidation, therefore, is selected for further study.

Dry thermal techniques (ex-situ)
In this category the three fluid bed ovens, one of the electric infra-red ovens and the plasmareactor are promising. The electric infra-red oven is being developed in the USA. It is recommended to wait for the results of this development. Fluid bed ovens are suitable for a large range of matrices and contaminants. Furthermore, they can be used for air stripping. In general, they are somewhat cheaper than rotating ovens, more flexible as to the material treated and the process conditions can be better controlled. Therefore, fluid bed ovens are selected for further research. Plasma techniques can be used for a variety of matrices using oxidative, reductive and pyrolysing process conditions. In the Netherlands this technique is rather new. It is therefore recommended to study the technique in more detail.

Thermal immobilization techniques (ex-situ)
These techniques have been incorporated in the study for completeness' sake. Within the framework of this project we will not take these techniques into account.

Physico-chemical immobilization (ex-situ)
See remarks under thermal immobilization techniques.

Dechlorination techniques (ex-situ)
Hydrothermal dechlorination does not lead to hazardous emissions and has, therefore, been selected for further study. The other techniques do not lead to sufficient dechlorination results or lead to hazardous emissions. Most of the listed dechlorination techniques have a limited field of application. The need for dechlorination taken into account, however, it was decided that some attention should be given to the other dechlorination techniques listed as well.

Particle separation techniques (ex situ)
Particle separation techniques in general look very promising. They are cheap and have proven their applicability in mining industry. Six of them will be studied in more detail (jig, shaking table, spiral, tilting-frame, vanner, Bartles-Mozley). Techniques that are expected to be applicable only to a few soils like heavy media separation, heavy media cyclonation, Reichert cone separation, pinched sluice process, revolving round table and high gradient separation, will not be considered for further study.

Extraction techniques (ex-situ)
In this category only extraction with complexing agents looks promising. This technique will be further investigated. The other techniques listed either have a lower status of development or do not solve high priority problems.

Other ex-situ techniques
In this category we find only chemical and fotochemical oxidation as promising. These, however, are rather water purification techniques than techniques for soil and sludge cleaning. In the framework of this srudy they will not be investigated further. It is recommended to incorporate these techniques in a research programme for water purification. Ex-situ stripping techniques are fairly expensive for high volatile

and, therefore, in principle easily removable contaminants. These techniques will not be investigated further.

Stripping and extraction techniques (in-situ)
In this category compressed air injection can be considered for further study. This technique, as well as the other stripping techniques, is frequently used in Germany and information on the technique becomes readily available. There is no need for stimulating this development. Within the framework of this study we will, therefore, not investigate this technique further. In-situ extraction is expected to be applicable only to very sandy soils and highly volatile contaminants; situations that very seldom occur.

Immobilization techniques (in-situ)
See remarks for thermal immobilization techniques.

Other techniques (in-situ)
In this category electroreclamation looks very promising. This technique has the possibility of cleaning clay contaminated with heavy metals. This technique will be further investigated. The other techniques listed have a rather limited field of application and do not solve high priority problems.

In phase 2 of the project the selected techniques will be studied in more detail. The findings will be described in 8 monographs entitled:
1. Supercritical oxidation
2. Fluid bed incineration
3. Plasma reactors
4. Dechlorination techniques
5. Particle separation techniques
6. Froth flotation
7. Extraction with complexing agents
8. Electroreclamation

Based on these monographs, a selection of techniques for further development in the Netherlands will be made.

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RECENT DEVELOPMENTS IN EXTRACTION AND FLOTATION TECHNIQUES FOR CONTAMINATED SOILS AND SEDIMENTS

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RECENT DEVELOPMENTS IN EXTRACTION AND FLOTATION TECHNIQUES FOR CONTAMINATED SOILS AND SEDIMENTS

Merten Hinsenveld, October 1991

1. INTRODUCTION

Extraction as presently applied in soil cleaning, refers to a combination of particle separation, dissolution and dispersion in an aqueous environment. The terminology "extraction" was adapted in the early stages of development, beginning 80's, because it was believed that contaminants could easily be extracted from the soil. At present we know that, due to the fact that contaminants are heavily adsorbed onto the fines (particles smaller than 63 μm), the cleaning in these installations is mainly due to the separation of these heavily contaminated fines from the bulk of the soil. Hence the terminology "classification" techniques would have been more appropriate.
The process of extraction-classification can economically be applied to soils with a combined fines and organic matter contents of less than about 30%. There is a simple reason for the limitation of 30% fines in the current extraction installations: fines are difficult to dewater and lead to huge amounts of sludge. For example: one ton of soil containing 30% fines leads to about 0.6 ton of contaminated sludge (compared to the original soil, the water content of the fines is roughly doubled), and 0.7 ton of clean soil, the waste stream being reduced by only 40%. Because sediments consist mainly of fines, these extraction techniques can not be used for sediments.
Experience has shown that, in some cases, intermediate fractions, e.g. fractions between about 30 and 63 μm, are much cleaner than the fraction below 30 μm. Separating these fractions in addition to the sand particles (> 63 μm), would result in a reduction of the amount of heavily contaminated sludge. Furthermore, it was discovered that the residual concentrations in the cleaned sand particles could sometimes be attributed to the presence of larger particles of lower density, that showed the same behavior in the separation equipment as the (clean) sand particles, e.g. coal particles contaminated with PAHs. It is not surprising, therefore, that current research is focussed on improving separation performance, e.g. by combining different types of cyclones, and on new separation techniques, Chapter 2.

A technique, which largely circumferences the above mentioned problems, is the flotation technique. Although strictly spoken a particle separation technique, it is worth a separate heading. Flotation is one of the most powerful techniques in soil cleaning. Basically any component can be removed by flotation. As opposed to many other separation techniques, the surface properties of the contaminants, rather than their particle size governs the separation. The technique, therefore, can be used to separate a mixture of particles of equal size and density, but different surface properties. Dissolved material must be flocculated prior to treatment. As for the process is contaminant specific, it is capable of cleaning a large part of the fine fraction as well. Hence the production of sludge is much smaller than in extraction techniques. Thus far flotation has found little application for treatment of sediments. The sludge fraction (particles smaller than about 16 μm) are difficult to clean, even by flotation techniques. Application of this technique requires more knowledge than extraction. This may well be the reason that application has been limited to a small number of installations, mainly in The Netherlands. The flotation techniques are described in Chapter 3.

Emerging extraction techniques, which do not rely on particle separation, may use different extractants, as well as a different types of processes. In aqueous environment, research is focussed on complexing agents and acids. Biological techniques, using acid producing bacteria, are also focus

of current research, Chapter 4.
The use of organic solvents has only recently been considered, but are gaining more and more attention. These techniques are generally referred to as solvent extraction or supercritical extraction, dependent on the conditions, Chapter 5. A brief evaluation is given in Chapter 6.

2. PARTICLE SEPARATION TECHNIQUES

2.1. Introduction

Particle separation techniques can be applied, when contaminants are present as discrete particles or adsorbed onto a particular particle fraction of soils or sediments. Mining technology is a major source of information for these techniques (see f.i. Weiss et al., 1985). Most particle separation techniques are effective in a certain range of particle sizes, making a combination of techniques necessary, to obtain an effective separation. Because the techniques are relatively inexpensive, applying more than one technique is quite feasible. In this section some techniques that are strong candidates for soils treatment are described. Although the techniques are standard in mining industry, their application in soils and sediments treatment has only recently been considered.

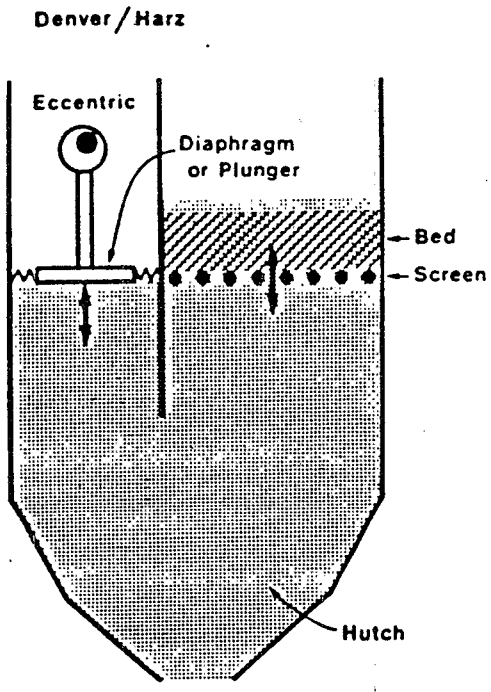

Figure 1: Jig separation (Spottiswood, 1982).

2.2. Jig Technique

In jigging, a bed of particles, supported on a perforated plate or screen, is subjected to an alternate rising and falling flow of fluid, Figure 1. The objective is to cause the particles of high specific gravity to travel to the bottom, while the particles of lower specific gravity collect at the top of the bed. The settling conditions can be described according to the concept of hindered settling. By jigging the different fractions again the separation can be improved. Because the separation is based on size as well as density, the feed to the system should preferably be sieved or cycloned into different fractions as to obtain a better result in the process. If fractions of equal size are jigged separately, the location of the particles in the stratified layers will be a function of density only. The technique has already been incorporated in a number of extraction and flotation installations in The Netherlands to remove particles having a diameter larger than 0.15 mm with a significant different density from the bulk of the soil. Practical experience in soil cleaning has shown that the technique is very useful for the separation of tar particles. These particles are larger but also lighter than sand. This causes the tar particles to show the same behavior as the clean sand particles in cyclones, thus contaminating the cleaned sand. The jig technique is a standard technique in mining industry and promises to become one in soil treatment as well.

2.4. Humphrey-spiral Separation

A downward winding gutter used to separate particles is called a Humphrey spiral, Figure 2. As the water flows down the spiral, it is subjected to centrifugal force which places much of the water near the outer rim until the flowing film reaches an equilibrium between centrifugal force outward and gravitational force downward. In such a curved channel, the bottom layer of water, retarded by friction, has much less centrifugal force and, consequently, will flow sideways along the bottom towards the inner edge, carrying with it the heavier particles. Simultaneously with this bottom flow of water inward, the upper mass of water must flow outward to replace it. In fact, the heavy particles in the spiral take the shortest way downward, while the lighter particles, with the bulk of the water at the outer radius, move downward. The different fractions can be collected via openings in the spiral at different distances from the center. Separation in more than two fractions is possible. The technique is applied in the alluvial mining industry for the winning of heavy metals from river and beach sands. The Humphrey spiral has recently been introduced in the extraction installations in The Netherlands and seems to perform quite well. There is, however, no official information on this performance available (since the technique is innovative in soil cleaning, the firms tend to keep silent about the performance). Optimum particle sizes range between 0.075 and 3 mm.

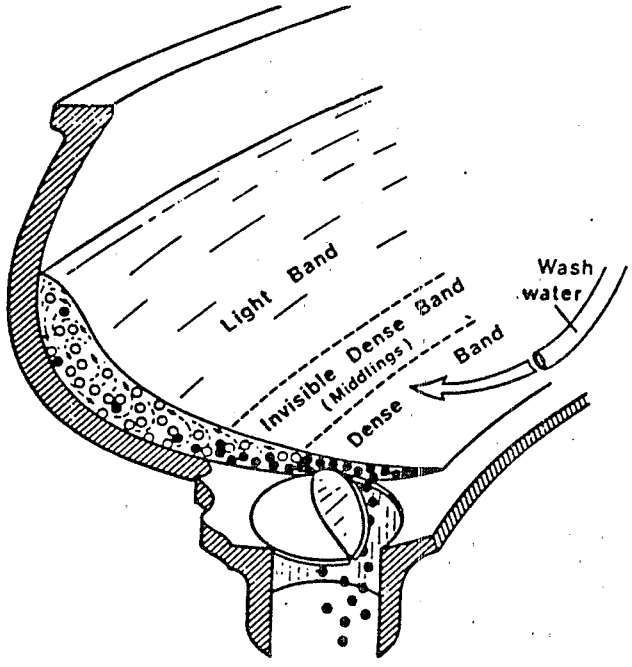

Figure 2: Humphrey-spiral separation (Spottiswood, 1982).

3. FLOTATION TECHNIQUES

3.1. Chemistry of Flotation

The addition of specific chemicals is one of the major factors in determining the success of this technique and it is worthwhile to look at the chemicals used in the flotation process. They are usually classified as (1) Collectors and Extenders, (2) Modifiers (pH-modifiers, activators, depressants, dispersants) and (3) Frothers.

Collectors and extenders. When components adsorb on the surface of the soil particles (mostly fine particles on which the contaminants are adsorbed), the surface energy at the solid-liquid and the solid-gas interfaces decreases. These interfacial energies are minimal upon saturation of the entire surface. Many organic components can in fact adsorb onto the surface, making the particles susceptible to flotation. Components that can do this are called collectors. It is important that the collectors adsorb onto the contaminated particles that must be removed. Collectors, therefore must be selected with care and be added to the slurry at the right conditions. Establishing these

conditions requires extensive laboratory investigation.
An important property of collectors is their polarity. They consist of a "head" and a "tail" with the polar tail directed away from the particle. In water the result is a decrease of the surface tension resulting in a hydrophobic particle. Collectors in water are characterized by the charge of the head that attaches to the particle as anionic (-) or cationic (+). By choosing the charge of the head, the collectors can attach to specific surfaces; anionic collectors attach to positively charged surfaces, whereas cationic collectors attach to surfaces that are negatively charged. The effect of collectors can be enhanced by extenders which in turn attach to the collector tail to enlarge the it or to give the tail different properties. The collectors used in soil treatment can be classified into as: (1) Anionic collectors for sulfidic contaminants such as xantates, dithiosulphates, thiocarbinilide and thiocarbamates; (2) Anionic collectors for non-sulfidic contaminants, mostly fatty acids of different kind; and (3) Cationic collectors for non-sulfidic contaminants, such as alkylamines and quaternary ammonium salts.

Modifiers. Different chemicals can be used to modify the collector action and the selectivity of the collector with respect to the contaminants. The most commonly used modifiers are pH-regulators, activators depressants and dispersants.

pH-regulators. These regulators change the pH of the solution. They change the properties of particles that have hydroxyl groups or hydrogen ions at the surface. Examples are: acids, chalk and soda.

Activators. These chemicals are added to improve the bond between collectors and particle surface. Examples are: sodium sulfide and copper sulfate.

Depressants. To improve the selectivity of the flotation process with respect to the contaminated particles, it may be necessary to depress flotability of certain other (non contaminated) particles. Examples are: dextrine, sodium cyanide and starch.

Dispersants. In substrates containing a large amount of fine particles it may be necessary to add chemicals that keep these fines in suspension. Examples are: sodium silicate

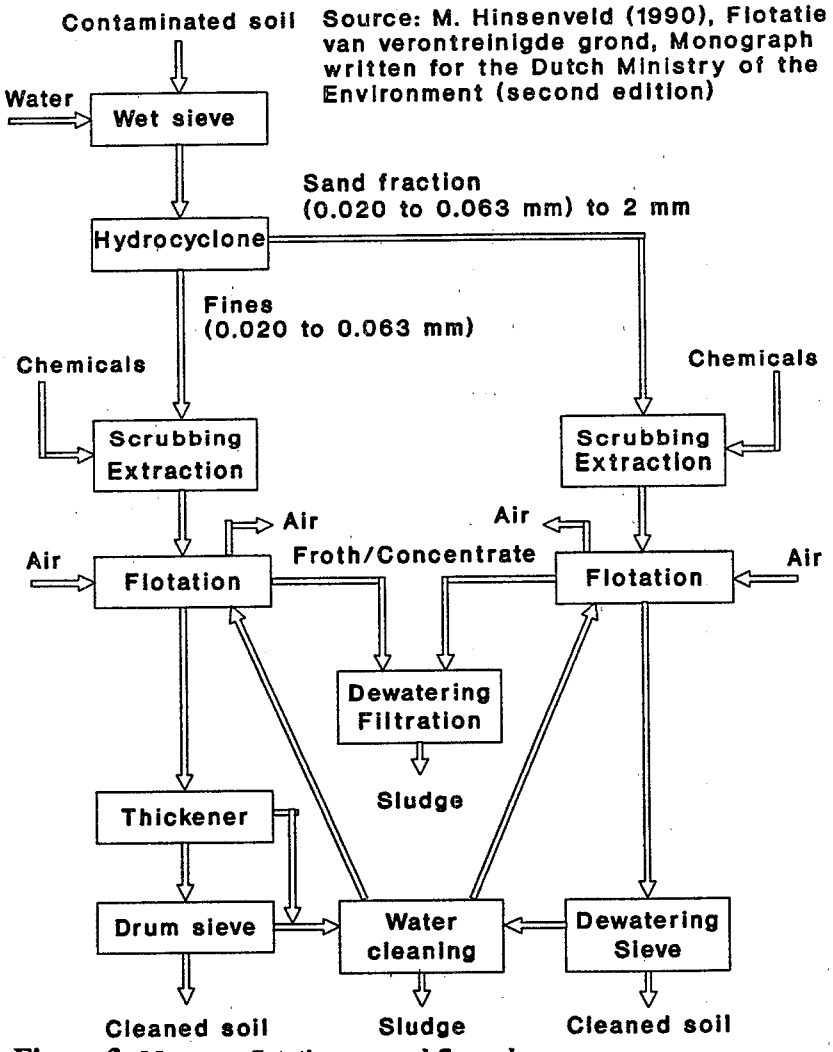

Figure 3: Mosmans flotation, general flow scheme.

(waterglass) and hexametaphosfate.

Frothers. Contaminants are captured in a foam that forms at the surface. In order to effectively be able to skim this foam and to prevent redisssolution of contaminants a resistant foam is needed. Examples are: cresylacid and methyl-isobutyl-carbinol. The latter one is a universal frother.

3.2. The Mosmans Process

In the Netherlands, three full-scale flotation installations are available, with cleaning efficiencies generally ranging from 75 to 99%. Lurgi, in Germany is presently developing a flotation plant. One of the most advanced flotation installations is the installation of Mosmans Mineraaltechniek (NL), the firm that introduced the technique in the field of soil cleaning in 1983. A general scheme of the process is given in Figure 3. At present, the company is cleaning the famous Sandoz site in Switzerland, that was contaminated by mercury compounds, pesticides and herbicides originating from a fire [de Boer, 1990]. The company has recently reached extremely high removal efficiencies in cleaning soil contaminated with HCH, including the congener lindane: from 1,600 to 0.03 mg/kg, with an efficiency of 99,99% [Mosmans, 1991].

3.3. Air-sparged Hydrocyclone

This technique is designed at the University of Utah to achieve fast flotation of very fine particles in a centrifugal field, Figure 4. Compared to a conventional flotation cell, the air-sparged hydrocyclone (ASH) has a high specific flotation capacity (up to 100 tons per day versus 1 to 2 tons per day for conventional flotation). The ASH consists of two concentric vertical tubes with a conventional cyclone header at the top and a froth pedestal at the bottom. The slurry is fed tangentially through the conventional cyclone header to develop a swirl flow of a certain thickness in the radial direction, and is discharged through an annular opening between the insides of the porous tube wall and the froth pedestal. Air is sparged radially through the inner porous tube and sheared into small bubbles that attach to the hydrophobic particles and form a froth phase in the cyclone axis. The outer tube serves only as an air jacket to provide for even distribution of air through the porous inner tube. The froth phase is stabilized and constrained by the froth pedestal at the underflow, moves towards the vortex finder of the cyclone header and is discharged as an overflow product. Research on the ASH has also been carried out at the University of Eindhoven (NL), but results for cleaning of soils or sediments are not known to me.

4. AQUEOUS EXTRACTION TECHNIQUES

4.1. Introduction

Extraction techniques are well developed in the Netherlands and Germany. A total of about ten full-scale installations is available. Developers of "innovative" extraction techniques often claim magical cleaning efficiencies of 99% and better. Generally not indicated is, that these contaminated soils hardly contained any fines (particles smaller than 63 μm) or that only a small clean fraction was obtained. The techniques described here aim at extraction rather than classification.

4.2. Extraction with Complexing Agents

Complexing agents have the ability of trapping metals in a structure and shielding them from interactions with other species. Different types of complexing agents can be used, such as EDTA, NTA and citric acid. The metal-complexes then have to be separated from the matrix. PBI (NL) applies a so-called heap leaching process for an extraction of sediments and the fine fraction in soils with EDTA [Olijve, 1988; PBI, 1989]. Prior to leaching, the sludges are treated with a flocculant. The flocculated material is then fed into a basin and flushed either upward or downward with a dissolved complexing agent in solution. PBI uses EDTA, but other complexing agents could be considered. Essential for the method is that the percolate is allowed to flush the material homogeneously, without clogging and channeling. In the PBI system, the soil is, therefore, slightly consolidated by mechanical vibration. The loaded complexing agent solution is regenerated by flocculation-sedimentation and/or, depending on the type of metals separated, electrochemical methods. The metals are being separated as hydroxides, sulfides or pure metals. The heap leaching method is applicable to metals like Pb, Zn, Cd, Cu and Co. Arsenic is very difficult to remove. In one experiment researchers reported to have reached the Dutch A-level for lead and zinc [Kollée and Van Dijck, 1989]. After the extraction is complete, the material must be flushed with water to remove residual EDTA.

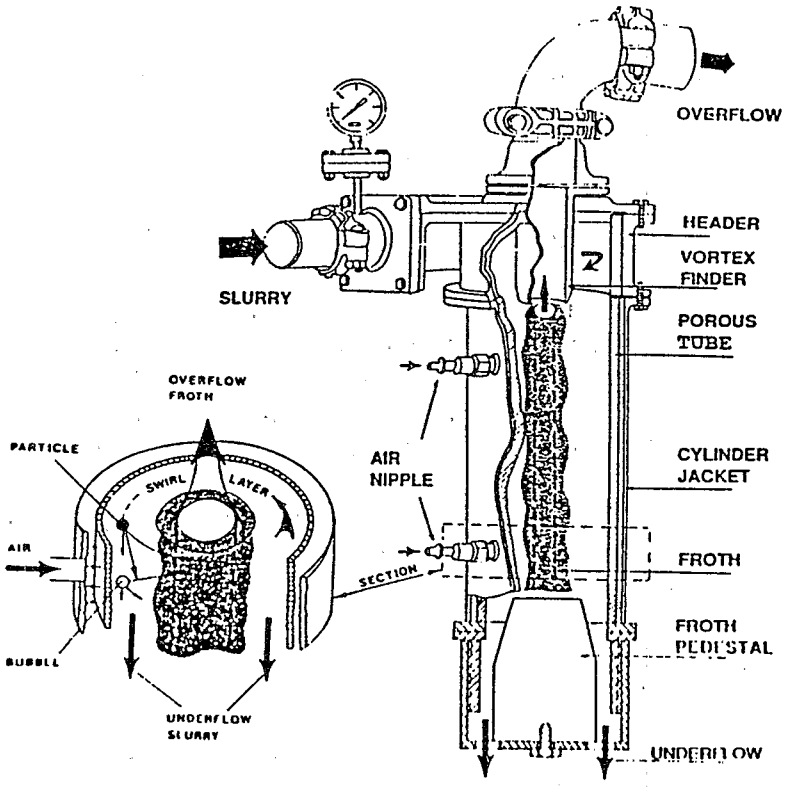

Figure 4: Air sparged hydrocyclone (EPA, 1990b).

4.3. Acid Extraction

Acid extraction is the extraction of contaminants at a pH lower than 3, without significant classification. Acid extraction can be used if the metals are bound in a soluble matrix or in an acid soluble form to the particles and cannot, or with low efficiencies, be extracted with sodium hydroxide, such as some forms of Pb, Cd, Zn, Cu and Cr(III). Two mechanisms in the acid extraction of heavy metals from soil and sediments are important: (1), the rapid exchange of reversible exchangeable metals (cations) with H^+ and the dissolution of oxides and sulfides and (2) a slow exchange from the crystal structure by dissolution of aluminum silicates. In many cases the amount of reversible bound metals and the soluble fraction, however, are very small compared to the amount that is bound irreversible.
In the full-scale installations in The Netherlands, acid is applied when tests indicate the positive

influence of its use. In general, however, the pH is not lowered to less than 5 to 4. Since addition of $FeCl_3$ is often necessary for the subsequent flocculation step in the process, the acidification generally is carried out by adding this chemical in the scrubber. An advantage of mild acidification is an improvement in settling properties in the solid-liquid separation unit. For more rigorous pH values, a protective coating must be applied to prevent corrosion of the installation. Acid extraction to a pH of 2.5 to 2 can be used on a full scale by Heymans (NL), but is hardly ever done [Hinsenveld, 1990a].

Different types of acids can be used: inorganic acids such as HCL, HNO_3 and H_2SO_4 and hypochloric acid, and organic acids such as acetic acid, lactic acid and citric acid. An advantage of organic acids is that they not only reduce the pH, but also have complexing properties, and the residuals can easily be biodegraded [Joziasse et al., 1990]. Nitric acid has also been considered, but it was found to create highly undesirable by products, such as tetroxide, and produced end products that were not amenable to further treatment [EPA, 1990c]. Florosilic acid, as an extractant for lead, has also been proposed [EPA, 1991b]. Of the inorganic acids, HCl is usually considered the most attractive extractant, because it is relatively cheap, less harmful than other inorganic acids, forms well-soluble chlorides and forms complexes with a number of metals (e.g. Cd, Zn, Cu). Extraction efficiencies in the literature range from 5 to 95% (the wide range indicates the importance of speciation). Extractions of lead from sediments was found to be greatly enhanced if, prior to acidification, an oxidation by H_2O_2 was performed. Large amounts of chemicals were needed to obtain the desired pH of 1: about 200 kg HCL and the same amount of NaOH per cubic meter to afterwards neutralize the cleaned sediment [Kelderman et al., 1991]. Chloride levels after treatment were also reported to be a problem. Although acid extraction offers possibilities for the extraction of metals from soils and sediments, some major disadvantages, e.g. corrosivity and handling problems, and excessive use of chemicals, may hold its implementation.

4.4. Microbiological Leaching

Microbiological leaching, which involves the use of microorganisms to extract metals from materials, has recently been introduced in the field of soil treatment. The process is used throughout the world to extract copper from low-grade ores and waste materials via a process called dump leaching. It is also widely used to extract uranium from sulfide-rich ores. The microorganism, initially thought to be the only organism important in the leaching of metals from ores was the rod-shaped Thiobacillus ferrooxidans, but many others have now been identified. They can be classified as gram-negative aerobic chemolithotrophic (rock eating) bacteria and include the species Thiobacillus thiooxidans, Leptospirillum ferrooxidans, Thiobacillus organoparus and the extremely acidophilic and thermophylic genus Sulfolobus. The importance of mixed cultures is now generally accepted. T.ferrooxidans and T.thiooxidans combined, for example, are more effective in leaching certain ores than either organism alone. Similarly, the combination L. ferrooxidans and T. organoparus can degrade pyrite (FeS_2) and chalcopyrite ($CuFeS_2$), a feat neither species can accomplish alone [Brierley, 1982]. Al bacteria mentioned endure a low pH (some enduring up to 7% sulfuric acid) and are very tolerant to concentrations of metals that are normally considered toxic. They may use different electron donors (energy source); the carbon source is limited to bicarbonate for the Thiobacillus thiooxidans, whereas T.ferrooxidans and Sulfolobus may also use organic components. The electron acceptor ordinarily is molecular oxygen, but Sulfolobus may also use Mo^{6+} or Fe^{3+}. Although the organisms degrade mineral structures by directly attacking sulfide and ferrous iron constituents, the resulting ferrous ion is itself a strong oxidizing agent of sulfide minerals and greatly enhances the metal dissolution process [Brierley 1984]. Since natural soils and sediments contain

limited amounts of sulfur compounds, addition of sulfur flower will be necessary. Remaining a sufficient concentration of oxygen is crucial to the process.

Two different leaching processes are generally distinguished: heap leaching (or vat leaching on a small scale), which consists of a heap of, in this case soil or sediment, which is sprayed with the leaching solution; and flood leaching, where the heap is completely submerged under the leaching solution. Stope leaching is a combination of both flood and heap leaching and is an intermittent flood and drain, Figure 5.

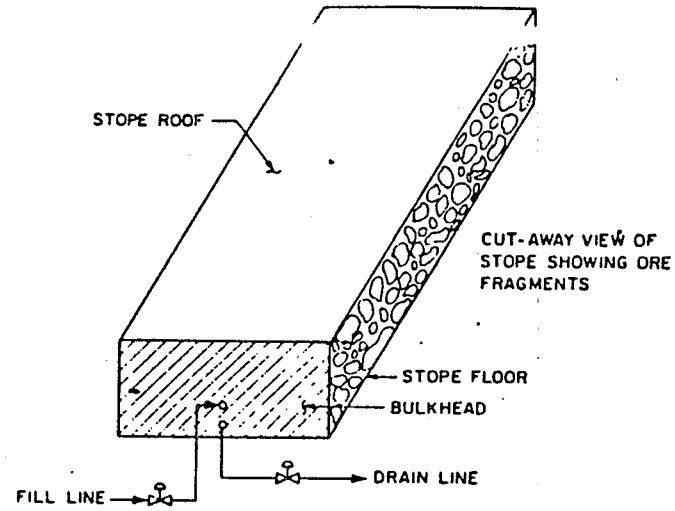

Figure 5: Stope leaching (Daniel et al., 1990).

A biological membrane reactor was investigated for use in cleaning of sediments in The Netherlands by Storm Environmental Consultancy (SEC). The process consists of two phases. In the first phase, Lactobacillus helveticus, producing lactic acid from sugar substrate (lactose) is used to leach and complex the metals that are readily available at a pH of about 3 to 3.5. (L. helveticus is a thermophylic bacterium, used for example to produce lactic acid from whey ultra filtrate or permeate and does not endure pH values lower than about 3). In the second stage, T. thiooxidans and T. ferrooxidans are used to extract the metals bound as sulfides from the sediments. A special membrane reactor was developed to combine bio-leaching in a slurry with simultaneous separation of fluid from silt particles and bacteria [Storm van Leeuwen, 1991]. A problem occurring was that L.Helveticus did not produce sufficient acid. Therefore, lactic acid was added. Extraction efficiency for metals of 85 to 100% are mentioned.

5. SOLVENT EXTRACTION

5.1. Introduction

Solvent extraction has been shown to be effective in treating sediments, sludges and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents and petroleum wastes [EPA, 1990d]. Full-scale application is still limited. Some of these systems use solvents that are either flammable or mildly toxic or both. However, there are long-standing standard procedures used by the chemical companies, gasoline stations, etc., that can be used to greatly reduce the potential for accidents [EPA, 1990d].

5.2. Extraction with Organic Solvents

Two main types of solvents can be distinguished.

- Non water-miscible solvents, such as hexane. An advantage of such a solvent is the relative simple separation of solvent and cleaned soil. A disadvantage is that the solvents generally do not reach the water filled pores of the soil particles and, therefore, only remove superficially

present contaminants, unless some measure is taken (e.g. intensive scrubbing, ultra-sonic vibrations). The latter disadvantage disappears if the solvent can be mixed with a phase transmitter that is soluble in both water and solvent.

- Water-miscible solvents, such as acetone. An advantage of these solvents is the intense contact with contaminants in the pores of the particles. A disadvantage can be the difficulty in separating water, solvent and contaminant. The latter disadvantage disappears if the solvent is extremely volatile compared to water.

Acetone has been successfully used by the US Department of Defence to remove explosives (TNT, DNT, etc.) from sediments. Unfortunately, the process concentrated the acetone dissolved explosives in a closed container, which may be very dangerous. For this reason, acetone extraction was abandoned in favor of rotary kiln incineration [EPA, 1991a]. The Sanivan Group (USA) has developed a mobile solvent extraction unit, the so-called Extraksol technology [EPA, 1990b]. The extraction is a batch process and is performed in a tumbling vat. No information is available as to what solvent is used, but the solvent is said to be a non-chlorinated and non-persistent organic solvent (perhaps acetone?). After the extraction the soil is separated from the extractant and dried by heating. The solvent is purified by distillation and recirculated in the process. Some limitations mentioned are a maximum clay fraction of 40%, a maximum water content of 30% and a maximum size of porous material of 5 cm. The technology has not yet been demonstrated.

A similar process, the so-called LEEP (Low Energy solvent Extraction Process) is subjected by Environ-Sciences (USA) to the US EPA Emerging Technologies Program, Figure 6. The contaminants are leached with a hydrophilic (water miscible) solvent from the soil or sediment and

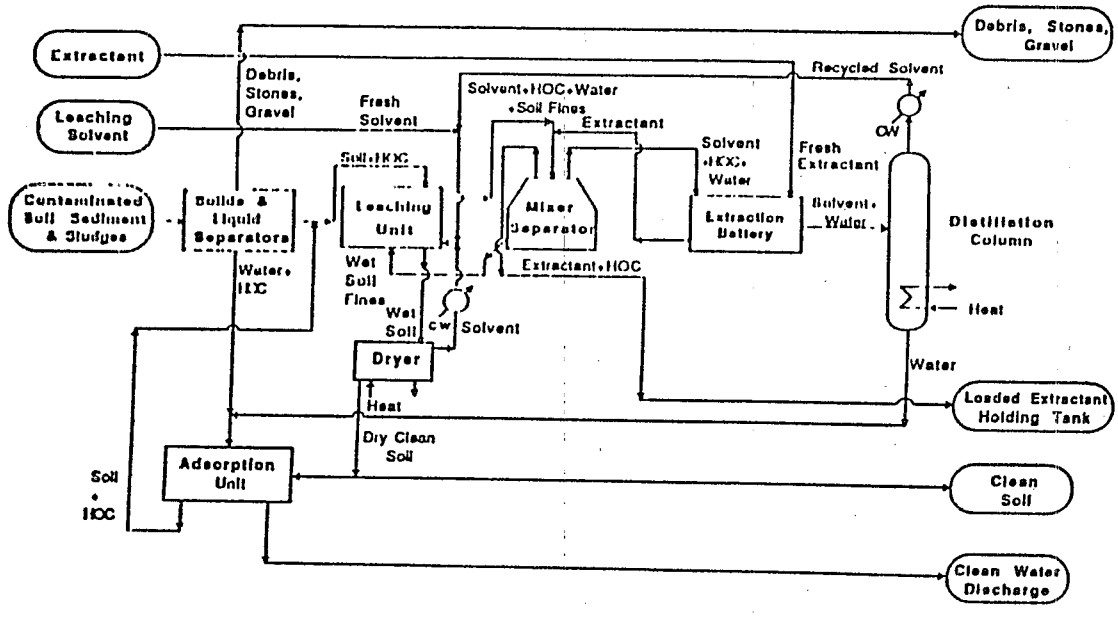

Figure 6: LEEP flow diagram (EPA, 1990b).

concentrated in a hydrophobic (water immiscible) stripping agent. Research was focused on acetone, isopropanol and methanol [EPA, 1990c]. The process was originally designed to remove PCBs from sediments, but was also used for PCB contaminated sludges, refinery sludges and oil contaminated solids. Bench-scale tests conducted on sediments reduced PCB concentrations from 3,200 mg/kg to 1 mg/kg. Plans exist, to test a pilot-scale unit capable of treating 30 to 50 tons/h [EPA, 1991a].

Another process in the Emerging Technologies Program is developed by Harmon Environmental Services (USA). In this process, a hydrophobic patent solvent blend is used to extract PCBs from soil. The solvent wash is cleaned by distillation. This process is still on a laboratory scale.
A continuous solvent extraction system using dichloromethane has been developed by Phønix Miljø (DK). The system is marketed under the name CONTEX. The system is specifically designed for soil treatment and has a throughput of about 10 tons per hour. The soil is pre-screened down to about 50 to 80 mm and transported through a tube system by schaftless augers, where it is flushed counter currently with the extracting agent [Haztech, 1991]. The bulk of the extracting agent is removed from the soil by gravity separation and regenerated by distillation. The extracting agent is fully recycled in the process. Residuals of dichloromethane in the soil are removed by volatilization at a temperature of about 100 °C, followed by steam stripping. These residuals are (after cooling) recovered and also recycled in the process. Contaminants remain in the distillation unit as an aqueous emulsion, which is sent for off-site treatment. Results reported are (all numbers in mg/kg): tar, from 270,000 to < 30; jet fuel/gasoline, 15,000 to < 10; heavy fuel/oil sludge, 22,000 to < 10; drilling cuttings, 400,000 to < 60; chlorinated solvents, 3,600 to < 1; BTX compounds, 5,000 to < 1.5; naphthalene, 5,300 to < 1.5 and phenanthrene 23,000 to < 1 mg/kg.

5.3 Extraction with Aliphatic Amines

Resources Conservation Company (USA) developed a so-called BEST-technology (Basic Extraction Sludge Treatment), Figure 7. This also is a solvent extraction technique, but the features of the technique are worth a separate heading. The technology is based on the inverse solubility of a number of secondary and tertiary amines: complete soluble in water at low temperatures and not miscible with water at higher temperatures. At present only TEA (triethylamine) is used, which has an inversion temperature of 20 °C. The process is applicable to most organic and/or oily contaminants in soil or sludges, including PCBs. In the process, the contaminated mineral matrix is mixed with the cold amines to extract the (chlorinated) hydrocarbons. After the solvent has broken the oil-water-solid bonds, the solids are allowed to settle from the suspension. Following the solid-liquid separation, the fluid phase is heated to separate water and TEA. The organics will be transferred to the organic phase and can, subsequently, be recovered in a stripping column. The solvent TEA is recycled in the process, whereas the water is discharged to a local waste water treatment plant. The oil product fraction is chemically unaltered by the process. At large concentrations, the oil can be recovered. A full-scale test (100 ton/day) was performed in 1986, on a sludge from a refining site. The sludge composition varied considerably, with an oil concentration ranging from 0-40%, water from 60-100%, solids from 2-30% and PCBs ranging from 1-13 mg/kg. It was reported that separation efficiencies, defined as the amount of desired product less the amount of all undesired products times 100, often exceeded 98% [Sudell, 1988]. Research on contaminated sediments in The Netherlands indicated that extraction of PAHs with TEA was more effective than extraction with toluene [van Dillen, 1991]. The presence of detergents can result in lower separation efficiency and emulsifiers can affect organics separation from the water fraction. Because TEA is flammable in the presence of oxygen, the treatment system must be sealed from the atmosphere and operated under a nitrogen blanket. Prior to treatment, it is necessary to raise the pH of the material above 10, to be able to effectively recycle TEA in the process. A research and development permit to operate the BEST pilot plant has recently been issued [Haztech, 1991].

5.4. Supercritical Extraction

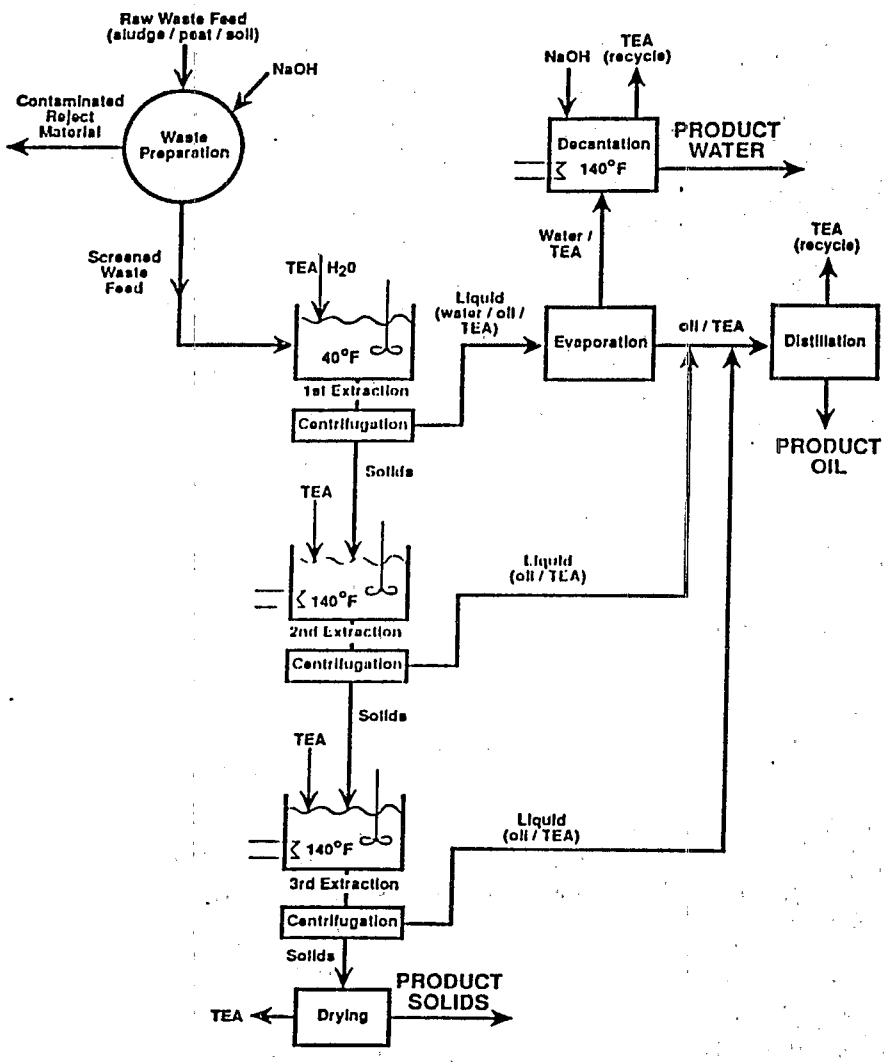

Figure 7: BEST extraction (Sandrin and Fleissner, 1990).

Liquified gasses can, similar to extraction to organic solvents, be used for the extraction of organic components. An advantage of the use of liquified gasses is the high volatility and the relative ease with which the solvents can be recycled. A disadvantage is that the extraction must be executed under pressure. Heated to their critical temperature, they also exhibit the properties of supercritical fluids. The properties of supercritical fluids, such as density, viscosity and diffusion coefficients are intermediate between those of the gas and liquid phases, and are dependent upon the fluid composition, temperature and pressure. The compressibility of supercritical fluids is large just above the critical temperature; at this point small changes in pressure result in large changes in the density of the fluid. The liquid-like behavior of a supercritical fluids results in greatly enhanced solubilizing capacities compared to subcritical gas, with higher diffusion coefficients, lower viscosity and an extended temperature range compared to the corresponding liquid [Wright and Smith, 1986]. Supercritical fluids possess a high solubilizing capacity for organic components and an extreme low solubilizing capacity for inorganic components. Many possible supercritical fluids are reported to be used, such as ethylene (32.2 °C), carbon dioxide (31.1 °C), ethane (32.2 °C), propane (96.9 °C), ammonia (132.4 °C), butane (152.0 °C), sulphur dioxide (157.6 °C), pentane (296.7 °C) and water (374.3 °C).

An advantage of using carbon dioxide or water to other gasses is, that no environmental hazardous components are introduced in the system. Supercritical extraction is mostly used for the extraction of components from fluids, but tests with soil and sediments have also been reported. Brady et al. (1987) report on the extraction of PCBs and dioxins from soil, using CO_2 as the extracting agent. They conclude that the extraction of PCBs is relatively simple, whereas the extraction of dioxins is

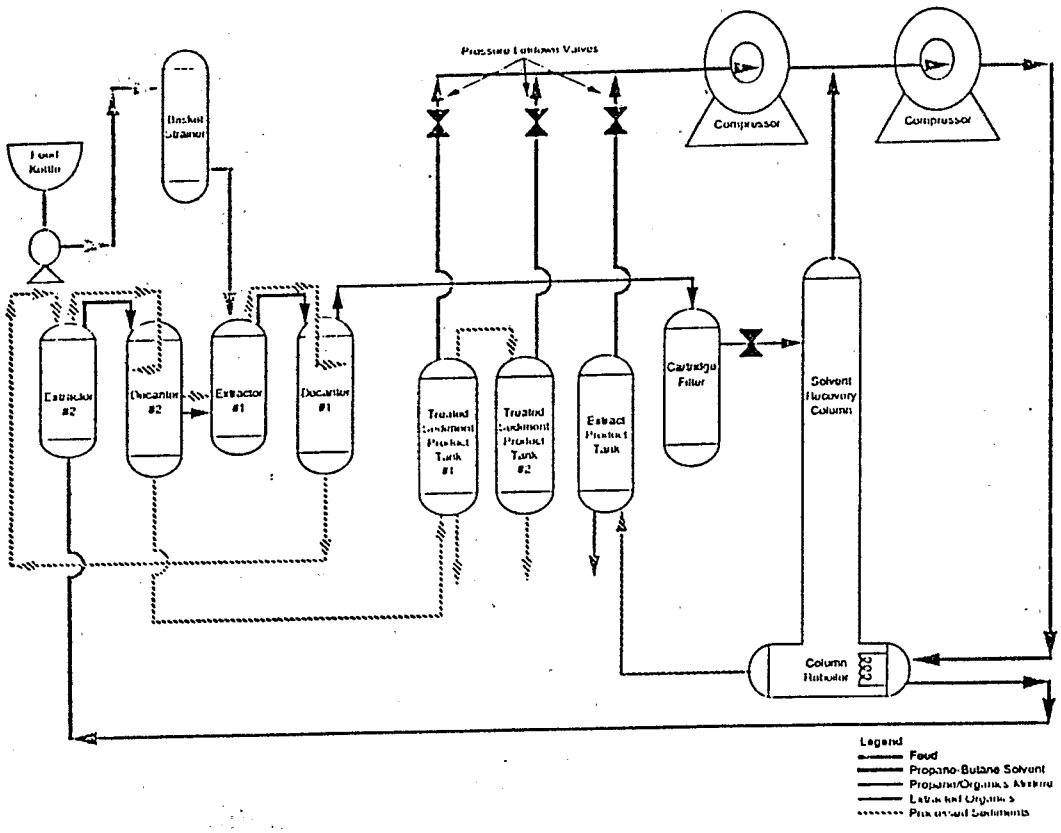

Figure 8: CF systems extraction (EPA, 1990b).

more difficult. The results also indicate that the extraction is inhibited by a high organic content of the soil. A high water content also slows down the extraction. PCBs seem to be easily extractable from sand.

CF Systems Corporation developed a system capable of extracting PCBs from soils, sediments and sludges [EPA, 1990a], Figure 22. A mixture of propane and butane at near critical temperatures is used as the extracting agent. Residue generation from the process, however, is reported to be significant [EPA, 1990c]. In demonstrations conducted concurrently with pilot dredging studies at the New Bedford Harbor superfund site in the US, the system achieved cleaning efficiencies varying from 90 to 98% for sediments containing between 350 and 2,575 mg/kg PCBs. PCB concentrations were as low as 8 mg/kg in the treated sediment. Projected costs for PCB cleanups are estimated at approximately $150 to 450 per ton, including material handling, pre- and post-treatment costs.

6. FUTURE STATUS OF EXTRACTION AND FLOTATION TECHNIQUES

Separation of fines from the soil leads to production of sludge, which is generally the main drawback of extractive methods. If contaminants are equally distributed over particle size and particle density, conventional extraction is not applicable. With regard to the contaminants, the extraction techniques are powerful techniques, because they can deal with a variety of contaminants and mixtures thereof. Some improvement of the extraction-classification techniques by using new

separation techniques is expected.
Flotation is probably the most powerful technique in soil cleaning. It cleans, rather than separates the fines from the soil and is suitable for almost any contaminant. Furthermore, performance of flotation keeps improving, whereas extraction techniques have shown little improvement over the years. However, the sludge fraction (<16 μm), is at present considered non cleanable.
The use of organic solvents and supercritical extraction techniques are being investigated at the moment and might further enlarge the applicability of the extraction techniques. This also holds true for extraction with acids. However, these techniques, will probably be more expensive than the ones used at present.
Heap leaching processes are likely to be used in future for soils and sediments cleaning. Example were given for extraction with complexing agents and microbiological leaching. Heap leaching techniques allow more time for the contaminants, to migrate from the matrix into the leaching solution.
New installations are likely to incorporate the advantages of the different methods into a treatment train. Flotation will probably play a larger role in these installations. It is expected that the cost of treatment will increase, since the easier techniques have already been tested.

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NATO/CCMS Fellow:

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Summary Report: NATO/CCMS Pilot Study on Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater

Not included here; this report was incorporated into Volume 1.

NATO/CCMS Fellow:

Wayne A. Pettyjohn, United States

Principles of Ground Water: Fact and Fiction

PRINCIPLES OF GROUND WATER FACT AND FICTION

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Introduction

All of us have an impression of ground-water quality or the manner in which an aquifer system functions. Not uncommonly these impressions are based on past experience, hearsay, published information, a single sample, perhaps on the basis of several samples representing a considerable difference in both space and time, or on an assumption formulated to simplify a physical phenomenon.

From these generalized impressions, the next step to using them as the basis for some plan, effort, initiative, guideline, or regulation, is a natural one.

Perhaps one of the reasons that our generalizations can lead us down a troubled path is that so many of them are exclusively based on theoretical concepts or laboratory studies, or are required to simplify a mathematical model; few have ever been extensively tested under field conditions. Not only are detailed field studies unusual, but adequate, long term ground-water monitoring, even of contaminated sites, is rare.

The following general principles are classified as "fact" and "fiction". They have been tested over a period in excess of six years at a field site in north-central Oklahoma.

Fiction

Ground-water recharge only occurs when field capacity is exceeded.

Fact

When a soil or rock unit has been saturated and then allowed to drain by gravity, it is said to be holding its field capacity of water. This implies that ground-water recharge can not occur if the moisture content is less than field capacity because the earth materials will absorb all of the water that infiltrates. Although the idea of field capacity is a useful concept, it ignores flow through fractures and other large openings called macropores.

A graph of precipitation and water-table elevation is shown in Figure 1. This rainfall event occurred in July, 1989 at a field site where the aquifer consists of a rather homogeneous mixture of very fine sand, silt, and clay (silt loam). The soil-moisture content was well below field capacity, and the water table was

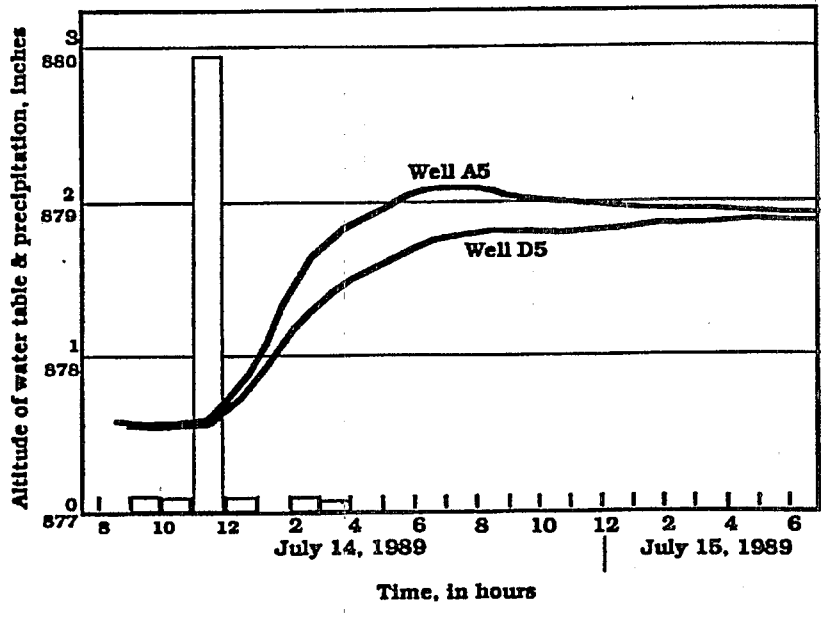

Figure 1. Relation Between Precipitation and Water-Table Rise.

Prepared for the NATO/CCMS Pilot Study on Demonstration of Remedial Action Technologies for Contaminated Land and Ground Water, Washington, D.C., November 18-22, 1991

about 7.5 feet below land surface. Most of the precipitation, amounting to nearly 3 inches, took place during a period of an hour. Within 30 minutes of the start of the rain, the water table began to rise, suggesting flow through the unsaturated zone at a rate of about 15 feet per hour. At the A-well cluster, which lies in an open area, drainage of water from the unsaturated zone largely ceased after about 7 hours, as indicated by the downward trend of the water table. At the D-well site, which lies under a line of large trees, the water-table response to the rain was less than the A site, and gravity drainage continued for several additional hours. This is probably related to interception by the trees and a greater fillable porosity at the D site.

Fiction

The water-table gradient is rather uniform, both in space and time, if the aquifer is not stressed by pumping.

Fact

In some surficial aquifers the direction and magnitude of the hydraulic gradient can change dramatically from one time to the next even though the aquifer is not stressed by pumping. The April water-table map, shown in Figure 2, suggests a flow direction to the southwest with a gradient of .003. By July (fig. 3) ground water was flowing to the south southeast and the gradient had doubled. Throughout the period of record the direction of flow ranges within about 125 degrees each year. There are no water-supply wells in the entire aquifer.

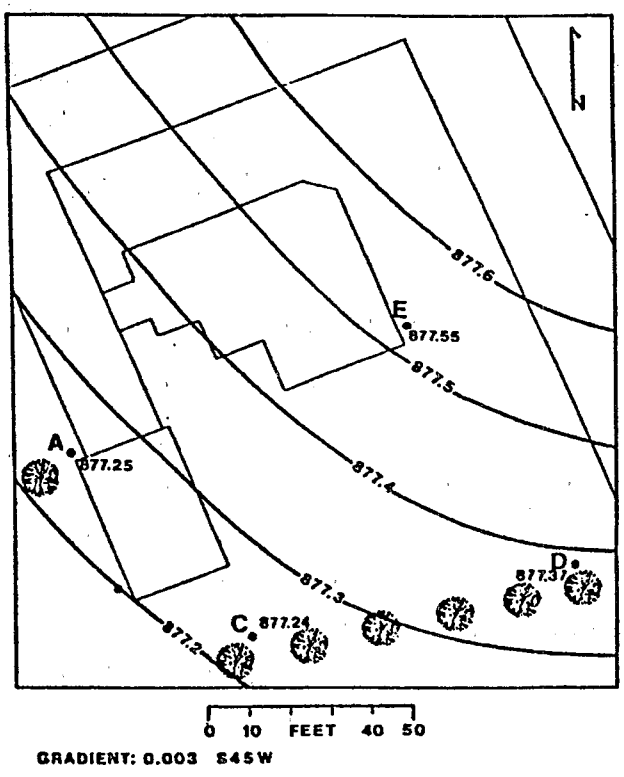

Figure 2. Water-Table Map for April 2, 1986.

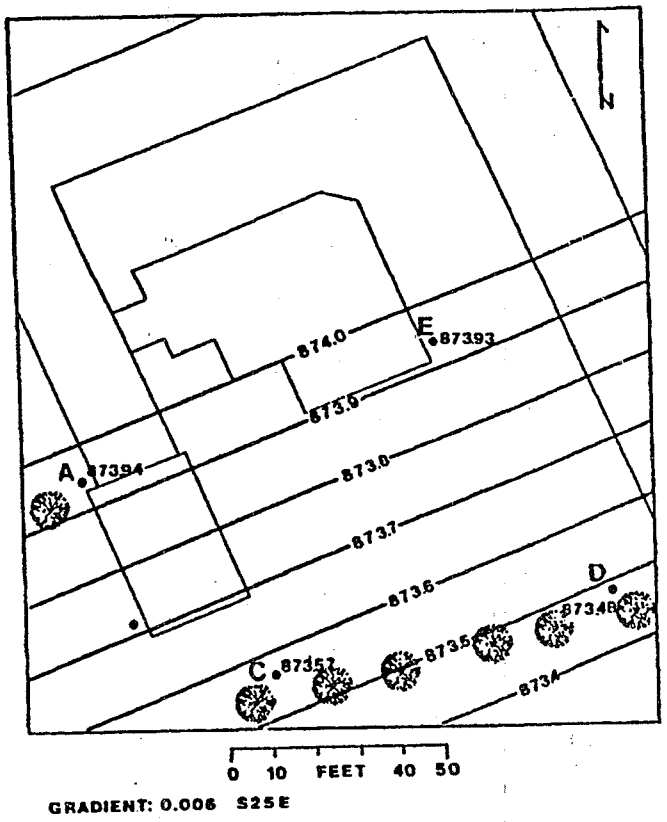

Figure 3. Water-Table Map for July 26, 1986.

At this site, when the water table is less than 7.5 feet below land surface, ground water discharges into a small stream that lies a few hundred feet to the west. When the water table declines below the bottom of the stream, the direction of flow changes so that the ground water can discharge into a larger and deeper stream that lies several hundred feet southward. The major cause of the water-table decline, averaging about 8 feet from March to October or about .1 feet per day in the absence of recharge, is transpiration by large trees.

Fiction

Fine-grained sedimentary strata are impermeable or nearly so.

Fact

Despite it's appearance, the fine-grained alluvial material at the field site is quite permeable, both vertically and horizontally. Aquifer and slug tests indicate that the hydraulic conductivity ranges from about 30 to 120 gpd/ft^2, and averages about 60. This is similar to many fractured sandstones. Tracer tests, velocity studies, the lack of head differences between wells of different depths during recharge events, and the response of the aquifer to pumping, suggest that the ratio between horizontal and vertical permeability is about one. Wells can produce as much as 10 gpm.

At this site, the fine-grained alluvial material fills a steep-walled valley cut into a massive shale unit. The top of two buried soil horizons occurs at about four and 27 feet below land surface; they have been dated as approximately 1300 and 10,300 years old. Although only two A-horizons are evident, soil characteristics, including macropores, are abundantly evident throughout the entire 43 feet thickness of the alluvial material. These features, however, are apparent only through the scrutiny of cores, and they were entirely missed during an examination of cutting derived from augering and hydraulic rotary drilling.

Fiction

Laboratory analyses of hydraulic conductivity of cores of unconsolidated fine-grained earth materials provide reliable or at least useful results.

Fact

Rather sophisticated laboratory analyses of cores from the field site indicate values of hydraulic conductivity that are three to six orders of magnitude smaller than values determined from aquifer tests. Regardless of the care used in sample preparation of the cores for the permeameter tests, the macropores were largely destroyed during packing, which resulted in exceedingly small values of hydraulic conductivity.

This suggests that laboratory analyses of unconsolidated material are, at best, open to serious question. This is of particular concern when the analyses are driven by regulatory controls. It is suggested that far more reliable values can be obtained by conducting aquifer tests, particularly by means of discharging wells. The discharge rate, commonly only 1 to 5 gallons per minute, needs to be merely sufficient to stress the aquifer. The low rate also has the advantage of producing only a meager quantity of water, which in some cases must be drummed or disposed of by some other approved method.

Fiction

Movement of solutes through a fine-grained unsaturated zone is very slow with residence times measured in months or years.

Fact

The rate of movement of chemical constituents through the unsaturated zone depends, at least in part, on the permeability of the materials. The migration commonly is envisioned in a manner similar to an intermittent wetted front moving through the bulk soil matrix (piston flow), in which the residence time may be measured in weeks, months, or even years.

With the exception of a continuous source, it is suspected that leachate movement is not continuous, but rather one that operates as a series of movements in response to changes in soil-moisture content, infiltration, and ground-water recharge. The leaching of a contaminant from the unsaturated zone may require many years, but the mass flow rate is caused by individual, short periods of flushing, each of which removes a small percentage of the remainder. Some preliminary data from oil-field brine disposal pits indicate that the leaching rate is in the vicinity of 10 percent of the remainder per year.

In fine-grained materials, much of the flushing occurs through macropores, in which case the residence time may be measured in minutes, hours, or a day or two. The latter can cause significant but short term changes in ground-water quality during or immediately following a rain, and this phenomenon can have a major impact on the interpretation of chemical analyses of ground-water samples.

As Figure 4 shows, the concentration of nitrate in ground water increased at least fourfold in less than two days following a rain that was immediately preceded by the application of fertilizer. Furthermore, the nitrate concentration decreased approximately fivefold to about half the pre-rain concentration within another two or so days. This event took place in September following a relatively long dry period. A similar event occurred in the following March, when the soil-moisture content was about twice as high as it had been in September (fig. 5). This example illustrates the same time related concentration distribution pattern but with a decrease in concentration with depth.

In both examples, the water table did not rise with the original increase in concentration, implying that the volume of water that infiltrated was relatively small but of high concentration. The subsequent water-table

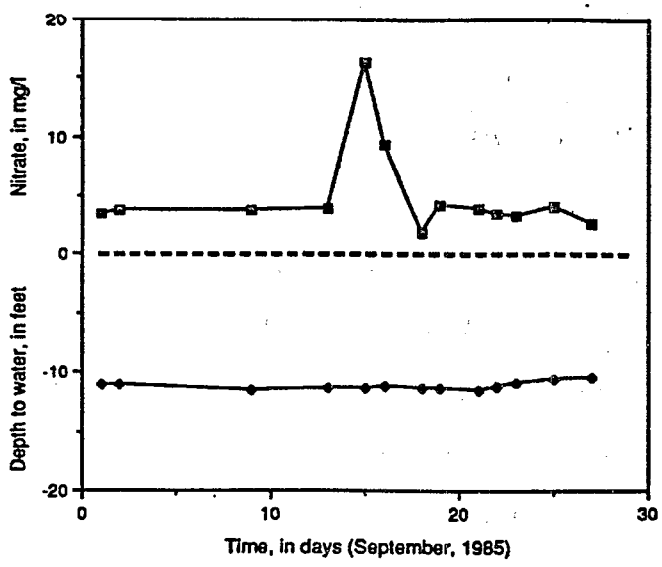

Figure 4. Relation Between Nitrate Concentration and Depth to Water Table.

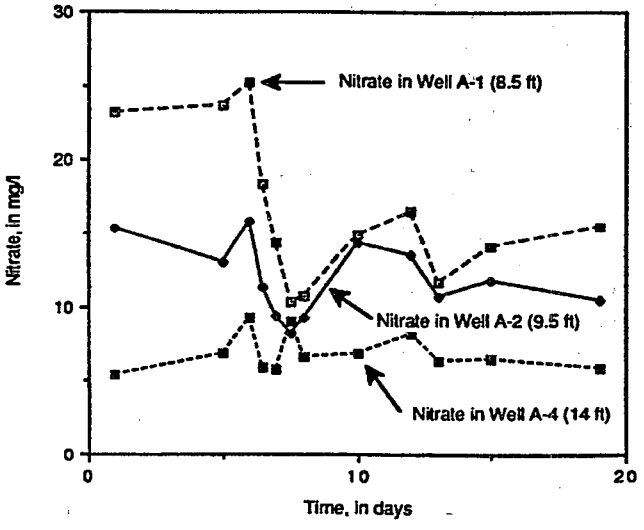

Figure 5. The Concentration of Nitrate Decreased with Depth Following a March Rain on Day Five.

rise, when compared with the concentration decrease, suggests infiltration of a more slowly moving but larger volume of water that was less mineralized.

The implications relative to ground-water monitoring are significant. If the pattern is similar in other geologic terrains, then the concentration in a monitoring well sample is related to well depth, construction, and when the sample was collected with respect to a rain. To determine a generalized background concentration, it would appear that samples should be collected after a week or two of dry weather, but this suggestion should be based on an understanding of the reaction rate of the system. The reaction rate can be determined only by continuous monitoring of the water table, which is best accomplished by pressure transducers/recorders, and by the closely spaced collection of water samples.

Fiction

Ground-water quality is nearly constant, both in space and time.

Fact

The quality of ground water in unstressed, confined aquifers should remain relatively constant, but in shallow or surficial aquifers, the quality can change significantly within a matter of days, hours, or even minutes, as well as throughout the year.

Figure 6 shows the variability of specific conductance throughout a period of several months in a well 14 feet deep. In this case extreme values ranged from about 800 umhos to almost 1175, a difference of nearly 50 percent. Superimposed on the graph of weekly measurements are quarterly samples, which ranged from about 920 to 1075 umhos. This figure clearly illustrates that quarterly measurements do not adequately express the degree or magnitude of variability.

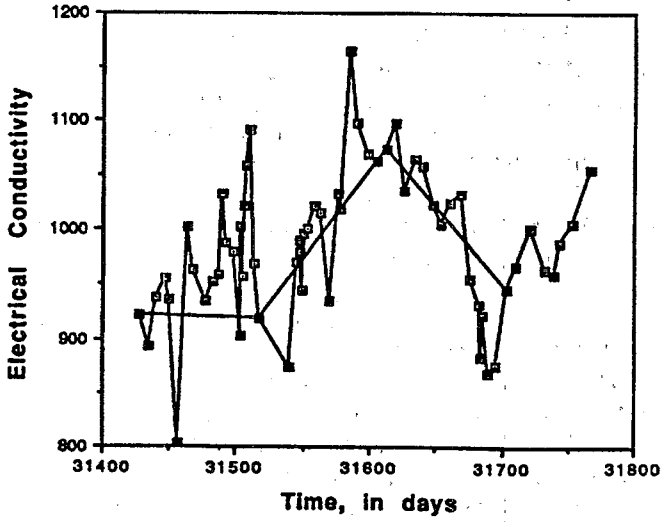

Figure 6. Electrical Conductivity Ranges Widely Throughout the Year, But This Is Not Evident from Quarterly Samples.

Fiction

Electrical conductivity can be used to estimate the concentration of selected chemical constituents.

Fact

Electrical conductivity provides an acceptable measure of the dissolved solids content of a water sample, but it does not allow one to estimate the concentration of minor constituents. Electrical conductivity is strongly influenced by the major chemical constituents, such as calcium, sodium, chloride, sulfate, and bicarbonate. Generally, minor constituents, which normally occur in concentrations less than 10 mg/L, have little impact on the measurement. Figure 7 shows the relation between nitrate and electrical conductivity. In this case nitrate, driven by a rainfall event, decreased with time as the electrical conductivity increased, then tended to follow the same pattern but at a reduced concentration, and finally nitrate began to increase as the electrical conductivity decreased.

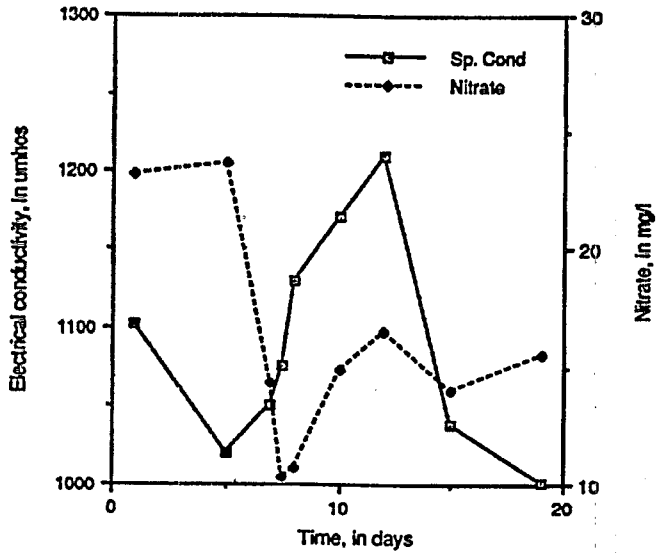

Figure 7. There is No Direct Correlation Between Nitrate and Electrical Conductivity Following a Recharge Event.

Fiction

Nitrate can be used as an indicator of the presence of other agricultural chemicals.

Fact

There is a high probability that a small percentage of fertilizer and other agricultural chemicals in some terrains can travel rapidly to the water table by means of preferred pathways, as previous examples have illustrated. On the other hand, nitrate can have several other sources, none of which are related to agricultural activities.

As one example, in the 1960's several water samples were collected from a shallow private well in North Dakota that tapped a mass of surficial sand and gravel. Livestock were excluded from several acres surrounding the well, the adjacent grasslands were but lightly grazed, and there were no other apparent sources of contamination in the near vicinity. Nonetheless, from one time to the next the nitrate concentration ranged from less than 2 to more than 100 mg/L. The owner noticed a relation between rain and high concentration. In this case the source of the nitrate was the leaching of decaying organic matter that occurs in abundance in the many shallow depressions that dot the land surface.

Fiction

The rise in the water table following a period of rain can be used to estimate the amount of ground-water recharge.

Fact

One approach to calculating ground-water recharge is to multiply the water-table rise by an estimated value of porosity or specific yield. On the other hand, a rain-induced response of the water table in a fine-grained, unconfined aquifer is related to the soil-moisture content and the fillable porosity in the unsaturated zone. Calculated values of fillable porosity at the Oklahoma field site range from less than 10 to as much as 24 percent.

Dry material can absorb substantially more water than can wet material because, in the latter case, part of the storage space is already occupied. The infiltration of one inch of water in a relatively dry unsaturated zone (fillable porosity of 25 percent) results in a water-table rise of about four inches, while the same quantity in a moist situation (fillable porosity of 10 percent) will cause a rise of nearly 10 inches (fig. 8).

Fiction

Cuttings of earth materials penetrated during well drilling provide an accurate representation of subsurface conditions.

Fact

Cuttings from holes drilled by auger, hydraulic rotary, or air provide a good indication of the lithology of

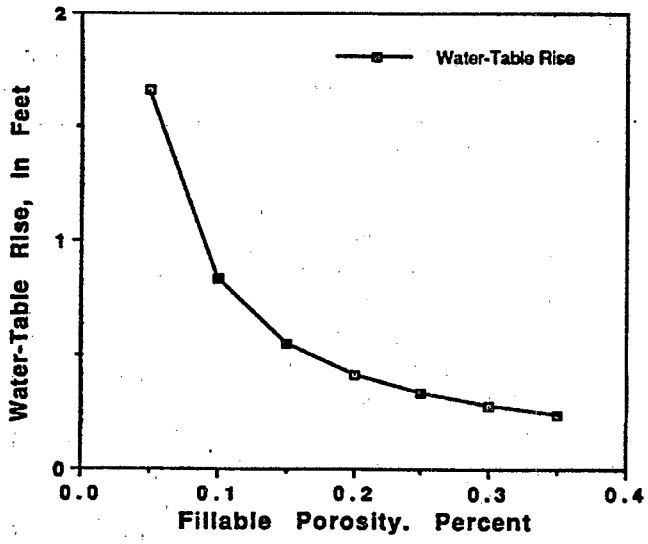

Figure 8. The Amount of Water-Table Rise Due to a Precipitation Event Is Related To Soil Moisture and Fillable Porosity.

the material being penetrated, but they do not furnish adequate information on the rock structure, which may control hydraulic conductivity. Cores impart far more detail than cuttings, but they too can be misleading, partly because the core represents an infinitely small sample of an infinitely large area.

Lithologic logs, based on cores acquired from a hazardous waste disposal site, are shown in Figure 9. The alternating layers of very fine-grained sandstone, siltstone, and mudstone suggest individual water-bearing zones that are separated by confining units. The cores display a few fractures, but presumably not enough to have much influence on hydraulic conductivity.

When the vertical head distribution is examined, however, it becomes clear that the entire upper 50 to 70 feet is so fractured that the entire thickness serves as a single hydrologic unit, regardless of rock type (fig. 10).

Conclusions

The conclusions to be reached from the above described hydrogeologic misconceptions should be quite obvious. The solution, however, boils down to at least two clear facts. First, adequate and long-term monitoring of field sites, representing different geologic conditions, is essential to justifiable interpretations of hydrogeologic data, and to the formulation of regulations and guidance documents. Secondly, results of the field studies must be made readily available to and used by the scientific/regulatory community in order to avoid the entanglements brought about by differences between fiction and fact.

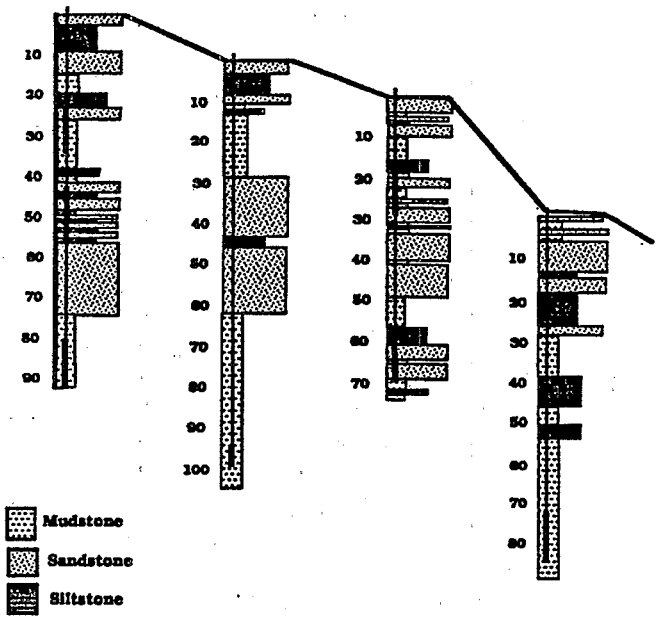

Figure 9. Cuttings and Cores Provide a Good Indication of Lithology but not Necessarily Hydraulic Conductivity.

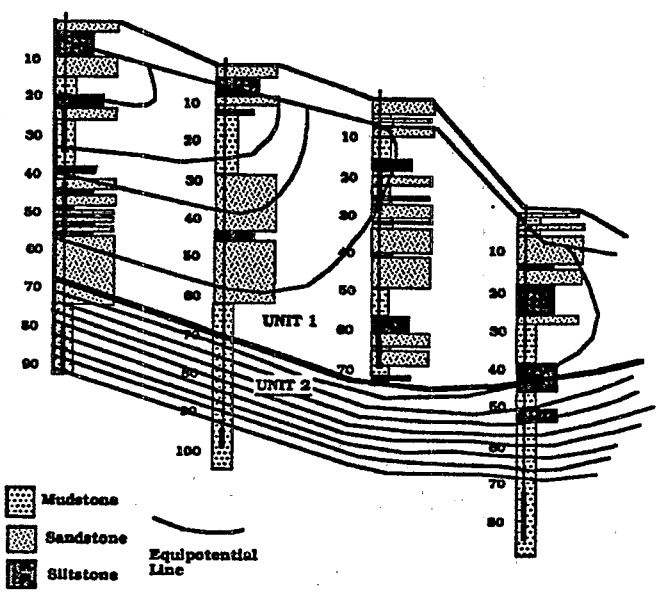

Figure 10. Hydrologic Cross-Sections are Based on the Vertical Distribution of Head and Indicate Zones of High and Low Hydraulic Conductivity.

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Appendix 2-A

Thermal Technology Case Studies

Rotary Kiln Incineration, The Netherlands

PRACTICAL EVALUATION OF A SOIL TREATMENT PLANT

INTRODUCTION

Since 1982 much experience has been gained in The Netherlands with soil cleanup techniques. Thermal and extraction processes in particular have passed the technological development stage and are applied on a large scale for various types of soil contamination.

At present, the government, industry and commerce, and the public need, first of all, information on:

- how to select the most suitable cleanup technique, depending on the type of soil contamination;
- environmental impact assessment and environmental auditing of remedial action technologies; and
- costs.

It is therefore essential to develop a standard methodology by which soil cleanup projects can be evaluated in practice. Within this framework the Ministry of Housing, Physical Planning, and Environment commissioned DHV, Consulting Engineers, in May 1987 to carry out a practical evaluation of a thermal soil treatment plant built by Ecotechniek. The objective of the study was:

- the development of a standard evaluation methodology for soil treatment plants in general, and
- the determination of the environmental aspects of the plant management and the cleanup performance of Ecotechniek's installation in particular.

The study was conducted during the period of August-October 1987.

This paper will discuss in turn:

- the state of the art of contaminated soil treatment in The Netherlands,
- the thermal treatment plant where the study took place,
- the evaluation study carried out, and
- conclusions about the evaluation of soil cleanup techniques.

Emphasis is laid on the framework and the design of the study. Only some of the measured results are presented, to illustrate the monitoring program which was undertaken to determine cleanup performance and emissions into the air.

POLICY ASPECTS OF CONTAMINATED SOIL TREATMENT IN THE NETHERLANDS

A national inventory taken in 1981 revealed that the soil contamination problem in The Netherlands was far greater than was first thought. The survey identified about 4,000 cases of possible soil contamination. However, this figure has since risen to around 7,500. The urgent nature of the soil cleanup operation ensured that the various parties concerned have made haste in looking for solutions. It involved legal, managerial, and financial as well as technical fields. The Soil Cleanup Interim Act came into force in 1983 to create a framework for action. The implementation of the measures stipulated in this Act necessitated, among other things, the rapid development of cleanup techniques. Thanks to the efforts of industry and the incentives policy of the government, the soil treatment capacity available in The Netherlands has increased from nil to about 400,000 metric tons a year in the past 6 years. There is, moreover, a considerable reserve capacity. Table 1 gives a summary of the processing capacity available in The Netherlands. A review and a description of the techniques are given in references 6 and 7.

Six years after its start, the soil cleanup operation has entered a new phase in which, in addition to the optimization of techniques, increasing attention is also being paid to the evaluation of these techniques and the remedial action solutions chosen. The objective of this evaluation is to point the direction in which solutions for observed bottlenecks should be sought. At the same time, the aim is to arrive at a more standardized approach to the treatment of contaminated soil and the qualitative management of soil flows.

It has become clear from the bottlenecks observed during the past year that in the methodological and technical fields the following aspects demand attention:

- a better definition of cleanup criteria;
- reuse, applicability of cleaned soil;
- layout and management of temporary storage sites; and
- streamlining of the supply and demand of contaminated soil.

Work on this is in progress at various levels and in several quarters. The activities that have been or will be carried out within this framework include:

- research into the leaching behavior of contaminants, among other things, for the purpose of standardization in reusing cleaned soil;
- setting-up a Service Centre for Contaminated Soil Treatment, a national management organization which will occupy a central position in redirecting soil flow resulting from the soil treatment operation. This organization will act as a coordinating point between suppliers and customers of contaminated and cleaned soil (ref. 2);
- the establishment of a testing procedure for cleaned soil, included in a standard specification for contaminated soil treatment (ref. 4); and

Table 1. Summary of Processing Capacity for Contaminated Soil Treatment in The Netherlands (ref. 2)

Company	Location	Type of Process	Capacity* in Metric Ton/Year**
Broerius	Voorthuizen	thermal, <400°C	25,000
ATM	Moerdijk	thermal, <800°C	60,000
Ecotechniek I	Utrecht	thermal, <800°C	55,000
Ecotechniek II	Rotterdam	thermal, <800°C	50,000
NBM	Schiedam	thermal, <800°C	40,000
BSN	Mobile	high pressure fraction	25,000
Heidemij	Den Bosch	flotation	34,000
Heijmans	Rosmalen	extraction	14,000
HWZ	Amsterdam	extraction	27,000
Mosmans	Mobile	flotation	8,000

* approximately, based upon 8h/day.

**$1m^3$ - 1.7 metric tons.

- drawing up the so-called provisional practical guidelines on sampling and analysis in soil contamination research (ref. 5).

In summary, it can be said that in The Netherlands, the soil cleanup policy pursued aims increasingly at the total environmental health and qualitative management of the soil flows released during soil treatment. Its background is the soil protection policy which has been taking shape since the Soil Protection Act came into force early in 1987. From 1988 on this Act will also regulate the soil cleanup operation.

A BRIEF DESCRIPTION OF THE ECOTECHNIEK SOIL TREATMENT PLANT

At the moment Ecotechniek has two thermal soil treatment plants in operation. One of these has been in Utrecht (the middle of the Netherlands) since 1982, and the other one has been operational in the greater Rotterdam area since early 1987.

The evaluation study described here concerns the latter installation, which has a maximum treatment capacity of 50 metric tons per hour. Figure 1 shows the process scheme of the plant.

The contaminated soil is treated in the rotary kiln by direct heating at a temperature of up to 550°C with a residence time of about 7-15 minutes. The resulting vapors are afterburned at a temperature of 850-1,000°C and a residence time of 1-2 seconds. The afterburner limits the emission of hydrocarbons, CO, and HCN. Heat exchangers permit the reuse of the energy released. Further measures to limit emission include a wet scrubber (SO_2) and a fabric filter (dust). The wash water from the wet scrubber is cleaned and partly recycled for cooling the cleaned soil.

The process is suitable for the removal of aromatic and aliphatic hydrocarbons (up to 10,000 mg/kg), cyanides (up to 400 mg/kg), and polynuclear aromatic hydrocarbons (PAHs) (up to 800 mg/kg).

To date, much experience has been gained for the treatment of contaminated soil from former gasworks sites and soil contaminated by leaking fuel tanks. A trial cleanup of soil contaminated with chlorinated hydrocarbons is planned for the end of 1987.

The installation is suitable for all types of soil. It is especially the moisture content, the organically-bound nitrogen and sulfur content of the soil, and the type of contamination that influence the costs. These vary between Dfl 100 and Dfl 190 per metric ton (One Dfl is approximately U.S. $0.5, October 1987).

EVALUATION STUDY

General

In 1985, The Netherlands Organization for Applied Scientific Research (TNO), commissioned by the consultative group on soil treatment of government and industry, developed a preliminary scheme for a standard evaluation methodlogy for soil cleanup techniques (ref. 1). It comprises two phases:

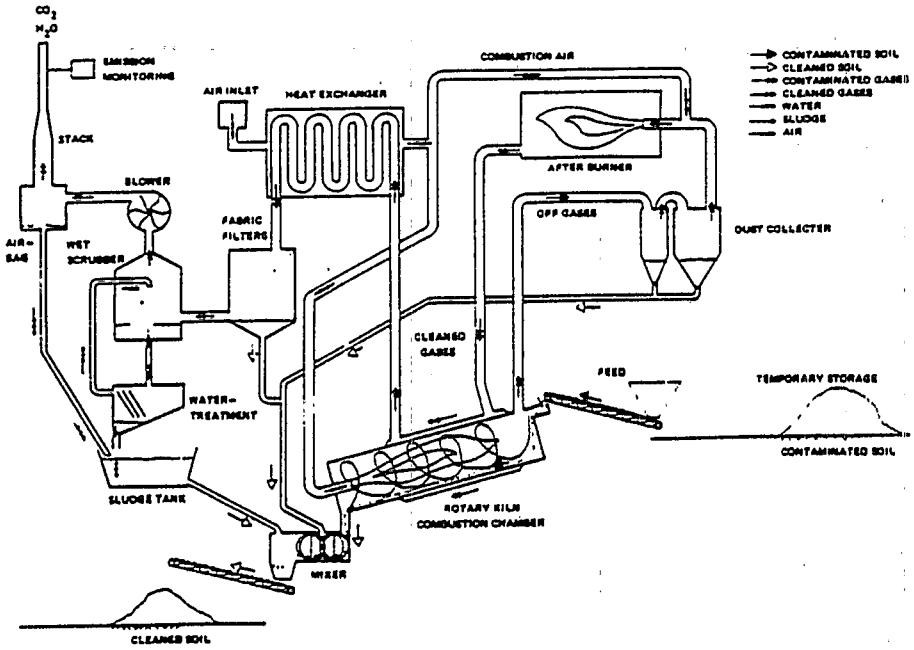

Figure 1. Process Scheme for the Ecotechniek Thermal Soil Treatment Plant

- an individual evaluation of actual cases, focusing on cleanup performance, environmental health and safety aspects, and costs, the results of which are to be summarized in public information papers; and

- an integral evaluation to be conducted once every 1-2 years by a central independent body, comparing the various cleanup techniques with each other.

It was recommended that the proposed scheme be tested in practice, the main focus of attention being:

- sampling and analytical techniques for soil and air emissions;

- the way in which the quality of the cleaned soil should be assessed; and

- the way in which reliable information can be obtained about the general procedure during the evaluation of the individual cases.

However, further development of the provisional scheme for a standard methodology was hampered by a variety of factors. At the beginning of 1985 relatively little experience had yet been gained from the treatment of contaminated soil on a practical scale, and it concerned thermal techniques only. The proposed testing procedure for cleaned soil met with both practical and financial objections by the contaminated soil treatment companies. Furthermore, there was as yet no clarity about the requirements to be set for cleaned soil. A number of matters has meanwhile contributed to the fact that by mid-1987 the time was considered ripe for resuming the development of a standard evaluation methodology. They were:

- the policy development outlined previously, aimed at an integral environmental hygienic and qualitative management of the soil flows;

- the greatly increased practical experience gained with various types of cleanup techniques, because in the Dutch soil cleanup operation the emphasis shifted from investigation and risk assessment to remedial action;

- the more favorable market prospects for the contaminated soil treatment industry; and

- the increased interest of government and industry in Environmental Auditing, resulting in pilot projects launched in 1986 in several industries.

A thermal treatment plant of Ecotechniek was chosen for the evaluation study, since most practical experience had been acquired with this technique and by this company. The two main parts of the study will be discussed below in turn, i.e., the measurement of the cleanup performance and the Environmental Audit.

Study of Cleanup Performance

Study design

The study focused on the treatment of two types of contaminated soil under practical circumstances. The two lots of soil can be characterized as follows:

- "easy to clean": sandy soil, chiefly contaminated with cyanides and polynuclear aromatic hydrocarbons (PAHs), derived from a former gasworks site; and
- "difficult to clean": clayish soil with rubble, chiefly contaminated with PAHs and mineral oil, derived from a site where various wastes had been dumped.

The study comprised:

- the determination of performance and residual concentrations during the cleanup of the soil; and
- the measurement of air emissions during the treatment.

The treatment was carried out under the normal conditions considered optimal by the company. The average processing capacity was approximately 40 metric tons per hour. The volume of the lots of soil investigated amounted to 400-600 metric tons each. The net sampling time was 9 hours for each lot.

Before treatment began the average composition of both lots of soil was determined by sampling and analysis of three mixed samples per lot. The parameters investigated were dry residue, organic matter content, grain-size distribution, cyanides (total and free), PAHs (U.S. Environmental Protection Agency (EPA) priority list), and volatile aromatics.

During the treatment a 1 kg sample of the outgoing cleaned soil was taken every 9 minutes during the net sampling period of 9 hours. A total of 60 samples was thus collected per lot. Next, the testing procedure prescribed in The Netherlands was applied in the selection of the samples to be analyzed (ref 4). This will be discussed in more detail in the next section, "Testing procedure of cleaned soil."

Parallel to this, the ingoing soil was sampled in the same way. Taking the average residence time of the soil in the treatment plant into account, 20 samples of ingoing soil corresponding to those samples of outgoing soil selected for chemical analysis were chosen. From these, 10 samples were chosen at random for chemical analysis. For financial reasons the number of samples of ingoing soil to be analyzed was kept as low as possible. The reason is that in practice the residual concentration in the cleaned soil is the main assessment criterion and to a lesser extent the cleanup performance.

The dry residue, the PAHs, and cyanide or mineral oil contents were determined in the samples of in- and outgoing soil. In addition, a mixed sample was composed of the 20 selected samples of cleaned soil, for supplementary investigation of several parameters that play a role in the possible uses and sales potential of this material, such as leaching behavior and ecological integration.

Storage, preservation, and chemical analyses were carried out in accordance with the provisional practical guidelines on sampling and chemical analysis in research on soil contamination (ref. 5).

Testing procedure of cleaned soil

Testing of the cleaned soil took place according to the standard procedure developed in The Netherlands for this purpose (ref. 4). The procedure for "once-only" lots of soil, not greater than 2,000 metric tons, was applied. Another procedure is applicable to larger lots, in which an initial sublot of between 500 and 2,000 metric tons is intensively analyzed. If the results of the first test are favorable, the following sublots are subsequently tested increasingly less exhaustively.

The testing procedure used here for "once-only" small lots is multi-stage, that is, in the first instance the residual concentration is deterined in 20 of the 60 samples of the outgoing soil. Next, depending on the results, another 20 samples or, finally, all 60 samples are included in the test. The calculated mean value of the residual concentration and its standard deviation are examined. The maximally permissible value for the estimated standard deviation (Se) is determined on the basis of the requirements set for the residual concentration:

$Se = (y-x)/2.39$
in which x and y are test requirements regarding the residual concentration:
x = mean value
y = 99th percentile

For the first stage of the testing procedure, the lot of soil is passed if:

- the calculated value $m_{20} \leq 0.8\ x$
- the calculated standard deviation $S_{20} \leq 0.5\ Se$

If this is not the case, then the number of observations is increased by selecting at random another 20 samples from the remaining 40 and determining the residual concentration in those. In the second stage the lot of soil is passed if:

$m_{40} \leq 0.9\ x$

$S_{40} \leq 0.65\ Se$

If necessary, all 60 samples may finally be tested, with as a requirement:

$m_{60} \leq x$

$S_{60} \leq Se$

The sampling procedure used here for in- and outgoing soil during the investigation can be represented schematically as shown in Figure 2.

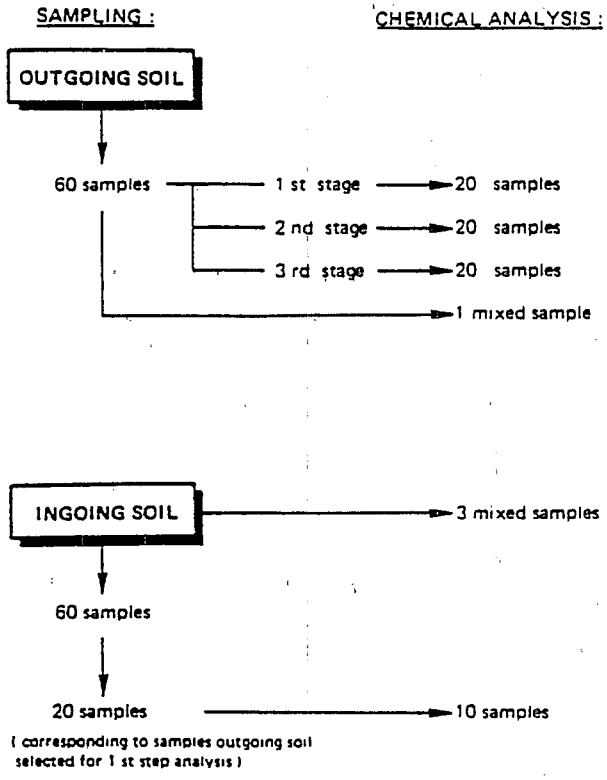

Figure 2. Sampling and Analysis Procedure

Air pollution monitoring

Hydrocarbons, SO_2, NO_x, fluorine, chlorine, and HCN in the waste gases were measured continuously by Ecotechniek, as a standard procedure. To supplement this, during the sampling period DHV measured dust, O_2, CO_2, CO, SO_2, fluorine, chlorine, mercury, HCN, volatile aromatic hydrocarbons, nitrous oxides, and hydrocarbons. PAHs and heavy metals were determined in a few dust samples.

Results

Cleanup performance

The principal process conditions during the treatment were:

	Soil From	
	Gasworks Site	Dump Site
Rotary kiln temperature (°C)		
.range	510–570	430–570
.average	540	510
Afterburner temperature (°C)	925	850

The requirements laid down in the specifications of the soil cleanup projects from which the lots of soil were derived, were:

	Mean Value (mg/kg d.wt.)	99th Percentile (mg/kg d.wt.)
Gasworks Site		
.cyanide (total)	10	20
.vol. aromatic hydroc.	0.1	2
.PAHs (Borneff)	20	-
Dump Site		
.PAHs (EPA priority list, individual)	0.1	0.3
.benzo(a)pyrene	0.05	0.15
.PAHs (EPA, total)	1	3
.mineral oil	100	200

Some of the results are summarized in Tables 2 and 3.

Table 2. Results of Treatment of Soil From a Gasworks Site

Soil from Gasworks Site (sandy soil)

Analyses	Ingoing n = 10	Outgoing n = 20	Requirements (mean)	Removal (%)	Results Testing Mean n = 20	Procedure For Standard Deviation s = 20
Moisture %	17.5	12.4				
Organic matter %	5.1	2.7				
PAHs (mg/kg.d.wt.)						
fenanthrene	5.41	0.07		98.8		
anthracene	1.13	0.10		91.5		
fluoranthene	8.73	0.08		99.1		
pyrene	8.45	<0.01		98.8		
benzo(a)pyrene	4.02	0.04		98.9		
total Borneff (6)	33.2	0.5	20	98.0	accepted	
total EPA-priority list (16)	133.04	4.88				
Cyanide (total) (mg/kg.d.wt.)	82	1.2	5	98.5	accepted	rejected
Volatile aromatic hydrocarbons (mg/kg.d.wt.)						
benzene	0.03	0.04				
toluene	0.03	0.03				
xylene	0.04	0.01				
Heavy metals (mg/kg.d.wt.)						
chrome	<20	<20				
copper	24	28				
zinc	110	130				
nickel	<20	<20				
cadmium	<20	<20				
lead	197	410				
mercury	<20	<20				
arsenic	<50	<50				

Table 3. Results of Treatment of Soil From a Waste Dump Site

Soil from Waste Dump Site
(clayish soil with rubble)

Analyses	Ingoing n = 10	Outgoing n = 20	Requirements (mean)	Removal (%)	Results Testing Mean n = 20	Procedure For Standard Deviation s = 20
Moisture %	21.1	11.1				
Organic matter %	8.4	5.0				
PAHs (mg/kg.d.wt.)						
fenanthrene	13.43	0.22	0.1	98.4	rejected	rejected
anthracene	1.65	0.03	0.1	98.5	accepted	accepted
fluoranthene	3.58	0.11	0.1	96.9	rejected	rejected
pyrene	3.70	<0.01	0.1	97.3	rejected	accepted
benzo(a)pyrene	1.09	0.05	0.05	95.5	rejected	rejected
total EPA-priority list (16)	76.91	1.86	1	97.0	rejected	accepted
Mineral oil (mg/kg.d.wt.)	2,602	10	100	99.5	accepted	accepted
Volatile aromatic hydrocarbons (mg/kg.d.wt.)						
benzene	0.03	0.06				
toluene	0.01	0.03				
xylene	0.03	0.02				
Heavy metals (mg/kg.d.wt.)						
chrome	24	28				
copper	36	42				
zinc	197	200				
nickel	<20	<20				
cadmium	<20	<20				
lead	110	140				
mercury	<20	<20				
arsenic	<50	<50				

The results show that removal rates above 95 percent were achieved for both lots of soil. Residual concentrations of mineral oil and cyanides amply meet the requirements. For some of the PAHs, the requirements were not met by soil originating from the dump site. In the case of the gasworks soil, higher residual concentrations of (Borneff) PAHs were allowed. As expected no removal of heavy metals took place. The testing procedure for cleaned soil (first stage: analysis of 20 samples) resulted in the rejection of the lot of soil from the dump site. Neither for the mean value nor for the standard deviation were the (quite strict) requirements met with regard to various PAHs. Although the mean value of the concentration of mineral oil was far below the required value, the requirement set for the standard deviation could not be met. This was due to one single value just above the required mean together with 18 values far below. This shows that the requirements for the standard deviation may need some adaptation in order to avoid this kind of illogical result.

Air pollution

Some of the main results are presented in Table 4.

These results show that the requirements set for emissions into the air were met during the treatment of both lots of soil.

ENVIRONMENTAL AUDIT

General

The limited audit conducted for this evaluation study fits into the framework of a number of pilot projects being implemented by order of the Ministry of Housing, Physical Planning, and Environment. The objective of these pilot projects is to explore the possibilities for setting up an environmental protection system in various industries. An environmental audit is an examination of the quality of plant management in the field of environmental protection. An audit can only succeed when it has the express support of the management of the company in question. It should be convinced of the value of the audit for its own company, and where it concerns a pilot project, as is the case here, for the entire branch of industry. All relevant information sources should be placed at the auditor's disposal. The necessary cooperation is also required of the personnel, who must be informed about the objective and the operating procedure.

The objective of the audit conducted at the thermal soil treatment plant of Ecotechniek was:

- to gain an insight into the way in which the company meets the environmental requirements set by the authorities; and
- to investigate whether the management of the plant, both from a technical and an organizational viewpoint, is geared to implementing its own corporate policy, its own corporate rules regarding the environment, and the regulations laid down by the government.

Table 4. Results of Air Pollution Monitoring

	Measured Value ($mg/m^{3}*$)	Requirement ($mg/m^{3}*$)
SO2	120-180	200
Dust	1-24	75
Cadmium (in dust)	0.02-0.03	0.1
Mercury (in dust)	0.006-0.0	0.1
PAHs (in dust)	n.d.	0.002
Volatile aromatic hydrocarbons	n.d.	5
Chlorine	<3	75
Fluorine	<0.3	5
HCN	2.4-3.3	10
Flow ($m^{3}*/h$)	31.000	38.000

n.d. = not detectable.
* = dry gas, temp. 273 K, press. 101.3 kPa.

The audit program focused on the following environmental aspects:

- acceptance of contaminated soil
- solid wastes
- emissions into air and soil
- waste water
- external safety

Noise, vibrations, and other nuisances, such as attracting traffic and vermin were not taken into account, because of the plant's location in an industrial area, adjoining a far bigger solid waste incineration plant.

Design of the Audit

The audit was conducted in three phases:

- pre-audit activities
- audit visits
- reporting

The pre-audit activities included:

- determining the required industrial information to be provided by Ecotechniek;
- studying the industrial information, the environmental licenses in force, and the other internal and external environmental regulations;
- drawing up the audit plan;
- discussing the plan thoroughly with the management; and
- holding an information meeting for the personnel of the plant.

During the audit visits, the audit was conducted on the spot in accordance with the plan drawn up. The examination concentrated on both organizational aspects and the operation and maintenance of the plant. The efficiency of the plant management was examined with regard to:

- prevention (maintenance, tests, registrations, internal control, environmental provisions, safety systems); and
- repression (fire extinguishers, scenarios, internal and external alarm systems, handling of complaints).

The information gathered during the audit was evaluated according to the following criteria:

- o environmental requirements set by the local authorities and the government (Nuisance Control Act, Surface Water Contamination Act, Chemical Wastes Act);
- o corporate policy regarding the environment and safety;
- o controlability of the activities at the plant; and
- o involvement of the personnel of the plant with the environmental policy of the company.

No measurements were made as part of the audit. A summary of the audit, intended for external use, will form part of the final report of the evaluation study. In addition, a more detailed report will be prepared, which will be confidential and available to the management only.

Results of the audit

The audit was effectuated with the full cooperation of the management and the personnel of the plant. During the collection of information and the audits visits, no problems had to be faced. The audit will result in recommendations to the Ecotechniek management with regard to environmental and safety policy. Recommendations to the ministry will refer to the setting up of an environmental protection system for the soil treatment branch of the industry especially.

CONCLUSIONS

Some of the main conclusions of the evaluation study are as follows:

- o The integral approach, combining the measurement of treatment performance and emissions with an environmental audit provides a valuable tool to assess a soil treatment process. The quality of the management of the plant in the fields of environment and safety strongly influences the cleanup performance and the reliability of the treatment plant process.
- o It would be desirable to determine uniform cleanup criteria based upon residual concentrations for those substances representative of the main contaminants which are present. Especially in the case of PAHs, a variety of requirements are laid down by the authorities (e.g., for total EPA-priority list PAHs, different individual PAHs, as well as total Borneff-group PAHs).
- o The standard testing procedure for cleaned soil which is used in The Netherlands may need some modification with regard to the requirements set for the standard deviation of the measured values.
- o The thermal treatment plant that was the subject of this study performed well with respect to cleanup results and emissions into the air during the treatment of both lots of soil. This shows that thermal treatment is a suitable process for the cleanup of similar contaminants and concentration ranges and for different types of soil varying from sand to clayish soils.

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Appendix 2-B

Thermal Technology Case Studies

Indirect Heating in a Rotary Kiln, Germany

Experience with the Decontamination of the Königsborn Coke-Oven Plant Site using a Pyrolysis Plant

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Under a research and development project support by the Federal Ministry for Research and Technology of the Federal Republic of Germany Ruhrkohle Westfalen AG operates a pyrolysis plant to contaminate a site of a former coke-oven plant decontaminated with hydrocarbons. The plant was erected on the site of Königsborn 3/4 coke-oven plant in Bönen (district of Unna), which was closed-down in 1977, by Deutsche Babcock Anlagen AG following detailed planning according to a Ruhrkohle AG concept and a simplified approval procedure possible on the basis of the Federal Act on Emission Control for such test plants in 1987/88. The initial approval for a test plant has, in the meantime, been replaced by a site-specific permanent approval following a procedure involving the general public. So far, some 85.000 t of soil have been treated.

The pyrolysis method was selected for this decontamination project because Ruhrkohle AG disposes of corresponding expert knowledge from coke-oven technology and the process moreover offers the possibility to dispense with the secondary treatment of the pure heating gases and the fire-resistant lining of the pyrolysis or carbonisation chamber. As the soil is not heated to the temperature required for complete pollutant destruction it does not ceramilize during the treatment and is not dead but only biologically inactive. The R&D-project will be terminated at the end of this year. The plant will continue its operation at this site. At the same time it will be investigated at which site the chamber may be used afterwards.

Plant Set-Up and Operation

The plant (fig. 1) is designed for a materials' throughput of 7 t/h with a soil humidity of up to 21 % and a volatile pollutant content of max. 5 %. It operates as follows: the material to be treated undergoes a preparation with crusher, overbelt magnets and screening plant in which the permissible maximum grain size is limited to 50 mm. Preliminary tests showed that smaller mesh sizes cannot be used because of the soil's structure which is in some cases characterized by high clay contents. Thus also the possible purification successes can only be utilized to a limited extent even if the crushing work is intensified. The treated material is supplied to a feed bunker with a downstream twin feed screw delivering to the alloyed steel rotary tube with a length of some 26 m, of which 20.6 m are indirectly heated, and a diameter of 2.2 m. The rotary tube rotates with an infinitely adjustable speed of up to 2.5 rpm. Staggered lifting rails transport the material through the rotary kiln in 1 to 1½ h. The permanently filled feed screw seals the entire rotary tube including the downstream system in such a way that a negative pressure of approx. 1.5 mbar generated by a fan operated at the end of the overall plant can be maintained to avoid the escape of both dust and pyrolysis gas. The plant is heated by means of 18 natural gas-fired burners distributed over 3 zones. They heat the kiln to a wall temperature of 600 to 650° C so that a lining is not required in the kiln. The observance of this maximum temperature is guaranteed by a limit switch reacting to the thermal elongation of the rotary kiln. Given an adequate residence time this temperature is sufficient to remove the soil humidity first and then the noxious PAH's mentioned in the EPA list which was selected as assessment criterium after consultations with the approving authority and the involved expert institutions (fig. 2). In this procedure the ring-

shaped polycyclic aromatics decompose almost completely into aromatic chain compounds (fig. 3). The decontaminated soil falls into a discharge chamber with a screening screw arranged below separating the material into the grain sizes > 10 mm and < 10 mm. The coarse grain size is supplied to a wet ash remover where it is cooled- down in a water bath to a temperature suitable for the safe further handling and transported to an interim storage bunker using a scraper conveyor. The fine grain size, which cannot be cooled directly in the water because of the complexe slurry treatment this would entrain, is supplied via a cooling screw system to an interim bunker where it is humidified and cooled-down further by adding water.

The pyrolysis gas is extracted at the top of the discharge chamber and supplied from below to the neighbouring post-combustion chamber with fire-resistant lining, in which 3 natural gas-fired burners are used for supporting firing and guarantee a temperature for a reliable combustion of the pyrolysis gases flowing through here for approx. 3 s to CO_2 and other harmless components (fig. 4). Because of the generally high water vapour content an autothermal post-combustion process could not be implemented so far. During the "test approval time" the post-combustion chamber was operated at a temperature of at least 1.000° C, in presence of chlorine above pre-defined limits also at a temperature of some 1.250° C, to guarantee the distruction of possible dioxines. Subsequently, the gases are channeled down a cooling tower (quenching) after fresh air addition with approx. 850° C where they are cooled-down to a temperature of 160° C to 190° C at an hourly water addition of up to 3.6 m^3 in short time, i.e. at approx. 1.7 s residence time. Behind the cooling tower slaked lime is injected into the flue gas stream which binds also pollutant gases, in particular SO_2 or fluorine, on the surfaces of the downstream "system Beth" filter system with 196

filter hoses corresponding to a filter area of 216 m^2 to separate entrained dust by reaction. The filter system guarantees the observance of the values defined by the technical instruction for air pollution control still effective until the end of 1992 in the outlet air. Together with the heating gases of the rotary kiln which are re-used in a heat exchanger to heat the combustion air to approx. 350° C the burned gases are vented into the environment via a stack.

In May 1988 the plant was heated for the first time and initially supplied with weakly contaminated material to test the mechanical components. After removing the deficiencies established in this context almost completely and after finalizing the measurements for a continous operation defined in the approval certificate through the "Technische Überwachungsverein (TÜV)" the test operation could be started. Initially, a two-shift operation per working day (6.00 - 22.00) and from mid August 1989 a three-shift operation had been approved. With the granting of the permanent approval time-related operating restrictions became ineffective.

Technical Aspects and Modifications

The preparation plant is so efficient that the material for a three-shift operation can be prepared in one shift. Only for the removal of all iron parts a second magnet had to be retrofitted. Additional tests and modifications related to different screen covers. Here the retrofitting to rubberized screen covers is worth mentioning in particular. They were used in tests to throughput smaller grain sizes than 50 mm but also to reduce noise emissions.

Initially, non-removed iron parts caused failures at the feed screws in the feed system. Moreover, additional failures and observations showed that also

the screws need to be wear-resistant and made of a specially hardened material. On the Königsborn site to be treated matter which act very corrosively on the screws is contained in the crushed material of former buildings and foundations in addition to the clay parts in the soil. Also for the discharge screws which in some cases lacked the lubricating properties of the soil humidity very short service lifes of only a few weeks were established initially. By means of special build-up welding the service lifes of all screws could be extended to several months.

In serveral inspections of the rotary tube connected with wall thickness measurements signifcant damages or changes could not yet be stated. In contrast one of the two compensators sealing the rotary tube against the environment at the feed and discharge openings had to be replaced because it had come defective as a result of frequent flexing work when heating-up and cooling-down during the regular two-shift operating phase.

In the post-combustion chamber modifications were required to provide for the execution of reliable temperature measurements. The residual dust quantities contained in the pyrolysis gas ceramalized on the temperature sensors and caused errornous measurements. Protective stones above the elements led to a significant improvement here. Another modification had to be effected in the cooling tower. It was only after installing additional guiding plates that it became possible to design the water addition in such a way that an optimal cooling effect could be reached and that the water used to this end was distributed also uniformly over the entire cross-section and thus in the full gas stream and not spotwise at individual wall zones.

At the connecting pipe between combustion chamber and cooling tower a flap is installed which is used as stack when starting-up the plant from the cold condition. Moreover, it acts as a safety device in form of a pressure relief valve. It is used for example if as a result of a failure in the cooling water addition hot gases with excessive temperatures reach the filter system and the filter bags may be destroyed by heat. In individual opening procedures also burned-out red fly ash deposited under the flap or in the pipeline escaped leading to irritation and protests in the public. To avoid repetitions compressed air pulse units known as "Big Blasters" were arranged at the outlet of the combustion chamber and below the flap (fig. 5) removing such dust depositions through regular operation and providing for a dust-free "opening" of the flap.

The filter systems with the glass fiber tissue filter bags met, with regard towards the dust emissions, the requirements of the "TA-Luft" effective at the date of plant construction. It does, however, not observe the limits of the 17th Federal Ordinance on air pollution control and noise abatement (BImSch VO) effective from 1993 onwards. In coordination with the plant manufacturer the old filter bags were therefore replaced by bags made of needle felt textile fibers. The subsequent emission measurements of "TÜV" confirmed that the former dust emissions could be reduced by some 90 % to less than 2 mg/m^3 and thus far below the future limit.

Thanks to the new filters it was also possible to replace the lime with a surface of approx. 17 m^2/g used so far by a more fine grained lime with a surface of approx. 36 m^2/g. This also improved the binding capacity for SO_2 and other pollutants.

Particular attention was given to the insulation of the noise emittors established in noise measurements. As an

upper noise limit of 40 dBA in the neighbouring residantial area was set for the night operation both different electric motors and the fan station had to be specially encapsulated. As a result of these measures it was possible to observe the required limits at the nearest houses - about a 100 m away from the plant - with unbuilt space in between. All listed improvements contributed to an increase in plant availability from some 75 % in the second half of 1988 to 95 % in the first half of 1989. This availability could also be achieved in the first quarter of the three-shift operation given good scheduled plant maintenance. A subsequent availability decrease to some 90 % today (fig. 6) can be explained exclusively by the unexpected high sulphur concentrations in the feed material for which the filter system without flue gas scrubber is not designed. Without this limiting factor a continued utilization of 95 % would be possible.

Available Operating Experience

Soil Excavation and Preparation

Almost 7 ha of the more than 16 ha site of Königsborn 3/4 are contaminated and need to be treated or secured in another form corresponding to the agreement between the owner and the municipality and the stipulations of the terminating operations approval procedure required under the mining law. In test drillings the contaminations were proven down to a depth averaging 2 to 3 m, in individual cases pollutants had also been found in 8 m and in one case even in 18 m depth. So far, 3 part areas were excavated completely, another 2 partly. The excavated material has undergone comprehensive treatment and, in some cases, was re-installed after cleaning.

The material is excavated by using an excavator applying the undercut method (fig. 7). The excavator is located at the upper edge of the excavation and loads the soil from the pit upwards onto a truck. In general, the personnel does not have to work in the pit and is thus also not exposed to the emitted volatile pollutants. Check measurements of the industrial hygiene agency and of an independent expert at the mentioned working places showed values in the inhaled air which range far below the MAC or TRK values. Only for napthalene the olfactory threshold is occassionally exceeded leading to initial irretations amongst observers from a general public which could, however, be removed (fig. 8).

Additional measurements were taken in the preparation area. The air measurements also produced positive data. In one case - in particularly dry weather - the dust measurements led to the recommendation to employ the operators mainly on the windward side, which does not cause any major difficulties because of the plant design. Moreover, suitable labour protection devices are available.

Rotary Kiln Operation

The two-shift operation turned out to be unfavourable for the plant. In numerous measuring series taken by the Institute for Thermal Process Technology of Dortmund university accompanying the R&D project it could be proven that an instable state for about 2 to 3 hours was created with each daily plant start-up (fig. 9). During this time the desired temperatures in the soil could presumably not be reached completely as the heat content of the already heated soil was lacking in the rotary tube. Independently from this it has to be noted that the regular start-up and shut-down - the kiln was operated at reduced capacity during the nights

at a temperature of approx. 350° C and the combustion chamber at approx. 800 to 850° C - resulted in an immense waste of energy and thus increased the process costs. Another negative observation was the freezing up of the gas pipe during a frost period after the burner at the rotary kiln had been switched off during night-time. A retrofitted insulation of the pipe removed this failure source. For the normal continous operation the Insitute for Thermal Process Technology of Dortmund university has established that, at the rotary tube, only 0.8 % of the energy in use is consumed for degasification, more than 60 % for water evaporation and almost 40 % for the heating of the inert soil (fig. 10).

The three-shift operation significantly improved the operating sequence and helped to reduce failures and to improve the operating sequences. To this end, however, a scheduled and adequate maintenance at work-free days is required.

Operating Results

The Institute for Thermal Process Technology of Dortmund university has set up a targeted examination programme and collected the data of this test programme in a computer. Data were also evaluated in some cases. So far, the following results are available:
Figure 11 shows the relation between natural gas consumption and soil throughput. The tests were run at soil humidities of 12 to 13 % with throughputs of 3.8 to 11.3 t/h. At the last mentioned feed quantity, however, the measurements had to be terminated prematurely because the cooling capacity of the discharge device was insufficient. However, the data show clearly that the specific gas consumption decreases with increasing throughput. A quantity of 25

to 30 m^3 STP per tonne of soil should be permanently required for this plant size.

The soil residence time in the rotary tube is mainly governed by the speed. Figure 12 shows how the residence time of the material in the kiln extent's with reduced speed. Normally the filling rate of the kiln ranges around 7 to 8 %. The graphs in figure 13 show the relation to the residence time and the hourly throughput. The extreme values at high filling rates are only theoretically calculated graphs as the rotary tube structure is only designed for a filling of max. 22 t.

The specific natural gas consumption was also established for the post-combustion chamber under consideration of different parameters (fig. 14). As the water content of the soil normally amounts to 10 %, often even 15 %, this straight line shows that an autothermal operation, i.e. a combustion resulting from the own energy potential of the pyrolysis gas, is not possible in general. If, in particular, the combustion temperature has to be increased to more than 1.200° C because of the presence of PCB or Cl a considerable natural gas quantity is required for supporting firing. However, the figure also shows that a reduction of the water content in the feed material may lead to significant energy savings, in particular if also the consequent savings resulting from the heating of the soil in the rotary tube are considered. The diagramme in figure 15 illustrates how the gas requirement of the supporting gas firing may vary according to the pollutant content, in this case by some 20 %.

In normal operation, i.e. as soon as the plant has been started up and left the heating-up phase completely, satisfying cleaning results are obtained. The PAHs are decomposed almost completely, i.e. to below the B value of the Holland list, often even below their A values

given an adequate residence time in the rotary kiln. If the soil discharge temperature is reduced by shortening the residence time of the soil in the oven or by reducing the rotary tube wall temperature residual contaminations remain in the soil as shown in figure 16. A statement of the cleaning rate in percent seems to be unsuitable because in that case different cleaning rates would have to be stated for low initial values. This shall be explained by using two extreme analysis series as examples. In the first sample (fig. 17) a very weakly contaminated soil with a load of 31.3 mg/kg soil was cleaned to a value of 3.9 mg/kg. This corresponds to a cleaning rate of 87.5 %. The second sample (fig. 18) has an initial value of approx. 17.500 mg/kg and a final value of < 3.2 mg/kg in a coarse grain after cleaning several individual components to < 0.1 mg/kg. In this case the cleaning rate reaches 99.98 % although the final value almost corresponds to the value of the first sample. As the operators became familiar with the plant today generally discharge values are obtained in which frequently all residual values for the individual components range around 0.1 mg/kg and below (fig. 19). Numerous samples were screened at 10 mm so that also a first assessment of the cleaning of different grain sizes is possible. However, the effect of grain crushing during the process cannot be taken into consideration. More than 90 % of the samples from treated soils show that the grain size fraction below 10 mm shows higher contaminations than the coarser grains. There are two explanations for this:
Firstly, it could be proven in numerous analyses separated by grain size fraction that, in the fine grain fraction, contaminated dust particles are still existant which are presumably extracted so rapidly from the rotary tube directly after evaporation of the soil humidity with the pyrolysis gas stream that they are not heated up to the temperature required for decocting the pollutants. In the discharge casing they then

sediment in the slowed down gas stream and thus reach the fine grains. A reduction of the discharge casing cross-section or an additional heating gas filter at the end of the rotary tube might help to remove this residual load.

The second explanation is based on the existing surface of the soil grains. With its quantity-related larger surface the fine grain also offers more adhesion possibilities for pollutants. The coarse grain only shows a higher contamination in individual special cases if it is very porous and may be permeated by pollutants. In a particularly impressive way this is shown for the already presented sample (fig. 18) taken from a former acid sludge store. In the fine grain size range of this sample the cleaning effect is not quite so excellent, but also here the individual components range below the Holland B value. When separating samples according to grain size ranges it has to be considered that the coarse to fine grain ratio may vary considerably. Individual examples show 20 to 25 % coarse material, others in contrast up to 55 %. The significance of this phenomenon has not been investigated completely. Certainly the crushing and preparation of residual foundations have an impact. In addition, samples are also examined with regard to other pollutants in regular intervalls. The BTX aromatics with their low boiling points are also decomposed completely in most cases. It should be mentioned that the test programme of Dortmund university also included a rotary kiln operation at lower temperatures. As already the first tests with lower wall temperatures showed insufficient cleaning rates additional tests were excluded from the programme.

Moreover, samples are also examined regularly with regard to their contents of cyanides and phenoles without being able to prove these substances in all

feed samples. In presence of cyanides in the feed they could never be proven in the discharge analyses (fig. 20). Generally, phenoles, if existing in the feed, can only be proven in small traces in the discharges but it has to be mentioned that the phenole analysis can be distorted by other components.

At least once a week also the ashes and filter dusts produced in the process, together accounting for less than 0.5 % of the feed, are included in the examination programme. As a result of the secondary treatment in the higher temperature range of the post-combustion chamber the PAH contents of these samples range below the detectability limits in almost every case (fig. 21).

Another examination series is to provide information on the question whether the heavy metal accumulations detected in individual samples were relocated or converted through the treatment of the material in the rotary kiln. First analyses showed that the contents of heavy metals with low boiling points decrease in the treated soil as expected. In contrast accumulations exist in the ashes and, in particular, the filter dusts. However, it is too early today to draw conclusions on the overall behaviour from these individual results, some of which are shown in figure 22. At present, analyses series are carried out in which dusts and fine grained material are examined separately. In this context also the elution behaviour of the individual components is determined in addition to the absolute pollutant contents as a basis for further decision making.

In some test series about 6.900 t of soil from other sites with in some cases differing contaminations were treated. Mineral oil contaminated soils of a former company-owned petrol station, sludges from canal cleaning and so-called "phenole sands" from a coke-oven

plant have to be mentioned. The mineral oil contaminated soil could be cleaned very easily, as also an analysis (fig. 23) shows. The sludges from the cleaning of former coke-oven plant sewer canals were, as expected, characterized by a high fine grain content and, in some cases, higher pollutant concentrations.

Individual batches had to be treated twice because the normal residence time at a rotary tube wall temperature of 600 to 620° C was insufficient to reach values below the B values in the Holland list. Here the high fine grain content and the above-average water content were assumed to be particularly influential.

With the strongly contaminated phenole sands from a filter system the energy offer in the combustion chamber was so high that the temperature occasionally increased to up to 1270° C. In this context fly ash fusion occurred so that the regular cleaning of the ash hopper below the combustion chamber became very complicated. In this case an upstream hot-gas filter would have been very helpful. For one batch a secondary treatment was required.

Emissions

In the first approval certificate it had been laid down that a series of emission measurements had to be carried out by "TÜV" prior to the final plant commissioning for test operation. In two larger measuring series the different operating units were examined under consideration of the pre-set limits. Amongst others "TÜV" produced the following emission measurement results:

Dust	max.	80 % of the 30 mg/m^3 limit
CO	max.	60 % of the 100 mg/m^3 limit
NO_x	max.	55 % of the limit
SO_2	max.	70 % of the 100 mg/m^3 limit.

Additional emission measurements for HCl and HF also produced values of approx. 30 % below the permissible values. The individual results are shown in figure 24. Other measurements related to the mass concentrations of pulverized anorganic substances according to article 3.1.4 of the "TA-Luft". Here cadmium, thallium, and mercury from class I, the metals arsenic, cobalt, nickel, selenium, and tellurium from class II, and lead, chromium, fluoride, copper, manganese, vanadium, and tin from class III as well as antimone, palatinum, palladium, and rhodium in an additional programme were examined. Also these values did not exceed the pre-set limits. In the meantime the measurements were repeated with similarly good results when treating another site.

Moreover, "TÜV" devoted its attention also to the question of air polluting emissions from the test plant and connected emissions in the environment by carcenogenic substances like dioxines and furanes. From class I of the carcenogenic substances special measurements were carried out for berylium, benzo(a)-pyrene (BaP), and dibenz(a, h)antracene (DBahA), from class II for arsenic, chromium, chromium (VI)-compounds, cobalt, and nickel - all including the corresponding compounds - as well as for all pollutants according to the list of class III. Also here it was stated that the values remained far beyond the pre-set emission limits.

The measurements for the dioxines and furanes were carried out in two series over several days by "TÜV". Moreover, a recognized expert institute carried out measurements for simulated failures following power drops. The measuring data are listed in figures 25 and 26. They show that the Nato recommended limits were observed so far with regard to dioxine and furane emissions.

In the framework of its measurements "TÜV" found a confirmation for an earlier statement saying that also in this plant benzo(a)pyrene takes on a certain "guiding function". This means that at only low concentrations of this substance also other carcenoganic substances frequently emitted together with this substance do not exhibit a significant relevance.

Moreover, "TÜV" produced an emission forecast for the neighbouring areas based on its examinations. In this context it refered to the spreading class statistics of the German meteorological service and its long-year measuring series selecting an area with a side length of 3 km which is larger than the area defined under article 2.6.2.2 of the "TA-Luft" so that this examination is even more comprehensive. Moreover, it assumed that the plant is operated throughout the year, i.e. for 8.760 hours instead of an operation at five working days per week (6.000 hours) according to the first approval certificate. Also in case of a permanent approval this utilization rate cannot be achieved as a result of standstills on sundays and bank holidays or for larger revisions. In its comments "TÜV" states that the daily take-up and the emission concentrations in the neighbouring hazardous areas range slightly more than 2 % above the recommended values which Menzel regards as tolerable in his report "Assessment aid for Dioxines" from the present view. Given this trace concentration the approving authority in the final instance also approved the operation without restrictions in this direction.

It should be pointed out that in the preliminary examinations for hazard assessment on the territory to be treated only one area was established in which pollutant concentrations (PCB) sufficient for the formation of dioxines and furanes might possibly exist.

Another problem may be caused by the occasional presence of mercury in the soil to be treated. Because of its low boiling point the mercury evaporates in the rotary tube and forms a constituent of the pyrolysis gas. In the cooler ash and the filter dust part quantities are present. To avoid a release of the remaining mercury into the atmosphere an additional retaining device has to be provided. At present, we are undertaking efforts to bind this mercury on activated carbon additions to the lime. To this end also a specially prepared activated carbon is used in some cases. Should these tests produce negative results the use of an activated carbon reactor will have to be investigated.

Utilization of the treated Soil

The opponents of thermal decontamination methods claim again and again that the decontaminated soil is sterile and unsuitable for a follow-up utilization. To contradict this assertion different test series - in some cases in cooperation with university institutes - concerning the recultivation of the treated areas are carried out in Bönen. After the plant constructor had already proven in small scale tests that in decontaminated soil shortly after the treatment seed germinate and plants grow a larger test was started in cooperation with the municipality of Bönen. The municipality market garden laid out several beds of which one with a depth of some 3 m consists exclusively of treated material. In the other beds compost or 20 cm and 50 cm top soil were used as top layers. So far, the thermally treated and normally fertilized and watered soil shows an only slightly weaker groth than the other beds (fig. 27). In autumn 1989 and spring 1990 the Institute for Plant Sociology/Ecology of Essen university laid out several beds on an approx. 5.000 m^2 test area in which also an at least 1 m mainly,

however, more than 2 m thick, thermally treated and decontaminated soil layer was used. With the experience gathered with the recultivation of waste heaps in the hardcoal industry it is tried to revive the growth on these biologically only inactive soils using special seed compositions and to accelerate a humus formation on natural waste through the multitude of the offered plants. In the meantime the first seeds have sprouted. As some beds also remained untreated the differences will be visible soon. Finally, the Institute for Edaphology of Hamburg university was charged to investigate the soil with regard to its soil physical properties. Under an R&D project to be dealt with there it is intended to compare soils of different decontamination projects and methods. The required soil samples from Königsborn have, in the meantime, been supplied to the institute. Detailed results like the determination of the water adsorption capacity, the proctor density, or the pore size distribution, in particular also compared to the other methods, are unfortunately not yet available completely. An advance information, however, said that the residual PAH contents amount to a maximum of only 3.8 mg/kg. Thus, the cleaning rate was confirmed. Also the data on the pore volume and the water adsorption capacity confirm the suitability of the cleaned soil for reuse.

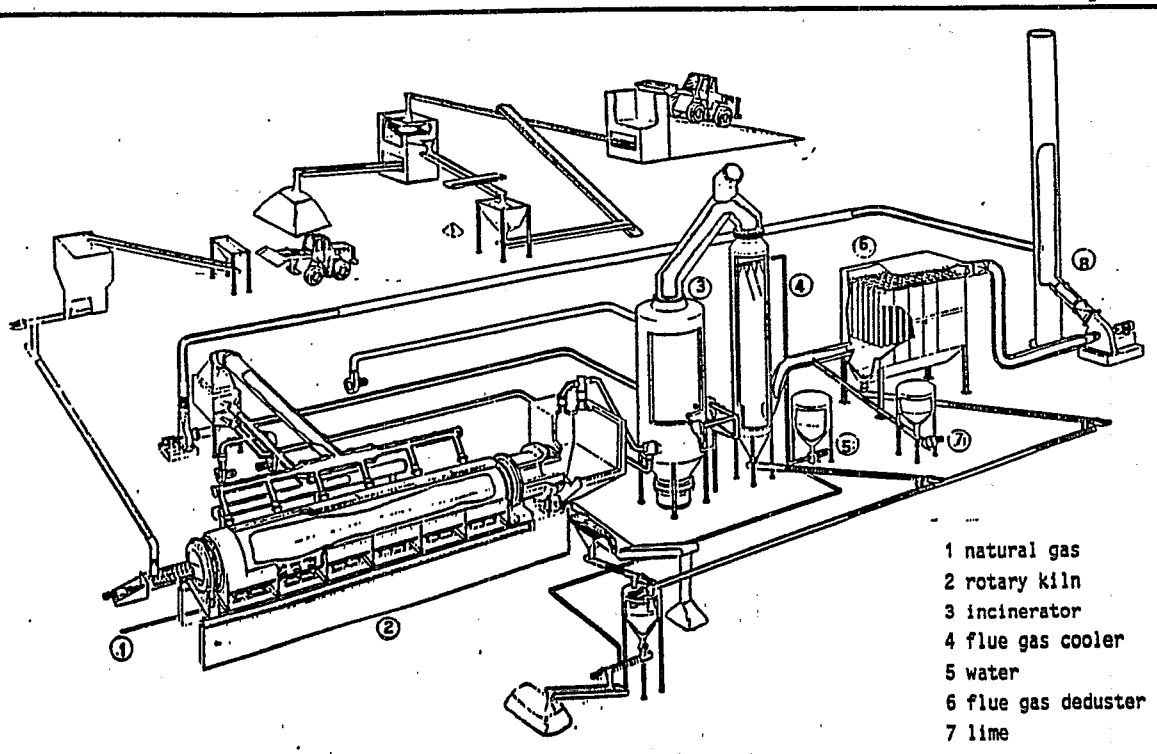
Internally a vegetable bed was layed out on the treated soil. After the harvest different plants were sent to LUFA (agricultural test and research institute) in Münster. This institute confirmed that the examinations with regard to arsenic and environmentally relevant PAHs did not supply any objectionable results under the aspect of food hygiene and that the measured concentrations also occurred in useful plants which grew in non-contaminated areas.

As some quantities were used for the construction of a noise protection dam samples of the cleaned soil were moreover submitted to comprehensive eluate examinations corresponding to the draft directive for the examination and assessment of wastes - part 2 - of the Northrhine Westfalian water and waste agency, the so-called landfill directive (fig. 29). All thresholds for landfill class 2 are observed. In contrast the eluate data for landfill class 1 are exceeded generally for about 5 parameters of which some regress to class 1 in the course of time under the influence of general environmental factors. This is particularly pronounced for the pH value which is positively influenced by the acid rain and for the chemical oxygen demand (COD value), which normalizes again under atmospheric conditions.

Conclusions

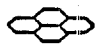
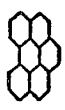
The Königsborn Pyrolysis plant has fully met the expections in the test period so far. In operation it was possible to clean also more severely contaminated soils to such an extent that the treated areas can be made available for a follow-up utilization. Moreover, the tests carried out so far also supplied a number of interesting detailed results which will certainly provide for statements concerning the limits of this methods in the framework of the R&D project still extending until the end of 1991. The plant operation will be continued also after the expiry of the supported R&D time.

Fig. 1



RAG RUHRKOHLE WESTFALEN AG	Degasing with incineration of contaminated soil	Lehmann Nov. 1991

Fig. 2

		°C	
Naphthalin	$C_{10}H_8$	218	
2-Methyl-Naphthalin	$C_{12}H_{12}$	241	
1-Methyl-Naphthalin		262	
Fluoren	$C_{13}H_{10}$	298	
Phenanthren	$C_{14}H_{10}$	338	
Anthracen	$C_{14}H_{10}$	340	
Fluoranthen	$C_{16}H_{10}$	384	
Pyren	$C_{16}H_{10}$	396	
Benz(a)anthracen	$C_{18}H_{12}$	438	
Chrysen	$C_{18}H_{12}$	441	
Benz(e)pyren	$C_{20}H_{12}$	493	
Benz(b)fluoranthen	$C_{20}H_{12}$	487	
Benz(k)fluoranthen	$C_{20}H_{12}$	481	
Benz(a)pyren	$C_{20}H_{12}$	496	
Dibenz(ah)anthracen		498	
Benzo(ghi)perylen	$C_{22}H_{12}$	500	
Indeno(1, 2, 3, cd)pyren		505	

RAG RUHRKOHLE WESTFALEN AG

Boiling points of PAH's

Lehmann
Nov. 1991

Fig. 3

			1	2	3
Wasser	H2O	Vol-%	65,10	71,60	75,00
Sauerstoff	O2	Vol-%	2,50	3,60	1,90
Wasserstoff	H2	Vol-%	0,75	0,37	0,11
Kohlenmonoxid	CO	Vol-%	0,45	0,23	0,29
Kohlendioxid	CO2	Vol-%	1,90	1,00	2,40
Methan	CH4	Vol-%	0,80	0,36	0,16
Ethan	C2 H6	Vol-%	0,14	0,08	0,02
Ethen	C2 H4	Vol-%	0,12	0,06	0,03
Ethin	C2 H2	vpm	8,00	3,00	4,00
Propan	C3 H8	vpm	436,00	230,00	62,00
Propen	C3 H6	vpm	759,00	400,00	199,00
iso-Butan	C4 H10	vpm	38,00	21,00	5,00
n-Butan	C4 H10	vpm	77,00	42,00	9,00
trans-Buten	C4 H8	vpm	144,00	77,00	15,00
1-Buten	C4 H8	vpm			
iso-Buten	C4 H8	vpm	131,00	70,00	32,00
cis-Buten	C4 H8	vpm	83,00	44,00	3,00
Butin	C4 H6	vpm	67,00	33,00	10,00
1,3-Butadien	C4 H8	vpm			
n-Pentan	C5 H12	vpm	38,00	20,00	4,00
Cyclopentan	C5 H10	vpm	104,00	55,00	7,00
2,2-Dimethylmethan	C6 H14	vpm			
2-Methylpentan	C6 H14	vpm	45,00	28,00	2,00
3-Methylpentan	C6 H14	vpm	21,00	16,00	2,00
Hexan	C6 H14	vpm	49,00	32,00	2,00
Heptan	C7 H16	vpm	18,00	37,00	4,00
Oktan	C8 H18	vpm	5,00	5,00	2,00
Benzol	C6 H6	vpm	82,00	77,00	73,00
Toluol	C7 H8	vpm	64,00	53,00	21,00
m-Xylol	C8 H10	vpm	7,00	6,00	5,00
p-Xylol	C8 H10	vpm			
o-Xylol	C8 H10	vpm	5,00	5,00	3,00

RAG RUHRKOHLE WESTFALEN AG

Pyrolysis Plant Königsborn 3/4
Analyses of Pyrolysis - gas

Lehmann
Nov. 1991

Fig. 4

$$C_m H_n + \left(m + \frac{n}{2}\right) O_2 \Rightarrow m\, CO_2 + \frac{n}{2} H_2O + \text{Heat}$$

$$2\, CO + O_2 \Rightarrow 2\, CO_2$$

RAG RUHRKOHLE WESTFALEN AG	Process in the incinerator	Lehmann Nov. 1991

Fig. 5

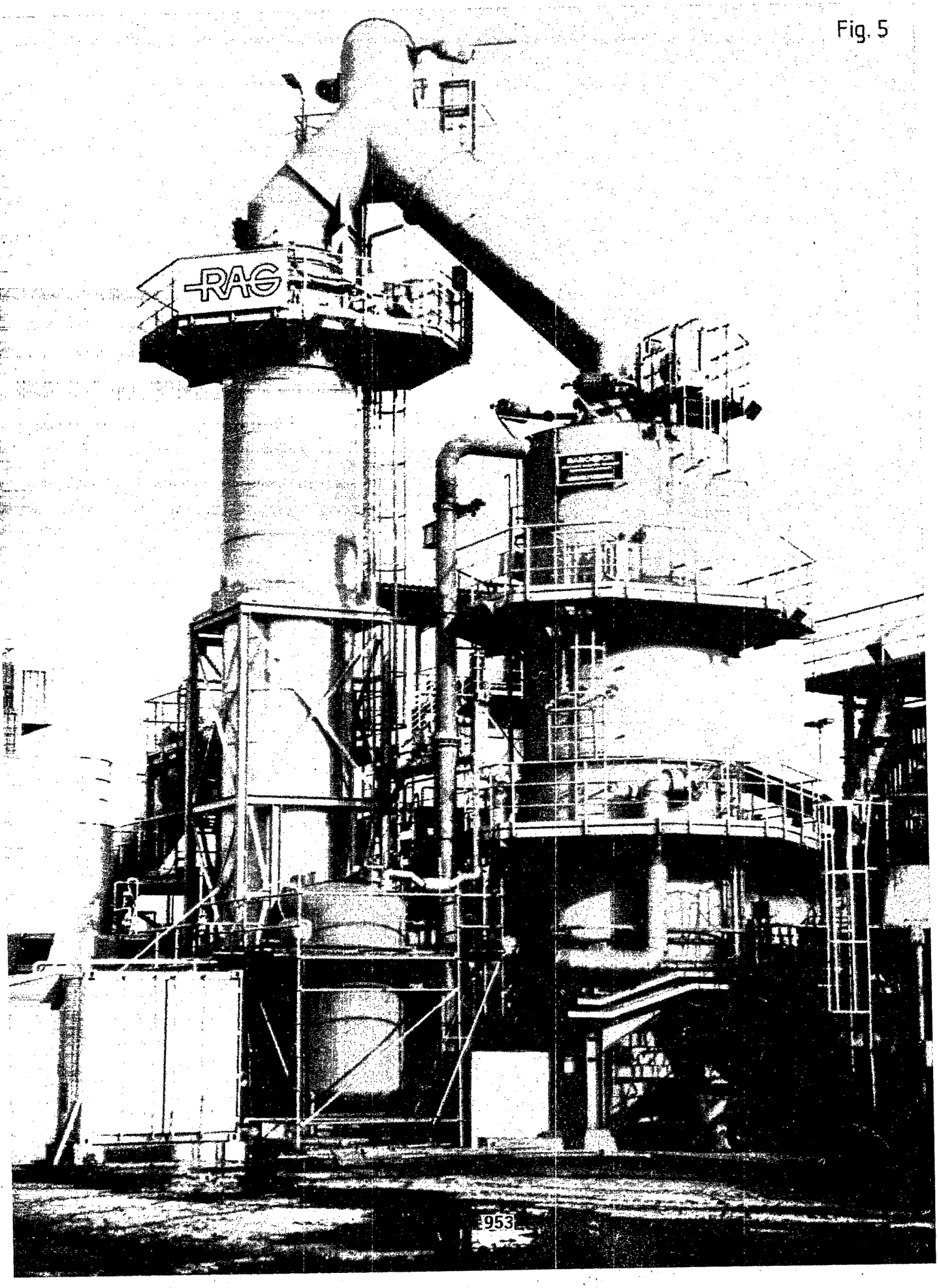
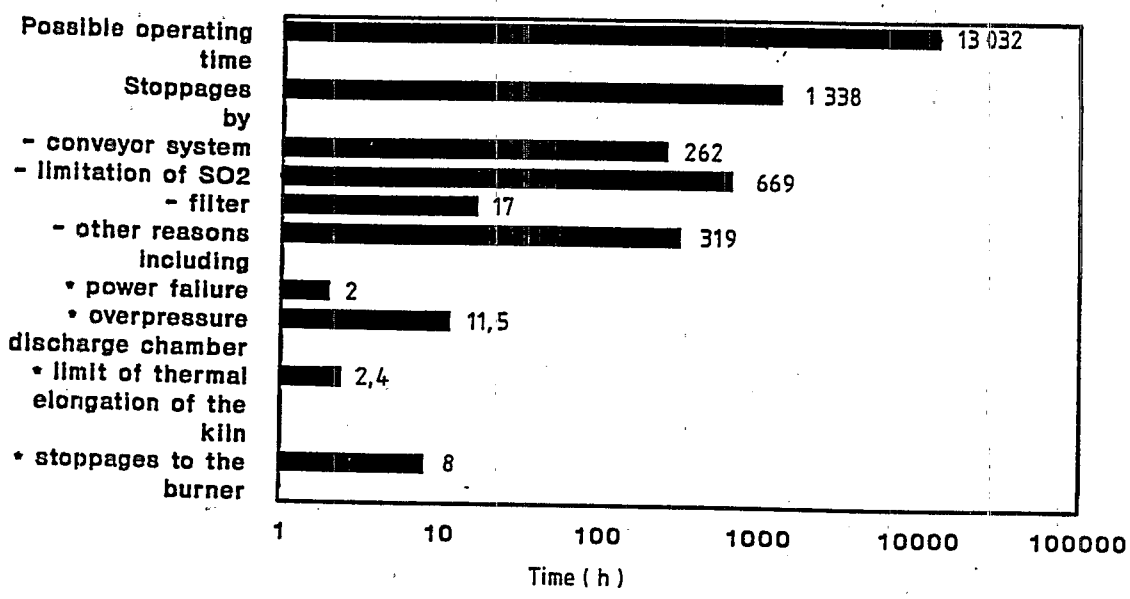


Fig. 6

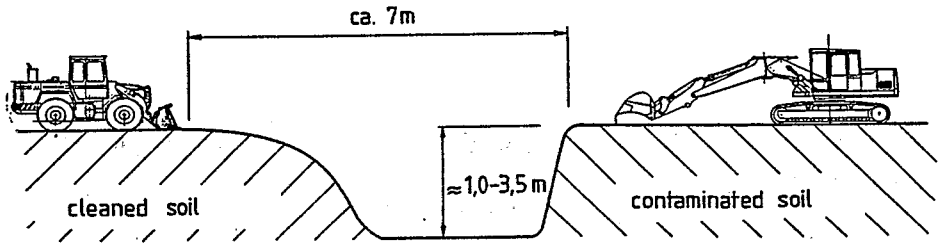


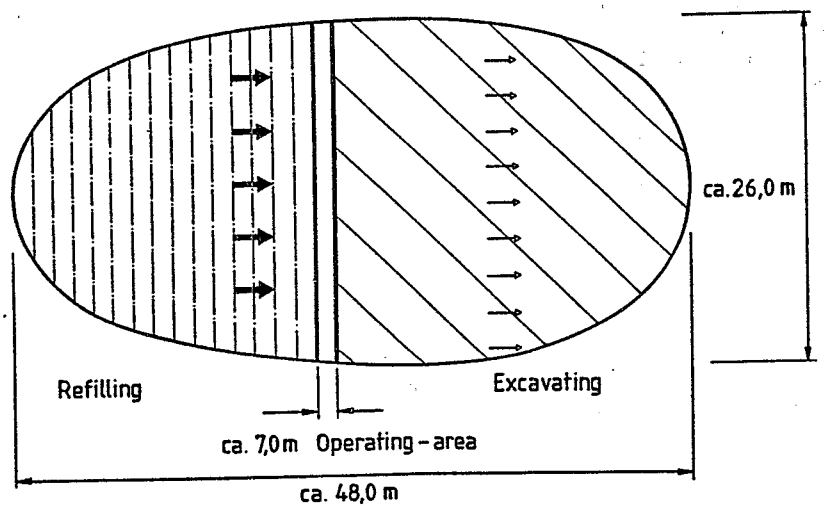
RAG RUHRKOHLE WESTFALEN AG

Königsborn 3/4
Thermal Treatment
Period: 14.08.1989 - 31.10.1991

Lehmann
Nov. 1991

Fig. 7





RAG RUHRKOHLE WESTFALEN AG	System of excavating and refilling the soil	Lehmann Nov. 1991

Fig. 8

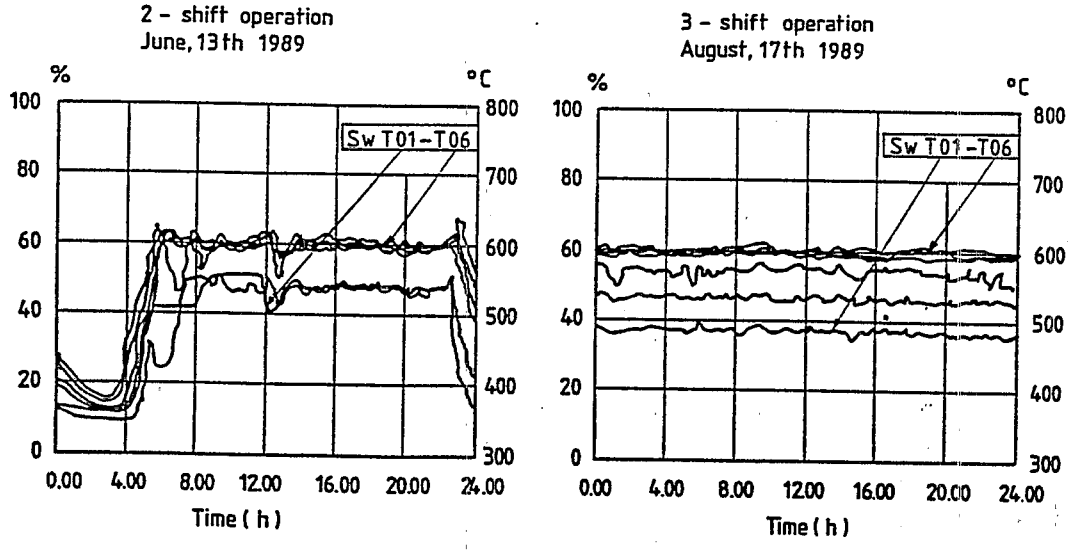
Place of test	Benzol µg/m3	Toluol µg/m3	Xylol µg/m3	Naphthalin µg/m3
Top of excavation area (pit)	17 - 23	28 - 29	39 - 47	240 - 440
Cabin of excavator	15 - 17	23 - 38	33 - 57	190 - 340
Cabin of truck	13 - 19	17 - 30	21 - 24	35 - 58
neighboured area	4	5	7	48
allowed working place concentration	16 000	380 000	440 000	50 000
Olfactory threshold (TÜV)	2 900	8 000	350	140
Olfactory threshold (Hyg. Inst.)		800	2 000	30
Olfactory threshold by "Roth"		200	200	4
Olfactory threshold by "Staub"				20

RAG RUHRKOHLE WESTFALEN AG

Pollutants content in the air during excavation works
May 1989, temperature 25° C
according to the german norm VDI 3482

Lehmann
Nov. 1991

Fig. 9

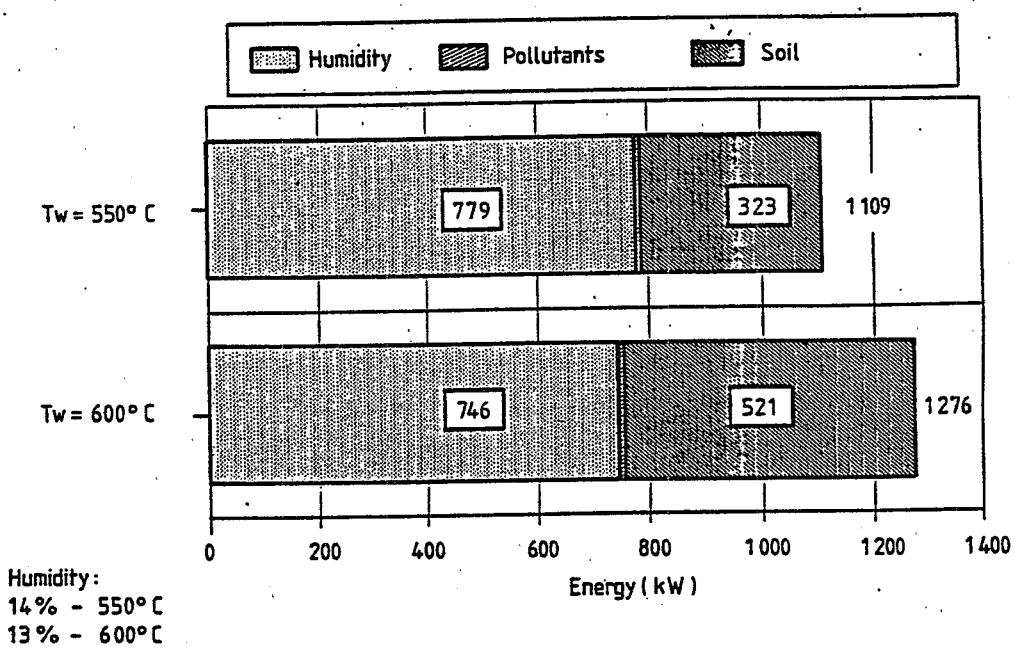


RAG RUHRKOHLE WESTFALEN AG

Temperature of the wall of the kiln
[Zone 1 (intake) - 6 (outlet)]

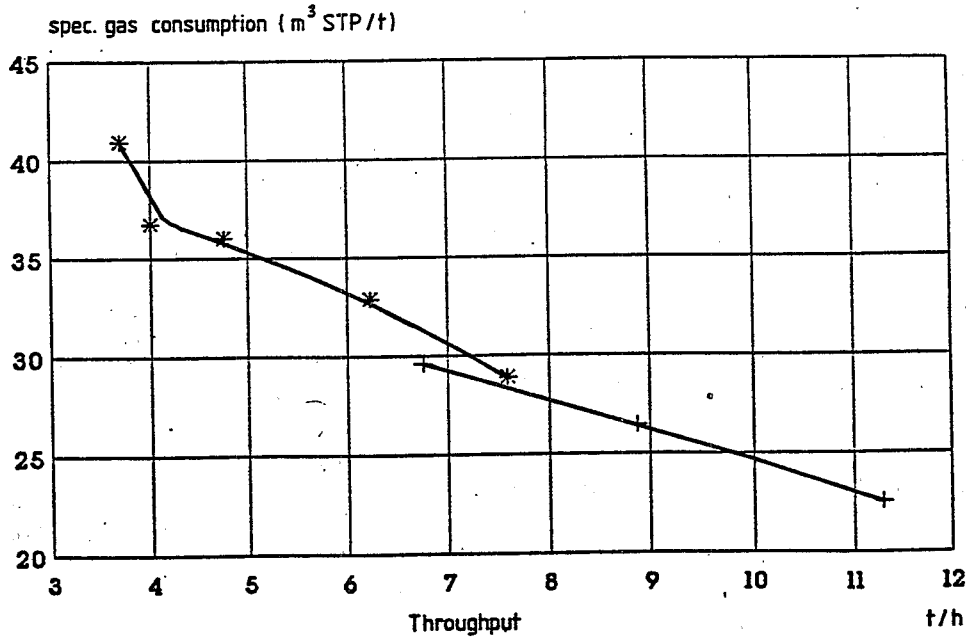
Lehmann
Nov. 1991

Fig. 10



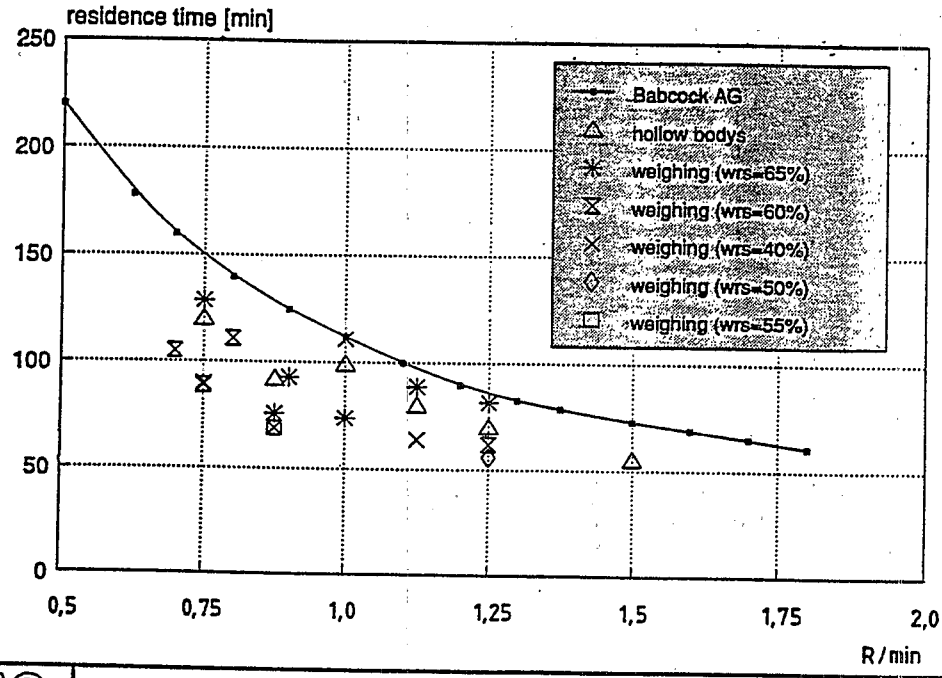
RAG RUHRKOHLE WESTFALEN AG	Used energy for water evaporation, degasification and heating the soil	Lehmann Nov. 1991

Fig. 11



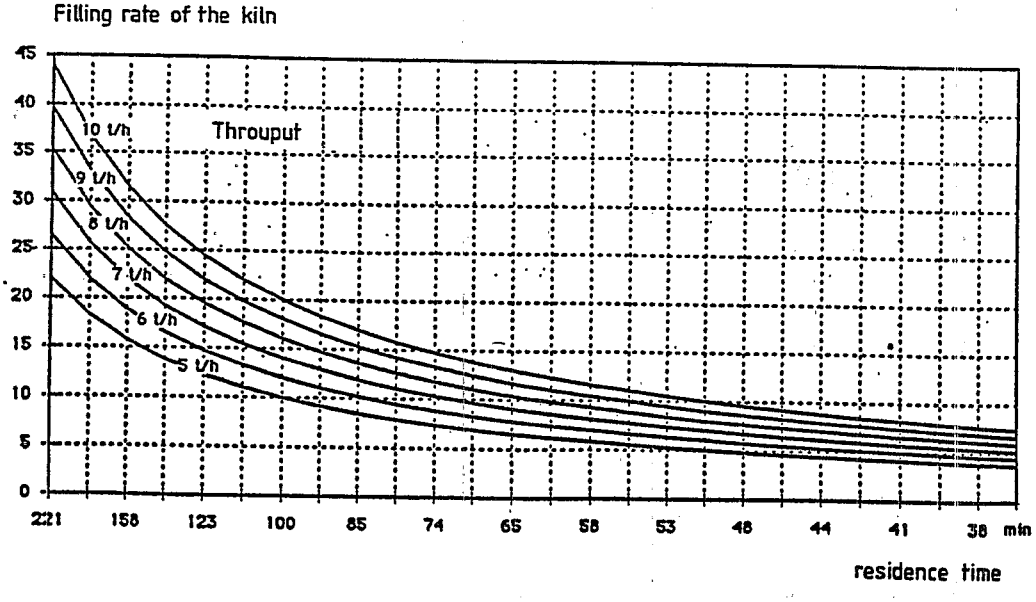
RAG RUHRKOHLE WESTFALEN AG	Rotary kiln - specific gas consumption	Lehmann Nov. 1991

Fig. 12



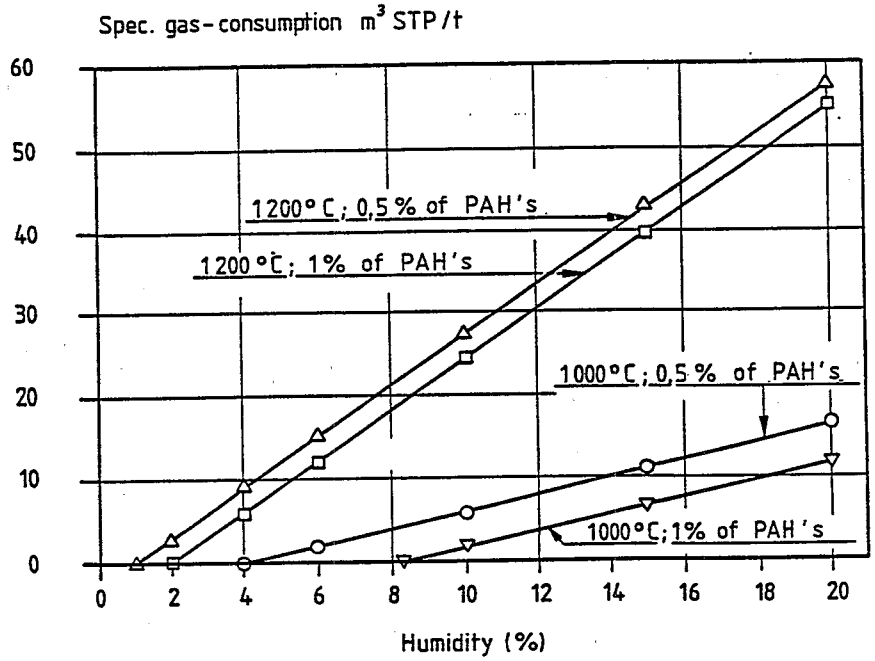
RAG RUHRKOHLE WESTFALEN AG	Residence time in the rotary kiln	Lehmann Nov. 1991

Fig. 13



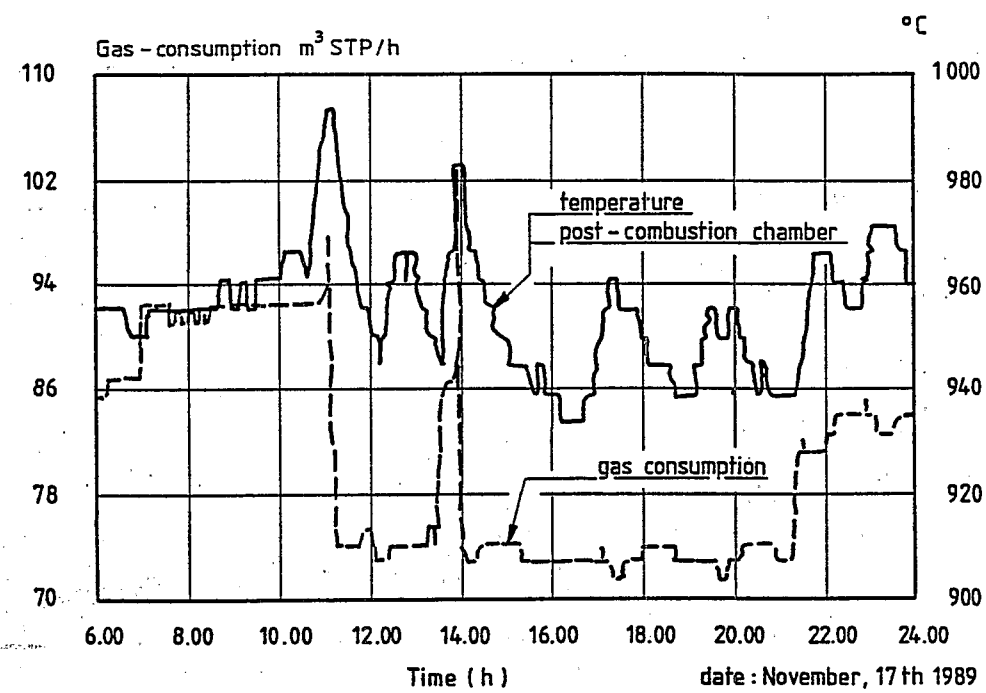
RAG RUHRKOHLE WESTFALEN AG	Connection of filling rate, throughput and residence time	Lehmann Nov. 1991

Fig. 14



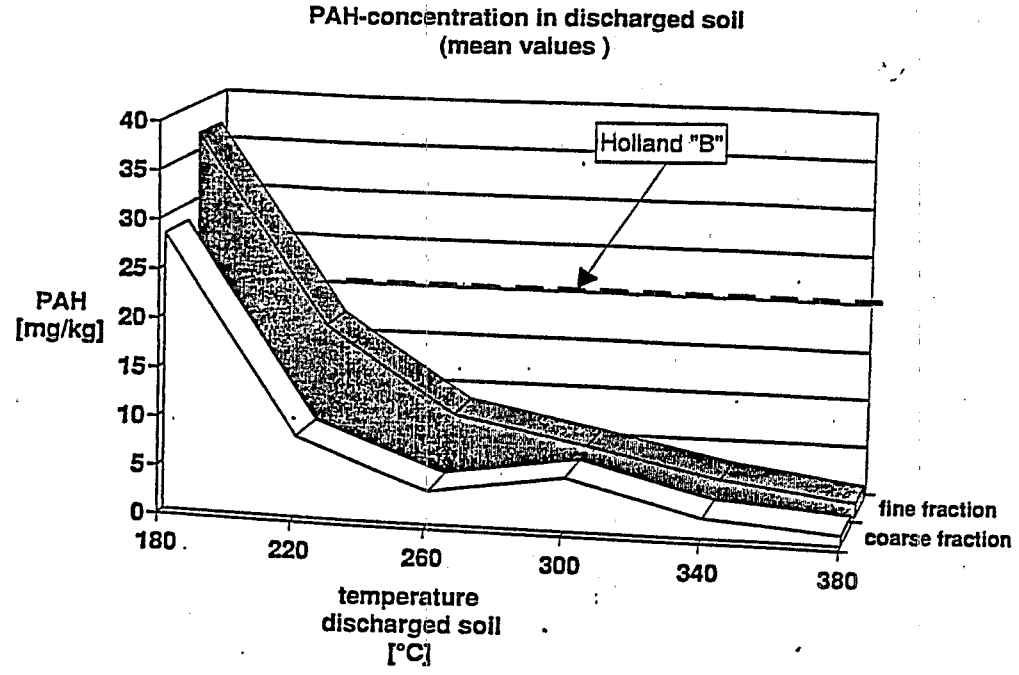
RUHRKOHLE WESTFALEN AG	Specific gas-consumption for heating the post-combustion chamber	Lehmann Nov. 1991

Fig. 15



RUHRKOHLE WESTFALEN AG	Influence to natural gas consumption in the post-combustion-chamber by pyrolyse-gas	Lehmann Nov. 1991

Fig 16



RAG RUHRKOHLE WESTFALEN AG	Influence of the temperature of discharged soil to the cleaning process	Lehmann Nov. 1991

Fig. 17

	Feed		Discharge
Naphthalin	1,1		0,1
2-Methyl-Naphthalin	0,5	<	0,1
1-Methyl-Naphthalin	1,3	<	0,1
Fluoren	0,6		0,2
Phenanthren	3,0		0,5
Anthracen	0,8		0,1
Fluoranthen	4,3		0,6
Pyren	3,6		0,4
Benz[a]anthracen	2,4		0,2
Chrysen	1,8		0,2
Benz[e]pyren	2,3		0,3
Benzo[b]fluoranthen	2,6		0,3
Benzo[k]fluoranthen	1,5		0,2
Benz[a]pyren	2,1		0,2
Dibenz[ah]anthracen	0,5	<	0,1
Benzo[ghi]perylen	1,4		0,2
Indeno[1.2.3.cd]pyren	1,5		0,1
Sum.:	31,3		3,9
Cleaning efficiency			87,5 %

RAG RUHRKOHLE WESTFALEN AG	Pyrolysis Plant Königsborn 3/4 Test August, 2nd 1988 (Results in mg/kg)	Lehmann Nov. 1991

Fig. 18

	Feed < 10 mm	Feed > 10 mm	Discharge < 10 mm	Discharge > 10 mm
Naphthalin				
2-Methyl-Naphthalin	312.0	3 160.0	4.1	0.7
1-Methyl-Naphthalin				
Fluoren	153.0	1 600.0	0.4	< 0.1
Phenanthren	566.0	1 080.0	2.9	0.9
Anthracen	117.0	451.0	0.2	< 0.1
Fluoranthen	439.0	3 720.0	2.4	0.4
Pyren	288.0	1 740.0	1.0	0.1
Benz(a)anthracen	148.0	1 230.0	0.9	< 0.1
Chrysen	78.0	456.0	1.1	0.1
Benz(e)pyren	64.7	660.0	1.1	< 0.1
Benzo(b)fluoranthen	91.9	862.0	1.9	0.1
Benzo(k)fluoranthen	76.4	577.0	0.7	< 0.1
Benz(a)pyren	93.1	824.0	0.4	< 0.1
Dibenz(ah)anthracen	14.8	130.0	0.5	< 0.1
Benzo(ghi)perylen	56.5	532.0	1.0	0.1
Indeno(1.2.3.cd)pyren	52.7	548.0	0.8	< 0.1
Sum	2 551.1	17 570.0	19.3	< 3.2
Cleaning Efficiency			99.25 %	99.98 %

RAG RUHRKOHLE WESTFALEN AG

Pyrolysis Plant Königsborn 3/4
Test No.829, 31th July'89
(Results in mg / kg)

Lehmann
Nov. 1991

Fig 19

	Feed < 50 mm	Discharge < 10 mm	Discharge > 10 mm
Naphthalin	36,1	< 0,1	< 0,1
Acenaphthylen	68,0	< 0,1	< 0,1
Acenaphthen	46,2	< 0,1	< 0,1
Fluoren	131,0	< 0,1	< 0,1
Phenanthren	624,0	< 0,1	< 0,1
Anthracen	363,0	< 0,1	< 0,1
Fluoranthen	602,0	< 0,1	< 0,1
Pyren	409,0	< 0,1	< 0,1
Benz[a]anthracen	300,0	< 0,1	< 0,1
Chrysen	458,0	< 0,1	< 0,1
Benzo[b]fluoranthen	187,0	< 0,1	< 0,1
Benzo[k]fluoranthen	133,0		
Benz[a]pyren	204,0	< 0,1	< 0,1
Indeno[1.2.3.cd]pyren Dibenz[ah]anthracen	139,0	< 0,1	< 0,1
Benzo[ghi]perylen	89,2	< 0,1	< 0,1
Sum.:	3789,5	< 0,1	< 0,1

RAG RUHRKOHLE WESTFALEN AG	Pyrolysis Plant Königsborn 3/4 Test July, 17th 1991 (results in mg/kg)	Lehmann Nov. 1991

Fig. 20

mg/kg	Feed	Discharge	Ash of quench	Dust of filter
Cyanide	20,0	< 0,1	< 0,1	< 0,1
Phenol	4,0	< 0,43	< 0,1	< 0,1

RAG RUHRKOHLE WESTFALEN AG	Pyrolysis Plant Königsborn 3/4 Test on Cyanide and Phenol (Results in mg/kg)	Lehmann Nov. 1991

Fig. 21

	1	2	3	4
Naphthalin	945,0	0,9	< 0,1	< 0,1
2-Methyl-Naphthalin	216,0	< 0,1	< 0,1	< 0,1
1-Methyl-Naphthalin	96,0	< 0,1	< 0,1	< 0,1
Dimethylnaphthaline	160,0	< 0,1	< 0,1	< 0,1
Acenaphthylen	196,0	< 0,1	< 0,1	< 0,1
Acenaphthen	789,0	< 0,1	< 0,1	< 0,1
Fluoren	480,0	0,6	< 0,1	< 0,1
Phenanthren	1764,0	1,4	< 0,1	< 0,1
Anthracen	649,0	0,3	< 0,1	< 0,1
Fluoranthen	1021,0	0,4	< 0,1	< 0,1
Pyren	589,0	0,2	< 0,1	< 0,1
Benz[a]anthracen	355,0	0,4	< 0,1	< 0,1
Chrysen	470,0	0,4	< 0,1	< 0,1
Benzo[b]fluoranthen	189,0	0,4	< 0,1	< 0,1
Benzo[k]fluoranthen	156,0	< 0,1	< 0,1	< 0,1
Benz[e]pyren	132,0	< 0,1	< 0,1	< 0,1
Benz[a]pyren	165,0	< 0,1	< 0,1	< 0,1
Indeno[1.2.3.cd]pyren	63,8	< 0,1	< 0,1	< 0,1
Dibenz[ah]anthracen	21,7	< 0,1	< 0,1	< 0,1
Benzo[ghi]perylen	51,1	< 0,1	< 0,1	< 0,1
Sum.:	8508,6	6,1	< 0,1	< 0,1

1. Feed 2. Discharge
3. Dust 4. Ash of quench

Date : February, 10 th 1989

RAG RUHRKOHLE WESTFALEN AG

Pyrolysis Plant Königsborn 3/4
Test of dust and ash (Results in mg/kg)

Lehmann
Nov. 1991

Fig. 22

			Feed	Discharge < 10 mm	Discharge > 10 mm	Dust of filter
Quecksilber	(Hg)	mg/kg	7,30	1,80	< 0,40	174,00
Cadmium	(Cd)	mg/kg	0,71	0,80	0,44	2,70
Arsen	(Ar)	mg/kg	116,00	151,00	48,00	543,00
Chrom	(Cr)	mg/kg	97,00	70,00	88,00	30,00
Nickel	(Ni)	mg/kg	48,00	37,00	41,00	22,00
Kupfer	(Cu)	mg/kg	45,00	53,00	30,00	30,00
Zink	(Zn)	mg/kg	151,00	155,00	121,00	174,00
Blei	(Pb)	mg/kg	149,00	236,00	91,00	800,00

RAG RUHRKOHLE WESTFALEN AG

Pyrolysis Plant Königsborn 3/4

Analysis of heavy metals

Lehmann
Nov. 1991

Fig. 23

	Feed < 50 mm	Discharge < 10 mm	Discharge > 10 mm
Mineraloil-Hydrocarbons	3800,0	< 5,0	< 5,0
Naphthalin	7,5	< 0,1	< 0,1
Acenaphthylen	3,7	< 0,1	< 0,1
Acenaphthen	2,4	< 0,1	< 0,1
Fluoren	6,0	< 0,1	0,1
Phenanthren	27,9	0,1	0,3
Anthracen	9,0	< 0,1	0,1
Fluoranthen	22,6	0,1	0,3
Pyren	17,3	< 0,1	0,2
Benz[a]anthracen	17,4	< 0,1	< 0,1
Chrysen	19,5	< 0,1	< 0,1
Benzo[b]fluoranthen Benzo[k]fluoranthen	18,2	< 0,1	< 0,1
Benz[a]pyren	11,9	< 0,1	< 0,1
Indeno[1.2.3.cd]pyren	9,8	< 0,1	< 0,1
Dibenz[ah]anthracen	4,3	< 0,1	< 0,1
Benzo[ghi]perylen	6,4	< 0,1	< 0,1
Sum.:	183,9	0,2	1,0

RAG RUHRKOHLE WESTFALEN AG	Pyrolysis Plant Königsborn 3/4 Test with soil contaminated by mineraloil - hydrocarbons (Results in mg / kg)	Lehmann Nov. 1991

Fig. 24

component	limit (mg/m3 STP)	measurement results (mg/m3 STP)
dust old filter	30	24/22/21/20/19/17
new filter (May-June 1991)	10	0,7/0,7/1,2/0,4/0,6/0,5/0,5/0,8/1,1
class I an.	0,2	0,00011
class II an.	1,0	0,00259
class III an.	5,0	0,11382
CO	100	20/35/22/15/13/16
SO2	100	62/26/15/23/39/16
C org. (total)	20	6/ 8/ 5/ 4/ 6/ 8
HCl	50	16/17/15/14/12/13
HF	2,0	0,8/0,6/0,5/0,7/0,6/0,6
NOx	only measurement	140/144/151/161/171/154

m^3 STP calculated on 11 % O_2

RAG RUHRKOHLE WESTFALEN AG	Measurements by TÜV January 1989 and May - Juni 1991	Lehmann Nov. 1991

Fig. 25

	Measurements by TÜV						..... by GfA	
	10.10.89 ng/m³*)	11.10.89 ng/m³*)	12.10.89 ng/m³*)	18.04.90 ng/m³*)	19.04.90 ng/m³*)	19.04.90 ng/m³*)	04.10.90 ng/m³*)	05.10.90 ng/m³*)
Tetrachlordibenzodioxine	0,24	0,26	0,15	0,29	0,17	n.n.	0,02	n.n.
Pentachlordibenzodioxine	0,14	0,20	0,14	0,31	0,07	n.n.	n.n.	n.n.
Hexachlordibenzodioxine	0,12	0,15	0,12	0,22	0,07	n.n.	n.n.	n.n.
Heptachlordibenzodioxine	0,24	0,24	0,16	0.54	0,06	n.n.	0,09	0,07
Octachlordibenzodioxin	0,36	0,33	0,29	0,76	0,04	n.n.	0,21	0,19
Summ. Tetra- bis Octachlordibenzodiozine	1,10	1,18	0,86	2,12	0,41	n.n.	0,32	0,26
Tetrachlordibenzofurane	0,10	0,16	0,09	0,82	0,21	n.n.	0,13	0,06
Pentachlordibenzofurane	0,21	0,17	0,13	0,46	0,18	n.n.	0,13	0.05
Hexachlordibenzofurane	0,12	0,12	0,09	1,02	0,12	n.n.	0,09	0,02
Heptachlordibenzofurane	0,20	0,17	0,15	1,24	0,25	n.n.	0,08	0,04
Octachlordibenzofuran	0,08	0,06	0,05	0,56	0,10	n.n.	<0,29	<0.19
Summ. Tetra- bis Octachlordibenzofurane	0,71	0,68	0,51	4,10	0,86	n.n.	0,43	0,17
2,3,7,8-Tetrachlordibenzodioxin	n.n. **)	n.n.	n.n.	n.n.	n.n.	n.n.	<0,002	<0,001
1,2,3,7,8-Pentachlordibenzodioxin	n.n.	n.n.	n.n.	0,02	n.n.	n.n.	<0,003	<0,001
1,2,3,4,7,8-Hexachlordibenzodioxin	n.n.	n.n.	n.n.	0,01	n.n.	n.n.	<0,010	<0,003
1,2,3,6,7,8-Hexachlordibenzodioxin	n.n.	n.n.	n.n.	0,02	n.n.	n.n.	<0,010	<0,003
1,2,3,7,8,9-Hexachlordibenzodioxin	n.n.	n.n.	n.n.	0,01	n.n.	n.n.	<0,010	<0,003
1,2,3,4,6,7,8-Heptachlordibenzodioxin	0,10	0,12	0,10	0,29	0,03	n.n.	0,047	0,042
2,3,7,8-Tetrachlordibenzofuran	n.n.	0,01	n.n.	0,03	0,02	n.n.	0,019	0,018
1,2,3,7,8-Pentachlordibenzofuran	0,02	0,02	0,01	0,08	0,02	n.n.	0,012	0.006
2,3,4,7,8-Pentachlordibenzofuran	0,01	0,01	0,01	0,05	0,01	n.n.	0,016	0,008
1,2,3,4,7,8-Hexachlordibenzofuran	0,02	0,02	0,01	0,14	0,02	n.n.	0,014	0,006
1,2,3,6,7,8-Hexachlordibenzofuran	0,02	0,02	0,01	0,11	0,02	n.n.	0,011	<0,004
1,2,3,7,8,9-Hexachlordibenzofuran	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	<0,007	<0,004
2,3,4,6,7,8-Hexachlordibenzofuran	n.n.	n.n.	n.n.	0,07	0,01	n.n.	<0,042	<0,026
1,2,3,4,6,7,8-Heptachlordibenzofuran	0,20	0,17	0,15	0,84	0,18	n.n.	0,060	0,040
1,2,3,4,7,8,9-Heptachlordibenzofuran	n.n.	n.n.	n.n.	0,11	0,02	n.n.	<0.005	<0.005
TCDD-Äquivalente nach BGA	0.02	0.02	0.01	0.09	0.02	n.n.	0.012	0.006
TCDD-Äquivalente nach NATO	0,013	0.02	0.01	0,09	0.02	n.n.	0.014	0.008

*) bezogen auf das Abgasvolumen im Normzustand (275 K, 1013 mbar) **) Die Nachweisgrenze für die Einzelisomere betrug < 0,01 ng/m³ n.n. = not evident

RAG RUHRKOHLE WESTFALEN AG	Contents of dioxines (PCDD) and furans (PCDF) in the filtered gas	Lehmann Nov. 1991

Fig. 26

	Measurements by GfA							
	10.10.90 ng/m³*)	11.10.90 ng/m³*)	12.10.90 ng/m³*)					
Tetrachlordibenzodioxine	0,09	n.n.**)	0,03					
Pentachlordibenzodioxine	n.n.	n.n.	n.n.					
Hexachlordibenzodioxine	n.n.	n.n.	n.n.					
Heptachlordibenzodioxine	0,17	0,09	n.n.					
Octachlordibenzodioxin	0,73	0,24	0,25					
Summ. Tetra- bis Octachlordibenzodiozine	0,99	0,33	0,28					
Tetrachlordibenzofurane	0,30	0,09	0,06					
Pentachlordibenzofurane	0,16	0,10	0,08					
Hexachlordibenzofurane	n.n.	n.n.	n.n.					
Heptachlordibenzofurane	0,04	0,04	0,02					
Octachlordibenzofuran	<0,41	<0,22	<0,27					
Summ. Tetra- bis Octachlordibenzofurane	0,50	0,23	0,16					
2,3,7,8-Tetrachlordibenzodioxin	<0,005	<0,003	<0,006					
1,2,3,7,8-Pentachlordibenzodioxin	<0,006	<0,004	<0,019					
1,2,3,4,7,8-Hexachlordibenzodioxin	<0,121	<0,011	<0,062					
1,2,3,6,7,8-Hexachlordibenzodioxin	<0,121	<0,011	<0,062					
1,2,3,7,8,9-Hexachlordibenzodioxin	<0,121	<0,011	<0,062					
1,2,3,4,6,7,8-Heptachlordibenzodioxin	0,102	0,052	<0,038					
2,3,7,8-Tetrachlordibenzofuran	0,039	0,020	0,020					
1,2,3,7,8-Pentachlordibenzofuran	0,009	0,009	0,012					
2,3,4,7,8-Pentachlordibenzofuran	0,021	0,022	0,013					
1,2,3,4,7,8-Hexachlordibenzofuran	<0,021	<0,021	<0,020					
1,2,3,6,7,8-Hexachlordibenzofuran	<0,021	<0,021	<0,020					
1,2,3,7,8,9-Hexachlordibenzofuran	<0,021	<0,021	<0,020					
2,3,4,6,7,8-Hexachlordibenzofuran	<0,083	<0,105	<0,036					
1,2,3,4,6,7,8-Heptachlordibenzofuran	0,039	0,034	0,024					
1,2,3,4,7,8,9-Heptachlordibenzofuran	<0,009	<0,010	<0,009					
TCDD-Äquivalente nach BGA	0.014	0.008	0.006					
TCDD-Äquivalente nach NATO	0,017	0.015	0.010					

*) bezogen auf das Abgasvolumen im Normzustand (275 K, 1013 mbar) **) Die Nachweisgrenze für die Einzelisomere betrug < 0,01 ng/m³ n.n. = not evident

RAG RUHRKOHLE WESTFALEN AG	Contents of dioxines (PCDD) and furans (PCDF) in the filtered gas during simulated failures	Lehmann Nov. 1991

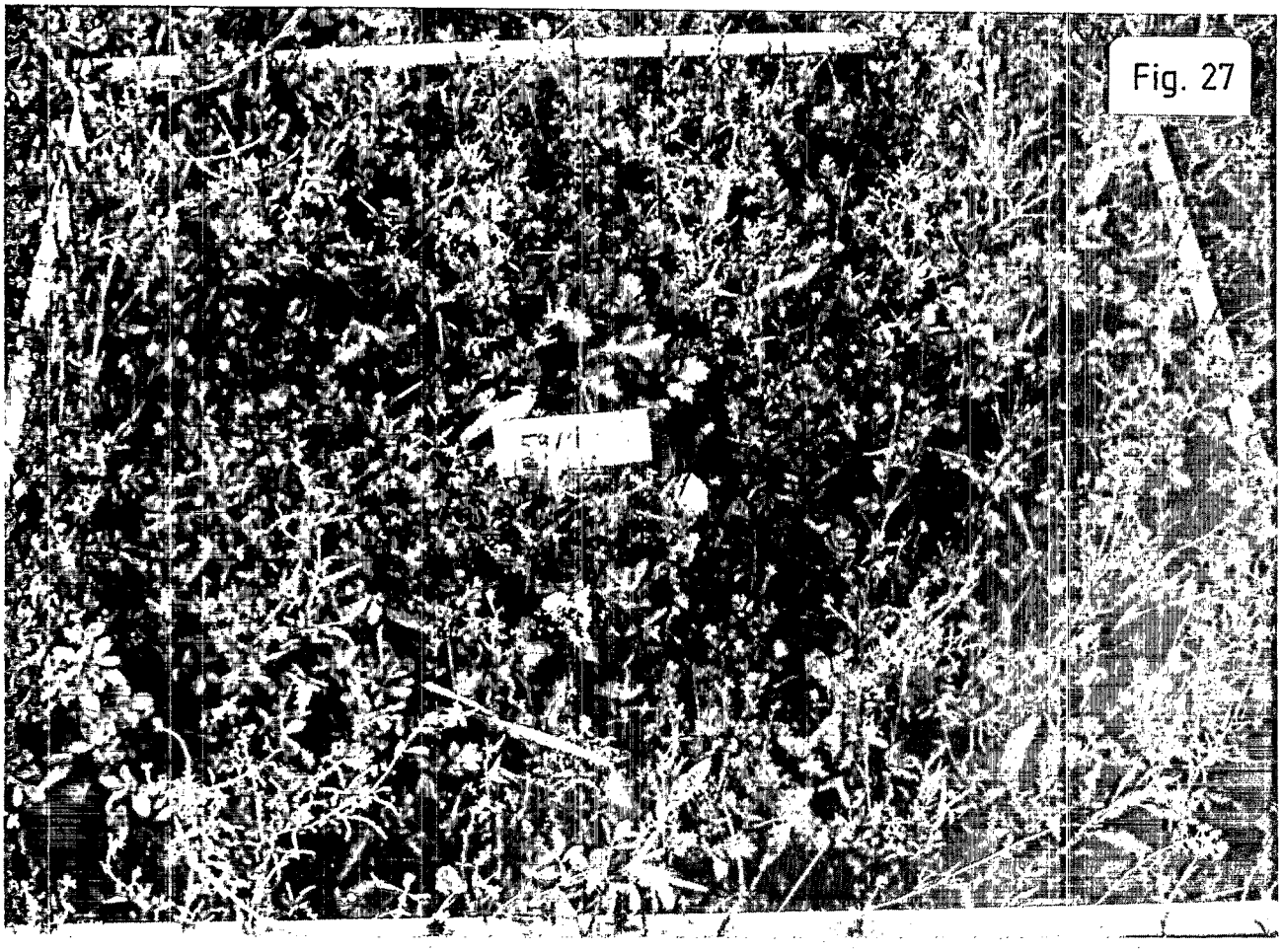


Fig. 27

Fig. 28

		after treatment	Refilled soil			
			after 20 months		after 30 months	
			in a depth			
			0 - 0,3 m	0,3 - 2,0 m	0 - 0,3 m	0,3 - 2,0 m
value		10,6	7,7	7,8	7,4	8,6
conductisity	mS/m	445	54	37	14	44
COD	mgO2/l	31	< 15	< 15	< 15	< 15
PAH	mg/l	< 0,001	< 0,001	< 0,001	< 0,001	< 0,001
Phenolindex	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
KW (n. DEV H 18)	mg/l	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
EOX (Cl)	mg/l	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Antimon (Sb)	mg/l	0,004	0,012	0,007	0,004	0,006
Arsen (Ar)	mg/l	0,028	0,08	0,029	0,027	0,021
Barium (Ba)	mg/l	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Beryllium (Be)	mg/l	< 0,001	< 0,001	< 0,001	< 0,001	< 0,001
Blei (Pb)	mg/l	< 0,001	< 0,002	< 0,002	< 0,002	< 0,002
Bor (B)	mg/l	< 1	< 1	< 1	< 1	< 1
Cadmium (Cd)	mg/l	< 0,001	< 0,001	< 0,001	< 0,001	< 0,001
Chrom (Cr) total	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Eisen (Fe)	mg/l	< 0,2	< 0,2	< 0,2	< 0,2	< 0,2
Kobalt (Co)	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Kupfer (Cu)	mg/l	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Mangan (Mn)	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Nickel (Ni)	mg/l	< 0,002	< 0,001	< 0,001	< 0,001	< 0,001
Quecksilber (Hg)	mg/l	< 0,0005	< 0,0005	< 0,0005	< 0,0005	< 0,0005
Selen (Se)	mg/l	0,004	0,021	0,008	0,002	0,002
Silber (Ag)	mg/l	0,001	< 0,001	< 0,001	< 0,001	< 0,001
Thallium (Tl)	mg/l	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005
Vanadium (V)	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Zink (Zn)	mg/l	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Zinn (Sn)	mg/l	< 0,005	0,006	0,005	< 0,005	< 0,005
Fluorid (F)	mg/l	0,7	0,87	0,72	1,3	0,55
Ammoniak (N)	mg/l	1,4	< 0,08	< 0,08	< 0,08	0,1
Chlorid (Cl)	mg/l	8,1	< 1	1,8	< 1	1,6
Cyanide (CN) total	mg/l	0,04	< 0,01	0,02	0,02	0,01
Nitrat (NO3)	mg/l	0,5	0,11	0,27	0,14	0,14
Nitrit (NO2)	mg/l	0,06	< 0,01	< 0,01	< 0,01	0,13
Phospat (P)	mg/l	0,19	< 0,1	0,1	0,12	< 0,1
Sulfat (SO4)	mg/l	385	255	157	34	190

RAG
RUHRKOHLE WESTFALEN AG

Results of tests according to the landfill directive (class I) of Northrhine Westfalia

(Eluat according to the German norm DEV S 4)

Lehmann
Nov. 1991

Appendix 2-C

Thermal Technology Case Studies

Off-site Soil Treatment, Japan

Thermal Treatment of Contaminated Soil with Mercury

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SUMMARY

The site of former electro-chemical industry in residential area of Tokyo was found to be highly contaminated with mercury and lead when the industry stopped its operation and dismantled facilities in order to move the factory to the suburb and redevelop the site in accordance with the urban planning of Tokyo Metropolitan Government. The mercury contamination was mostly limited within surface soil with average concentration of 3.68 % (max. 15.6 %). About 56,000 m^3 soils with mercury level of above 2 mg/kg were considered to be processed before redevelopment of the site. Underground containment with and/or without stabilization using with Na_2S for slightly contaminated soil and thermal treatment (roasting) for heavily contaminated soil were taken for the remedial technologies of the site. About 840 m^3 (ca.1260 tons) heavily contaminated soils with mercury were railed to off-site mercury roasting plant to process and recover mercury. Total cost of soil roasting including pakaging and transportation was about $374/ton soil.

1. INTRODUCTION

A. Site Description

The problem site, a former electro-chemical industry site was situated in dense residential area on the bank of the Sumida River in Arakawa Ward, northeast part of Tokyo Metropolitan Area where many small industries and residential premises have been coexited (see Figure 1). The soils in the site were alluvium and hence soft with a few organic material and composed of mainly silty sand. N value of soil strata between 0 m and -21 m ranged from 0 to 4 and cohesive strength was 2-3 tons/m^3. Hydraulic conductivity was around 10^{-4} cm/sec in silty sand and 10^{-5}-10^{-6} cm/sec in silt

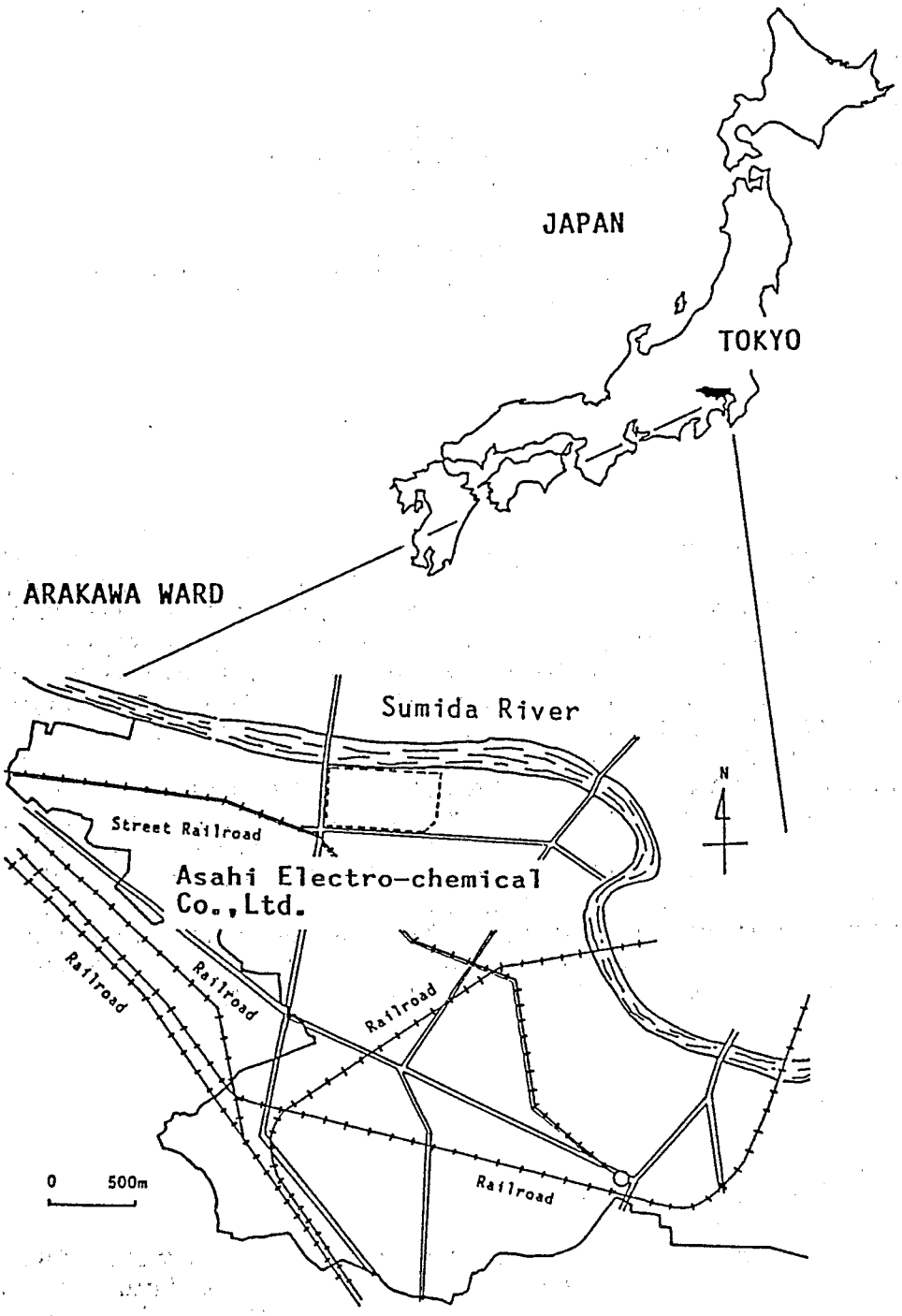

Figure 1. Location Map of the Former Asahi Electro-chemical Co., Ltd. Site

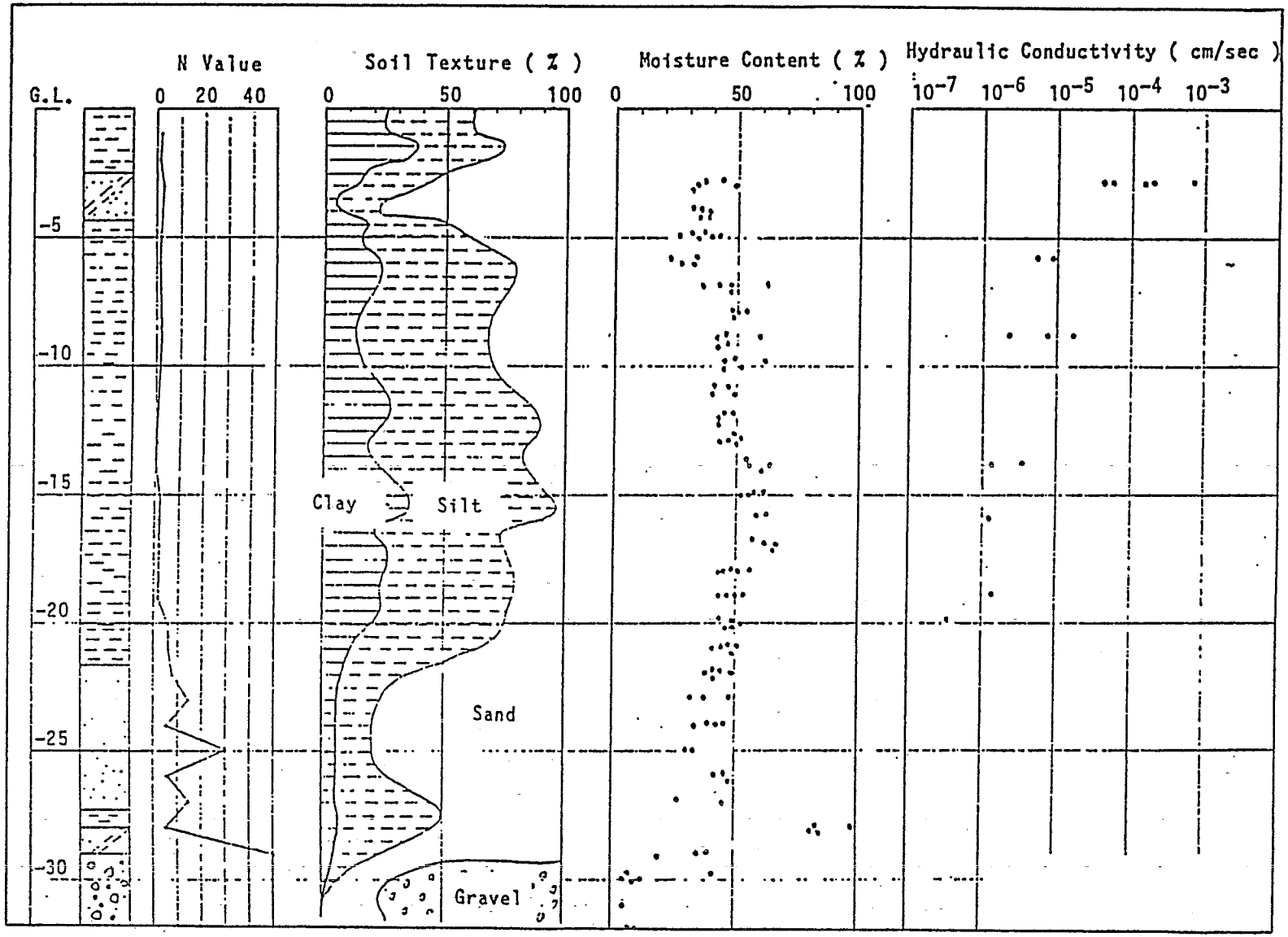

Figure 2. Soil Texture and Hydrogeology of the Site

(see Figure 2). Groundwater level was high (i.e. 0.2-0.8 m below surface) and groundwater flow in horizontal direction could not be recognized.

B. Site History

The industry, Asahi Electro-chemical Co., Ltd. began its operation at this site in 1917 to produce primarily sodium hydroxide and breaching powder as a leading industry in Japan at that time. Using hydrogen and chlorine, by-products of sodium hydroxide, they also produced soap, margarine, hydrogen chloride, and chlorinated organic compounds as well as another industrial materials.

In 1955, the company developed mercury-electrolysis process to obtain high quality sodium hydroxide to meet requirements of chemical textile industry which had developed rapidly after World War Two in Japan. By the time when closed system was introduced into mercury-electrolysis process in 1966, mercury had spilled out of plant in the form of gas, wastewater and stains on various materials. As a result, the site of 20 ha was widely contaminated with mercury and lead.

In the early 1970's, Tokyo Metropolitan Government decided to remove heavy chemical industry located in residential area to industrial area or another prefecture. Asahi Electro-chemical Co., Ltd. was included in this project. After removing, the site was planned to be used for college, pubilic park, municipal wastewater treatment plant, and community complex. The plant was closed in March 1979.

During dismantling the factory equipments in 1978, highly contaminated soils with mercury of max. 15.6 % (3.68 % mean) were detected under electroysis vessel. These soils with a volume of 840 m^3 (ca. 1,260 tons) were excavated and packed into about 6,000 drums and stored on site. Several alternatives were considered to treat these highly contaminated soil and finally these were railed to off-site mercury roasting plant at Hokkaido to recover mercury in 1979 and 1980.

C. Initial Sampling and Analysis Results

In 1977 the company analysed mercury and lead level of soil core samples and groundwater in the site. Results of initial analysis are shown in Figure 3 and Table 1. Among 980 soil samples at 188 points, maximum mercury concentration was 1,250 mg Hg/kg soil, while 79 samples showed above 5 mg Hg/kg soil. Form of mercury was mostly sulphide . A 97 % of groundwater sample showed the concentration of below 0.005 mg/1. Only top soils (i.e. 50 cm below surface) were severely contaminated and groundwater contamination outside the site was not recognized. Maximum lead concentration of

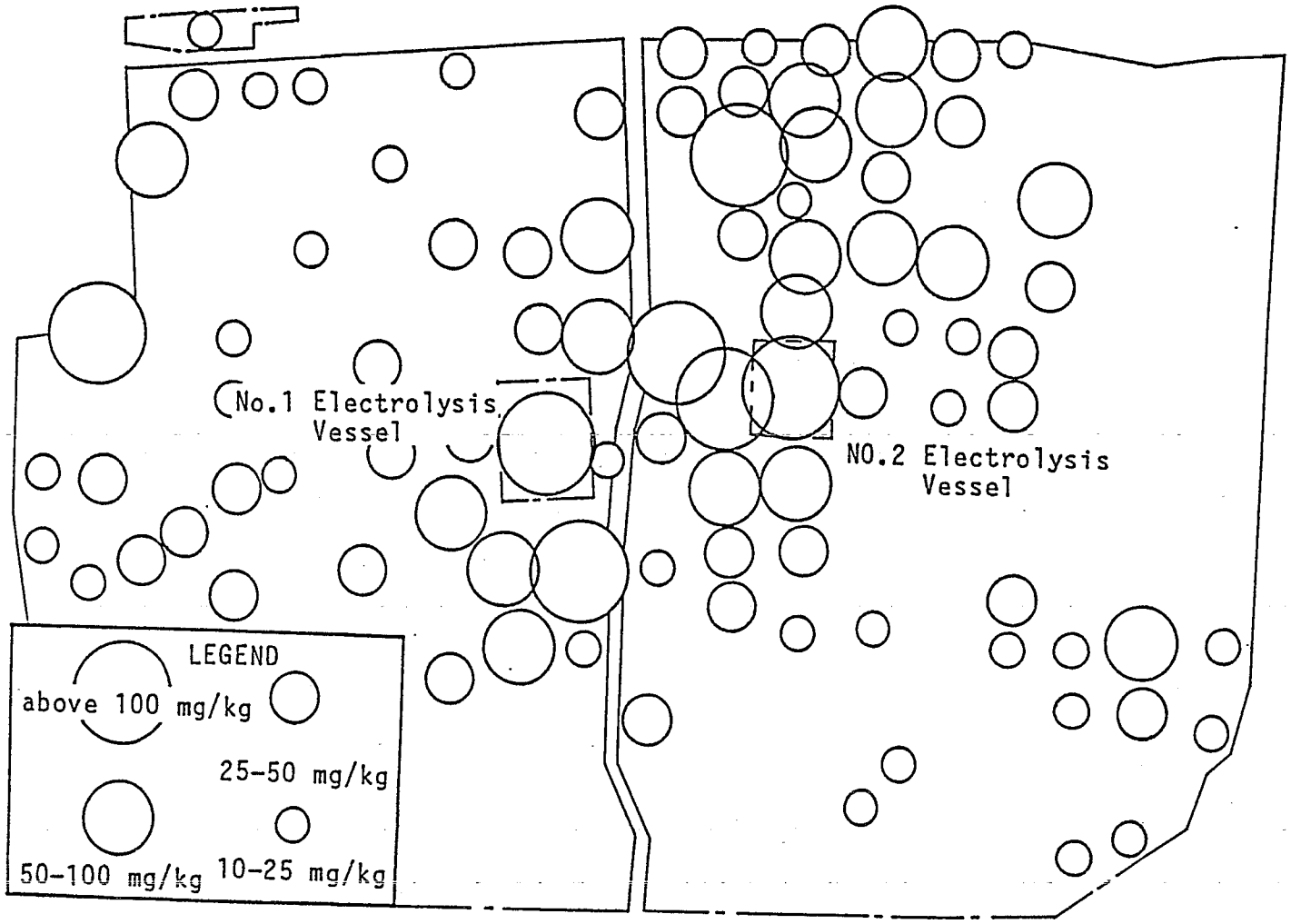

Figure 3. Mercury Distribusion in the Site

Table 1. Initial Sampling Results of Soil and Groundwater

(a) Soil

Depth (m)	Hg Concentration (mg/kg) <5	5-25	25-100	100-500	500-1,000	>1,000	No. of Sample
0	109	48	25	4	1	1	188
0.5	132	40	11	5	–	–	188
1	172	12	2	2	–	–	188
2	94	2	2	–	–	–	98
3	84	2	–	–	–	–	86
4	85	1	–	–	–	–	86
5	84	2	–	–	–	–	86
7-15	60	–	–	–	–	–	60
No. of Sample (%)	820 (83.7)	107 (10.9)	40 (4.1)	11 (1.1)	1 (0.1)	1 (0.1)	980 (100)

(b) Groundwater

Depth (m)	Hg Concentration (mg/l) <0.005	>0.005	No. of Sample
0	179	9	188
0.5	179	9	188
1	181	7	188
2	97	1	98
3	85	1	86
4	85	1	86
5	85	1	86
7-15	60	–	60
No. of Sample (%)	951 (97.0)	29 (3.0)	981 (100)

soil was 2,610 mg Pb/kg soil. No further information on lead contaminaton was available. Mercury in highly contaminated soil which were detected under the two electrolysis vessel during dismantling factory was metal mercury. Mean concentration of mercury in these soils were 3.68 % and mostly distributed between 1 and 7 % as shown in Figure 4.

D. Technology Selection

There was no statutory criteria for clean-up decision of mercury contaminated soil at that time. Therefore Tokyo Metropolitan Government sampled soils at 71 non-contaminated area through Tokyo and analysed mercury to show that most of the data distributed between 0.02 and 2 mg Hg/kg soil. Hence they took 2 mg Hg/kg soil as a maximum background level of non-contaminated area and critera for remedial action.

Underground containment with or without stabilization/solidification has been considered so often as a basic treatment method for contaminated soil in Japan. However, it was impossible to keep the level of mercury in solution of highly contaminated soil under the certain level even if solidified with Na_2S and $FeCl_2$. Moreover recovering mercury from these soils were judged to be economically feasible and preferable from the view point of resource conservation. Fot these reasons, remedial technologies were selected according as the level of contamination as follows:

(1) Thermal treatment (i.e. roasting) for highly contaminated soil with above 10 mg Hg/kg soil.

(2) Underground containment after immobilization for highly contaninatead soil with above 10 mg Hg/kg soil.

(3) Underground containment without any pre-treatment for moderately contaminated soil with 2-10 mg Hg/kg soil.

2. THERMAL TREATMENT TECHNOLOGY

Initially, Ashahi Electro-chemical Co., Ltd. planned to construct on-site rotary kiln with a total throughput of 0.3 t/day to roast contaminated soil using light oil as a fuel. Due to the strong opposition of nearby residents and immature technology to control gaseous mercury under the level of regulation, they had to withdraw this plan and decided to transport contaminated soils to mercury recovery plant in mountainous site of Hokkaido, about 1,000 km north of Tokyo. This plant was owned by mercury refining company , Nomura Kosan Co. and was used for treatment of mercury bearing waste to recover mercury at that time.

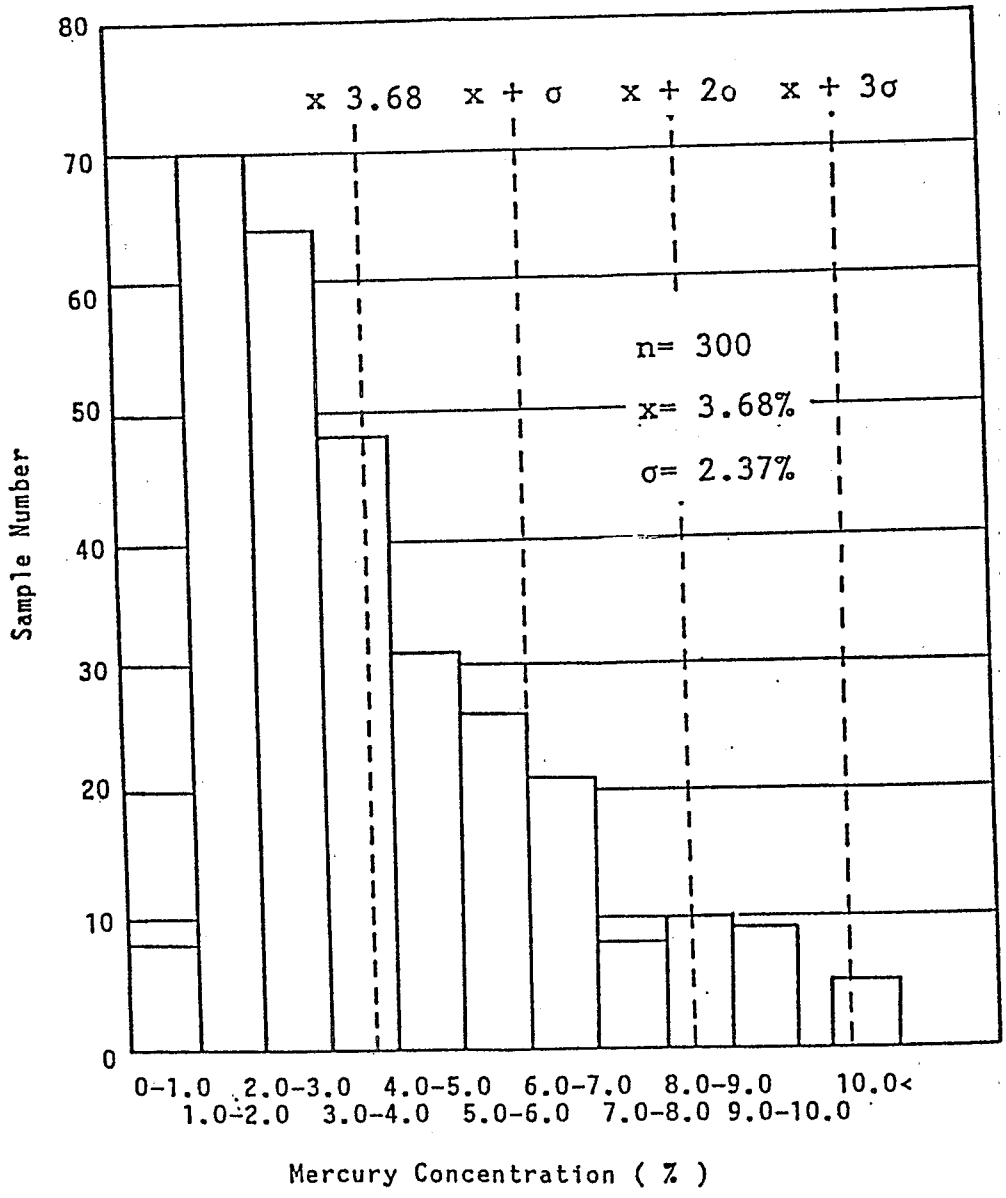

Figure 4. Mercury Distribution in Highly Contaminated Soil

This plant is equipped with vertical multistage roasting furnace (called as Herreshoff Furnace) with an annual gross teatment capacity of 3,600 tons. The plant is primarily composed of roaster, condenser to recover mercury and flue gas cleaning devices. Schematic flow diagram of this plant is shown in Figure 5.

Mercury-contained waste or soil is roasted at temperature of 600-800 C using heavy oil. Volatiled mercury in flue gas condensed on the inner wall of condenser subsequent to dust removal equipment. Crude mercury is recovered from soot at constant intervals and refined into commercial grade groducts with a purity of 99.99 % or more either by thw wet or the vaccume distilling. Trace amount of mercury and acid gas components in flue gas are removed by adsorption and neutralization. Slag from roasting furnance are disposed of at on-site secure landfill and sludge from flue gas treatment processes, dust collected by cyclone, residue from mercury recovery are returned into roaster.

Recently this plant has been partly expanded to recover mercury and other metals from used dry cell generated from individual home.

3. DEMONSTRATION RESULTS

About 6,000 drums packed with highly contaminated soil were transporated everyday except Sunday during March and July in 1980. Cost of soil roasting was 65,000 yen/ton ($300/ton), and transportation cost including package was 16,000 yen/ton ($74/ton). Another mercury bearing waste were processed simultaneously at this plant, hence technical data of soil roasting were not available separately.

About 54,500 m^3 soils contaminated with mercury of above 2 mgHg/kg soil were contained in on-site underground pit after immobilization by Na_2S for the soils with mercury level of above 10 mg Hg/kg soil. Excavation and immobilization followed by underground containment were conducted from December 1983 to August 1984. To minimize environmental pollution during clean-up action, air, dust, effluent, noise, and vibration were monitored around the site and if any environmental deterioration was recognized, clean-up had to be stopped or modified. Groundwater and rainfall inside site were treated in the manner described in Figure 6. Groundwater has been monitored at 4 monitoring wells of 20 m depth just outside the site and no groundwater pollution has been reported so far.

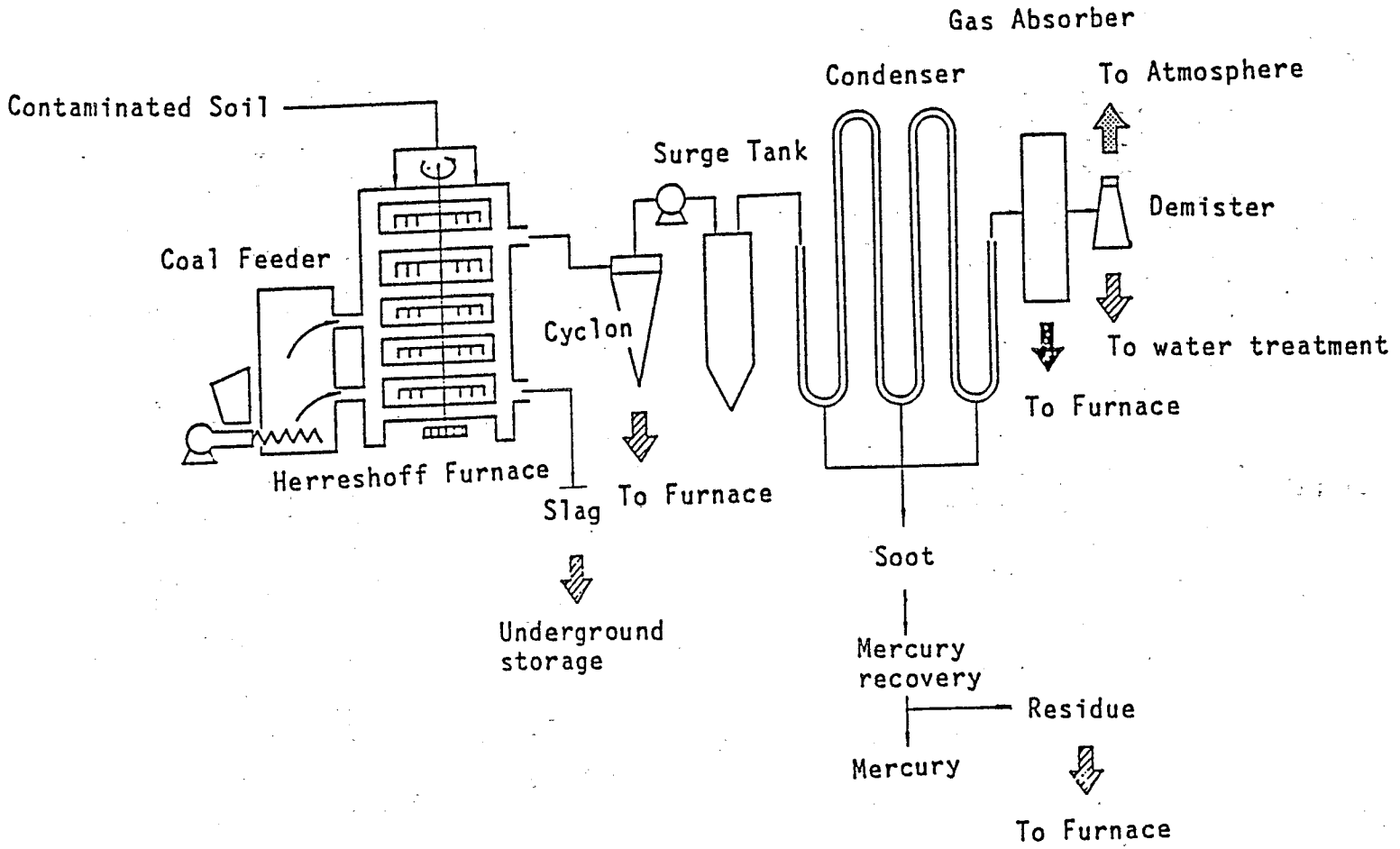

Figure 5. Mercury Roasting Facility

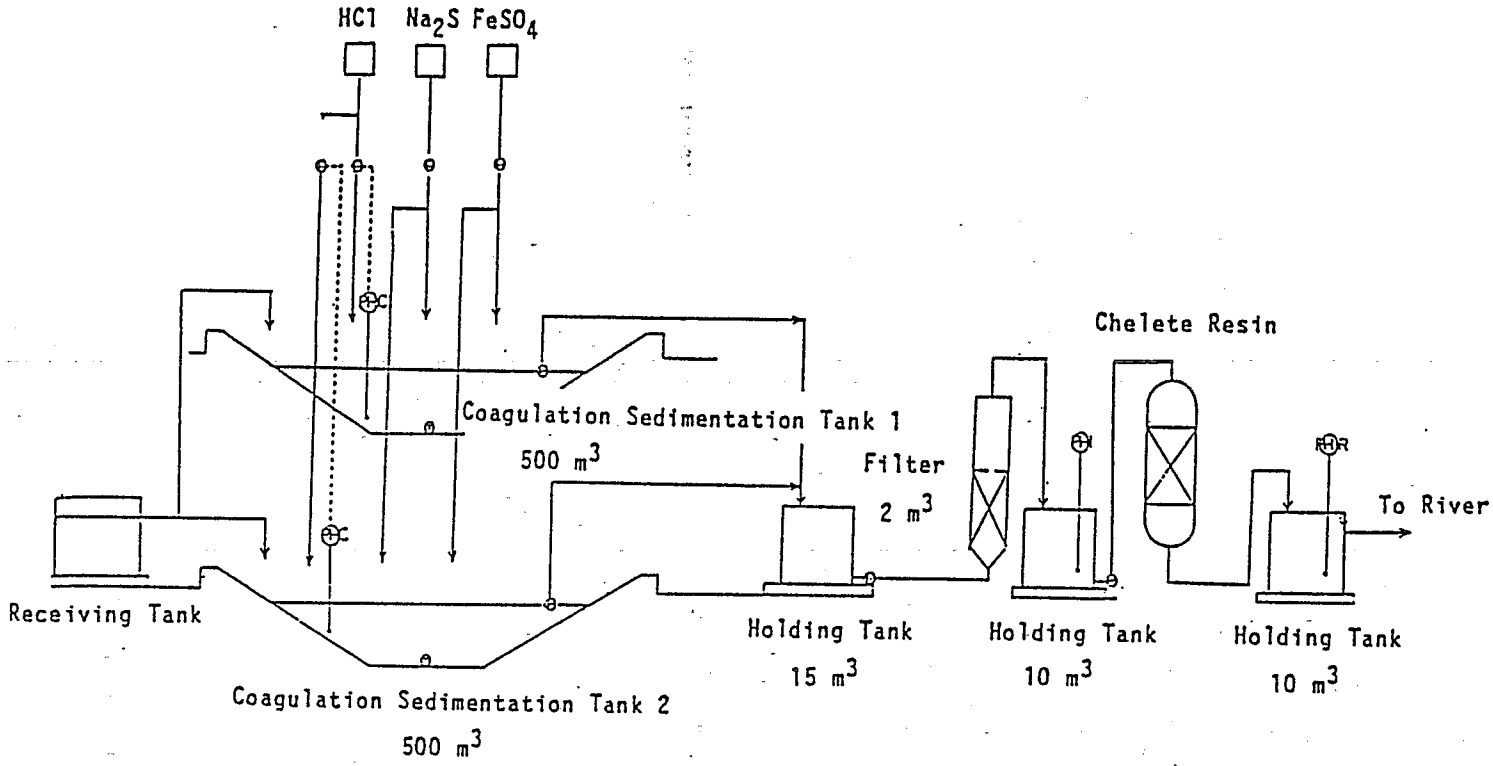

Figure 6. On-site Wastewater Treatment Facility

4. CONCLUSION

Soil pollution in Japan was focused on the agriculture field so far, however with urban redevelopment at former industry site or national institution, soil pollution at these site has been reported recently. In Tokyo, for example, several soil contaminations have been identified at these sites including the case of this paper. Major pollutants are heavy metals such as Hg, Pb, Cd and restoration has been completed at all cases identified.

In the light of these facts, Environment Agency has been conducting preliminary study of soil contamination resulted from human activities at residential area and clean-up criteria of these soils as well as clean-up technologies. Such criteria for soil clean-up has been set up at some local government already.

Remedial technologies used so far are disposal at secure landfill site or underground containment with or without immobilization in principle. These technologies are, however not detoxification method but mere isolation which renders future potential hazard and therefore development of both on-site and off-site detoxification technology of contaminated soil are required now.

Roasting of contaminated soil and mercury recovery of this paper are the only case of detoxification that has been ever tried in Japan. This example was off-site thermal treatment and economically feasible because the mercury level in soil was extremely high, as high as mercury ores. On-site roasting, however is technically and possible as the company originally planned, provided that nearby residents accept such facility.

ACKNOWLEDGMENT

Authors thank the Department of Environment Control, Tokyo Metropolitan Government and Arakawa Ward Office for offering informations.

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Appendix 2-D

Thermal Technology Case Studies

Electric Infrared Incineration, United States

United States
Environmental Protection
Agency

EPA/540/S5-88/002
January 1989

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Technology Demonstration Summary

Shirco Electric Infrared Incineration System at the Peak Oil Superfund Site

Under the auspices of the Superfund Innovative Technology Evaluation or SITE Program, a critical assessment is made of the performance of the transportable Shirco Infrared Thermal Destruction System* during three separate test runs at an operating feedrate of 100 tons per day. The unit was operated as part of an emergency cleanup action at the Peak Oil Superfund site in Brandon, Florida. The report includes a process description of the unit, unit operations data and a discussion of unit operations problems, sampling and analytical procedures and data, and an overall performance and cost evaluation of the system.

The results show that the unit achieved destruction and removal efficiencies (DREs) of polychlorinated biphenyls (PCBs) exceeding 99.99% and destruction efficiencies (DEs) of PCBs ranging from 83.15% to 99.88%. Acid gas removal efficiencies were consistently greater than 99%. Particulate emissions ranged from 171 to 358 mg/dscm, exceeding 180 mg/dscm during two of the four tests. The Extraction Procedure (EP) Toxicity Test on the furnace ash exceeded the RCRA EP Toxicity Characteristic standard for lead. Small quantities of tetrachlorodibenzofuran (TCDF) were detected in one of the four stack gas samples. Also detected were low levels of some semivolatile organics and a broader range of volatile organics, which can be considered products of incomplete combustion (PICs). Ambient air monitoring stations detected quantities of PCBs, which appear to be caused by the transport of ash from the ash pad to the ash storage area. Waste feed and ash samples were not mutagenic according to the standard Ames Salmonella mutagenicity assay. Unit costs are estimated to range from $196 to $795 per ton with a normalized cost per ton of $425 for the Peak Oil cleanup.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Program demonstration that is fully documented in three separate reports (see ordering information at back).

Introduction

The SITE Program demonstration test of the Shirco infrared incineration system was conducted from July 1, 1987 to August 4, 1987 at the Peak Oil Superfund site in Brandon, Florida during a removal action by EPA Region IV. The Region had contracted with Haztech, Inc., an emergency removal cleanup contractor, to incinerate approximately 7,000 tons of waste oil sludge contaminated with PCBs and lead after determining that high temperature thermal destruction of the nonrecyclable sludge was capable of destroying the PCBs in a cost-effective and environmentally sound manner. Metals that concentrated in the ash residue would be dealt with after the thermal destruction of the sludge. The removal action offered an ideal opportunity for the SITE program to obtain specific operating, design, analytical, and cost information to evaluate the performance of the unit under actual operating conditions. Also, the SITE program studied the feasibility of utilizing the Shirco transportable infrared incinerator as a viable hazardous waste treatment system at other sites throughout the country. To this end, specific test objectives of the Shirco system were:

- To determine the system's destruction and removal efficiency (DRE) for PCBs.
- To report the unit's ability to decontaminate the solid material being processed and to determine the destruction efficiency (DE) for PCBs based on the PCB content of the furnace ash.
- To evaluate the ability of the unit and its associated air pollution control/scrubber system to limit hydrochloric acid and particulate emissions.
- To determine whether heavy metals contaminants in the waste feed are chemically bonded or fixated to the ash residue by the process.
- To determine the effect of the thermal destruction process in producing combustion byproducts or products of incomplete combustion (PICs).
- To determine the impact of the unit operation on ambient air quality and potential mutagenic exposure.
- To provide unit cost data for effective development of a cost/economic analysis for the unit.
- To document the mechanical operations history of the unit and analyze and provide potential solutions to chronic mechanical problems.

Facility and Process Description

Solid waste processed at the Peak Oil site was incinerated in a transportable infrared incinerator, designed and manufactured by Shirco Infrared Systems, Inc. of Dallas, Texas and operated by Haztech, Inc. of Decatur, Georgia. The overall incineration unit consists of a waste preparation system and weigh hopper, infrared primary combustion chamber, supplemental propane-fired secondary combustion chamber (afterburner), emergency bypass stack, venturi/scrubber system, exhaust system, and data collection and control systems, all mounted on transportable trailers. The system process flow and the overall test site layout are presented schematically in Figure 1.

Solid waste feed material is processed by waste preparation equipment designed to reduce the waste to the consistency and particle sizes suitable for processing by the incinerator. After transfer from the waste preparation equipment, the solid waste feed is weighed and conveyed to a hopper mounted over the furnace conveyor belt. A feed chute on the hopper distributes the material across the width of the conveyor belt. The feed hopper screw rate and the conveyor belt speed rate are used to control the feedrate and bed depth.

The incinerator conveyor, a tightly woven wire belt, moves the solid waste feed material through the primary combustion chamber where it is brought to combustion temperatures by infrared heating elements. Rotary rakes or cakebreakers gently stir the material to ensure adequate mixing, exposure to the chamber environment, and complete combustion. When the combusted feed or ash reaches the discharge end of the incinerator, it is cooled with a water spray and then is discharged by a screw auger/conveyor to an ash hopper.

The combustion air to the incinerator is supplied through a series of overfire air ports located at various locations along the incinerator chamber; combustion air flows countercurrent to the conveyed waste feed material.

Exhaust gas exits the primary combustion chamber and flows into the secondary combustion chamber where propane-fired burners combust any residual organics present in the exhaust gas. The secondary combustion chamber burners are set to burn at a predetermined temperature. Secondary air is supplied to ensure adequate excess oxygen levels for complete combustion. Exhaust gas from the secondary combustion chamber is quenched by a water-fed venturi/scrubber to remove particulate matter and acid gases; the exhaust gas is then transferred to the exhaust stack by an induced draft fan, and finally discharged to the atmosphere.

The main unit controls and data collection indicators comprising the data collection and control system are housed in a specially designed van.

An emergency bypass stack is mounted in the system directly upstream of the venturi/scrubber for the diversion of hot process gases under emergency shutdown conditions.

Results and Discussion

A detailed summary of the SITE demonstration test results is presented in Table 1. Based on the test objectives outlined in the Introduction, the following results and conclusions were obtained.

PCB Destruction and Removal Efficiency

PCBs were analyzed in the solid waste feed, furnace ash, scrubber effluent solids, stack gas, scrubber liquid effluent, and scrubber water inlet. The DRE calculation for PCBs is based on the following:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

where: W_{in} = mass rate of PCBs fed to incinerator

W_{out} = mass emission rate of PCBs in stack gas

The unit achieved a DRE for PCBs of 99.99%.

It should be noted that the unit was operated to produce an ash that contained 1 ppm or less of PCB. The PCB concentration in the waste feed to the unit varied from 5.85 to 3.48 ppm during the tests. These low PCB concentrations in the waste feed were the result of mixing the original oily waste having up to 100 ppm of PCBs with the PCB-free surrounding soil, lime, and sand so that the resulting material could

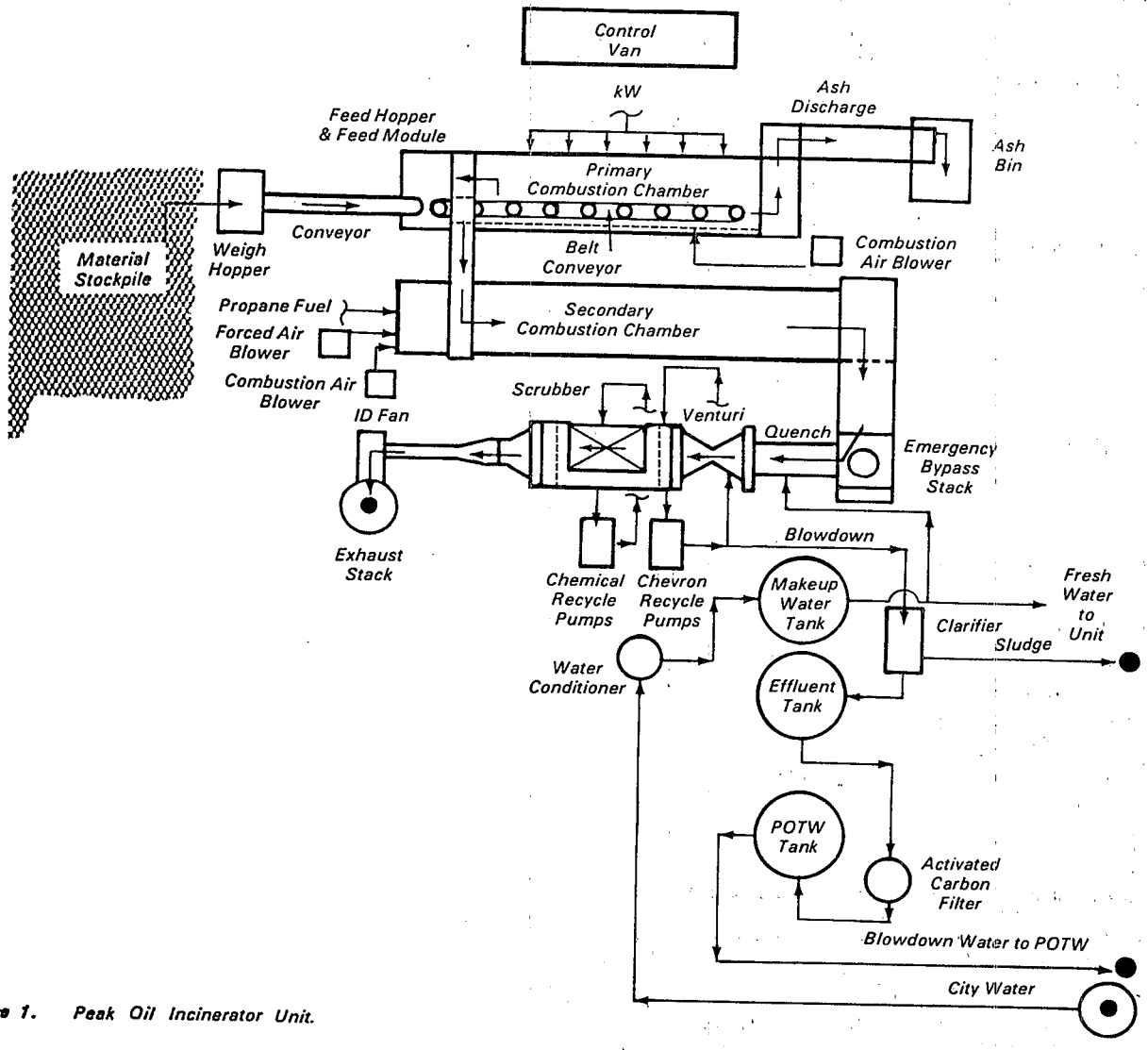

Figure 1. Peak Oil Incinerator Unit.

be handled and processed as a solid waste. It was not possible to calculate the DRE beyond two decimal places because of the detection limits associated with the analytical procedures employed.

Decontamination of Solid Waste and Destruction Efficiency

Residual PCBs in the furnace ash were below the 1 ppm operating standard, ranging from 0.007 ppm on August 1 to 0.900 ppm on August 3. DE was determined by the formula

$$DE = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

where: W_{in} = mass rate of PCBs fed to incinerator

W_{out} = mass rate of PCBs in stack gas, furnace ash, and scrubber effluent

A basis for calculating DE was based on the PCB concentrations in the waste feed and the furnace ash. The DE or removal of the PCBs from the waste feed ranged from 99.88 wt% (August 1) to 83.15 wt% (August 3).

Acid Gas Removal

Measured HCl emission rates ranged from less than 0.8 to 8.6 g/hr. Since the chlorine concentration in the solid waste feed was below the 0.1% detection limit, it was impossible to determine actual HCl removal efficiency. However, SO_2

Table 1. *Site Demonstration Test Results Summary*

	8/1/87	8/2/87	8/3/87	8/4/87
Waste Feed Characteristics				
Moisture, wt. %	16.63	16.06	14.24	14.37
Ash, wt. %	69.77	69.80	72.40	75.21
HHV, Btu/lb	2064	1639	1728	2018
PCB, ppm	5.850	3.850	5.340	3.480
Pb, ppm	5900	4900	5000	4400
Chlorine, ppm	<1000	<1000	<1000	<1000
Sulfur, ppm	25300	17800	18900	16700
Chlorine (as HCl), kg/hr	<5	<5	<5	<5
Sulfur (as SO_2), kg/hr	200	132	138	125
EP Tox (Pb), mg/L, ppm	27.00	29.00	--	24.00
TCLP (Pb), mg/L, ppm	8.60	2.50	3.00	3.50
Stack Gas				
HCl, ppmv	<0.051	0.60	0.22	0.20
SO_2, ppmv	0.99	41.80	0.96	0.91
HCl, g/hr	<0.8	8.60	2.90	2.70
SO_2, g/hr	27.40	1070.0	22.0	20.6
Particulates (@ 7% O_2), mg/dscm	358	211	173	171
PCB, µg/hr	57.70	174.50	58.10	126.20
Ash				
PCB, ppm	0.01	0.240	0.900	0.540
Pb, ppm	7100	6000	6400	6200
EP Tox (Pb), mg/L, ppm	25.0	28.0	36.0	36.0
TCLP (Pb), mg/L, ppm	0.01	0.01	0.02	0.01
Operating Conditions				
Waste Feedrate (avg. daily), kg/hr	3328	3287	3626	3600
DRE (PCB), wt. %	99.99	99.99	99.99	99.99
DE (PCB), wt. %	99.88	93.77	83.15	84.48
Primary Combustion Chamber				
Exhaust Temperature (avg.), F	1797	1836	1922	1885
Residence Time, min.	19	19	18	19
Secondary Combustion Chamber				
Chamber Temperature (avg.), F	1886	1887	1889	1907
Residence Time, sec.	>3	>3	>3	>3
Acid Gas Removal Efficiency, wt. % SO_2	>99.9	>99.1	>99.9	>99.9

emissions were less than 1100 g/hr, with an average 149 kg/hr SO_2 feedrate giving an average removal of SO_2 in excess of 99%. SO_2 is more difficult to remove than HCl in a caustic scrubber, and the tests show that HCl removal should be in excess of the 99% determined for SO_2 removal.

Particulate Emissions

The particulate emissions during the first day were 358 mg/dscm. The unit was cleaned and mechanical adjustments were made resulting in an emission rate of 211 mg/dscm during the second day. The emissions during the third day were 172 mg/dscm (average of duplicate measurements). These values exceeded the RCRA standards during two of the four sampling periods. Particulate emissions were about 60% lead, when analyses of all samples were averaged.

Leaching Characteristics

The solid waste feed, furnace ash, and scrubber effluent solids were subjected to the EP Toxicity and proposed TCLP tests to evaluate the toxicity characteristics of these materials.

The EP Toxicity and the TCLP data present a contradictory picture regarding leaching of metals. The EP Toxicity data did not indicate that the process "encapsulates" or ties up heavy metals (lead) in the ash to prevent leaching. The EP Toxicity data show that lead content in the ash was 30 ppm and exceeded the 5 ppm toxicity characteristic standard. The measured lead content of leachates for feed material and ash are almost equal, indicating that the process appears not to affect leaching characteristics for lead.

In contrast to the EP Toxicity data, the TCLP data show that the lead content for both the feed and ash were less than the proposed toxicity characteristic standard of 5 ppm. Measured lead concentrations were an order of magnitude lower in the TCLP leachate (about 2 ppm compared to about 30 ppm for EP Toxicity).

The significant differences in results from these two analytical techniques have been documented in a recent Oak Ridge National Laboratory report (ORNL, "Leaching of Metals from Alkaline Wastes by Municipal Waste Leachate," ORNL/TM-11050, March, 1987). It appears that the differences in the test procedures and alkalinity of the matrix provide a difference in the pH environment that is sufficient to affect the solubility and leachability of heavy metals, particularly lead.

Products of Incomplete Combustion

Small quantities of products of incomplete combustion (PICs) were identified in the sampled streams from

the unit. No polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) were identified in any of the sampled streams above detection limits with the exception of trace quantities (2.1 ng) of tetrachlorodibenzofuran (TCDF) found in the stack gas sampled on August 2.

Low levels of some semivolatile organic compounds were identified in all streams. These compounds were primarily phthalates, which may be the result of contamination from plastic components in the process, sampling equipment, or laboratory apparatus. Other semivolatile compounds included aromatic, polyaromatic, and chlorinated aromatic hydrocarbons. Low levels of pyrene, chrysene, anthenes, naphthalenes, and chlorinated benzene were identified in the waste feed stream; although possible PICs, their presence must be discounted to some extent, because they were originally introduced into the unit with the waste feed.

Low concentrations of volatile organics were measured in the stack gas and included halogenated methanes, chlorinated organics, and aromatic hydrocarbons including BTX compounds. No volatile organics were identified in the water streams. Low levels (ppb) of chlorinated hydrocarbons and BTX compounds were measured in all solid streams. Low levels of BTX compounds, carbon disulfide, chloroform, ditrichlorofluoromethane, and trichlorofluoromethane, dichloroethane, and trichloroethane, and methylene chloride were identified in the waste feed. Methylene chloride, a solvent used during testing, was also detected in laboratory and field blanks. These compounds, although possible PICs, must also be discounted to some extent based on their introduction to the unit from an external source and because of possible contamination.

Ambient Air Sampling and Mutagenic Testing

Ambient air monitoring stations placed upwind and downwind of the Shirco unit were designed to collect airborne PCB contaminants. Based on the downwind sampler data, it appears that the Peak Oil site boundaries limited the location of the downwind sampler to an area that was significantly exposed to fugitive emissions during the transport of ash from the ash pad to the ash storage area.

Samples of the waste feed and ash were collected on August 2 and forwarded to the EPA Health Effects Laboratory, Research Triangle Park, North Carolina for mutagenic testing. The results of these tests indicate that although the samples contain hazardous contaminants, they are not mutagenic based on the standard Ames Salmonella mutagenicity assay.

Cost/Economic Analysis

Several cost scenarios examined were based on a model for a Shirco unit operation equivalent in processing capacity to the unit that operated at Peak Oil, and on cost data available from Shirco and other sources. The economic analysis concludes that in using currently available Shirco transportable infrared incineration systems, commercial incineration costs will range from an estimated $196 per ton for a Shirco unit operation at an 80% on-stream capacity factor to an estimated $795 per ton for the operation at the Peak Oil site at a 19% on-stream capacity factor. A normalized total cost per ton of $425 represents a more realistic interpretation of the costs accrued to the Peak Oil cleanup action based on a 37% on-stream capacity factor.

Unit Problems

A review of the Haztech, EPA Technical Assistance Team (TAT), and EPA logbooks and progress reports, plus discussions with unit and project personnel, provided a summary of mechanical and operating problems encountered in this first application of a full-scale commercial Shirco incineration system at a Superfund site. These problems were categorized by unit operating sections, and a profile of the major problem areas within the unit were defined and analyzed to ascertain the reasons for and possible solutions to these specific operational difficulties. The review revealed that materials handling and emissions control were the most significant problem areas affecting operation of the unit. Prior to the operation of such a unit, extensive pretest analysis should be conducted on the waste feed matrix. The characteristics of the feed, including the nature of contaminants plus the feed's effect on incineration system chemistry, must be defined to allow appropriate assembly of the unit. The unit must be equipped with the proper feed preparation system and materials handling capabilities and adequate emissions control capacity and effectiveness. At the Peak Oil site, the solidified sludge feed continually agglomerated, clogged, bridged, and jammed feed preparation and handling equipment. The high levels of lead contaminant and the excessive carryover of calcium and magnesium salts were a continuous source of problems for the emissions control system, which had difficulty in meeting stack emissions criteria.

Conclusions and Recommendations

Based on the above data and discussions, the following conclusions and recommendations can be made concerning the operation and performance of the transportable Shirco infrared thermal destruction system.

1. The unit achieved DREs of PCBs greater than 99.99%. Detection limits were used for this calculation so actual DREs were greater.
2. The unit achieved DEs of PCBs ranging from 83.15 to 99.88%. The unit was operated to produce an ash that contained 1 ppm or less of PCB.
3. Acid gas removal efficiencies were consistently greater than 99%. Particulate emissions during two days of testing were 358 mg/dscm and 211 mg/dscm, which contained 60% lead. The unit's emissions control system experienced particulate removal problems due to a combination of excessive fines carryover from the waste feed matrix and scrubber-washer and an overall emissions control system design that was not able to operate efficiently at abnormally high particulate loadings. As a result, two of the four samples taken exceeded the 180 mg/dscm RCRA standard.

   Pretest analysis of the waste feed and its combustion and emissions control chemistry and mechanisms must be performed to identify potential emissions control problems. A more flexible and adaptable emissions control system should be developed that can respond to and control a wider range of particulate and stack gas flows.
4. The furnace ash failed to meet the toxicity characteristic standard for lead for the EP Toxicity Test Procedure. Although the ash passed the similar standard for the proposed TCLP, its failure under EP Tox indicates that the unit did not immobilize lead in the ash product.

5. Small quantities of PICs were identified in the sampled streams from the unit. In addition to trace quantities of TCDF on one sample, low levels of semivolatile compounds, including aromatic, polyaromatic, and chlorinated aromatic hydrocarbons were identified. Low concentrations of a broader range of volatiles including halogenated methane, chlorinated organics, and BTX compounds were also identified.

6. Ambient air monitoring stations detected quantities of PCBs, which appear to be caused by the wind transport of ash resulting from the nearby roadway. Waste feed and ash samples were not mutagenic based on the standard Ames Salmonella mutagenicity assay.

7. Overall costs ranged from $196 per ton with the unit operating at an 80% on-stream capacity (292 days per year) to $795 per ton with the unit operating at a 19% on-stream capacity (70 days per year). A normalized cost per ton for the Peak Oil cleanup was estimated at $425.

8. In addition to the particulate emissions control system problems, waste feed handling and materials handling problems consistently affected the unit's ability to treat the waste feed at design capacity. Pretest analysis of the waste feed and its handling characteristics must be performed to identify and design for any potential materials handling or feeding problems that the waste matrix may present at a specific site.

The EPA Project Manager, ***Howard Wall****, is with the Risk Reduction Engineering Laboratory, Cincinnati, OH 45268 (see below).*

The complete report consists of two volumes, entitled "Technology Evaluation Report, SITE Program Demonstration Test, Shirco Infrared Incineration System, Peak Oil, Brandon, Florida:"

"Volume I" (Order No. PB 89-125 991/AS; Cost: $21.95, subject to change) discusses the results of the SITE demonstration

"Volume II" (Order No. PB 89-116 024/AS; Cost: $42.95, subject to change) contains the technical operating data logs, the sampling and analytical report, and the quality assurance project plan/test plan

These two reports will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Applications Analysis Report: Shirco Infrared Thermal Destruction System," which discusses application and costs, is under development.

The EPA Project Manager can be contacted at:

Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

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Appendix 3-A

Stabilization/Solidification Technology Case Studies

In Situ Lime Stabilization (EIF Ecology), and Petrifix Process (TREDI), France

AGENCE NATIONALE POUR LA RÉCUPÉRATION ET L'ELIMINATION DES DÉCHETS

Département INDUSTRIE
RG/BP/MFB/OTAN/1

NOVEMBRE 1988

EVALUATION OF SOLIDIFICATION-STABILIZATION PROCESSES

I - OBJECTIVES OF THE PROJECT

The objective of the present study is to evaluate, some years after their application in France, for the treatment of different types of contaminated sites, the efficiency of solidification stabilization techniques.

II - SAMPLING AND ANALYSIS PROGRAMS

1 - Sampling

In order to get significant but rather simple evaluation of the treated sites, it was decided to carry out sampling procedure by digging trenches in the treated material by using a backhoe. This method was prefered to drilled boreholes because it is easy to carry out and moreover it allows easy visual observations and can give wide sections showing the treated material, its contacts with the surrounding soil and possible heterogeneousnesses.

For every site, three sampling trenches were realized and for every trench three samples of three kilograms of material were taken : one of the treated material from the upper layer of the treated section ; one of the treated material from the middle layer, and one from the ground material located under the treated zone. The upper sample may be considered as representative of the treated material in contact with biosphere conditions : freezing, leaching by infiltrated water, the middle sample may be considered as representative of the average treated material and lower sample would give an estimation of possible releases of contaminants from the treated material. However, on the field, it appeared sometimes that the material underlaying the treated area remained much or less contaminated by the orignal pollutant. In such cases the corresponding sample was not considered as significant.

2 - Analysis program

For every site it was made three average samples conrresponding to the three sampling levels by mixing the corresponding samples taken on the site. The specific analysis performed on samples included :

- measuring of physical properties

  . water content
  . permeability
  . compressive strength

- leaching tests

In France, at the present time, there are no specific standardized tests for the evaluation of contaminated material treated by stabilization-solidification. However, investigations are now carried out that will propose such tests within less than one year. Consequently, it was decided :

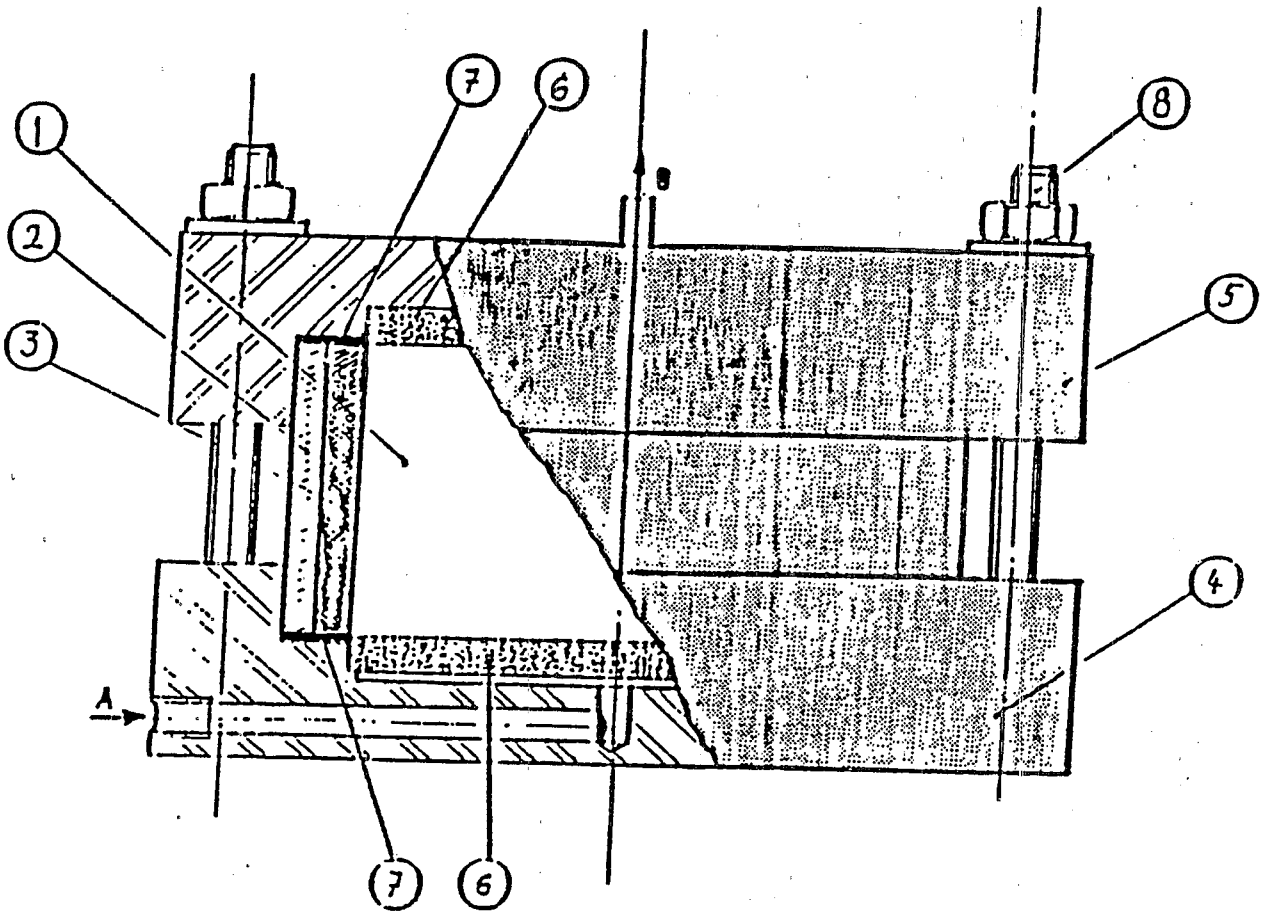
a) To perform, for every average sample the present leaching test (called INSA test) applicable to waste material candidate for landfilling in special industrial waste landfills. The main features of this test are :

   - extraction solvent : demineralized water saturated with CO2 and air - (ph about 5),
   - tested material crushed in parts smaller tham 4 mm,
   - 100 g of material mixed with 1 liter of extraction solvent,
   - extraction of solutionfor analysis after 16 hours of agitation.

   This test was choosen although it is going to be replaced as standard for waste acceptation in landfills by a similar one excluding the saturation of solvent extraction by CO2 because it has been performed for samples taken from two of the sites considered in the present study at the time of their treatment, thus allowing more significant comparisons. For every sample two successive extractions have been carried out.

b) In addition, in order to take in account the specific characteristics of solidification techniques it was decided to perform the new test which is now prepared to be later standardized for evaluation of solidified material.

This test called oedometric pressure leaching test is based on the use of a pressure permeater, a section of which is represented on the following figure.



1 - Sample
2 - Cylinder of confinement
3 - Contact resin
4 - Lower baseplate
5 - Upper baseplate
6 - Porous stone
7 - Filler joint
8 - Stud bolts

The test is performed first to give an evaluation of the permeability of the treated material, then the oedometer is operated for leaching test. The pressure is adjusted in order to get a discharge of 0.01 cm³/s (36 cm³/hour). Successive extractions are carried out and it is possible to add separately the extracted quantities of every contaminant and to represent their variation in fuction of the quantity of the liquid discharged through the sample.

This function is hyperbolic and its interpretation allows the evaluation of the total quantity of the considered contaminant which can be extracted if the volume of extraction liquid or the time of extraction was infinite. The resulting figure will be considered as the maximum extractible quantity of the considered contaminant (mg/kg).

III - EVALUATION OPERATIONS

1 - SITE A : MARAIS DE PONTEAU-LAVERA (50 km west of Marseille)

a - Site history and treatment

Old salt marsh on the seaside in which were dumped various industrial residues of the Lavera petro-chemical plant. About 30 000 m^3 of wastes (sludges, sediments) had been disposed there for more than 15 years (1955-1974). After a first estimation of the quantities and nature of the wastes to treat, many possibilities of treatment were tested :

- incineration in an industrial waste incinerator,
- recycling as stock feed in a cement factory,
- incinerator in a thermal power plant,
- recycling in an oil refinery.

All these treatments were unsuccessfull, mainly because of the heterogeneity of the material to treat. Consequently, on site treatment by stabilization-solidification was decided. The treatment operation was carried out in september and october 1978 by EIF ECOLOGIE using a solidification patented process based mainly on the use of lime as reactive agent. The total amount of material treated was 22 000 m^3.

Laboratory tests were carried out, involving lixiviation of samples of treated material agitated during 24 hours in water with a pH of 6. The analysis gave figures of 3 to 64 mg/l for COD and total hydrocarbons < 0,2 mg/l.

b - Evaluation of efficiency

Sampling operation : The sampling procedure has been carried out on sept 23, after a rainy night. The site is covered with sandy and graveled material without vegetation. It is shaped in a slignt dome the top of which is 2 or 3 meters above the sea level. The sampling has been performed according to the procedure described in chapter II.1. Two ditches have been digged in the central part of the treated site, for both the vertical section was :

0 - 15 cm : coverage of sand and gravel
15 - 100 cm : treated material, dry and hard, grey in the upper part and black in the middle ; slignt smell of hydrocarbons. The extracted black material became rapidly grey after contact with the air.

A third ditch has been digged at the limit of the treated zone. A first hole was digged in which black liquid and black soil appeared. According to the information given by the representatives of the waste generator and of the local authority who were present during the present sampling operation and who took part to the treatment realization ten years ago, this might be considered as water and original untreated material which remained outside the dikes surrounding the treated area.

The digging was resumed in the direction of the center of the treated area and the treated material appeared in a shallow hard slice located at a level clearly above which of the untreated material. Because of the limited thickness of the treated layer it was decided to take only one sample from this section.

Results of tests and analysis

- Physical characteristics

Sample	water content (%)	permeability (m/s)	compressive (strength) kg/cm^2
A1 (upper)	18	-	-
A2 (middle)	17	$7.9\ 10^{-6}$	4.7
A3 (bottom)	21	-	-

- Lixiviation tests

Landfill lixiviation test (figures given in mg/kg except pH, conductivity, alcalinity)

Sample	Extraction	pH	Conductivity mS/s	TOC mg/kg	COD	Alkalinity m mol/kg	Cu	Pb	Cd	Co	Va	Ni	HC
A1	1	12.7	5.6	900	2800	440	6.2	25	0.4	<0.5	<0.5	1.0	12
	2	12.7	5.4	490	2000	400	3.7	21	0.2	<0.5	<0.5	0.8	8
	Total			1390	4800	840	9.9	46	0.6	<0.5	<0.5	1.8	20
A2	1	12.7	6.4	1170	3200	440	11.1	24	0.3	<0.5	<0.5	1.3	11
	2	12.7	5.6	419	1400	420	4.6	19	0.4	<0.5	<0.5	0.8	7
	Total			1589	4600	860	15.7	43	0.7	<0.5	<0.5	2.1	18
A3	1	12.1	5.9	3080	9100	280	3.6	<2	0.4	<0.5	<0.5	1.2	5
	2	9.3	1.6	846	2100	18	1.5	<2	0.5	<0.5	<0.5	0.5	3
	Total			3926	11800	298	5.1	-	0.9	<0.5	<0.5	1.7	8

Pressure test : maximum releases (long term)

Sample a2	pH	Conducti-vity ms/s	TOC mg/kg	COD	Alkalini-ty mimol/	Fe	Cu	Pb	Cd	Cr	Co	Va	Ni	HC
	12.7	5.6	1166	3200	850	-	4.8	> 10.6	> 0.11	0.06	0.08	-	1.27	> 11.8

2 - SITE B : BOURRON MARLOTTE - Seine et Marne (70 km south-east of Paris)

a - Site history and treatment

Ancient sand pit located in BOURRON MARLOTTE at the south eastern limit of the forest of Fontainebleau which had been used as dumping site until 1971 for the wastes generated by an old refinery pland (mainly acid tars and filtration residues). The surface of the lagoon was about 4 200 m^2 and the dumped material had stratified in three main layers :

- upper layer light and viscous
- middle layer made of aqueous liquid
- bottom layer of sticky material

Many analysis of these material were performed, including lixiviation tests according to the INSA test utilized for the present investigation. The following table summurizes the results of analysis carried out before treatment.

	Upper layer (lixiviation) 1200 m^3	middle layer 1300m^3	bottom layer (lixiviation)
Ph.....	3.5	2.05	2.10
Resistivity	7 900	232	232
COD.....	4 800 mg/kg	1 960 mg/kg	52 000 mg/kg
Sulfates...	260 mg/kg	1 829 mg/kg	41 220 mg/kg
Hydrocarbons	15 mg/kg	20 mg/kg	< 0.1 mg/kg

It was decided to restore the site by using the EIF Ecologie stabilization process. The treatment was performed during summer 1985 and about 25 000 tons of contaminated material has been treated.

D - Evaluation of efficiency

Sampling operation : the sampling operation has been performed on october 4th in the morning by rainy weather. The treated area has a slight slope from its southern part besides a surelevated railway to its northern limit surrounded by the forest. the site is covered with soil without any vegetation. Three ditches have been digged, two in the center of the treated area, one out its western limit. The total thickness of the treated section is about 6 to 7 meters, the treated material is colored in brown, homogeneous and compact with a very slight smell of hydrocarbons.

For every ditch, three samples have been taken at the top, in the middle and under the treated section. However, the sandy soil under the treated material seemed to be still contaminated by untreated tar and in the third ditch there was a seepage of liquids from an untreated zone remaining at the western limit of the dumping pit.

Results of tests and analyses

Physical characteristics

Sample	water content (%)	permeability (m/s)	compressive strength kg/m^2
B1 (upper)	33	-	-
B2 (middle)	24	$1.2\ 10^{-5}$	3.8
B3 (bottom)	31	-	-

- Lixiviation tests

Landfill lixiviation test (figures given in mg/kg except pH, conductivity, alcalinity)

Sample	Extraction	pH	Conductivity ms/s	TOC mg/kg	COD	Alkalinity mimol/kg	Fe	Pb	Cd	Ni	HC	S_2^-	SO_4
B1	1	8.4	1.7	2100	5400	15	0.6	<0.2	-	-	5.	<0.5	-
	2	7.8	1.6	1270	3050	60	0.4	<0.2	0.3	-	23	0.6	4350
	Total			3370	8450	75	1	<0.2	0.3	-	28	-	
B2	1	12.5	5.3	1440	3500	310	0.5	4.0	0.4	-	11	1.8	10310
	2	11.1	1.8	2040	6100	260	0.6	-	0.3	-	10	<0,5	10550
	Total			3480	9600	570	1.1	4.0	0.7	-	21	-	20860
B3	1	7.8	2.15	2920	7700	66	0.5	<0.2	0.3	-	4.	<0.5	12170
	2	7.7	1.95	898	3600	68	0.6	-	0.2	-	5	<0,5	934
	Total			3818	10300	134	1.1	-	0.5	-	9		11169

- **Pressure test** : maximum releases (long term)

Sample B2	pH	Con-ducti-vity mS/m	TOC	COD	Fe	Pb	Cd	Ni	Alkali-nity m.mol/kg	Cl	SO_4	S^{2-}
	12.6	5.8	1690	4760	>0.26	3.26	> 0.12	-	> 165	>5.9	>5434	<0.5

3 - SITE C - NESLE - Somme (100 km north of Paris()

a - Site history and treatment

During the first national inventory of hazardous dumps carried out in 1978, contamination of the chalky aquifer by nitrogen compounds and salts was pointed ou in the region of NESLE where an industrial dumping site was found to be at the origin of the pollution. The waste dumping had occured in pits digged in silty material laying above the chalk.

In order to restore the safety of the site and of its environment, the firm who generated the wastes and owned the dumping site decided to carry out its tratment by stabilization-solidification.

The waste consisted mainly of black colored sludges and silty material. Analysis of leachates indicated COD up to 450 mg/l iron up to 47 mg/l amonia up to 80 mg/l and traces of copper and zinc. The treatment was performed by TREDI (Petrifix Process) and a total of about 7 500 tons of contaminated material has been treated beetween mid-october and mid-december 1980.

A control of the mecanical stability of the treated site performed in october 1981 concluded to a variable resitance to compressive strength, which was found generaly good or even very good but with weak layers in some places. These weak parts of the site have been re-treated later.

In 1985 a new construction has been built at the south-eastern limit of the treated site.

b - Evaluation of efficiency

Sampling operation : the sampling operation has been carried out on october 4th, in the afternoon by rainy wather. The site is rather flat, covered with lush grass. Three sampling points have been choosen, each corresponding to one of the ancient lagoons of residues. The two first sampling points showed a similar log : down to 1,50 meter, coverage of humus soil, then about 4 meters of treated material which appeared blackish and crumbly with a rather strong smell (of organics and ammonia).

The third sampling point has been located near the newly constructed building and its section can be described as follows : 0,80 cm of soil, treated materieal compact and strong down to about 3 meters, then down to about 5 meters, again crumbly treated material.

For the three points, the sampling operation has been performed according to the definition given in part II.1.

Results of tests and analyses

Physical characteristics

Sample	water content (%)	permeability (m/s)	compressive (strength) kg/cm^2
C1 (upper)	45	-	-
C2 (middle)	16	3.410^{-8}	1.1
C3 (bottom)	16	-	-

- Lixiviation tests

Landfill lixiviation test (figures given in mg/kg except pH, conductivity, alcalinity)

Sample	Extraction	pH	Conductivity Ms/s	TOC mg/kg	COD	Alkalinity m mol/kg	NH4	Fe	Cu	Zn
C1	1	7.6	1.1	411	1000	52	549	0.8	<0.5	<0.2
	2	7.6	0.57	105	280	31	144	1.0	<0.5	0.5
	Total			516	1280	83	693	1.8		0.5
C2	1	7.8	0.92	61	120	36	513	0.8	<0.5	0.6
	2	7.9	0.49	16	60	31	108	0.9	<0.5	0.5
	Total			77	180	67	621	1.7		1.1
C3	1	7.7	0.94	35	130	71	522	0.5	<0.5	0.5
	2	7.8	0.41	9	70	3	126	0.4	<0.5	0.9
	Total			44	200	74	648	0.9		1.4

- Pressure test : maximum releases (long term)

Sample C2	pH	Conductivity Ms/m	TOC	COD	Alkalinity m.mol/kg	NH4	Fe	Cu	Zn
	8.5	0.4	60	160	65	271	5.1	0.06	0.03

4 - SITE D : BELLAY - Ain (80 km east of Lyon)

a - Site history and treatment

At the end of 1980, the lagoons used for the storage of sludges of wastewater treatment of a tanning plant were full and it became urgent to proceed to the disposal of these sludges. However, because pretreatment before disposal was required by the local authorities in charge of environment protection.

Analysis performed by the Centre Technique du Cuir (Leder Technical Center) indicated contents of 8,7 g/kg cromium, 0,475 g/kg sulfide, 0,5 g/kg sulfates and 0,35 % nitrogen.

Treatment operation was carried out by TREDI using its PETRIFIX patented process beetween april and june 1982 about 9 000 tons have been treated.

b - Evaluation of efficiency

Sampling operation : the sampling operation has been carried out on september 30 th by rainy weather. The site where the treated material was disposed is a low swampy area with lush vegetation. Three ditches have been digged, the first one at the supposed limit of the treated area presented a first layer of about 80 cm of humus soil then about 1,20 meter of treated material under which some material which seemed untreated appeared until the original soil was reached at a depth of about 2,50 meters.

On that point, two samples were taken : one from the upper part and one from the middle of the treated material.

For the two other ditches digged in the central part of the treated area, the section was similar but without the appearance of any apparently untreated material underneath. Consequently, three samples were taken, according to the sampling procedure described in part II.1. Noticeable smell (mainly ammonia), especially in the first ditch. For the three sections of sampling the treated material presented a noticeable difference beetween a first layer (about 15 cm thick) colored in grey and hard and compact and a second much thicker layer rather crumbly and colored in dark blue.

Results of tests and analyses

Physical characteristics

Sample	water content (%)	permeability (m/s)	compressive (strength)
D1 (upper)	55	-	-
D2 (middle)	57	-	0.95 + 0.1
D3 (bottom)	16	-	-

- Lixiviation tests

Landfill lixiviation test (figures given in mg/kg except pH, conductivity, alcalinity)

Sample	Extraction	pH	Conductivity mS/s	TOC mg/kg	COD	Alkalinity mimol/kg	NH4	Fe	Cr	Ca
D1	1	7.7	1.1	230	800	45	<1	0.4	0.8	1280
	2	7.8	0.72	161	220	36	<1	0.5	<0.5	1150
	Total			391	1020	81		0.9	0.8	2430
D2	1	9.6	0.82	1260	3200	16	234	0.3	0.9	560
	2	8.2	0.48	260	750	9	27	0.6	1.1	410
	Total			1520	3950	24	261	0.9	2.1	970
D3	1	7.8	0.92	55	250	86	801	1.4	<0.5	620
	2	7.9	0.56	31	150	37	130	0.5	<0.5	850
	Total			86	400	123	931	1.9		1470

***- Pressure test** : maximum releases (long term)*

Sample D2	pH	Conductivity mS/m	TOC	COD	Alkalinity m.mol/kg	NH4	Fe	Cr	Ca
	9.2	0.44	1200	2680	24	131.6	0.6	<0.05	315

III - REMARKS AND CONCLUSIONS

Some remarks may be pointed out about these investigations

- It appears that some of the sites has apparently not be completely treated (A,B,D). This may be understood as the necessity to fix a limit to the treatment, but this limit seems rather approximative and may left some significant quantities of untreated material. However this situation results from the position of the owner of the site and of the authorities responsible for the control of the rehabilitation project, it is not representative of the treatment process itself. As a consequence, it appears that the upper and bottom samples are probably not always realy representative of the treatment process efficiency at the limits of the treated layer, therefore our opinion is that only the middle sample very be considered without douot as representative of this efficiency.

- With the exception of site B, that has been more recently treated, it was not possible to find figures representatives of the characteristics of the initial contaminant material, and when some datas are available, the evaluation tests performed (specialy leading tests) are not sufficiently defines to allow a significant comparison with the result of the present investigation. If we considerer the site B and the results of lixiviation test it should be kept in mind that the main part of initial material is comparable to bottom layer characteristics and the test of this material is comparable to the first extraction performed on the middle sample of treated material.

- In connection with the previous remarks, it appears that the treatment performance required by the responsible of the sites were far from acurately defines. For example, for sites C and D, the enterprise who carried out the treatment project indicates that the requirement, of the owners of the sites were only dealing with the physical stability of the treated sites. From the present sampling operation it appears clearly that the compact ness and the mechanical efficency can be adjusted to reach a high level by increasing the proportion of the reactive agent (and consequently the cost of treatment).

- The evaluation of the efficiency of a treatment of stabilization solidification relies greatly upon the choice of tests and analysis. The present study, which is based on the use of two different lixiviation tests shows a relative uniformity of figures of general parameters of the leachates like pH and conductivity. for the release of the pressure tests as more singificant because this test is concerned to give an estimate of the maximum release on a long term basis.

- Comparaison between the two solidification processes, is not possible because of the differences of nature and characteristics of the waste that has been treated. However some systematic differences can be mentionned for the physical characteristics : water content (generaly higher for Petrifix), mechanical resistance (higher for EIF), permeability (higher for EIF), and for the chemincal characteristics of leachates, the pH and alkalinity of which remains high for EIF, as a consequence of the use of line as reactive agent.

- *As a conclusion it may be mentionned :*

. *that a significant evaluation of the efficiency of the stabilization-solidification treatment of these old contaminated site remains difficult, mainly because of the lack of knowledge of initial characteristics of the treated material*

. *that the results of the present investigation give an evaluation of the present state of the treated sites and a tentative estimation of their potential of evolution in the future. As a whole it appears that the treated sites are presently and will remain in the future in a satisfactory state according to their use and their environmental condition*

. *that the present investigation will participate to the efforts of adjustement of the methods of evaluation of on site efficiency of stabilization-solidification.*

This last point might be one of the most positive of our conclusions and be usefull for the future projects of treatment.

Appendix 3-B

Stabilization/Solidification Technology Case Studies

Portland Cement (Hazcon, presently IM-Tech), United States

United States
Environmental Protection
Agency

EPA/540/S5-89/001
March 1989

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Technology Demonstration Summary

Technology Evaluation Report, SITE Program Demonstration Test, HAZCON Solidification, Douglassville, Pennsylvania

The major objective of the HAZCON Solidification SITE Program Demonstration Test was to develop reliable performance and cost information. The demonstration occurred at a 50-acre site of a former oil reprocessing plant at Douglassville, PA containing a wide range of organic and heavy metal contaminants. The HAZCON process mixes the hazardous waste material with cement, a proprietary additive called Chloranan, and water. The Chloranan is claimed to neutralize the inhibiting effect that organics normally have on the hydration of cement.

The technical criteria used to develop the effectiveness of the HAZCON process were contaminant mobility, based on leaching and permeability tests; and potential integrity of solidified soils, based on measurements of physical and microstructural properties.

Extensive sampling and analyses were performed showing (1) the concentration of the organics were the same in the TCLP leachates of the untreated and treated soils, (2) heavy metals reduction was achieved, and (3) structural properties of the solidified cores were found to indicate good long-term stability.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Program demonstration that is fully documented in two separate reports (see ordering information at back).

Introduction

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the Environmental Protection Agency's Offices of Research and Development (ORD) and Solid Waste and Emergency Response (OSWER) have established a formal program to accelerate the development, demonstration, and use of new or innovative technologies as alternatives to current containment systems for hazardous wastes. This new program is called Superfund Innovative Technology Evaluation or SITE.

The major objective of a Demonstration Test Program is to develop reliable cost and performance information. One technology, which was demonstrated at the Douglassville, PA Superfund Site, is the HAZCON proprietary solidification

process. The process involves the mixing of hazardous waste material and cement with a patented nontoxic chemical called Chloranan. The Chloranan is claimed to neutralize the inhibiting effects that organic contaminants normally have on the hydration of cement-based materials. For this treatment, the wastes are immobilized and bound by encapsulation into a hardened, leach-resistant concrete-like mass.

The Douglassville, PA Superfund Site, No. 102 on the National Priority List, was selected as the location for the Demonstration Test. This is a 50-acre rural site of an oil recovery facility that includes: two large lagoons once filled with oily sludge, an oily filter cake disposal area, an oil drum storage area, an area where generated sludge was landfarmed into the soil and the plant processing area. More than 250,000 cu yd of soil is contaminated.

The major objectives of this SITE Project were to determine the following:

1. Ability of the stabilization/solidification technology to immobilize the site contaminants, which included volatile organics, base neutral/acid extractables (BNAs), oil and grease, polychlorinated biphenyls (PCBs), and heavy metals.
2. Effectiveness of the technology for treating soils with contaminant concentrations varying over the range 1%-25% by wt. oil and grease.
3. Performance and reliability of the process system.
4. Probable long-term stability and integrity of the solidified soil
5. Costs for commercial-scale applications

Project documentation will consist of two reports. This Technology Evaluation Report describes the field activities and laboratory results. An Applications Analysis will follow and provide an interpretation of the data and conclusions on the results and potential applicability of the technology.

The following technical criteria were used to evaluate the effectiveness of the HAZCON process:

1. Mobility of the contaminants:
   a. Leachability of the contaminants and oil and grease before and after treatment.
   b. Relative permeability of the treated and untreated soil.
2. Integrity of the solidified soil mass:
   a. Physical properties - unconfined compressive strength, bulk density, etc.
   b. Microstructure of the hydrated matrix.

The above criteria were used to develop the sampling program.

Procedure

The Demonstration Test utilized contaminated soil from six plant areas, referred to as Lagoon North (LAN), Lagoon South (LAS), Filter Cake Storage Area (FSA), Drum Storage Area (DSA), Plant Facility Area (PFA), and Landfarm Area (LFA). The intent was to process 5 cu yd from each of five areas and then perform an extended duration run for the sixth area. The purpose of the extended run was to confirm the reliability of the operating equipment. The extended run, which was intended to process approximately 25 cu yd from FSA, was performed on LAS feed, due to very difficult access to FSA and convenience of access and high contaminants level at LAS. The runs used less feedstock than anticipated, and produced approximately 5 cu yd from the short runs and 25 cu yd from the extended run of treated soil.

The contaminated soil was excavated and screened to remove aggregate and debris greater than 3 inches in diameter. It then was fed to the HAZCON Mobile Field Blending Unit (MFU) along with cement, water, and Chloranan. Cement was used on an approximately 1:1 ratio with soil, and the soil-to-Chloranan ratio was 10:1. The four feed components were blended in a mixing screw and fed into five 1-cu-yd wooden molds for the short tests and three 1-cu-yd molds plus two 12-cu-yd pits for the LAS run.

While the contaminated soil was processed and cured, the excavation holes were enlarged, lined with an impervious plastic liner, and partially filled with clean soil. After the 1-cu-yd blocks cured sufficiently to be moved (48-96 hours), they were removed from their molds and placed into the pits. The blocks then were covered with clean soil. The blocks were sampled 28 days later and will be sampled at 6 or 12 month increments for 5 years, along with the surrounding clean soil, which is to be checked for contaminant leaching from the blocks.

Soil samples were taken in three phases: before treatment, as a slurry exiting the MFU for analysis after 7 days of curing, and from the buried blocks after 28 days of curing. For the first five runs, two untreated soil composite samples, three sets of slurry samples, and three solidified cores were taken. For the extended run on LAS feed, additional samples were taken.

Physical property measurements performed were:

- bulk density
- moisture content
- permeability
- unconfined compressive strength of the solidified cores
- weathering tests–freeze/thaw and wet/dry

Chemical analyses were performed to identify the organic and metal contaminants in the soil. In addition, three different leaching tests were run:

- Toxicity Characteristic Leaching Procedures (TCLP)–standard leaching procedure used for measuring leachability of the contaminants.
- ANS 16.1 - simulates leaching from the intact solidified core with rapidly flowing groundwater
- MCC-1P - simulates leaching from the intact solidified core in relatively stagnant groundwater regimes.

These latter two tests were drawn from the nuclear industry and modified to suit hazardous waste analysis.

In order to obtain information on potential long-term integrity, microstructural studies were performed on the untreated soil and solidified cores. These analyses included:

- X-ray diffractometry–identifying crystalline structures in the solid
- Microscopy–scanning electron microscope and optical microscope–characterizing porosity, hydration products, fractures, and the presence of unreacted soil/waste material in the treated soil.

Results and Discussion

The following observations were made and summarized in Tables 1 and 2:

- The six plant areas offered a wide diversity of feedstock. The oil and grease ranged from 1% by wt. at DSA

Table 1. Physical Properties

Location	Untreated Soil		28-Day Cores		
	Bulk Density, g/ml	Permeability, cm/sec	Bulk Density, g/m	Permeability cm/sec	UCS, psi
DSA	1.23	0.57	1.95	1.8×10^{-9}	1113
LAN	1.40	1.8×10^{-3}	1.61	4.0×10^{-9}	523
FSA	1.60	Impermeable	1.51	8.4×10^{-9}	219
LFA	1.68	2.0×10^{-2}	1.84	4.5×10^{-9}	945
PFA	1.73	7.7×10^{-2}	2.07	5.0×10^{-10}	1574
LAS	1.59	1.5×10^{-5}	1.70	2.2×10^{-9}	889

Table 2. Chemical Properties

Location	Leachate Concentrations, mg/l					
	Untreated Soil			28-Day Cores		
	VOC*	BNA*	Pb*	VOC	BNA	Pb
DSA	0.92	ND	1.5	0.38	ND	0.007
LAN	0.02	1.02	31.8	0.06	1.45	0.005
FSA	1.03	2.81	17.9	0.72	2.79	0.400
LFA	5.10	0.010	27.7	0.37	0.10	0.050
PFA	1.10	0.010	22.4	0.84	0.11	0.011
LAS	0.06	0.010	52.6	0.11	0.73	0.051

*VOC - Volatile Organic Carbon
BNA - Base Neutral/Acid Extractable
Pb - Lead

to 25% at FSA. Polychlorinated biphenyls (PCBs) were detected up to 52 ppm by wt., with the maximum value detected at LAS. Lead contamination concentrations ranged from 0.3% to 2.3% by wt. at FSA. Volatiles and base neutral acid extractables (BNAs - semivolatiles) organics reached levels in excess of 100 ppm by wt. at FSA.

- The volume of the solidified soil was more than double that of the undisturbed feedstock. Optimization by HAZCON could reduce this volume increase, but other physical and chemical properties may change.
- Permeabilities of the treated soil, after curing for more than 28 days, were very low, in the range of 10^{-8} to 10^{-9} cm/sec.
- The unconfined compressive strengths (UCS) of the solidified soils ranged from about 220 psi for FSA to 1570 psi for PFA, and the values were inversely related to the oil and grease level.
- The wet/dry and freeze/thaw weathering tests showed small weight losses (0.5%-1.5%) at the end of the 12 cycle test for the test specimens and their controls. Unconfined compressive strengths, performed after the final weathering cycle, showed no loss in strength compared to the unweathered samples. No other analyses were performed on the weathered samples.
- The TCLP leaching tests compared leachate concentrations in the treated soil with that from untreated soil. Due to the addition of cement, Chloranan, and water, the treated soil contaminant concentration levels, on average, was 40% of the untreated soil concentrations. The results were as follows:

  - Metals–The leachate from the solidified soils showed metal levels at or near the detection limits. The results for lead, the predominant metal, were lower by a factor of about 500, from 20 to 50 mg/l in the leachates from the untreated soils to less than 0.1 mg/l in the treated soil leachates. The other five metals were at or near the detection limits for both untreated and treated soils.
  - Volatile Organics–The primary compounds detected were trichloroethene, tetrachloroethene, toluene, ethyl benzene, and xylenes. The leachate concentrations of the contaminants appear to be approximately the same in both the untreated and treated soils at levels of less than one milligram per liter (mg/l).
  - BNAs–The compounds detected in the leachates were phthalates, phenols, and naphthalene. The phthalates were reduced to near their detection limits of 10 µg/l in both the treated and untreated soil leachates. The total phenols in the leachates reach 3-4 mg/l for FSA where the feedstock had phenol concentrations as high as 400 mg/l with similar concentration levels seen in both the untreated and treated soil leachates. The values for naphthalene were less than 100 µg/l for both the treated and untreated soil leachates.
  - Oil and Grease–Leachate concentrations for treated soils were slightly greater than for untreated soils in each case. The values for the untreated soil were 0.2 to 2.0 mg/l and for the treated soil 2 to 4 mg/l.

- PCB analyses of all leachates, both for untreated and treated soil, were all below the detection limits of 1.0 µg/l.

- The special leaching tests, ANS 16.1 and MCC-1P, which simulate leaching of the solidified soil cores, were performed on the treated soil samples from each plant area except DSA and LFA. Experience with these tests on hazardous waste is limited. Results are compared to the TCLP results for treated soils, but this may not be relevant as a performance measure. The results are as follows:

  Metals–For ANS 16.1 the values in the leachate increased with leaching time. They were of the same order of magnitude as for TCLP leachates. The MCC-1P leachates also increased with time; for the largest time interval (28 days) they were greater by a factor of about 10 than the TCLP leachates.

  Volatile Organics–For ANS 16.1, the total concentrations of all the volatiles in the leachates were lower than the TCLP leachates by a factor of about 2. For MCC-1P the leachate concentrations were approximately the same as for the TCLP leachates. In both tests, no discernible trend between leachate concentration and time interval was noted.

  BNAs–The leachate concentrations for ANS 16.1 were less than for TCLP leachates, while the MCC-1P leachate concentrations were approximately equal. Leachate concentrations for the dominant components, phenols, appeared to increase with leaching time interval for MCC-1P, but no trends for ANS 16.1 were observed.

  Oil and Grease–MCC-1P leachate concentrations were about the same as for TCLP and ANS 16.1.

  PCBs–For both leaching tests, all leachate concentrations were below detection limits.

- Microstructural analysis are proven methods for understanding the mechanism of structural degradation of soils, cement, and soil-cement mixtures. However, there have been relatively few studies of complex waste/soil mixtures for stabilization/solidification processes. Consequently, in some cases, interpretation of the observations may be difficult. The microstructural studies provided the following information:

  - Mixing did not appear to be highly efficient.
  - There were many pores; some including air bubbles.
  - Soil components survived the solidification/stabilization process unchanged and appeared in the cores. The factors that suggest this were the presence in the cores of unaltered brownish aggregates, and observations of x-ray diffraction peaks, which cannot be identified with minerals constituents of the soil and are also present in the core, suggest that contaminant materials are being carried through the solidification process in an unaltered form. Since the two features being referred to are apparently major components of the contaminated soil, it appears that encapsulation is a major part of the mechanism of solidification/stabilization.

- The operations for the first five runs (5 cu yd) required many startups due to unscheduled shutdowns caused primarily by plugging in the soil feed screw.

  In addition, the consistency of the slurry mix was quite variable, running the gamut from powdery to a very thin slurry. However, physical property changes due to this variation were not observed. For the extended time run (25 cu yd) at LAS, operation was more uniform, with only a few short-term outages.

- The economic analysis was based on the 70% on-stream factor and a 300 lb/min operating capacity observed for the HAZCON equipment. A cost of $205/ton was calculated for the Mobile Field Blending Unit during the Douglassville, PA demonstration. The process is very intensive in labor and chemical additives, with these items amounting to approximately 90% of the total costs. Substantial cost reductions are expected with process and chemical optimization.

Summary

A Demonstration Test on the HAZCON solidification technology was performed on a wide range of hazardous waste feedstocks. Test runs producing 5 cu yd of treated soil were performed in five plant areas, and an extended run producing about 25 cu yds of treated soil in a sixth area. Many samples were taken and a wide range of laboratory analyses were performed to obtain a comparison of physical properties and contaminant mobilities before and after soil treatment. Highlights of the results are as follows:

- The volume of the solidified soils compared to the untreated soils increased by approximately 120%. HAZCON could reduce the volume increase by optimizing the quantity of cement and Chloranan, but other physical and chemical properties may change.

- The unconfined compressive strength ranged from 220-1570 psi and is inversely related to the oil and grease concentration.

- Permeabilities of 10^{-8} to 10^{-9} cm/sec were obtained which surpass the generally accepted permeability of 10^{-7} cm/sec for soil barrier liners.

- The TCLP leach test showed that heavy metals were immobilized over the range of oil and grease encountered.

- TCLP leach tests performed on untreated and treated soils showed equivalent concentrations of volatiles organics and BNAs in their respective leachates.

- The leachates from MCC-1P contained greater concentrations of metals and organics than ANS 16.1 for an equivalent time interval. There are no protocols for these tests on unsolidified waste and no attempt was made to run the ANS and MCC procedures on untreated waste.

- PCBs were not detected in any leachates, whether the soil was treated or untreated.

- The microstructural study of the solidified soil showed the following:

  - high porosity
  - brownish aggregates passed through the process unaltered
  - mixing was not highly efficient
  - encapsulation is a major part of the mechanism of solidification/stabilization

- Startup operating difficulties were encountered by HAZCON during the Demonstration Test.

- A cost of $205/ton was calculated for the Mobile Field Blending Unit during the Douglassville, PA demonstration.

The EPA Project Manager, **Paul de Percin**, *is with the Risk Reduction Engineering Laboratory, Cincinnati, OH 45268 (see below).*

The complete report consists of two volumes, entitled "Technology Evaluation Report, SITE Program Demonstration Test, HAZCON Solidification, Douglassville, Pennsylvania:"

"Volume I" (Order No. PB 89-158 810/AS; Cost: $21.95, subject to change) discusses the results of the SITE demonstration

"Volume II" (Order No. PB 89-158 828/AS; Cost: $36.95, subject to change) contains the technical operating data logs, the sampling and analytical report, and the quality assurance project plan/test plan

Both volumes of this report will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Applications Analysis Report: HAZCON Solidification," which discusses application and costs, is under development.

The EPA Project Manager can be contacted at:

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Appendix 4-A

Soil Vapor Extraction Technology Case Studies

In Situ Soil Vacuum Extraction, The Netherlands

Soil Vapour Extraction of Hydrocarbons In Situ and On Site Biological Treatment at a Gasoline Station

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Presented at
NATO/CCMS International Meeting
(Soil Remediation)
Washington DC, 18-22 November 1991

1 INTRODUCTION

1.1 Background

In the industrialized countries the extent of soil contamination is enormous. The overall costs of soil remedial action in the Netherlands is estimated to be in excess of 30 billion dollars. This corresponds with 150 million m^3 excavated soil, emanated from more than 100,000 polluted sites (Committee 10 Year Scenario, 1990).
The number of sites contaminated with hydrocarbons, in the Netherlands, is estimated to be at least 6,600 in 1990. The costs of soil remedial action (excavation) and improving the gasoline stations, with regard to these sites, amounts to approximately 750 million dollars. Excavating the contaminated soil is a very effective method of removing the contamination.

Treatment or disposal of the excavated soil is necessary. Nevertheless excavation can be difficult or even impossible under certain circumstances e.g.:-

- the presence of buildings and civil engineering works (roads, bridges etc.);
- certain cables, power lines and pipe lines in the subsurface;
- contamination has spread to great depths (i.e. > 4 m);
- shortage of space and traffic problems (city centres);
- irreplaceable function of the site (e.g. railway station, production plant).

Generally the criteria favourable for applying in situ techniques are the following:-

- the permeability of the soil is reasonable;
- less disturbing layers of clay/peat appear in the subsoil;
- the contamination is infiltrated (i.e. not buried);
- only one contaminant is present (e.g. toluene) or comparable component (e.g. gasoline);
- the quantity of contaminated soil is substantial;
- the contaminant can be biodegraded;
- the contaminant can be leached and/or volatilized.

The presence of above and underground infrastructure is unfavourable for conventional excavating techniques; this often occurs at sites situated in city centres and industrial areas. Therefore more effort has to be put into developing new innovative remedial action techniques.

In this article attention is paid to the soil vacuum extraction (SVE) as a remedial technique in general and in particular to SVE and the air based biodegradation of gasoline hydrocarbons underneath a road in Raalte. A new developed combined soil vapour/groundwater treatment system (BIOPUR®) will also be discussed.

Soil Vapour Extraction (SVE)

The mechanism by which SVE operates is relatively simple. By creating negative pressure gradients in a series of zones within the unsaturated soil a subsurface air flow is induced (figure 1). This flow volatilizes the contaminants present in the unsaturated soil. This process, in theory, continues until all volatile components are removed. The extraction wells are individually connected to the transfer pipes, then manifolded to a vacuum unit and the soil vapour is transported to a soil vapour treatment system. Figure 1 gives an outline of three different SVE performances.

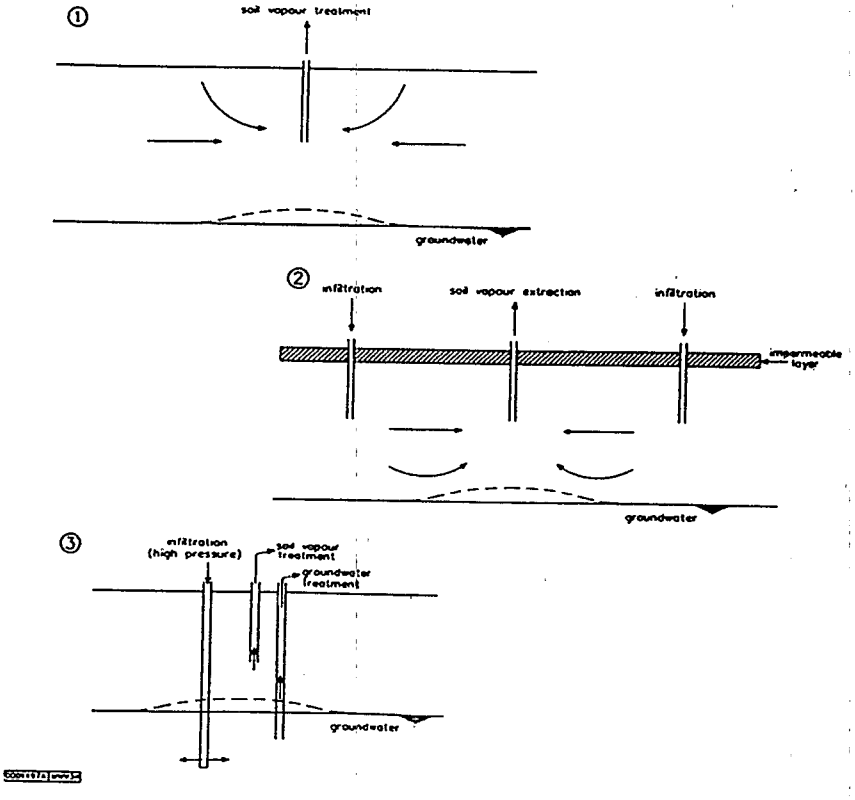

Figure 1: Three Different Performances of SVE

The withdrawn soil vapour is often treated by charcoal adsorption or catalytic incineration. The groundwater is usually treated by stripping and/or charcoal adsorption. In order to minimize the treatment costs of both groundwater and soil vapour TAUW Infra Consult B.V. applied (since 1989) a biological system for combined aerobic treatment (see section 4.2).

Meanwhile experience with soil vacuum extraction (SVE) is so wide that it can be considered as a proven technology. A review on SVE techniques is given by Hutzler (1989). The treatment costs of withdrawn soil vapour are substantial, usually more than 50% of the total remediation costs (Miller 1990). The air based biodegradation is applied with the aim of reducing SVE costs. This is a new innovative technique as indicated by an international review of in situ bioreclamation practice (Stapp 1990). Only 2 of the 23 studied sites used air based technology, most of the applied bioreclamation was water based. In recent literature (Miller, November 1990 and Hinchee, October 1990) air based enhanced biodegradation is described.
Apart from the mentioned advantage of lower hydrocarbon concentration in the withdrawn soil gas, substantially less carrier media is needed when air is used as an oxygen carrier. This is indicated in Table 1.

Table 1: Mass Requirements to Deliver Sufficient Oxygen or Nitrate for Biodegradation to Mineralization (derived from Hinchee 1990)

Electron Acceptor	Carrier Medium	Mass Requirements (kg carrier/kg hydrocarbon)
Oxygen (in air)	8 mg/l in water	400.000
Oxygen (pure)	40 mg/l in water	80.000
Oxygen (in H_2O_2)	100 mg/l H_2O_2 in water	65.000
Oxygen (in H_2O_2)	500 mg/l H_2O_2 in water	13.000
Nitrate	50 mg/l in water	90.000
Nitrate	300 mg/l in water	15.000
Oxygen	20.9 percent in air	13

An additional advantage of using air as an oxygen source in the vadose zone (gas phase) is the fact that diffusion rates are much higher in air than in the water filled saturated zone.

Furthermore one has to realize that during SVE soil vapour (with low oxygen content) is continuously replaced by fresh air (with high oxygen content). This oxygen source does not require additional expense!

An indication of the biological activity in the soil is given by several biological parameters such as TPC (total plate counts), OUR (oxygen uptake rate) and NCR (nitrogen consumption rate).

2 ESTIMATED DURATION OF SVE

To select the most suitable remedial action technique for a specific site it is necessary to estimate the costs of 3 or 4 chosen techniques. In order to give a good estimate the duration of the SVE also has to be calculated. For this purpose TAUW Infra Consult B.V. developed a relatively simple "spread sheet" model. The most important input parameter can be distinguished in groups related to:-

- the contaminants(s)
  * estimated amount of contaminants;
  * molecular mass, vapour pressure;
    solubility of contaminants (3 maximum);
  * adsorption/desorption coefficients (k_{oc});
- soil
  * volume of contaminated soil;
  * density, porosity, moisture;
  * fraction organic carbon in the soil;
- biodegradation
  * zero order biodegradation rate;
- application SVE
  * estimated effective air flow in the subsoil.

In addition to the model and even to validate the model it is recommended to carry out column tests with contaminated soil from the site. The application of column tests can give detailed information on volatilization, biodegradation and possible remedial action limit concentrations.

3 SITE CHARACTERISTICS

During soil remediation at a petrol station, it appeared that contaminants were found underneath a provincial road. Excavation of this part of the contaminated soil was not feasible due to financial and technical (traffic) reasons. The most favourable solution was a SVE system in combination with biostimulation. This system not only had to remove the volatile compounds from the gasoline but also had to stimulate biodegradation, of particularly the non volatile components, by the (passive) infiltration of air (oxygen). The unsaturated zone of the soil consisted of fine to gravel sand. The groundwater surface had to be lowered from 2 m to 3 m below ground surface in order to enlarge the unsaturated zone and make the smear zone available for SVE. Figure 2 is a diagram of a cross section of the site. On one side of the road there are several soil vapour extraction wells (perforated 2-2.75 m below ground surface) and on the other side seven infiltration wells (passive). To prevent direct air infiltration at the extraction side of the road, a plastic liner was placed between the road and the sheet pile wall. The biological system applied for combined soil vapour and groundwater treatment is shown on the left hand side of Figure 2 (above the excavated soil) and is called BIOPUR®.

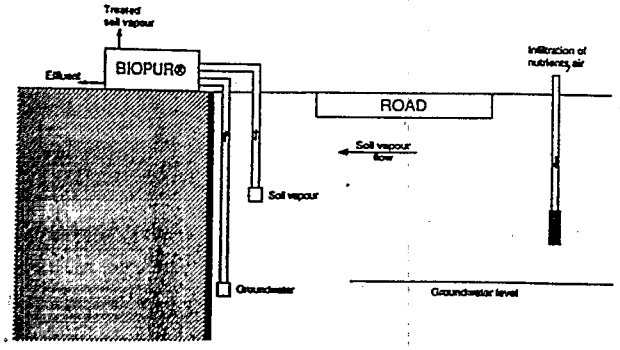

Figure 2: Cross Section of the site at Raalte

4 RESULTS AND DISCUSSION

4.1 SVE and Air Based Biodegradation

The under pressure applied in the soil vapour extraction wells and the corresponding soil vapour flow are outlined in Figure 3.

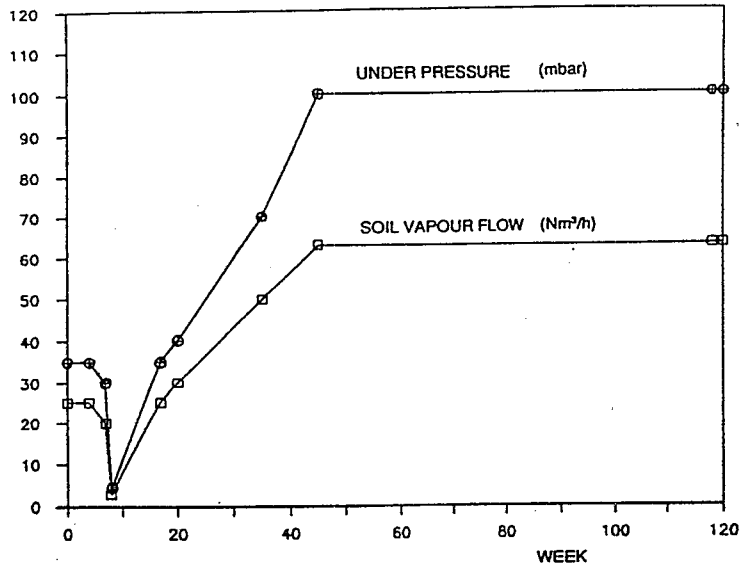

Figure 3: Under pressure (mbar) and corresponding soil vapour flow (Nm^3/h)

The concentration of volatile hydrocarbons in the withdrawn soil vapour is outlined in Figure 4. (Remark: Y-axis logarithmic).

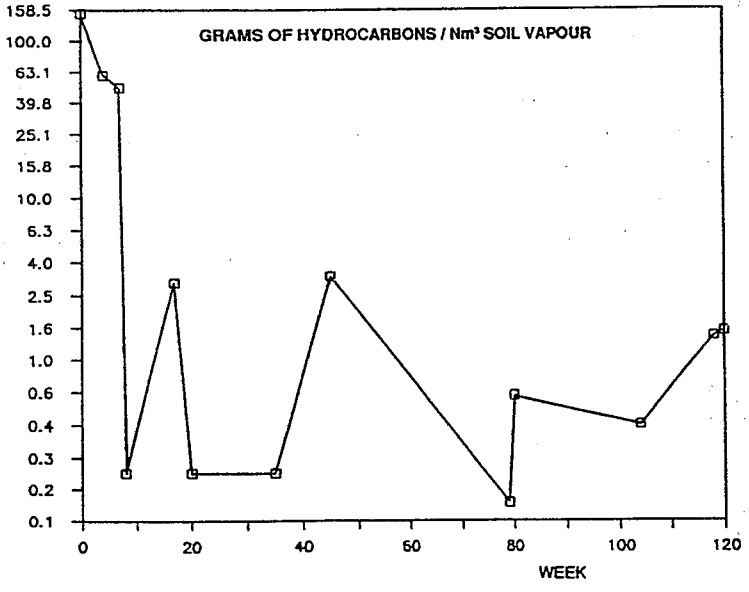

Figure 4: Concentration of volatile hydrocarbons in the withdrawn soil vapour

In Figure 5 the cumulative amount of vapourized and biodegraded hydrocarbons is given as well as the sum of both of them. The vapourized amount is the result of the combination of figures 3 (air flow) and 4 (concentration).
The biodegraded amount is derived from the withdrawn mass flow of carbon dioxide. The concentration of carbon dioxide in the withdrawn soil vapour amounted to approximately 0.5% (v/v) over weeks 0-37, increased till approximately 1% (v/v) in weeks 37-47 and gradually decreased till 0.25% (v/v) over weeks 47-118.

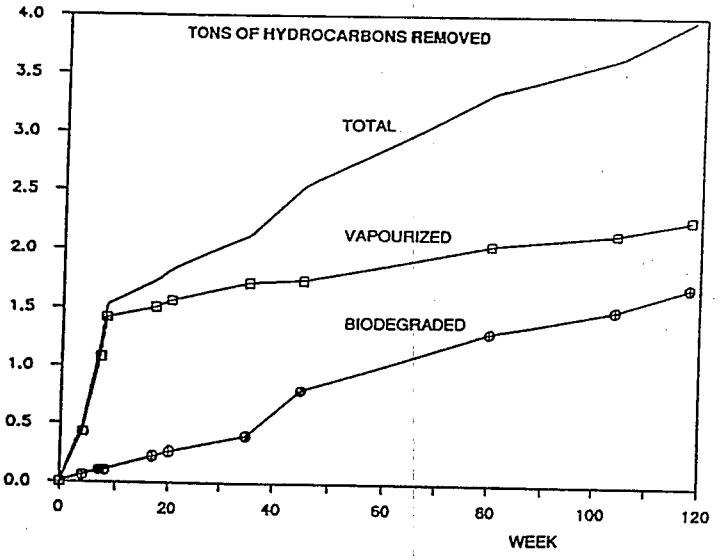

Figure 5: Cumulative amount of vapourized and biodegraded hydrocarbons

Figure 6 is an outline of the average hydrocarbon content of the soil during SVE and biodegradation. The removal of the volatile hydrocarbons was according to expectations. However, the removal rate was too slow. It was therefore decided to take additional measures (commencing week 78) to speed up the in situ bioremediation. The measures consisted of (heated) air injection (35-40°C), fluctuation of the groundwater level and infiltration of nutrients (N/P).

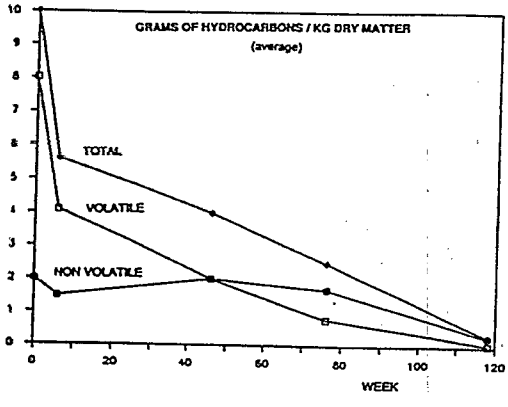

Figure 6: The average hydrocarbon content of the soil during SVE and biodegradation

In Table 2 the biological activity (in week 92) is expressed as TPC (total plate count), OPC (oil plate count), determined by applying specific gasoline degradable micro-organisms and the oxygen uptake rate (OUR) at different depths.

Table 2 Concentrations Measured and Biological Activity in Week 92

Depth (m)	Non Volatile Gasoline (mg/kg dw)	Volatile Gasoline (mg/kg dw)	Total Plate Count (CFU/g soil)	Gasoline Degraders (CFU/g soil)	Oxygen Uptake (mgO_2/kg dw)
0.5			2.7×10^3		3.6
0.9				3.4×10^4	1.3
1.5				1.6×10^6	6.8
2.0	100	1,200	0.7×10^6	0.9×10^6	18
2.5	2,700	1,300	4.6×10^6	5.6×10^6	34
2.7	130	< 100	0.3×10^6	0.4×10^6	14

CFU = Colony Forming Unit

The highest activity (TPC, OUR and gasoline degraders) and the highest concentration left in the ground is at the groundwater surface (2.5 m below ground surface).

4.2 Combined Air and Water Treatment (On Site)

The bioreactor, based upon a sludge on carrier type, can mineralize the vapours in the withdrawn soil vapour as well as the dissolved contaminants in the pumped groundwater. The first treatment unit with an effective volume of 10 m^3 was tested at the site in Raalte and functions beautifully. The residence time is approximately 15 minutes for groundwater and less than 10 minutes for soil vapour. The addition of N- and P- nutrients takes place in the influent stream. In the different compartment of the reactor ambient air is supplied. The mixing type of the reactor can be described as a plug flow. The treatment efficiency concerning the total load offered (soil vapour and groundwater) amounts to in excess of 98%. All the requirements regarding groundwater discharges are met, i.e. 100 μg aromatics per litre and 1 mg mineral oil per litre. In the search for metabolites with couples gaschromatography mass-spectrometry techniques no components could be detected at μg/l level.

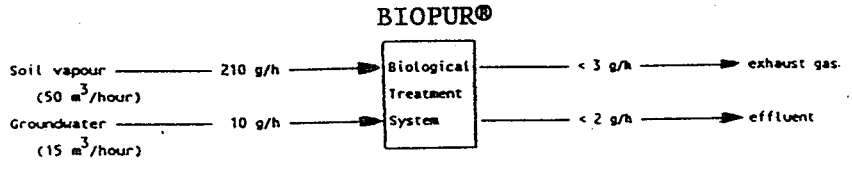

Figure 6: Gasoline mass balance at a steady state

In the purified soil vapour (exhaust gas) no aromatics or other volatile hydrocarbons were detected. The detection limit for these matters is 0.1 ppm. In the effluent no aromatics (BTEX) could be detected (detection limit 0.5 μg/l). Discharge of the effluent was suggested by the Water Board.

In Figure 6 the input and output of the on site BIOPUR® unit are outlined. In Figure 7 chromatograms of GC analysis are presented.

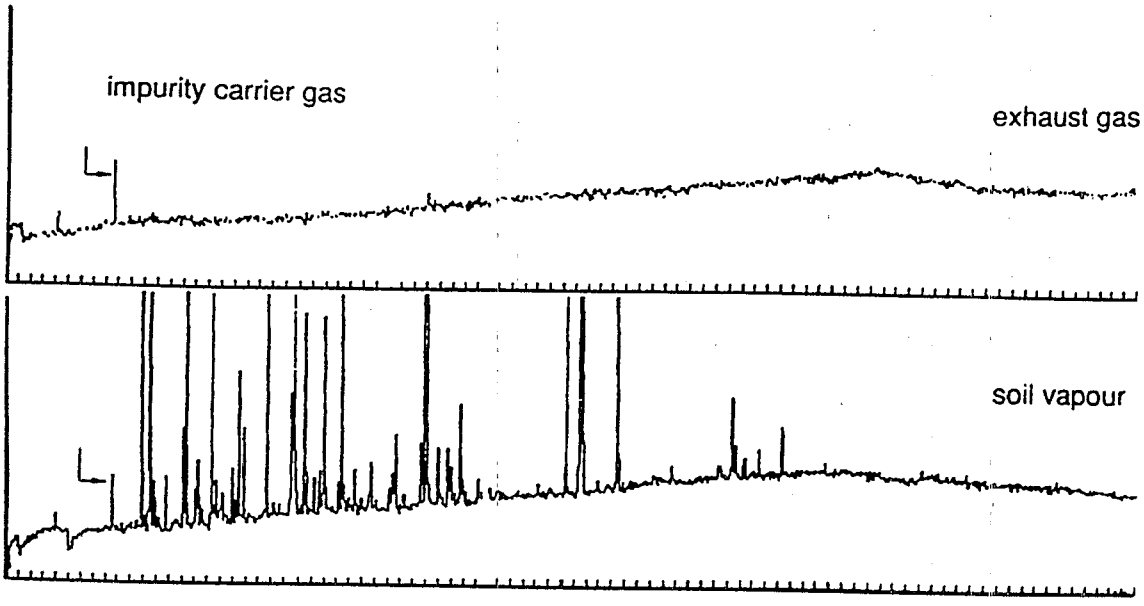

Figure 7: Chromatogram of soil vapour (untreated) and exhaust gas (after biological treatment)

5 CONCLUSIONS AND DISCUSSION

SVE and Air Based Biodegradation

Within a period of 1.5 years approximately 3,200 kg of gasoline was removed. Initially based on limited soil analysis, the estimated amount at the beginning of the soil vapour extraction/biorestoration was about 700 kg! At the end of this period, the average gasoline content of the soil decreased from roughly 10 to 2.5 g/kg dw. This decline was mainly due to the removal of the volatile fraction of the gasoline. To speed up the removal of the non volatile fraction several additional measure were taken. These measures consisted of (heated) air injection (35-40°C), fluctuation of the groundwater level and infiltration of nutrients (N/P). The results were significant. A further decrease of the average gasoline content of the soil was realized from roughly 2.5 to 0.26 g/kg dw within six months. This decline corresponded with the removal of approximately 800 kg gasoline.

Thus some 4,000 kg of gasoline was removed within two years. Approximately 50% of the removal was due to mineralization by the micro-organisms in the contaminated soil.

Combined Air and Water Treatment (On Site)

The bioreactor - BIOPUR ® - has functioned beautifully. A mass flow of more than 5 kg of gasoline hydrocarbons per day was converted into carbon dioxide and water, with a residence time of approximately 15 minutes for groundwater and less than 10 minutes for soil vapour. The degree of conversion amounted to more than 98%!

Related to the entire remedial action the treatment costs of soil vapour and groundwater were less than Dfl. 0.40 per m^3 of groundwater. For calculation purposes only, the treatment of the soil vapour was free of charge.

In Table 3 a comparison of the treatment costs of four types of groundwater purifying plants is given.

Table 3: Comparison of the treatment costs of four types of groundwater purifying plants

Type		Costs (Dfl.) per m^3 of groundwater		
		10 m^3/hour	20 m^3/hour	40 m^3/hour
1	BIOPUR®	0.53	0.44	0.35
2	Rotating Biological Contactor	0.78	0.65	0.59
3	Stripper/active carbon	0.85	0.54	0.36
4	Stripper/compost filter	1.16	0.87	0.72

Estimated Remediation Costs

On the supposition that an in situ remedial action takes approximately two years and excavation, including treating the groundwater takes one year, the estimated costs for in situ remediation of the site will be approximately 75% of the excavation variant.

Furthermore one has to take the two additional advantages of an in situ remediation action into account. These advantages are that no extensive excavation is required and that the exact soil contamination boundaries do not have to be known. In the case of excavation one has to know the exact boundaries.

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Appendix 4-B

Soil Vapor Extraction Technology Case Studies

Vacuum Extraction of Soil Vapor, Verona Well Field Superfund Site, United States

In-Situ Soil Vacuum Extraction System
Verona Well Field Superfund Site
Battle Creek, Michigan

Draft Final
Final Report for NATO/CCMS Pilot Study on Remedial Action Technologies for Contaminated Land and Groundwater
Presented at the Third International Meeting
November 6-9, 1989

Margaret M. Guerriero
U.S. EPA Region V

I. INTRODUCTION

Site Description

The Verona Well Field is located in Battle Creek, Michigan in the south central portion of the State. The Verona Well Field (VWF) site consists of four distinct problem areas within approximately 100 acres. The municipal well field is located in the northeast corner of the City and lies on both sides of the Battle Creek River (Figure 1). The well field consists of 30 production wells that supply drinking water for 50,000 residents and several major food industries. The Thomas Solvent Raymond Road (TSRR) facility, the Thomas Solvent Annex (TSA) facility, and the Grand Trunk Western Railroad (GTWRR) have been identified as sources of well field contamination. Figure 1 shows the location of these sources relative to the well field. The site is located in an urban setting which is primarily residential with some light industry.

Site History

The contamination problem at the VWF site was first discovered in August 1981, during testing of the City water supply. Test results revealed that 10 of the City's 30 supply wells were contaminated with volatile organic compounds (VOCs). Concentrations ranged from 1 to 100 ug/l. During the same period, private residential wells were also tested. Several of these wells were found to contain VOCs in excess of 1,000 ug/l. The highest level found in a private well was dichloroethylene at 3,900 ug/l. A bottled water program was implemented in this area and residents were connected to the City's water supply system.

In the Fall of 1983, the first phase of a Remedial Investigation (RI) was initiated to determine the extent of contamination in the well field and potential sources. Sample results from the initial RI work confirmed the existence of a contaminant plume with VOC concentrations ranging from 1 ug/l to 100 ug/l in the well field. The investigation also identified the three major sources of contamination.

Remedial Measures

In May 1984, U.S. EPA signed a Record of Decision (ROD) calling for an Initial Remedial Measure (IRM) to implement a blocking

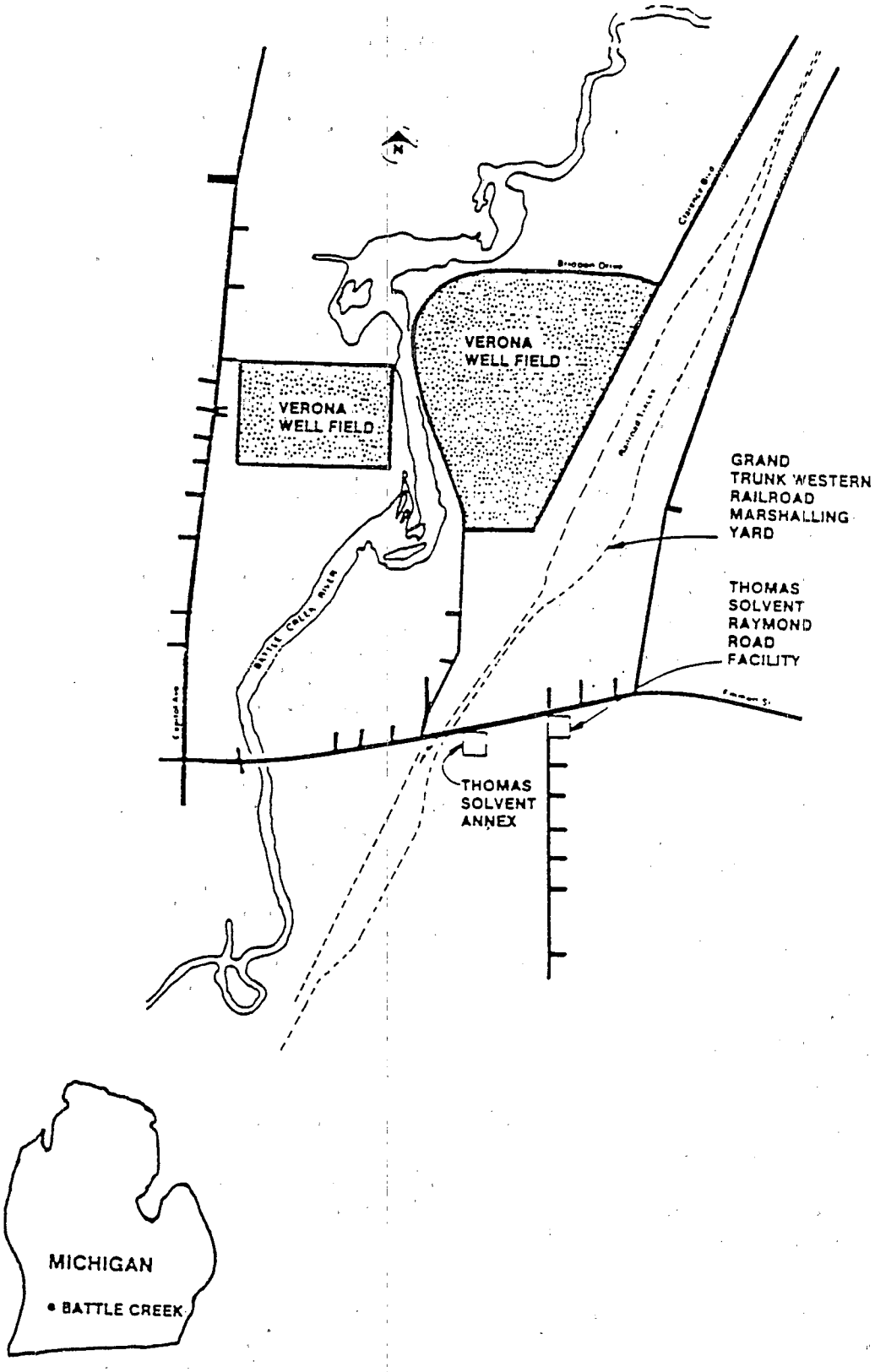

FIGURE 1
VICINITY MAP

well system in the well field. The blocking system consists of a line of converted supply wells that extract contaminated water from the southern end of the VWF. The system prevents contaminants from migrating further into the well field. An air stripper with vapor phase carbon treatment was also installed to treat contaminated water prior to discharge to the Battle Creek River.

In August 1985, U.S. EPA signed a second ROD that addressed the most contaminated of the three sources, the Thomas Solvent Raymond Road facility. The ROD included a groundwater extraction system to remove contaminated groundwater, treatment of extracted water utilizing the existing air stripper at the well field, demolition of the existing warehouse and loading dock, and a soil vapor extraction system to remove VOCs from contaminated soils.

Site Characteristics and Sampling Results

The Thomas Solvent Raymond Road (TSRR) facility is a former solvent repackaging and distribution facility that operated from 1970 to 1984. Solvents were stored in 21 underground storage tanks, of which 19 were later discovered to be leaking. There has also been documented reports of surface spillage during operation. The site contained an office building, a warehouse with a loading dock, and the 21 underground tanks (see Figure 2).

Site geology consists of a fine-to coarse-grained alluvial-glacial sand with traces of silt, clay, and pebbles underlain by a fine-to medium-grained sandstone with minor lenses of shales and limestones. The unconsolidated sand unit ranges in thickness from 10 to 50 feet and the sandstone varies from 100 to 120 feet in thickness. The hydraulic gradient is primarily north to northwest from the identified sources toward the VWF. The depth to water is approximately 20 to 25 feet. The hydraulic conductivity of the unconsolidated material ranges from 2.7×10^{-3} to 4.0×10^{-2} cm/sec. The hydraulic conductivity of the sandstone ranges from 7×10^{-3} to 2×10^{-2} cm/sec.

Samples collected at the TSRR facility indicate that both soils and groundwater are highly contaminated with a variety of organic compounds. Table 1 lists organic compounds detected in soils at TSRR. Groundwater samples showed concentrations as high as 100,000 ug/l VOCs. The total estimated volume of organics in groundwater and soils was 3,900 lbs., and 1,700 lbs., respectively.

It should be noted that these total mass estimates were based on sample data obtained using an accepted soil sampling procedure which is now known to produce VOC results lower than actual values. The total mass in groundwater and soils is now estimated

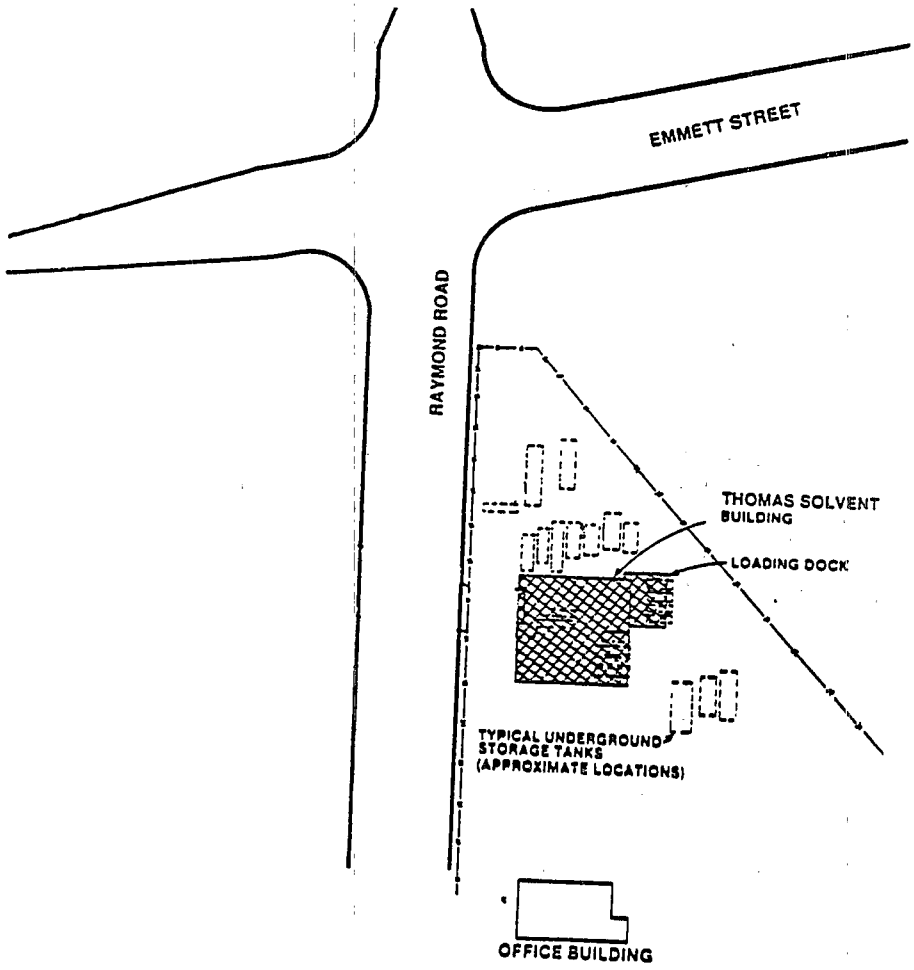

FIGURE 2
LOCATION OF
UNDERGROUND TANKS

TABLE 1

PRINCIPAL SOIL CONTAMINANTS DETECTED AT TSRR

CHLORINATED HYDROCARBONS	MAX. CONC. (ug/l)
- METHYLENE CHLORIDE	60,000
- CHLOROFORM	2,000
- 1,2-DICHLOROETHANE	27,000
- 1,1,1-TRICHLOROETHANE	270,000
- TRICHLOROETHYLENE	550,000
- TETRACHLOROETHYLENE	1,800,000
AROMATICS	
- TOLUENE	730,000
- XYLENE	420,000
- ETHYL BENZENE	78,000
- NAPHTHALENE	9,400
KETONES	
- ACETONE	130,000
- METHYL ETHYL KETONE	17,000

to be significantly greater based on the results of the operating groundwater extraction system and the soil vacuum extraction system.

Conventional subsurface soil sampling procedures involving the use of split spoon samplers require the sampler to be opened and the sample transferred to a bottle prior to shipment to the laboratory. This allows for significant amounts of VOCs to volatilize before analysis. This problem, coupled with the lack of sampling in the capillary zone and beneath the former warehouse building, resulted in estimates of VOC-contaminated soils being considerably lower than actual. This has had a significant effect on the operation of the soil vacuum extraction system. These effects will be discussed in detail in a later section of this report.

Technology Selection

Due to the significant mass of contaminants in the soil and groundwater at the TSRR facility, alternatives that employed both groundwater and soil remediation were developed in the feasibility study. A two step approach to remedial action was used at the TSRR facility in which each alternative developed for the feasibility study included both a groundwater and a soils portion. The selected alternative for the site includes a groundwater extraction (GWE) system and the soil vacuum extraction (SVE) system.

The groundwater extraction system includes 9 extraction wells which pump a total of 300 gallons per minute. The extracted water is pumped to the existing air stripper at the well field and discharged to the Battle Creek River after treatment. Figure 3 shows the layout of the GWE system. Initially, VOC concentrations in groundwater were so high that extracted water was passed through pretreatment carbon units prior to being pumped to the air stripper. The system has been operating since March of 1987.

Several alternatives for soil cleanup were evaluated, including SVE, excavation of soils with on/off site disposal, site capping, and soil washing (flushing water through the unsaturated zone with subsequent groundwater extraction).

SVE was chosen based on a number of reasons. Although it was considered an innovative technology, it was felt that it had a good likelihood of success given the site conditions and contaminants. Excavation was considered unacceptable due to its potential to release high concentrations of VOCs into the air, which would create a health hazard to residents in close proximity to the site, and significantly violate Michigan Air Quality Standards for VOCs. Therefore, alternatives that would

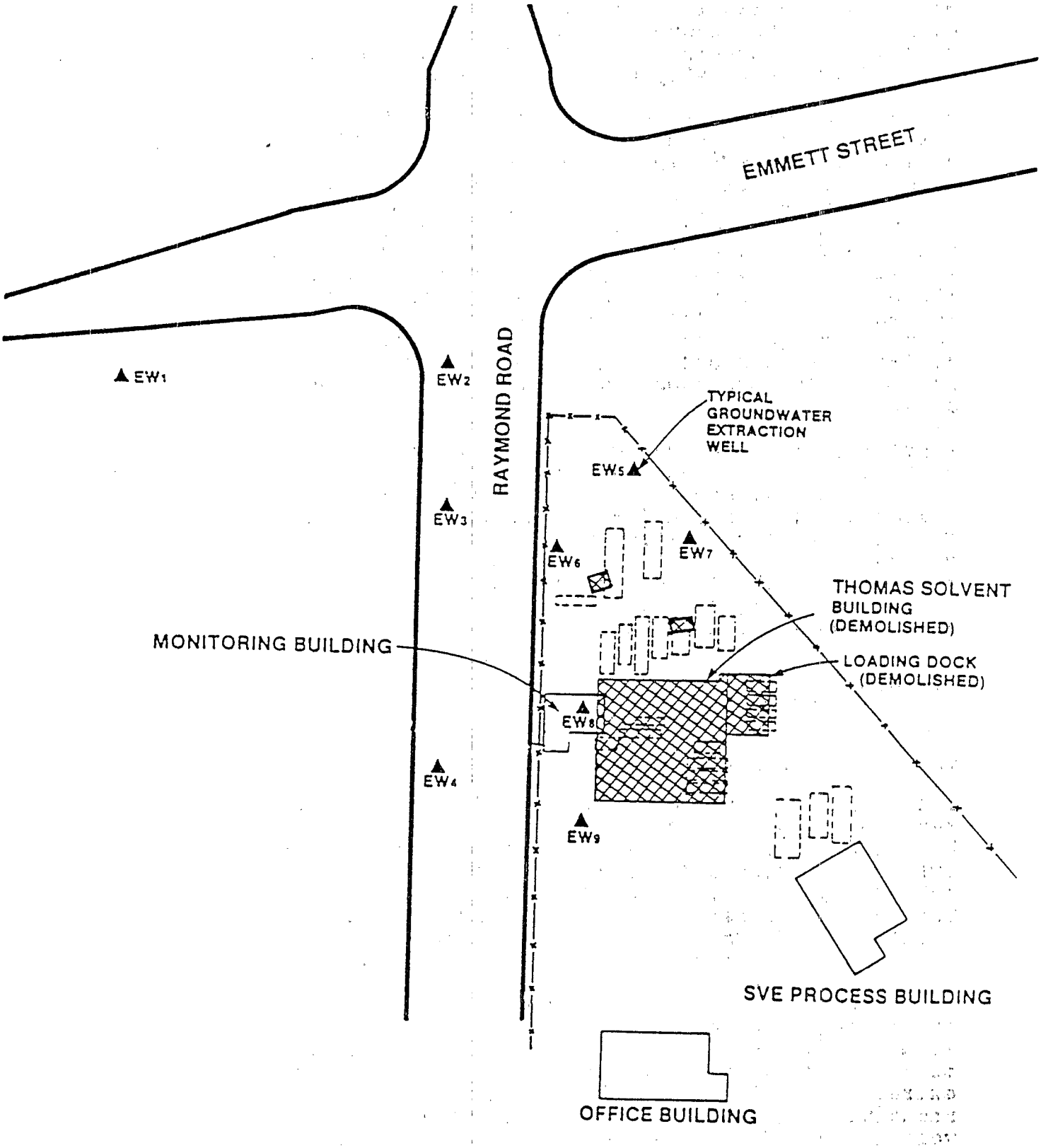

FIGURE 3
GWE SYSTEM LAYOUT

not disturb soils were favored. Capping was not considered to be consistent with future actions because of the high level of contamination present at the site and because the underground tanks would eventually have to be removed.

Of the two soil treatment alternatives, SVE was calculated to take less time to remediate the site than soil flushing. It was estimated that SVE, in conjunction with GWE, would reduce the groundwater contamination to 100 ug/l within three years. The contaminant mass would be reduced to 2% within 1 1/2 years (based on 1700 lbs. of VOCs). Soil washing was estimated to require 8 years to reach 100 ug/l in groundwater and 8 years to reduce contaminant mass to 2%. This was significant in the selection of SVE because it was not less expensive than soil washing. The estimated capital cost of SVE was $413,000, with operation and maintenance (O&M) of $90,000. Soil washing capital cost was estimated at $58,000, with O&M of $6,000. SVE was, however, considerably less expensive than the excavation and capping alternatives.

Since SVE is an innovative technology, the procurement of a SVE contractor was accomplished using a performance specification which contained certain minimum requirements but left the major design details to the discretion of the bidding SVE contractors. Contract documents called for the construction, operation, and maintenance of the SVE system. The performance standards require that the SVE would operate until all soil samples showed VOCs below 10 mg/kg, with no more than 15 percent of the samples above 1 mg/kg total VOCs.

II. TECHNOLOGY

Process Description

The soil vapor extraction process is designed for use in removing VOCs from the unsaturated zone in soils. The mechanism by which SVE operates is fairly simple and straight forward. The system is designed to create negative pressure in the unsaturated zone using wells that are connected to a vacuum extraction unit. The vacuum induces a flow of air through the soils, thereby volatilizing VOCs that are absorbed on soil particles and extracting the contaminants in the vapor phase.

A vacuum extraction system generally consists of several extraction wells screened throughout the unsaturated zone or within discrete units of the unsaturated soils. The wells are connected by transfer pipes which are manifolded to the vacuum extraction unit. The vacuum applied at the wellhead creates a negative pressure or vacuum in the subsurface which cause VOCs to volatilize and migrate to the extraction wells. A vapor/water

separator is also incorporated to remove water from the contaminated air stream.

The materials used for an SVE system are generally readily available and not specialized. Equipment requirements include PVC/stainless steel wells and piping; conventional vapor phase carbon treatment units; a conventional air/water separator; and an induction blower.

The design of the SVE system is critical in order to insure adequate cleanup of the soils. The design requires expertise in modeling vapor flow, understanding site lithology, determining contaminant mass and areal extent of contamination. These factors are used to determine system variables such as well spacing, number of wells, and depth of screened interval.

Site conditions, soil properties, and the contaminant's chemical properties are the important factors to consider in determining whether to use soil vapor extraction. Information on soil permeability, moisture content, and porosity is needed to make a determination on whether the soils have sufficient air-filled porosity. Insufficient air-filled porosity results from the presence of excess water in the pore spaces which reduces the effectiveness of vacuum extraction. Depth to groundwater is an important cost consideration because if the vadose zone is less than 10 feet, it may not be cost-effective to use SVE (excavation of less than 10 feet may be less costly).

In order for a contaminant to be stripped from the soil using SVE, it must have a Henry's Constant of 0.001 or greater. The higher the Henry's Constant, the easier the compound is removed by vacuum extraction. Figure 4 shows relative extraction rates for compounds found at the TSRR facility.

Design and Construction of the TSRR System

Prior to full-scale construction of the SVE system at TSRR, a preconstruction investigation was performed. The investigation included a geophysical survey, a soil sampling program, and a soil gas survey.

The geophysical survey was conducted to confirm locations of underground tanks and to check for additional buried objects in the effected area. The soil sampling program was conducted to investigate the horizontal and vertical extent of contamination, and to estimate the mass of VOCs in the vadose zone. As a result of this activity, a revised estimate for VOCs ranging from 13,000 to 16,500 pounds was calculated. This did not include estimates for a floating product layer that was discovered during the sampling. The objective of the soil gas survey was to investigate the extent of VOC contamination in shallow soils in

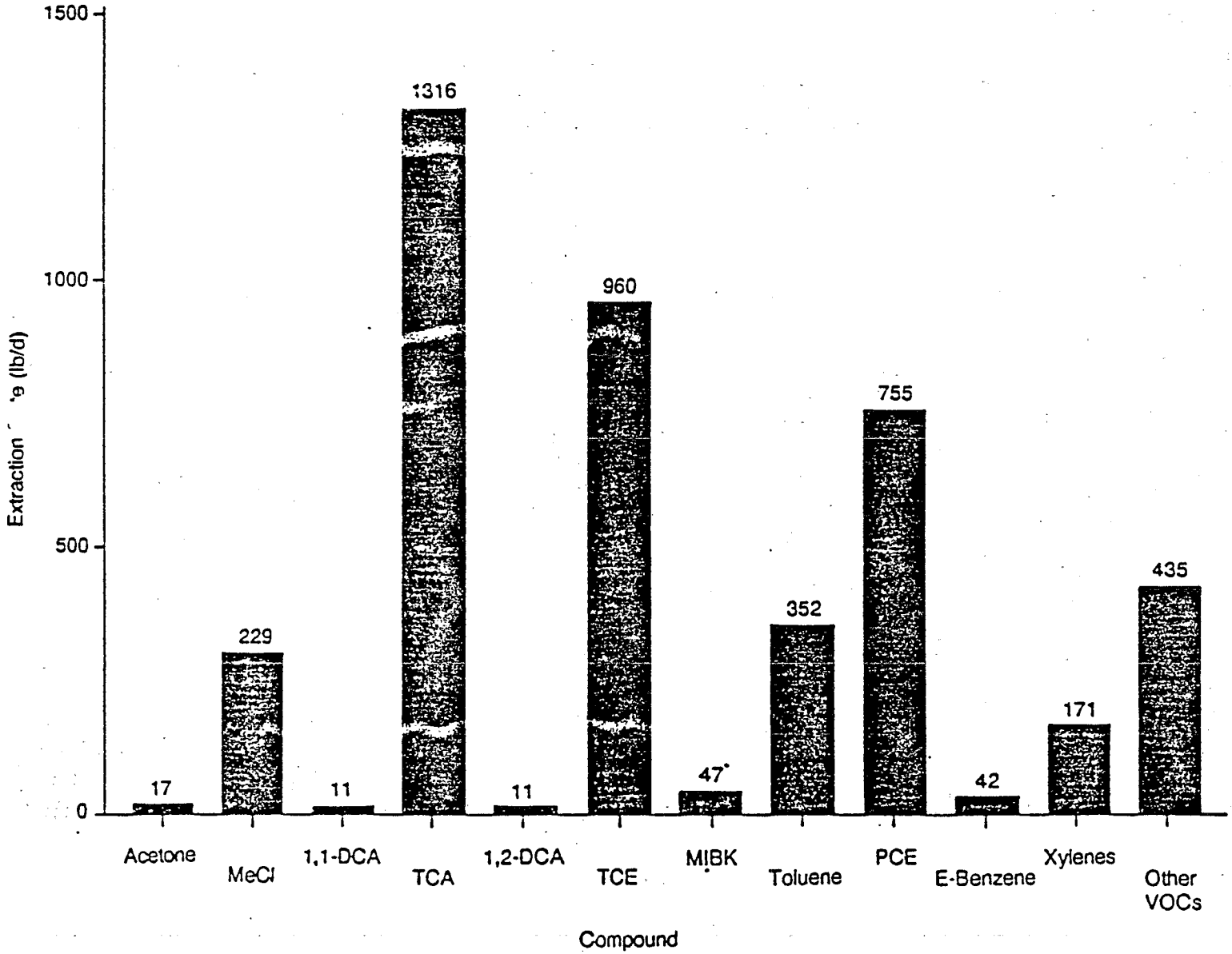

FIGURE 4
Relative extraction rates.

areas not previously investigated at the site. Results confirmed that the major area of contamination was in the vicinity of the underground tanks and loading dock, however, contamination was also detected along the northeast and southern parameters of the site.

Results of the investigation were used to determine locations of additional SVE wells, revise estimates of the mass of VOCs in the soils, and to make determinations on system parameters.

Following the preconstruction investigation, a pilot phase SVE system was installed. The system consisted of 11 wells that were operated for a total of 70 hours. The objectives of the pilot phase were to verify the radius of influence of the wells and determine the vapor flow rate/vacuum pressure relationship at each well, investigate the effect of the underground tanks on the vacuum pressure distribution in the vadose zone, and identify the VOC loading rates form individual wells as a function of vacuum pressure and flow rate.

Results of the pilot phase were used to determine process variables and locations of wells. Extracted airflow rates range from 60 to 165 standard cubic feet per minute (scfm) from individual wells, with wellhead vacuums of 3 to 4 inches of mercury. VOC extraction rates vary between wells with the highest measured concentration at 4,400 lbs/day during the pilot phase. The radius of influence for the wells was measured to be greater than 50 feet.

The full-scale system consists of a network of 23 4-inch diameter PVC wells with slotted screens from approximately 5 feet below grade to 3 feet below the water table. The wells are packed with silica sand and sealed at the screen/casing interface with bentonite and then grouted to existing grade to prevent short circuiting. Each well has a throttling valve, a sample port, and a vacuum pressure gauge. The wells are connected by an above ground PVC piping manifold system. Figure 5 shows the location of the SVE wells and the piping layout.

The piping manifold is connected to a centrifugal air/water separator. This is connected to the vapor phase carbon absorption system which is followed by the vacuum extraction unit (VEU). The VEU is responsible for inducing extraction of soil vapors from the subsurface, through the extraction wells and into the treatment unit. After treatment, air is discharged through a 30 foot stack located on site. Figure 6 is a schematic of the SVE system.

The carbon absorption system consists of eight stainless steel carbon canisters with four in the primary system and four in the secondary or backup system. The primary carbon system is the main unit for absorption of VOCs, with the secondary carbon

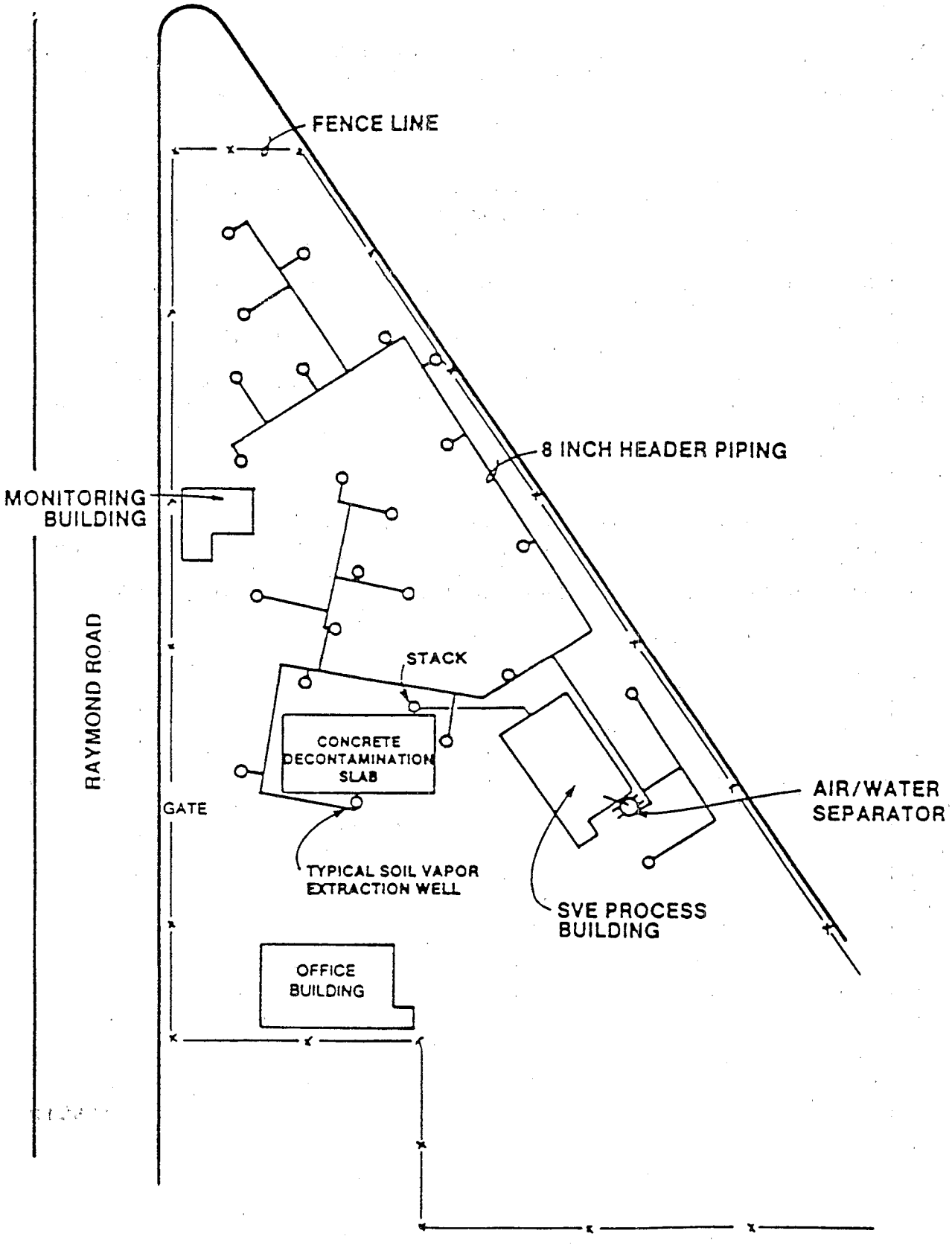

FIGURE 5
SVE WELLS AND PIPING LAYOUT

system acting as a backup when breakthrough of the primary system occurs. Each carbon canister holds 1000 pounds of vapor-phase granular activated carbon and are connected to the header piping with flexible hoses and couplings that are easily disconnected for ease in canister change outs. Figure 6 shows the various sample ports, pressure gauges and temperature probes located before, between, and after the carbon units. A carbon monoxide monitor is installed between the carbon units to detect combustion in the primary carbon unit and trigger an automatic system shutoff upon detection.

The carbon system was installed on the negative pressure side of the VEU to minimize leaks and eliminate the potential for emissions to the atmosphere. During the pilot phase of operation it was determined that carbon adsorption efficiency was equivalent under positive and negative pressure.

Breakthrough of the primary carbon system is measured by an in-line HNu photoionization detection meter. Four contaminants are used as indicator compounds, tetrachloroethylene, trichloroethylene, methylene chloride, and benzene. The breakthrough point was determined using the relationship between total VOCs measured by the HNu and the compound-specific concentrations measured in the air flow. When breakthrough occurs, the primary carbon canisters are changed out and replaced with those from the secondary system and a new set of four canisters are put into backup in the secondary system. This allows maximum loading of the primary carbon system prior to rotating the carbon units, while minimizing the possibility of breakthrough in the backup system.

Samples are collected from both carbon systems as well as at the individual wellheads. Results are used to determine VOC loading rates and predict rates of breakthrough. Sample analysis is performed on-site using a gas chromatograph with dual flame ionization detectors and capillary columns.

III. RESULTS

The SVE system began full operation in March 1988. Results discussed in this report are for the period of March 1988 through September 1989.

Vacuum Extraction System Performance

To date, approximately 40,250 pounds of VOCs have been removed from the soils. On-site gas chromatography has been used to monitor VOC concentrations extracted by SVE. Off-site analysis of spent carbon has confirmed that on-site monitoring is accurate to within approximately 5 percent.

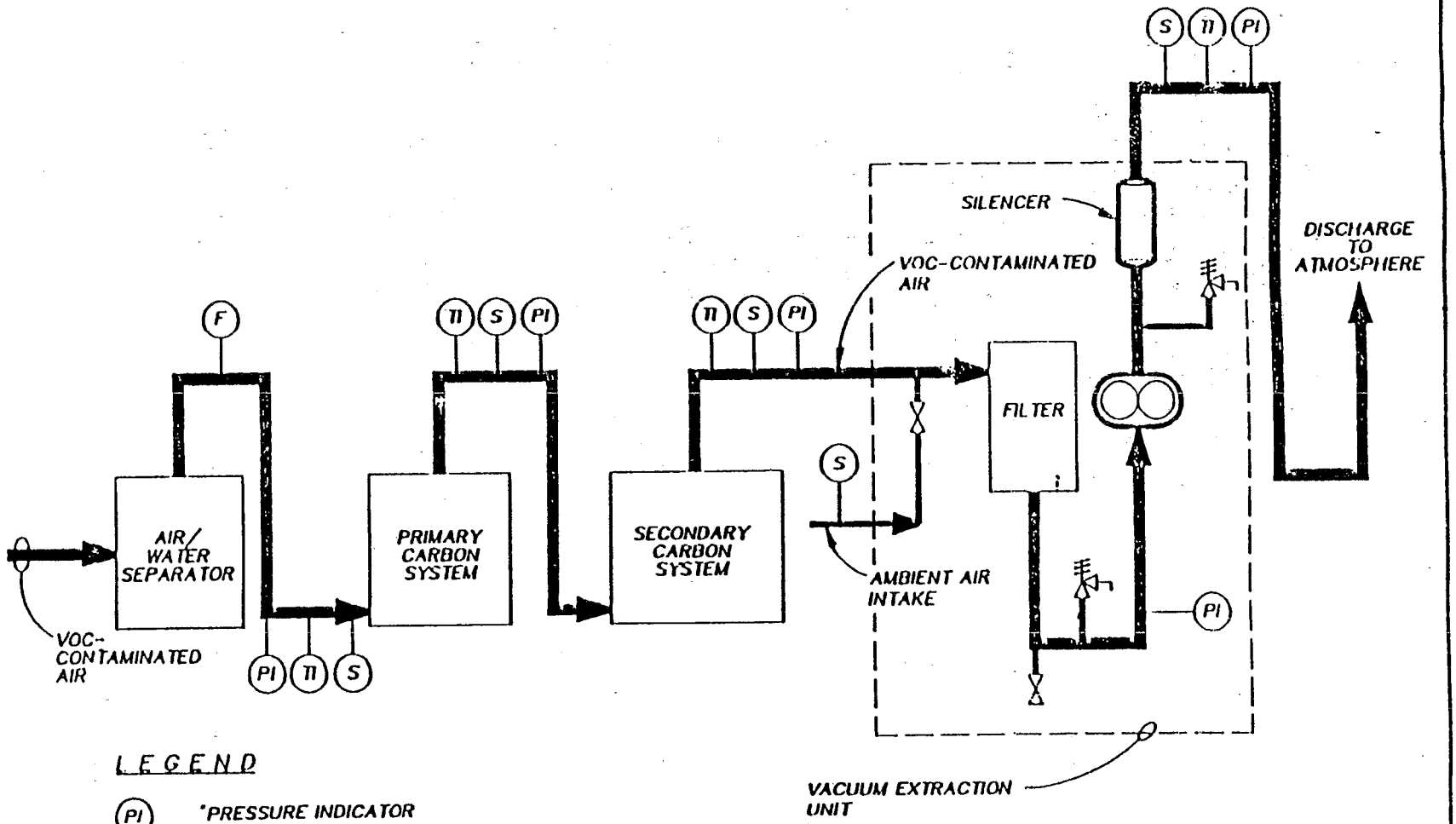

FIGURE 6
SCHEMATIC OF SOIL VAPOR EXTRACTION SYSTEM

The initial loading rate of total VOCs has declined over the period of operation from an initial level of approximately 45 pounds per hour (pph) to below 10 pph. The floating product layer that was detected during preconstruction and during the initial operation perice has not been detected since October 1988; however, at that same time, a 0.5- to 1.0 foot increase in the water table was recorded.

The average VOC concentrations measured at the air discharge stack is approximately 1.35 mg/l, with an average flow rate in the stack of 1060 standard cubic feet per minute (scfm). This has dropped from an initial VOC concentration of approximately 23 mg/l. Over the course of operation of the system, an average efficiency rate of greater than 99.8 percent removal has been measured.

Technology Evaluation and Performance Monitoring

Since SVE is an innovative technology, careful consideration was given to the method by which the system's performance would be monitored and to confirm that the performance objectives would be met. A Quality Assurance Project Plan (QAPP) and Sampling Plan were developed for the sampling events. Three soil sampling episodes were planned. One prior to startup, one at the mid-operation point, and the last to confirm that performance objectives have been met.

Since conventional soil sampling methods cause volatilization of VOCs prior to analysis, a special sampling and analysis procedure was developed for collection of samples. Samples are taken by driving a split spoon sampler fitted with four, 3-inch brass liners, through hollow stem augers. To prevent excess handling, and thus volatilization of contaminants, one brass liner is removed from the split spoon, immediately wrapped in aluminum foil, sealed, and sent to the laboratory for analysis. Samples are analyzed using a core of the undisturbed sample for extraction.

To date, the pre-operational and mid-operational sampling events have occurred. The pre-operational samples verified that the volume of VOCs in the soils had been underestimated during the remedial investigation at the site. Based on sample results, VOC concentrations were estimated to be between 12,800 and 16,500 pounds. This did not include estimates for the floating layer of product that was identified during the startup work.

Data from the mid-operational sampling event have not yet been received from the laboratory. It is hoped that this data will be available for incorporation into the final version of this report.

Process factors

Carbon handling requirements have been the limiting factor in performance of the SVE system. Because the estimate of VOCs present in the soils was significantly underestimated, the amount of carbon needed was also underestimated. The amount of contaminants extracted to date has resulted in the use of 250,000 pounds of carbon in the treatment system at a cost of $541,000. It is estimated that a total of more than 400,000 pounds will be needed to complete the project at a cost of approximately $886,000.

In addition to the increased costs, the additional carbon requirements have caused delays in the operation of the system. Although the system has been operational for more than 18 months, actual number of days of operation is approximately 100. This due to the need for frequent carbon change outs and transporting the spent carbon off-site for regeneration. It is estimated that an additional 50 days will be needed to attain the levels required in the performance objectives. It is also expected that carbon change outs will become less frequent as the loading rates decline.

The equipment needed to operate the system has proven to be very reliable and down time due to equipment failure has not been a factor in SVE operation. As discussed, the materials used to operate the SVE system are conventional and easily replaced if necessary. Although Terra Vac, the vendor, has been required to be on site for 8 to 10 days per month due to the frequent need to change out carbon and monitor the system, the system was designed for unattended operation. It is expected that as loading rates decline, Terra Vac will be required to spent less time at the site per month.

Instrumentation and controls have been installed to monitor the system and trigger shut down if necessary. These include the carbon monoxide monitor in the carbon system, a high water-level shut down in the air/water separator, high temperature shut down triggers, and an on-line HNu with a shutdown mechanism for detecting VOC breakthrough of the primary carbon system. In addition, the system contains an automatic dialer that contacts Terra Vac when any of the shutoff mechanisms are triggered.

Costs

A summary of the costs to install and operate the SVE system, current and projected future carbon costs, and the unit costs for operation of the system are listed in Table 2. It was not possible to separate out the cost of the pilot phase portion from the cost of the full-scale system because the bid was received as

TABLE 2

SOIL VAPOR EXTRACTION COSTS

SVE Lump Sum Bid - For Construction & Operation (excluding cost of carbon)	$1,265,535
Cost of SVE/Cubic Yard of VOC-Contaminated Soil (excluding cost of carbon)	$22.50
Unit Cost/pound for Carbon (removal/transport/regeneration)	$ 2.16
Carbon Costs to Date (250,000 pounds used)	$541,000
Projected Total Carbon Costs (estimated 400,000 pounds)	$886,000

a lump sum for the project. The original cost estimate was revised to account for the additional days per month Terra Vac is required to be on-site, due to the increased contamination at the site.

As previously discussed, carbon costs have been quite high due to the increased level of contamination found at the site. Initially, it was estimated that 20,000 pounds of carbon would be needed to remediate the site. To date, 250,000 pounds have been used and it is estimated that an additional 150,000 pounds more are needed to complete the project. Table 2 lists the actual and projected future carbon costs for project completion. No long term maintenance costs are expected.

Lessons Learned

Vapor Treatment

As has been discussed throughout this report, the underestimation of the total mass of VOCs in the soils at this site has complicated the remediation of the site. The increased levels have effected the project expense, the time to remediate, and the operation of the technology.

During evaluation of the treatment options for the project, it was determined that, based on a total VOC volume of 1,700 pounds, carbon absorption was the least expensive treatment option. If contamination estimates were closer to the actual, carbon absorption would not have been the least costly and would likely not have been considered. In addition, the cost of operating the system is more expensive because Terra Vac must be at the site many more days per month than estimated.

The underestimation of VOC mass has also effected remediation time and the operation of the technology. Due to the frequent number of change outs required during operation, the system is operational as little as five to ten days per month. This has resulted in only 100 days of system operation in a period of 18 months.

In order to prevent this situation, it is imperative that accurate estimates of subsurface contamination be obtained prior to design of the system. Specifically, accurate mass estimates must be obtained for amount of floating product present, and the amount of VOC contamination in the capillary fringe, the zone immediately above the water table, and in the smear zone, the zone within which the water table fluctuates. Based on data collected during operation of the SVE at TSRR, it was estimated that 70 percent of the mass of VOCs occurs as floating product and in VOC saturated soils in the smear zone and capillary fringe.

Radon Gas

A somewhat unexpected contaminant detected was radon gas, which occurs naturally in the site soils. Measurements of the carbon vessels indicate the presence of radioactivity on the spent carbon. The presence of radon gas is not too unusual since it is readily volatilized and activated carbon is a good collection medium for radon. Concentrations measured to date at the TSRR facility are not considered to present a public health or worker hazard. However, the handling, transportation and regeneration of radioactive spent carbon may need to be considered for SVE operation in areas where radon occurs at high levels.

Future Plans

U.S. EPA's contractor, CH_2M Hill, is currently evaluating the use of a catalytic oxidation (CATOX) system for the destruction of VOCs in the soil vapor. This would replace the carbon absorption system. While other treatment options have been looked at during the life of the project, the cost for removing the carbon system and installing another treatment system has not been shown to be cost-effective. However, cost-effective CATOX systems have recently been developed that can treat chlorinated VOCs without generating dioxins or suppressing catalyst performance.

In addition to the reduction in cost to treat contaminants, two other major benefits from switching to a CATOX system are the destruction of contaminants on-site, which eliminates the transporting of wastes off-site, and the ability to run the SVE system continuously, thereby attaining site cleanup faster.

IV. CONCLUSIONS

Since the project is still in operation, certain conclusions sould not be considered definite. However, based on evaluation of the operating data from the site and on the recent literature regarding SVE, the following conclusions have been drawn:

* SVE is a viable technology for the removal of VOCs in unsaturated soils. The fact that over 40,000 pounds of VOCs have been removed from the soils at TSRR indicates that the technology works.

* SVE will operate in a wide range of soil types. Based on work at the site, SVE is very effective in removing contaminants from sandy soils. Recent literature on SVE performance indicates that it is effective for soils with measured permeabilities of 10^{-4} to 10^{-8} cm/sec.

* The major considerations in determining the technology's

applicability are soil properties, depth to ground water, and the contaminant's chemical properties. Soils that have a low air-filled porosity and high moisture content may not provide adequate conditions. In addition, at sites where groundwater is encountered at less than 10 feet, it may be more cost-effective to excavate contaminated soils. Chemicals with a Henry's Constant of less than 0.001 may not be sufficiently volatile for the SVE process.

* The SVE system has operated well in all weather conditions at the site. Cold weather operation has not proved to be a problem. The system has operated through an entire winter in the midwest with temperatures that range from 0 degrees celsius to -26 degrees celsius.

* The SVE system can be designed to operate for the majority of the time without an on-site operator. Under most circumstances, the system would be sized to provide unattended operation with vendor personnel on-site 1 to 4 days per month depending on the size of the system and the monitoring requirements.

* Based on experience at the TSRR facility, SVE appears to be the only technology that can effectively remove the VOC saturation remaining after free product is removed from the capillary fringe and smear zone of VOC-contaminated soils.

* The costs of SVE at the site for 1 cubic meter of soil is approximately $50.00 to $60.00. This includes the cost of treatment of vapors using carbon absorption. If treatment of vapors is not required, costs could be as low as $20.00 per cubic meter of soil.

The overall prognosis of the SVE process is that it offers an economical, reliable, and rapid cleanup technology for remediating soils contaminated with volatile organics. The technology enhances groundwater extraction systems and greatly reduces the time and cost for groundwater remediation. The process works on most soil types and has a limited number of factors for consideration in determining applicability. There is no limit on size of the site, or on the level of VOC contamination (except in considering the need for treatment of off-gases). The system is easily installed and removed, and does not require specialized equipment for operation.

V. CONTACTS FOR MORE INFORMATION

Information useful to potential SVE technology users can be provided by the following sources:

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Appendix 4-C

Soil Vapor Extraction Technology Case Studies

Venting Methods, Air Force Bases, United States
- Bioventing
- Catalytic Oxidation Emissions Control
- *In-situ* Soil Venting of JP-4 Jet Fuels
  (no final paper available)

A FIELD SCALE INVESTIGATION OF ENHANCED PETROLEUM HYDROCARBON BIODEGRADATION IN THE VADOSE -ZONE AT TYNDALL AFB, FLORIDA

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ABSTRACT

Soil venting is effective for the physical removal of volatile hydrocarbons from unsaturated soils, and is also effective as a source of oxygen for biological degradation of the volatile and non-volatile fractions of hydrocarbons in contaminated soil. Treatment of soil venting off-gas is expensive, constituting a minimum of 50% of soil venting remediation costs. In this research, methods for enhancing biodegradation through soil venting were investigated, with the goal of eliminating the need for expensive off-gas treatment.

A seven-month field investigation was conducted at Tyndall Air Force Base (AFB), Florida, where past jet fuel storage had resulted in contamination of a sandy soil. The contaminated area was dewatered to maintain approximately 1.6 meters of unsaturated soil. Soil hydrocarbon concentrations ranged from 30 to 23,000 mg/kg. Contaminated and uncontaminated test plots were vented for 188

days. Venting was interrupted five times during operation to allow for measurement of biological activity (CO_2 production and O_2 consumption) under varying moisture and nutrient conditions.

Moisture addition had no significant effect on soil moisture content or biodegradation rate. Soil moisture content ranged from 6.5 to 9.8%, by weight, throughout the field test. Nutrient addition was also shown to have no statistically significant effect on biodegradation rate. Initial soil sampling results indicated that naturally occurring nutrients were adequate for the amount of biodegradation observed. Acetylene reduction studies, conducted in the laboratory, indicated a biological nitrogen fixation potential capable of fixing the organic nitrogen, observed in initial soil samples, in five to eight years under anaerobic conditions. Biodegradation rate constants were shown to be effected by soil temperature and followed predicted values based on the van't Hoff-Arrhenius Equation.

In one treatment cell, approximately 26 kg of hydrocarbons volatilized and 32 kg biodegraded over the seven-month field test. Although this equates to 55% removal attributed to biodegradation, a series of flow rate tests showed that biodegradation could be increased to 85% by managing air flow rate. Off-gas from one treatment cell was injected into clean soil to assess the potential for complete biological remediation. Based biodegradation rate data collected at this field site, a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would have been required to completely biodegrade the off-gas from the contaminated soil.

This research indicates that proper ratios of uncontaminated to contaminated soil and air flow management are important factors in influencing total biodegradation of jet fuel, substantially reducing remediation costs associated with treatment of soil venting off-gas.

INTRODUCTION

Background Information

Approximately 3.6×10^{12} kg (4 billion tons) of hazardous materials are transported annually in the United States, and of this amount about 90% consists of gasoline, fuel oil, and jet fuel. Massachusetts officials report, that in 1984, 58% of reported spills in their northeast region were petroleum products, of which 28% were gasoline, diesel, or fuel oil. Assuming that Massachusetts is representative of the rest of the United States, transportation and transfer of petroleum products, particularly fuels, pose a major risk to the environment (Calabrese et al.,1988a).

In addition to transportation of fuels, leakage of stored fuel has proven to be a serious environmental problem, particularly as a source of ground water contamination. The United States Environmental Protection Agency (U.S. E.P.A.) estimates that there are three million underground storage tanks in the United States, of which, 78% (2.3 million) are used to store fuel products. Based on a random sampling, EPA estimates that 35%, or approximately 820,000 underground fuel tanks are leaking (Calabrese et al.,1988a).

A recent report indicates that there are three to five million underground storage tanks used to store liquid petroleum and chemical substances and that EPA estimates 100,000 to 400,000 of these tanks may be or have been leaking. The majority of these tanks have been gasoline or other petroleum distillates (Camp, Dresser, and Mckee, 1988). Based on the percentages quoted above, the estimate for leaking underground fuel tanks could go as high as 1.4 million. The disparity in estimating the number of leaking underground fuel tanks underscores our inability, to date, to accurately quantify the magnitude of the problem. Even using minimum estimates, leaking underground fuel tanks pose a significant threat to the environment.

Hazards Associated With Fuel

Although the general public appears less concerned with fuels than with industrial chemicals, regulatory agencies have long been aware of the threat to public health that these fuels pose. The U.S. Coast Guard and U.S. E.P.A. have attempted to characterize the toxicological hazards associated with petroleum contamination. They concluded that exposure to petroleum products resulting from contaminated soils may occur via the following routes: inhalation, dermal absorption, ingestion from consuming contaminated soil, consumption of plants and animals that have assimilated petroleum products, and by consumption of contaminated drinking water (Calabrese et al.,1988b).

A combination of U. S. Coast Guard and U. S. E.P.A. ranking systems resulted in a list of 25 priority contaminants of public health concern found in petroleum products as shown in Table 1. Hoag's findings support the U. S. Coast Guard and U. S. E.P.A. He reports finding at least eight listed hazardous constituents in gasoline (Hoag et al., 1984).

Table 1. Priority contaminants identified in petroleum products.

Heavy Metals	Halogenated Hydrocarbons	Nonhalogenated Aromatic Hydrocarbons	Nonhalogenated Aliphatic Hydrocarbons
Cadmium	1,2,-dibromoethane	Benzene	Heptane
Chromium	Dichloroethane	Benzo (alpha) anthracene	Hexane
Tetraethyl lead	Dichlorobenzene	Benzo (beta) pyrene	Isobutane
Tetramethyl lead	Tetrachloroethylene	Phenol	Isopentane
Zinc	Trichloroethylene	Toluene	1- Pentene
	PCBs	Xylene	

Adapted from Calabrese et al. (1988b).

Jet fuels have received less attention in the literature than has gasoline. The reason for this is unknown but may be related to the circumstances under which jet fuel is transported and used. Millions of liters of jet fuel are transported daily. However, most jet fuel is delivered by underground pipeline or rail car directly from the refinery to the user. There have been major jet fuel releases, although most have not been published in the literature. Approximately half of the chemically contaminated sites on Air Force installations are associated with fuels, most of which are JP-4 (Downey and Elliot, 1990).

Lead is not added to jet fuels for octane enhancement, but one analysis revealed 0.09 ppm lead and 0.5 ppm arsenic (Riser, 1988). All other metals were below detectable levels, and no halogenated compounds were found. Normal hexane and heptane were measured at 2.21 and 3.67 % by weight, respectively, and the benzene, toluene, ethylbenzene, and xylenes (BTEX) fraction constituted 4.5 % by weight. Aromatics totaled 17.6% of the mixture by weight (Riser, 1988). Seventy-six major components of JP-4 were identified in this analysis, but as many as 270 different components have been reported in other studies (Mason et al., 1985).

There may be significant environmental health and safety hazards associated with subsurface fuel spills. Pathways for human exposure are through ground water contamination resulting from solubilization of normal and substituted alkane, alkene, and aromatic hydrocarbons and exposure to toxic levels of vapors trapped in occupied, confined spaces. Explosion from vapors, which move by advection and diffusion to a confined space containing a source of ignition (i.e., basements), is the greatest potential safety hazard resulting from subsurface fuel spills (Hoag and Cliff, 1988).

BTEX Contamination of Ground Water

BTEX are the contaminants in fuels which most often result in contamination and abandonment of subsurface drinking water supplies. This fact results from the relatively high solubility of these aromatics in water, coupled with the low allowable aqueous-phase maximum-contaminant levels (MCLs) due to their known or suspected carcinogenicity.

Dissolved benzene, toluene, and xylene resulting from gasoline contamination have been reported in domestic water wells at concentrations of 14, 10, and 10 mg/L, respectively (Hoag and Cliff, 1988). A 38,000 L (10,000 gallon) release from a gasoline station in Bellview, Florida caused the abandonment of the entire Bellview drinking water well field based on the BTEX fraction found in water samples. BTEX concentrations in soils collected during construction of monitoring wells ranged from 894 to 388 mg/kg (Camp, Dresser, and McKee, 1988).

Conner (1988) indicated that fuel leaks as large as 1 million L (270,000 gallons) have occurred but that leaks in the 75,000 to 200,000 L (20,000 to 50,000 gallon) range are more

common. Considering the damage resulting from the 38,000 L (10,000-gallon) release at Bellview, Florida, the typical 75,000 to 200,000 L (20,000 to 50,000 gallon) spill is environmentally significant. He also stated that soil can hold up to 70 L of gasoline/m^3 (0.5 gallons of gasoline/ft^3) and that 3.8 L (1 gallon) of gasoline can render 3.8 million L (1 million gallons) of water unsuitable for consumption. This conclusion results from the fact that if 3.8 L (1 gallon) of gasoline containing 1% benzene were added to 3.8 million L (1 million gallons) of water, the benzene concentration would be approximately 7 µg/L (ppb) and would be unfit for human consumption based on the current MCL of 5 µg/L (ppb) (Pontius, 1990). However, this analysis assumes complete benzene solubilization and ignores partitioning and kinetics.

One percent benzene in fuel is not uncommon, and much higher levels have been measured. The American Petroleum Institute (API)/EPA reference fuel, PS-6, contains 1.7 % benzene, 4 % toluene, and 9.8 % ethylbenzene and o- m- p- xylene by volume. The total aromatic fraction was measured at 26.08 % by volume (Calabrese et al.,1988b). The BTEX and total aromatic concentration in gasoline varies significantly from refinery to refinery and batch to batch. The fraction of BTEX in gasoline has been reported to range from 6.4 to 36.4% by weight (Riser, 1988).

Additional research indicates that the Bellview well field and others affected by fuel spills will be closed for long periods of time unless remediation of the unsaturated-(vadose-) zone is successful. First, work by Wilson and Conrad (1984) shows that 15 to 40% of the pore space can hold fuel. This means that 38,000 L (10,000 gallons) of gasoline can be held in a cube 9mx12mx9m (30ftx40ftx30ft). Malot and Wood (1985) describe a multi-phase transport model by Baehr and Corapcioglu that predicts benzene from a typical gasoline spill will be leached into water for about 20 years, and other components would take several decades longer to be removed through water flushing. Although natural biodegradation may eventually mineralize most fuel contamination, the process is frequently too slow to prevent ground water contamination. High-risk sites require rapid removal of the contaminants to protect drinking water supplies and public health.

Vadose-Zone Remediation

The realization that contaminated soil is a long-term source of ground water contamination has shifted the focus of remediation from treating contaminated ground water (pump and treat) to treating the source of the contamination in the vadose-zone. The initial remediation method employed by consulting firms was excavation of contaminated soil with placement in landfills or for use in asphalt plants. Fuel-contaminated soil is not a listed or characteristic hazardous waste, and disposal in sanitary landfills is often recommended to reduced disposal costs. The cost of this alternative ranges from $400 to $660 per m^3 ($300 -$500 per yd^3) of contaminated material (Clarke, 1987). This type of recommendation has been made without consideration of the listed hazardous waste components in fuels and the future costs associated with being identified as a potentially responsible party (PRP) in the clean-up effort of the hazardous waste or sanitary landfill. Increased restrictions by EPA on landfilling of hazardous waste and the risk of being identified as a PRP in a hazardous waste or sanitary landfill cleanup have led to the emergence of excavation coupled with incineration technology. However, this approach is extremely expensive at $1300 to $2600 per m^3 ($1000 to $2000 per yd^3), making this alternative cost prohibitive for large volumes of contaminated soil (Clarke, 1987).

Excavation is not only expensive but may be impossible if contamination extends beneath buildings or across property lines. If contamination is deep, the size of safe excavations may be prohibitive (Bennedsen et al., 1987). Numerous failures at hazardous waste landfills together with the inability to excavate many sites has sparked increased emphasis for on-site clean-up technologies. In many cases, on-site treatment technologies have proven to be less expensive than off-site alternatives and, if feasible, are usually preferred by U.S.E.P.A. (U.S.E.P.A., 1989). Technologies for *in situ* remediation of vadose-zone fuel hydrocarbon contamination include soil washing, radio frequency (RF) heating of soil, soil venting, and enhanced microbial degradation.

Soil venting is a technology that has been proven effective for the physical removal of volatile compounds such as gasoline and TCE from the unsaturated-zone. However, soil venting produces an effluent which may require expensive treatment prior to discharge. This off-gas treatment step frequently constitutes a minimum of 50% of total remediation costs. In addition, volatilization of contaminants through soil venting alone is not effective in the removal of nonvolatile or low volatility components of jet fuel. This research explored the possibility of reducing or eliminating expensive

off-gas treatment while remediating low volatility jet fuel contamination of vadose-zone soils through enhancing *in situ* biodegradation.

AIR FORCE RESEARCH OBJECTIVES

The Air Force stores and transports 11×10^9 L (3×10^9 gallons) of JP-4 jet fuel annually and an estimated 1,500 fuel spills have been identified during Phase II investigations conducted under the Air Force Installation Restoration Program (IRP). JP-4 is less volatile than gasoline and contains a considerable nonvolatile fraction (Mason et al., 1985). This research, funded by the Air Force, builds upon earlier work with enhanced bioreclamation through soil venting at Hill Air Force Base (AFB), Utah (Hinchee et al. 1989). This research direction resulted from the apparent failure of hydrogen peroxide (H_2O_2) to adequately deliver oxygen at JP-4-contaminated sites studied at Kelly AFB, Texas, and Eglin AFB, Florida (Downey and Elliot, 1990). As an alternative approach, Air Force research is presently concerned with evaluating soil venting as an economical process for supplying oxygen for enhanced biodegradation in the subsurface.

The objective of this project was to investigate the potential for enhanced biodegradation of JP-4 jet fuel in the vadose-zone by providing oxygen through soil venting combined with moisture and nutrient addition. This project is a field evaluation and demonstration of this *in situ* technology. Specific objectives were:

1. to evaluate the potential for enhanced biodegradation of JP-4 in the vadose-zone as the result of soil venting and incremental effectiveness observed with addition of nutrients and moisture,

2. to evaluate the relationships among air flow rate, biodegradation, and volatilization to determine minimal aeration rates required to maintain aerobic conditions for maximizing biodegradation and minimizing volatilization, and

3. to evaluate the potential for biodegradation of hydrocarbon vapors (off-gas) in uncontaminated or less contaminated vadose-zone soil as an alternative to expensive above-ground off-gas treatment.

The intended result was to develop sufficient information to allow the Air Force and/or other large users of similar fuel mixtures to progress to full-scale implementation of the technology.

MATERIALS AND METHODS

Site Description

An *in situ* field demonstration of enhanced biodegradation through soil venting was conducted at the site of an abandoned tank farm located on Tyndall AFB, Florida. The site is contaminated with fuel, primarily JP-4, and free product has been observed floating on the shallow ground water table. Tyndall AFB is located on a peninsula that extends along the shoreline of the Gulf of Mexico in the central part of the Florida Panhandle. The highest ground on the peninsula is 7.6 to 9.1 m (25 to 30 ft) above mean sea level. The uppermost sediments, at Tyndall AFB, are sands and gravels of Pleistocene to Holocene age (Environmental Science and Engineering, Inc., 1988). Soils at the site are best described by the Mandarin series consisting of somewhat poorly drained, moderately permeable soils that formed in thick beds of sandy material (U.S.D.A., 1984).

The climate at the site is sub-tropical with an annual average temperature of 20.5° C (69° F). Average daily maximum and minimum temperatures are 25° C and 16° C (77° F and 61° F), respectively. Temperatures of 32° C (90° F) or higher are frequently reached during summer months, but temperatures above 38° C (100° F) are reached only rarely. Average annual rainfall at Tyndall AFB is 140 cm (55.2 inches) with approximately 125 days of recordable precipitation during the year. The depth to ground water on Tyndall AFB varies from about 0.3 to 3.0 m (1 to 10 ft). The water-table elevation rises during periods of heavy rainfall and declines during periods of low rainfall. Yearly

fluctuations in ground water elevations of approximately 1.5 m (5 ft) are typical (Environmental Science and Engineering, Inc., 1988). Prior to dewatering at the site, the water table was observed to be as shallow as 46 cm (1.5 ft).

Field Testing Objectives

A seven month field study (October, 1989, to May, 1990) was designed to address the following areas:

1. Does soil venting enhance biodegradation of JP-4 at this site?
2. Does moisture addition coupled with soil venting enhance biodegradation at this site?
3. Does nutrient addition coupled with soil venting and moisture addition enhance biodegradation at this site?
4. Will the hydrocarbons in the off-gas biodegrade when passed through uncontaminated soil?
5. Evaluation of ventilation rate manipulation to maximize biodegradation and minimize volatilization.
6. Calculation of specific biodegradation rate constants from a series of respiration tests conducted during shutdown of the air extraction system.
7. Determination of the effects of biodegradation and volatilization on a subset of selected JP- 4 components.
8. Determination of the potential for nitrogen fixation under aerobic and anaerobic conditions.
9. Evaluation of alternative vent placement and vent configuration to maximize biodegradation and minimize volatilization.

Test Plot Design and Operation

In order to accomplish project objectives, two treatment plots and two background plots were constructed and operated in the following manner:

1. Contaminated Treatment Plot 1 (V1) - Venting only for approximately 8 weeks, followed by moisture addition for approximately 14 weeks, followed by moisture and nutrient addition for approximately 7 weeks.
2. Contaminated Treatment Plot 2 (V2) - Venting coupled with moisture and nutrient addition for 29 weeks.
3. Background Plot 3 (V3) - Venting with moisture and nutrient addition at rates similar to V2, with injection of hydrocarbon contaminated off-gas from V1.
4. Background Plot 4 (V4) - Venting with moisture and nutrient addition at rates similar to Vent 2.

Air Flow

Air flow was maintained throughout the field test duration except during *in situ* respiration tests. Flow rates were adjusted to maintain aerobic conditions in treatment plots, and background plots were operated at similar air retention times. Off-gas treatment experiments in one background plot (V3) involved operation at a series of flow rates and retention times.

Soil gas was withdrawn from the center monitoring well in V1 and V2 and from the only monitoring well in V3 and V4. This configuration was selected to minimize leakage of outside air observed when air was withdrawn from the ends of the plots. In all but one plot, V3, atmospheric air was allowed to passively enter at both ends. Off-gas from V1 was pumped back to the upstream ends of V3. Flow rates through all test plots were measured with calibrated rotameters.

Water Flow

To allow control of soil moisture, tap water was applied to the surface of the treatment plots. The design flow rates allowed variation from 10 to 100 mL/min in the contaminated treatment plots, and 2.5 to 25 mL/min in the background vents. This corresponds to average annual surface application rate of 43 to 430 cm (17 to 170 in). Based on vacuum and oxygen measurements in the soil gas monitoring probes, it was determined that a flow rate of 100 mL/min in the Treatment Plots inhibited air flow and oxygen transfer. Using the same technique, a flow rate of 50 mL/min (215 cm/yr surface application rate) was selected as the final water application rate. This rate did not appear to inhibit oxygen transfer to the soil gas monitoring points.

Nutrient Addition Rates

The objective of nutrient addition was to apply sufficient inorganic nitrogen (N), phosphorus (P), and potassium (K) to ensure, as far as possible, that these nutrients would not become limiting during the biodegradation of fuel hydrocarbons in the test plots. Optimizing nutrient addition rates was not the primary objective of this phase of the study. Sodium trimetaphosphate (Na-TMP), ammonium chloride (NH_4Cl), and potassium nitrate (KNO_3) were used as sources of P, N, and K, respectively.

RESULTS AND DISCUSSION

Operational Monitoring of Treatment Plots V1 and V2

Treatment plots were operated for 188 days between October 4, 1989 and April 24, 1990. Operation was interrupted only for scheduled respiration tests. Discharge gases were monitored for oxygen, carbon dioxide, and total hydrocarbons throughout the operational period. The biodegradation component was calculated using the stoichiometric oxidation of hexane. Oxygen consumption was calculated as the difference between oxygen in Background Plot V4 and oxygen in the treatment plots. Using the oxygen concentration in the background plot, rather than atmospheric oxygen concentration, the natural biodegradation of organic carbon in uncontaminated soil was accounted for. This method ensures that the biodegradation of fuel hydrocarbons was not overestimated. Biodegradation based on carbon dioxide production was similarly calculated. As the more volatile compounds are stripped from the soil, biodegradation becomes increasingly important over time as the primary hydrocarbon removal mechanism (Figure 1). As illustrated in Figure 1,

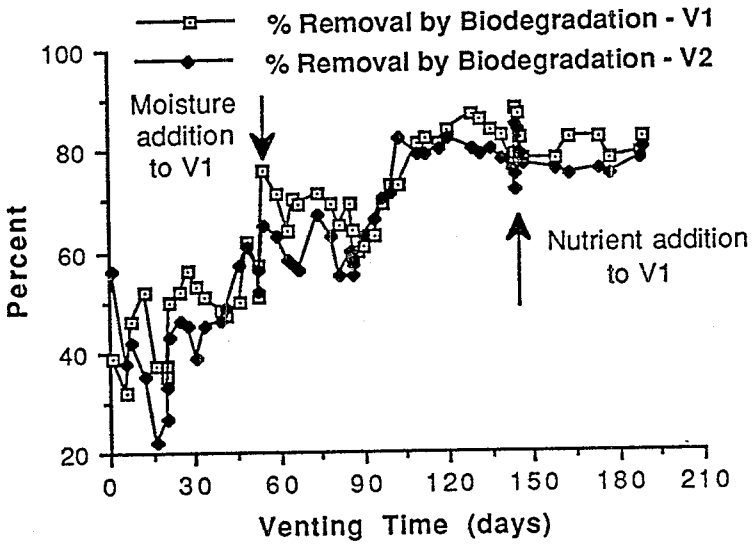

Figure 1. Comparison of the percent of combined volatilization and biodegradation hydrocarbon removal rates attributed to biodegradation (oxygen basis) in Treatment Plots V1 and V2 during the field study.

percentages of combined hydrocarbon volatilization and biodegradation removal rates attributable to biodegradation were similar in Treatment Plots V1 and V2 throughout the experimental period, and neither moisture nor nutrient addition appear to have increased biodegradation rates.

Respiration Tests

Respiration Tests, 1 through 5, were conducted October 24 through 26; November 28 through December 1, 1989; January 3 through 8; March 3 through 11; and April 24 through 26, 1990, respectively. In addition, two limited respiration tests, 3A and 4A, were conducted from January 25 through 26, and March 9 through 12, 1990. The respiration tests were designed to determine the order and rate of hydrocarbon biodegradation kinetics under varying conditions of moisture and nutrient addition. Treatment Plot V2 received moisture and nutrients throughout the experimental period and therefore served as a control for kinetic changes due to soil temperature and other factors not related to moisture and nutrients. The respiration tests were conducted by first shutting down the air delivery system to both the treatment and background plots, followed by measurement of oxygen consumption and carbon dioxide production over time. Biological respiration in Treatment Plots V1 and V2 was most consistently modeled by zero order kinetics during all respiration tests. In a system not limited by substrate, such as fuel contaminated soil, biodegradation is likely to be best modeled by zero-order kinetics (Riser, 1988).

Figure 2 graphically illustrates the zero order rate constant data obtained from the respiration tests. In Treatment Plot V1, the rate constant showed a significant drop between Test 1 and Test 2, and between Test 2 and Test 3. The rate constant significantly increased between Test 3 and Test 4 in Treatment Plot V1, but did not significantly increase between Tests 4 and 5. Since moisture was added to Treatment Plot V1 after Test 2 and nutrients after Test 4, their addition would seem, without further analysis, to be of no benefit and even detrimental, in the case of moisture addition. In Treatment Plot V2, there was a statistically significant drop in the rate constant from Test 2 to Test 3 and a statistically significant increase in the rate constant between Test 3 and Test 4. Although a depression appears in the rate constant data, there were no other statistically significant differences in Treatment Plot V2 rate constants.

Statistically significant differences in respiration rate between Treatment Plots V1 and V2, and the Background Plot V4, on all tests, and between Off-Gas Treatment Plot V3 and Background Plot V4, on Tests 3, 4A, and 5 are illustrated in Figure 2. From the data presented, it is concluded that

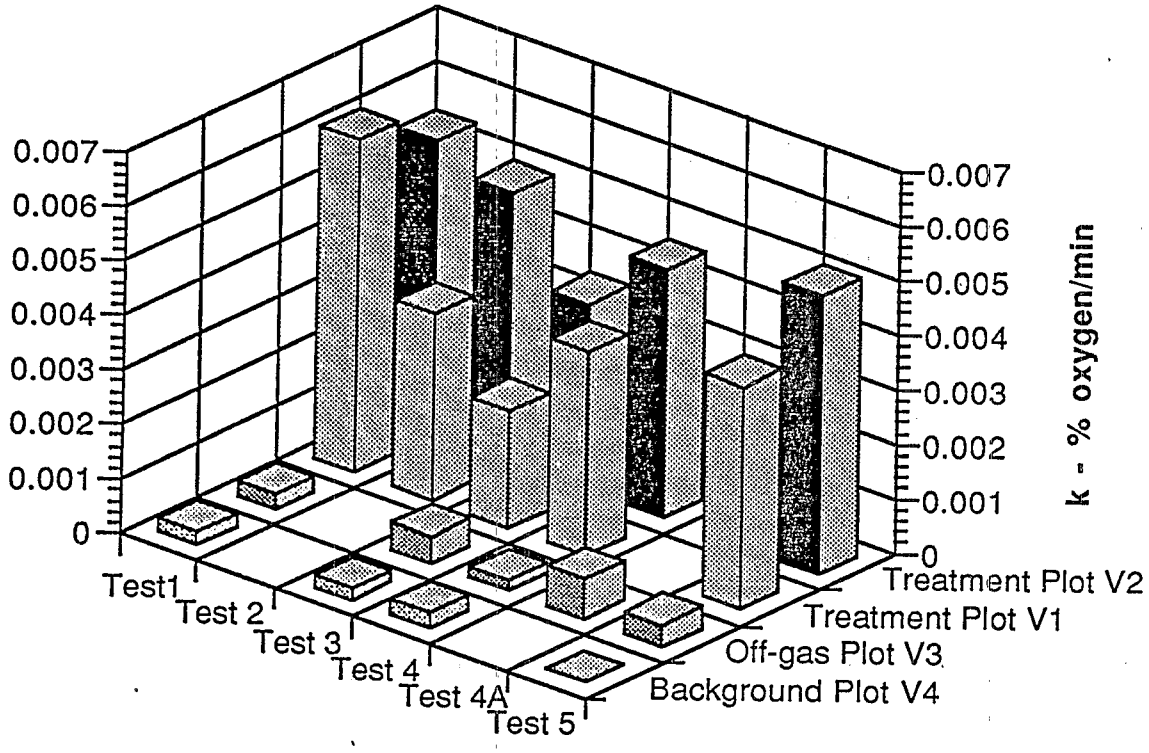

Figure 2. Average zero order rate constants determined by respiration tests.

biodegradation of jet fuel in contaminated soil, and biodegradation of hydrocarbon off-gas, resulted in statistically significant increases in respiration over that observed in uncontaminated soil.

Potential Temperature Effects on Respiration Tests

In aquatic systems, the van't Hoff -Arrhenius equation predicts a doubling of the rate constant with each temperature increase of 10°C, assuming typical activation energy values (Benefield and Randall, 1980). Using the Arrhenius constants determined from soil temperature data, the rate constants for Treatment Plot V1 were corrected to 23 °C, the soil temperature of Test 1 (Figure 3). The Arrhenius correction for temperature resulted in insignificant rate constant differences between Tests 2, 3, 4, and 5 in Treatment Plot V2. Although a statistically significant difference in rate constants remained between Test 3 and Tests 2 and 5 in Treatment Plot V1, the magnitude of the difference is not important from a practical application standpoint.

CONCLUSIONS

This field scale investigation has demonstrated that soil venting is an effective source of oxygen for enhanced aerobic biodegradation of petroleum hydrocarbons (jet fuel) in the vadose-zone. Specific conclusions are:

1. Operational data and respiration tests indicated that moisture (6.5 to 9.8% by weight) and nutrients were not a limiting factor in hydrocarbon biodegradation. Soil and water samples indicated that nutrients were delivered to the treatment plots and passed through the vadose-zone to the ground water.

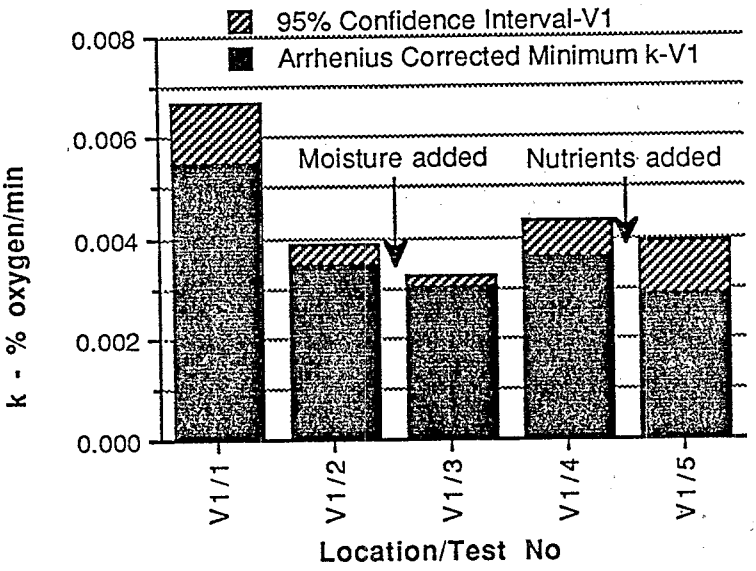

Figure 3. Temperature corrected (23 °C based on Arrhenius Plot) oxygen consumption rate constants (k) determined by respiration tests for Treatment Plot V1. Mean k is at the center of the 95% confidence interval.

2. Air flow tests documented that decreasing flow rates increased the percent of hydrocarbon removal by biodegradation and decreased the percent of hydrocarbon removal by volatilization. Under optimal air flow conditions (0.5 air void volumes per day) 82% of hydrocarbon removal was biodegraded and 18% volatilized. Biodegradation removal rates ranged from approximately 2 to 20 mg/(kg day), but stabilized values averaged about 5 mg/(kg day). The effect of soil temperature on biodegradation rates was shown to approximate effects predicted by the van't Hoff-Arrhenius equation.

3. Off-gas treatment studies documented that uncontaminated soil at this test site could be successfully used as a biological reactor for the mineralization of hydrocarbon vapors (off-gas) generated during remediation of fuel contaminated soil using the enhanced biodegradation through soil venting technology investigated in this field study. The average off-gas biodegradation rate was 1.34 (SD $\pm$ 0.83) mg/(kg day), or 1.93 (SD $\pm$ 1.2) g/(m^3 day). The percent of off-gas biodegradation was inversely related to air flow rate (retention time), and was directly related to hydrocarbon loading rate, at the 95% confidence level. Based on data collected at the field site, a soil volume ratio of approximately 4 to 1, uncontaminated to contaminated soil, would be required to completely biodegrade the off-gas from a bioventing system operated similar to this field project. However, if air flow rates in contaminated soil were designed to maximize biodegradation, the ratio of uncontaminated to contaminated soil required would be proportionally less.

4. Respiration Tests documented that oxygen consumption rates followed zero-order kinetics, and that rates were linear down to about 2 to 4 % oxygen. Therefore, air flow rates can be minimized to maintain oxygen levels between 2 and 4% without inhibiting biodegradation of fuel, with the added benefit that lower air flow rates will increase the percent of removal by biodegradation and decrease the percent of removal by volatilization.

5. Initial soil samples indicated that naturally available nitrogen and phosphorus were adequate for the amount of biodegradation measured, explaining the observation that nutrient addition had an insignificant effect on the rate of biodegradation. Acetylene reduction studies revealed an organic nitrogen fixation potential that could fix the observed organic nitrogen, under anaerobic conditions, in five to eight years.

6. Soil moisture levels did not significantly change during the field study. Soil moisture levels ranged from 6.5 to 7.4%, and 8.5 to 9.8%, by weight, respectively, in Treatment Plots V1 and V2. Neither venting nor moisture addition had a statistically significant effect on soil moisture at this site.

RECOMMENDATIONS FOR FUTURE STUDY

To further pursue the development of an enhanced biodegradation of petroleum hydrocarbons through soil venting technology, the following studies are recommended:

1. Further investigate the relationship between soil temperature and hydrocarbon biodegradation rate.

2. Investigate methods to increase hydrocarbon biodegradation rate by increasing soil temperature with heated air, heated water, or low level radio frequency radiation.

3. Investigate the effect of soil moisture content on biodegradation rate in different soils with and without nutrient addition.

4. Investigate nutrient recycling to determine maximum C:N:P ratios that do not limit biodegradation rates.

5. Investigate different types of uncontaminated soil for use as a reactor for biodegradation of generated hydrocarbon off-gas and determine off-gas biodegradation rates.

6. Investigate gas transport in the vadose-zone to allow adequate design of air delivery systems.

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CATALYTIC OXIDATION EMISSIONS CONTROL FOR REMEDIATION EFFORTS

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INTRODUCTION

The soils and groundwater under airfield facilities are often contaminated with jet fuel components, chlorinated solvents, and degreasers. This contamination has resulted from past disposal practices, leaking storage tanks, and accidental spills. As a primary solution to this problem, the Air Force established the Installation Restoration Program (IRP) to identify contaminated areas, determine the type and extent of contamination, and initiate appropriate cleanup actions. There are now over 3,500 IRP sites at 243 installations with an estimated 60% of the sites requiring cleanup action (Reference 1). The Engineering and Services Laboratory (ESL), part of the Air Force Engineering and Services Center, is responsible for environmental quality research and development of more effective, cost-efficient remedial actions. This research targets the development of chemical, biological, and physical treatment systems to meet this challenge. This paper reports the findings from several field tests of remediation technology where catalytic oxidation was used to control or treat the off gasses from the effort.

CONTAMINATED GROUNDWATER REMEDIATION

WURTSMITH AFB STUDIES

In the late 1970's, trichloroethlyene (TCE), a degreasing agent, was discovered in the drinking water at Wurtsmith AFB, Michigan. Chemical analyses of the groundwater showed levels of TCE exceeding 6,000 micrograms per liter (ug/L). The U.S. Environmental Protection Agency maximum contaminant level for TCE is 5 ug/L. The source of the TCE was traced to a leaking 500-gallon underground storage tank. Since the leaking tank went undetected for years, the quantity of TCE leaked could only be estimated. The subsequent plume of TCE was determined to encompass approximately 9 million cubic meters, with a maximum concentration approaching 10,000 ug/L.

A review of the literature identified countercurrent packed-bed air stripping as a possible treatment alternative. Countercurrent packed-bed air stripping involves flowing contaminated water down a packed column, while forcing air upward through the column. The packing breaks up the flow of water and air, increasing the air/water contact and enhancing transfer of the contaminant from the water into the air. In many states air emission controls are required to prevent release of these volatiles to the environment.

The Environics Division of the ESL performed laboratory and pilot-scale tests at Wurtsmith AFB to verify the operating performance of packed-bed air stripping. As a result of the study Wurtsmith AFB currently has two air stripping operations underway removing TCE from the groundwater from two separate plumes. A third unit, under construction, will remove benzene from

another plume of contaminated groundwater. The initial air stripper does not have any emissions control device while the other two have (or will have for the benzene unit) catalytic oxidation for emissions control. Catalytic oxidation is a combustion process where the contaminant-laden air stream is preheated and passed through a catalyst bed. Final products of the oxidation are typically carbon dioxide, water, and inorganics.

Evaluations are underway at Wurtsmith AFB on the catalytic oxidation unit installed to control the air stream coming from the 200 gallon per minute air stripper used to remove TCE from the groundwater. The preliminary findings are shown in Table 1. The catalytic unit is a fluidized bed reactor. The catalyst particles are spherical shaped and the contaminated air stream is passed through the reactor at sufficient velocity to churn or fluidize the catalyst bed. This motion causes the particles to collide into one another which breaks off small pieces of the surface. Since catalyst fouling occurs on the surface, this type of reactor is contiuously self-cleaning. This catalyst attrition is slow and at Wurtsmith AFB they are still running on the same catalyst charge from 1988.

There is some concern though because the Wurtsmith AFB catalyst appears to be forming a small amount of benzene when operating. Simultaneous sampling of the preheater effluent and the stack emissions show an 40 - 60 percent increase in the benzene concentrations. This is based on one sampling effort and is a preliminary, and puzzling, finding. The Engineering and Services Laboratory is looking further into the situation to understand the reaction mechanisms. The vendor indicates that the benzene formation is due to a low catalyst bed volume (not enough residence time for the air to contact the catalyst). This will be verified in the near future.

TABLE 1. PRELIMINARY DATA FROM THE EVALUATION OF A CATALYTIC OXIDATION CONTROL UNIT AT WURTSMITH AFB MI

AIR STREAM CONCENTRATIONS: 1 part per million Trichloroethylene; 10 parts per billion of 1,2 Dichloroethane

CATALYTIC OXIDATION UNIT SPECIFICATIONS:
- CAPACITY: 1200 cubic feet per minute
- OPERATING TEMPERATURE: 700 °F
- NATURAL GAS CONSUMPTION (ave): 800 cubic feet per hour
- TIME ON STREAM: SINCE JUNE 1988
- DESTRUCTION EFFICIENCY OF TCE (as of Feb 1990): >97%
- PURCHASE PRICE: $113,000

EGLIN AFB STUDIES

In 1988-1989, at a large jet fuel spill site on Eglin AFB, Florida, we evaluated (Reference 2) different packing materials for conventional counter-current air stripping operations and compared their performance to a new rotary air stripper. In addition several emissions control options were also evaluated. The groundwater at the site contained a large variety of soluble jet fuel components as well as inorganic materials that greatly affected the research effort. Table 2 lists some selected parameters from the Eglin site.

TABLE 2 SELECT CONTAMINANTS AT THE EGLIN AFB FUEL SPILL SITE

CONTAMINANT	AVE. CONC. (ppb)	HENRY'S LAW CONSTANT ($atm-m^3/mole$)
BENZENE	78	.0047
NAPHTHALENE	70	.00041
TOLUENE	60	.0059
O-XYLENE	220	.0040
IRON (as Fe^{+2})	8500	Not Applicable
SULFUR (as H_2S)	>500	Not Applicable

The rotary air stripper is a new approach to countercurrent air stripping. The unit utilizes a spinning rotor to move the water out radially from the center of the unit as shown in Figure 1. Clean air is forced from the outside towards the center, maintaining the countercurrent air/water flow. While removal efficiencies were similar, the rotary stripper has the added flexibility of rotor speed to meet changing feed stream concentrations. The disadvantage is the added cost to spin the rotor, the increased complexity and the requirement to have the rotor perfectly balanced during operation.

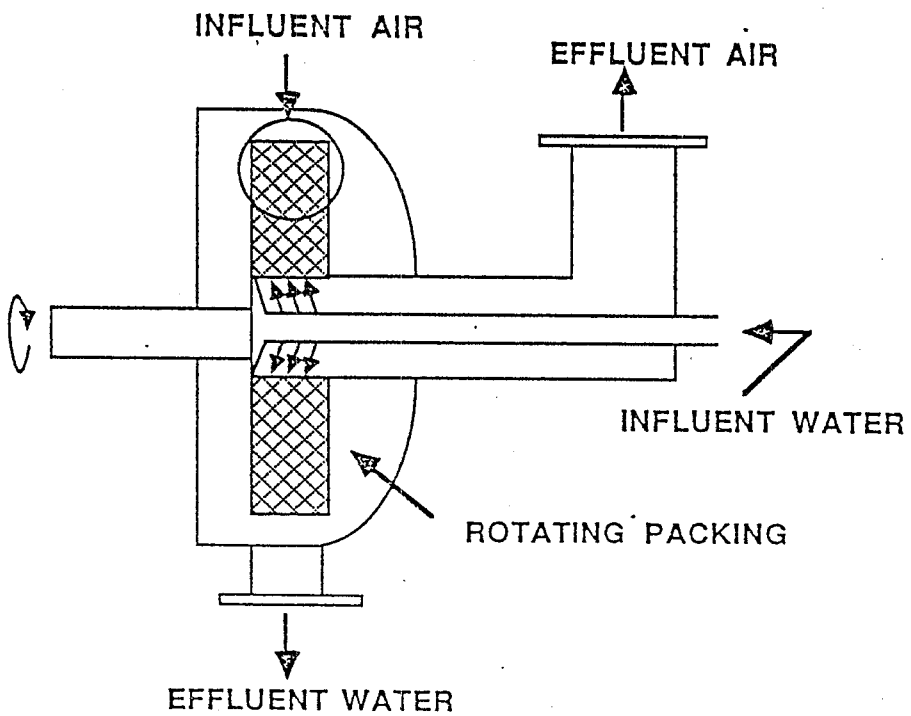

Figure 1. Cross section, rotary air stripper

Catalytic oxidation, carbon adsorption and molecular sieves were evaluated for the control of the emissions from the air stripping units at the Eglin site. The carbon units had a very low capacity for the lower molecular weight compounds (C_4 and below). In addition the excess humidity from the air stripping effluents further reduced the carbon adsorption capacity. Thus, a carbon bed large enough to adsorb the emissions from the air stripping operations would have a large capital and operating cost, making carbon a very expensive alternative at this site. Two molecular sieve materials, Union Carbide's type 9102 and 1387-53, were tested because they are not impacted by humidity effects and they could be regenerated on-site with ozone. Our data showed that both molecular sieve materials were unsuccessful for adsorbing the contaminants in the air stripping emissions. The unfavorable performance of the molecular sieves may have been because their pore sizes were too small to allow the contaminant molecules access to the active adsorption sites.

Another emission control technique evaluated was catalytic oxidation. An Engelhard pilot-scale catalytic oxidation unit was tested at the Eglin site. The unit uses an electric preheater to raise the inlet gas temperature to 1000 ^{o}F before passing it through a precious metal fixed bed catalyst reaction chamber. The result is on-site destruction of the organic contaminants. Enough of the hydrogen sulfide (see Table 2) was stripped out of the water to cause a chemical reaction in the catalytic oxidation unit which effectively and rapidly deactivated the catalyst. Total capital, operations and maintenance cost estimates for a 100 gallon per minute air stripping unit, based on 99% removal of benzene from contaminated groundwater, are: $3.19/1000 gallons just for the air stripping unit, $1.70/1000 gallons for catalytic oxidation of the emissions (based on other fluidized bed data) or $6.47/1000 gallons for activated carbon emissions control.

CONTAMINATED SOILS REMEDIATION

There are several methods to remediate a site contaminated with volatile organics such as jet fuel. The ESL tested the efficacy of using in situ soil venting to remove JP-4 from a contaminated sandy soil site at Hill AFB UT. During the ten months of operation 115,000 pounds of hydrocarbons were removed from the site. The emissions from this effort were sent through one of two catalytic oxidation units.

The first unit was a 500 cubic foot per minute fluidized bed unit that operated for eight months. The second was a 1000 cubic foot per minute fixed bed unit that used a precious metal catalyst and was operated for six months. Thus there was a period of four months where the two units operated together to treat the venting off gases. The fixed bed was operated between 470 and 625 ^{o}F while the fluidized bed unit was operated between 625 and 700 ^{o}F. The results (reference 3) show that the fluidized bed unit had an average 89% destruction efficiency and the fixed bed unit had a 97% destruction efficiency. This gives a cost-per-volume-treated rate of $23.80/million ft^3 air and $29.80/million ft^3 air for the fixed and fluidized bed units, respectively.

While the fixed bed unit appears economically feasible it has it's limitations. The unit would not be able to handle a large flow rate of the initial highly concentrated air stream. This is because the process is one of oxidation or burning of the contaminants. That means releasing heat in the process. Fixed beds could get so hot that they actually melt the end of the bed. Temperature safety controls prevent this from happening, however it does limit the amount of contaminant you can treat. The fluidized bed unit, because of the better heat transfer, can handle the higher concentration flow rates, up to a point. The draw back is the need to add catalyst. Approximately 150 pounds of catalyst were added to the reactor over the eight month operation at Hill AFB UT.

CATALYST DEVELOPMENT AND TESTING

Two laboratory studies are now being conducted to investigate catalysts resistant to deactivation. The University of Akron is developing a catalyst that resists deactivation when challenged with a chlorinated air stream. Akron researchers have found that chromium oxide and vanadium oxide materials can reach greater than 95 percent conversion of chlorinated organics to water, carbon dioxide, and dilute hydrogen chloride (Reference 4). They are continuing their research to find a superior catalyst that is resistant to chlorinated organics and sulphonated compounds present in air-stripping emissions.

The second study is being done by the Research Triangle Institute (RTI), N.C. They are evaluating off-the-shelf catalyst formulations from five manufacturers. The initial step was to create a standard catalyst testing protocol from which future catalyst formulations can be compared to this study. The goal is to find out which catalyst is the best for a given contaminated air stream.

After the catalyst has deactivated from constant exposure to a synthesized air-stripper emissions stream, RTI will determine what caused the catalyst to deactivate, which operating procedures will minimize deactivation, and whether the catalyst can be effectively regenerated. This information will be used in in an economic comparison of the different catalysts. Catalyst formulations being tested are the ARI Econocat, a copper chromite formulation from Harshaw, Carulite from Carus Chemical, three supported noble metal catalyst formulations from UCI, and a Haldor-Topsoe catalyst.

WHERE WE'RE HEADED - CROSSFLOW AIR STRIPPING WITH CATALYTIC EMISSIONS CONTROL

Crossflow air stripping is a packed-column aeration process which involves changing the air flow path of a conventional countercurrent tower. The main change is the placement of baffles inside the tower which causes the air to flow in a crisscross pattern up through the packing (Figure 2).. This forces the air to flow at 90 degrees to the flow of contaminated water rather than in completely opposing directions, as in a countercurrent tower. Proper selection of baffle spacing can produce a marked reduction in gas velocity, lowering gas-phase pressure drop, and reducing blower energy costs compared to conventional countercurrent mode of operation.

Results show the crossflow tower can greatly reduce the blower energy costs (Reference 5). However, for the highly volatile compounds, the blower energy cost is not a significant factor in the total cost; therefore, a countercurrent tower would be just as cost-effective as a crossflow tower. Blower energy costs do have a significant impact on the total cost of air stripping for the low and moderately volatile contaminants such as 1,2 Dichloroethane and Methyl Ethyl Ketone. Therefore, the crossflow tower could be more cost-effective for removing these compounds from groundwater.

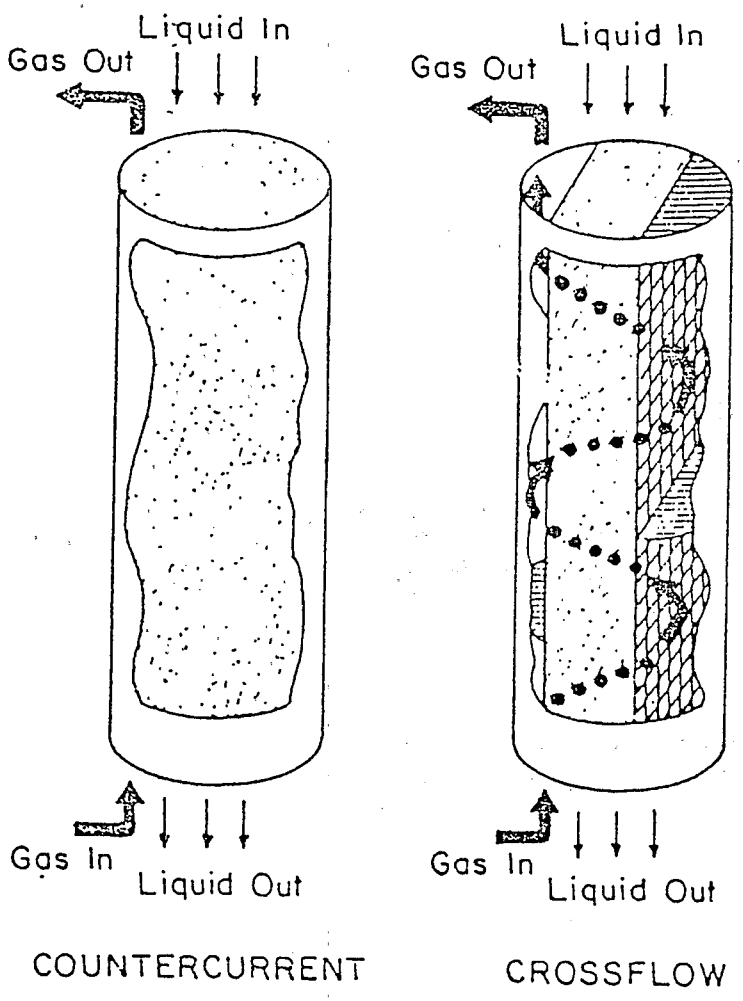

Figure 2. Comparisons of Crossflow and Countercurrent Air Strippers

A field study demonstrating the removal efficiency of crossflow air stripping for low and semi-volatile organics will be conducted during 1991 and 1992. During this test field validation of the RTI catalyst selection procedure and the University of Akron formulations will be carried out as emissions control from the crossflow air stripping operations.

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Appendix 4-D

Soil Vapor Extraction Technology Case Studies

Additional Case Studies, United States

APPENDIX 4-D

ADDITIONAL CASE STUDIES, UNITED STATES

Appendix 4-D.1 Groveland Well Site

Located in Groveland, Massachusetts, this site is contaminated principally with cutting oils, and chlorinated degreasing solvents. Contamination appeared to be the result of a leaking storage tank and improper practices in machine shop operations and in handling of cutting oils and degreasing solvents. The total contaminant level was estimated to be 1,350 to 13,500 kg (3,000 to 30,000 lbs) of VOCs, by the Massachusetts Department of Environmental Quality Engineering and EPA Region I.

The site is underlain with a sloping bedrock about 12 to 15 meters (40 to 50 ft) below the higher elevations of the site. The soil above the bedrock consists of medium sand and gravel near the surface, a clay layer 0.9 to 2.1 meters (3 to 7 ft) in depth and below this, coarser sand with gravel.

The results of VOC analysis from 27 soil borings indicated that heavy subsoil contamination existed below the southeastern portion of an existing building on the site. The primary contaminants detected in the soil were trichloroethylene (TCE) and methylene chloride (MC). The compounds 1,2 trans-dichloroethylene (TDCE), 1,1-trichloroethane (TCA), and tetrachloroethylene (TTCE) were detected in lesser concentrations. Although these compounds were not used at the site, they could have been components of the TCE and MC degreasing agent solution or could have resulted as biodegradation products of these degreasing agents. The highest concentration of VOCs were detected at a depth of between 1.2 to 3.6 meters (4 to 12 ft) in the vicinity of the oil storage area. This area generally lies above a clay lens. The clay lens is located approximately 1.5 to 3.7 meters (5 to 12 ft) below grade and extends under the same area in which the highest concentration of VOCs were detected and served as a barrier against infiltration of VOC into underlying subsoil strata.

This site was the location of a U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) demonstration test. SVE system test objectives were to determine how well the technology would remove VOCs from the vadose zone; to assess effectiveness in various soil types; to correlate declining recovery rates with time; and, to correlate VOC concentration in soils with those in extracted vapors. The tests were designed to focus on the periphery of the main zone of contamination. The system consisted of four extraction wells and

four monitoring wells. Each well was installed in two sections, one section just above the clay lens and one section just above the water table. Extraction wells were screened above the clay and below the clay with each section operating independently of the other. The collected vapors were passed through a vapor/liquid separator and then passed through activated carbon columns prior to discharge to the atmosphere. The separated liquid was stored and periodically removed for appropriate disposal by a tank truck.

The results of gas sampling indicates a total of 588 kg (1300 lb) of VOCs were extracted over the 56-day period of SVE operation. Subsequently, soil borings were taken and the VOC levels in these samples were not detectable.

Appendix 4-D.2 Paint Warehouse Fire Site, Dayton, Ohio

In 1987, a fire occurred at a paint warehouse in Dayton, Ohio. The warehouse had an inventory estimated at 5.7 million liters (1.5 million gallons) of paint, paint thinners, and associated products. Because this facility was located over the drinking water well field, water was not used to extinguish the fire. However, uncombusted material still penetrated the soil and spread through the unsaturated zone. Several VOCs were detected in nearby city wells less than six weeks after the fire.

The site is made up of glacial outwash material and the water table is approximately 14 to 15 meters (45 to 50 ft) below grade. The soil types were principally sand and gravel with occasional thin strata of cobbles or clay. The ground water flows toward the Great Miami River, however, the river contributes to the aquifer recharge by the pumping the municipal wells.

Soil contamination was comprised mainly of acetone, methyl isobutyl ketone (MIBK), methyl ethyl ketone (MEK), benzene, toluene, xylenes, and other volatile aliphatic and alkylbenzene compounds. More than 45 VOCs were identified in gas samples from the soil. Due to infiltration, the presence of the water soluble VOCs such as acetone, MEK, and MIBK, represented a threat to the groundwater supply.

The soil vapor extraction system, employed at this site, consisted of injection and extraction wells, heated headers from extraction wells, 8 blowers, various plumbing, valves, gauges and sampling ports, an air/water separator, and monitoring wells. The system was installed as four identical modules with 2 blowers each -- one for extraction and one for injection. Concrete, which was already in place and a clay cover were used to provide an impermeable cap. Initially, vapor treatment consisted of burning the extracted vapor. Vapor treatment was discontinued when the emissions rates decreased to State of Ohio approved levels. An air/water separator had to be installed when excessive water was pulled from the soil along with the vapors.

After 56 weeks of operation, over 3600 kg (8000 lb) of VOCs had been recovered. By April 1988, composite off-gas VOC measurements had fallen to less than 1 ppm. All perched water extracted from the vacuum wells yielded VOC concentrations below action levels accepted by Ohio EPA. At the same time, VOC concentrations in the unconfined aquifer had, for almost two months, been at nondetectable levels for all hydrocarbon species identified prior to treatment. As closure levels, developed in a risk assessment during the fall months of 1987, were met, the SVE operations in that area of the site was halted. (Ground water VOC action levels established were: acetone, 810 ug/L; MIBK, 260 ug/L; and, MEK 450 ug/L.) Thus in April 1988, two of the four systems were shutdown. By June 1988, all off-gases extracted from the shallow, unsaturated soil were below 1 ppm. Extraction operations were then halted and the site was subsequently closed.

Appendix 4-D.3 Twin Cities Army Ammunitions Plant Sites

This case study covers two sites (Site D and Site G) located at the Twin Cities Army Ammunitions Plant (TCAAP), in New Brighton, Minnesota. Site D was a solvent leaching pit/burn area and Site G was an active landfill from the 1940's to the 1970's.

Site D covers an area of 0.2 hectare (0.5 acres) and the surface soils are composed of Arsenal sand, stained sediments, and residues from burning activities. The Arsenal sand extends below the site to a depth of approximately 36 meters (120 ft). Below this is a layer of Hillside sand. The groundwater lies approximately 49.5 meters (165 ft) below ground surface. Two separate pilot systems were installed to test several design and performance variables. System 1 was designed to evaluate TCE removal from soils with relatively low VOC contamination (less than 2.3 mg/kg). This system operated at an extraction rate of 1.1 to 1.6 m^3/min (40 to 55 cfm) and had a vent pipe spacing of 6 meters (20 ft). The second system was designed to remove TCE at concentration levels up to 5,000 mg/kg. System 2 operated at an extraction rate of 5.7 to 6.2 m^3/min (200 to 220 cfm) and had a vent spacing of 15 meters (50 ft). The SVE process successfully demonstrated removal of 750 kg (1650 lb) of TCE. Soil sampling and analysis indicated that TCE removal from the stained, less porous soils were not as effectively removed as from the unstained soils (soils in close proximity to burning activities).

Site G consisted of landfill material such as cinder, slag, tar, brick, glass, metal and wood. Contamination consisted primarily of VOCs, although some metals (lead, chromium, and cadmium) were also detected. A full-scale SVE system was designed and installed at Site G consisting of 89 air extraction vents, ranging in depth from 9.6 to 10.2 meters (32 to 34 ft); an air manifold; four centrifugal blowers; and, a building to house the blowers and motor controls. Operation of the system was periodically interrupted for carbon change out. Sixteen batches (119,700 kg or 264,000 lb) of activated carbon were used for off-

gas treatment. The removal rates showed a sharp decline during the first few months of operation and they gradually declined during later operations. In April 1987, the activated carbon off-gas treatment was discontinued (due to the lower removal rates) and the extracted gases were vented to the atmosphere. As of May 17, 1990, approximately 45,000 kg (100,000 lb) of VOCs have been removed from Site G since remediation began in January 1986.

Appendix 5-A

Physical/Chemical Extraction Technology Case Studies

High Pressure Soil Washing (Klöckner), Germany

FINAL REPORT ON THE AFU (ANWENDUNGSGESELLSCHAFT FÜR UMWELTTECHNIKEN), BERLIN, MOBILE PLANT FOR SOIL DECONTAMINATION BY HIGH-PRESSURE SOIL WASHING

Contents

1. Introduction
2. The High-Pressure Soil Washing Process
3. Chemical Analyses by the "Bundesanstalt für Materialforschung und -prüfung (Referat Umweltschutztechnologien)"
4. Conclusion and Prospects

(Distributed at the Third International Meeting 6-9 November 1989, Monteal, Canada)

1. Introduction

Since 1986 AFU (Anwendungsgesellschaft für Umweltechniken mbH) is running a mobile plant for the cleaning of contaminated soil by use of high-pressure jets of water in Berlin. First located on a former scrap yard on Treidelweg, the high-pressure soil washing plant is now in its third location in Berlin.

During the pilot project on Treidelweg 1986 through 1988, 7,000 tons of contaminated soil from three different industrial sites have been successfully cleaned. The soil had been polluted with chlorinated hydrocarbons, polycyclic hydrocarbons, phenoles, benzene, mineral oil, lindan, lead, and cyanides.

Permanent tests by order of AFU show that the limits which had been set for the reduction of pollutants have been reached in most cases. These results have been supported by expertises on random samples ordered by the independent "Bundesanstalt für Materialforschung und -prüfung" (Federal Agency for Material Research and Material Testing).

2. The High-Pressure Soil Washing Process

The high-pressure soil washing process has been developed in the Netherlands and adapted to German requirements by Klöckner Umwelttechnik, Duisburg, FRG. The process is aiming at the complete separation of pollutants from contaminated soil by by means of washing. The remaining fractions are clean soil and a small amount of concentrated contaminants, the latter having to be disposed in a toxic waste dump or incinerated.

Prior to the development of the high-pressure soil washing process, pollutants adherent to soil could only be seperated with the help of wash active additives, i.e. tensides, which created new threats to the environment. In the high-pressure soil washing process, the soil first gets broken up by high-pressure jets of water, and then is cleaned from the adherent pollutants. This seperation takes place within a high-pressure jet pipe.

Within the jet pipe, water is shooting from a ring of nozzles with pressures of up to 350 bar. The jets conically focus, creating suction by which the homogenized soil is sucked through the jets' focal point. During the acceleration, the soil is chrushed to grains and the pollutants are separated from it. Easily volatile pollutants are exhausted and absorbed by activated carbon filters. The other pollutants are dissolved in the process water, dispersed and emulsified. The water gets processed and recirculated into the washing process.

First, the humose particles are separated from the process water. Then the non-soluable pollutants together with the fine particles (sand, clay with a diameter < 0.03 mm) are removed. The process water is chemically and physically treated through several stages, i.e. oxidation, reduction, cleavage, neutralization, solid material separation, and activated carbon filtering. Thereby the soluable pollutants are transformed into a non-soluable stage and removed.

3. Chemical Analyses by the "Bundesanstalt für Materialforschung und -prüfung (Referat Umweltschutztechnologien)

By order of the "Bundesanstalt für Materialforschung und -prüfung" (Federal Agency for Material Research and Material Testing) random samples of contaminated and cleaned soil have been chemically analyzed.

3.1 Preparation of the samples

Samples of about 30 kg were taken either from the running conveyor belts prior to and after the washing process or from the dump, and then automatically divided into portions of about 1.2 kg.

In order to prepare the required number of portions, each sample was homogenized first. The homogenization was carried out in minimal time so that the easily volatile substances would not evaporate. Then the samples were dried and the content of water was analyzed. Finally the samples were extracted by extraction solvent, and the solution was concentrated if necessary and analyzed.

3.2 Analytical results

Contaminated and cleaned soil are classified into three groups:

Class I - usable
Class II - polluted, to be disposed of
Class IV - heavily polluted, to be disposed of.

The analytical results (in mg/kg [ppm resp. ppb] of air-dried soil) are as shown in the following tables.

Sample 1

Three samples of contaminated (con.) and three samples of cleaned (cl.) soil were taken from the running conveyor belt on Kanalstraße on May 11, 1987 and analyzed.

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
Lead	18.3	18.1			4.0	
Cadmium	0.2	0.1			<0.1	
Phenole	3.1	2.7	1.5		<0.1	
AHC		< 0.1	for all samples			
MOHC	474	250	341	18	16	16
org. Cl	< 1	2.1	< 1	< 1	< 1	< 1
PAHC:						
Naphtaline	1.6	1.7	2.1	0.4	0.3	0.4
Acenaphtene	8.6	7.0	14.5	0.3	0.1	0.2
Fluorene	6.0	6.2	12.2	0.2	0.2	0.2
Phenanthrene	2.5	6.3	14.8	0.7	0.5	1.3
Anthracene	5.9	7.9	12.8	0.4	0.3	0.5
Fluoranthene	31.3	24.6	37.5	1.9	1.8	2.3
Pyrene	25.7	21.0	27.8	1.4	1.5	1.9
Benzo(a)anthracene	9.7	11.2	16.0	0.8	0.7	0.7
Chrysene	8.0	8.2	9.9	0.6	0.6	0.8
Benzo(b+k)fluoranthene	17.0	17.9	20.1	1.1	1.1	1.2
Benzo(e)pyrene	8.9	9.4	12.0	0.6	0.5	0.6
Benzo(a)pyrene	11.5	11.8	13.9	0.7	0.6	0.7
Perylen	2.0	2.2	3.1	0.1	0.1	0.1
Indeno(1,2,3-cd)-pyrene	5.4	5.4	6.7	0.2	0.2	0.2
Benzo(ghi)perylen	6.2	5.2	7.4	0.2	0.3	0.4
Sum of all PAHCs:	150.3	140.8	210.8	9.6	8.5	11.5
PCB (in µg/kg = ppb)						
No. 28	-	-	-	-	-	-
No. 52	-	-	-	-	-	-
No. 101	-	-	2.0	-	0.1	0.1
No. 153	1.0	0.1	8.0	1.0	0.1	1.0
No. 138	48.0	0.2	5.0	5.0	0.1	11.0
No. 180	62.0	0.1	1.0	4.0	0.1	4.0
Sum of all PCBs:	112.0	0.5	16.0	10.0	0.2	16.0

For these samples, the cleaning results can only be assessed referring to the polycyclic aromatic hydrocarbons (PAHC) because the initial concentrations of other pollutants have already been very low before the washing process. Referring to the PAHCs the cleaning result is better than 99%. Also referring to the mineral oil content a result better than 90% is achieved.

While the contaminated samples are 'Class II' soil (polluted, to be disposed of), the samples of cleaned soil belong to 'Class I' (usable). Thus the cleaning has been successful.

Sample 2

Three samples of contaminated (con.) and three samples of cleaned (cl.) soil were taken from the running conveyor belt on Kanalstraße on May 27, 1987 and analyzed.

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
Lead		15,3			5,3	
Cadmium		<0,1			<0,1	
Phenole	1,8	2,1	1,8	0,1	0,1	0,1
AHC	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
MOHC	414	420	346	16	15	11
org. Cl	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
PAHC:						
Naphtaline	1,3	0,7	3,9	0,3	0,3	0,4
Acenaphtene	0,9	1,7	14,5	0,3	0,1	0,8
Fluorene	0,8	0,8	9,3	0,3	0,1	0,7
Phenanthrene	6,0	6,0	20,5	1,0	1,0	1,6
Anthracene	1,2	0,9	7,8	0,3	0,2	1,0
Fluoranthene	11,9	10,4	38,4	1,8	1,3	3,7
Pyrene	27,1	14,8	31,8	1,4	1,1	2,7
Benzo(a)anthracene	5,6	5,8	14,6	0,8	0,7	1,6
Chrysene	6,7	6,1	11,6	0,6	0,6	1,1
Benzo(b+k)fluoranthene	28,6	30,7	25,0	1,9	1,9	2,3
Benzo(e)pyrene	13,5	14,5	10,9	0,9	0,9	1,1
Benzo(a)pyrene	18,0	19,5	15,8	1,2	1,2	1,4
Perylen	3,1	4,4	2,4	0,2	0,2	0,2
Indeno(1,2,3-cd)pyrene	10,0	9,3	7,0	0,6	0,6	0,7
Benzo(ghi)perylen	9,4	9,6	7,1	0,6	0,5	0,6
Sum of all PAHCs:	144.1	135.2	220.5	12.2	10.7	19.9

PCB (in µg/kg = ppb)

No. 28	10	3	4	1	1	1
No. 52	15	4	4	1	1	1
No. 101	5	3	4	1	1	1
No. 153	7	4	5	1	1	2
No. 138	9	4	4	1	1	3
No. 180	5	3	2	1	1	2
Sum of all PCBs:	51	21	23	6	6	10

While the contaminated soil belongs to 'Class II', the cleaned soil is ranking 'Class I'. Thus the cleaning has been successful with a ratio of more than 90% reduction of pollutants.

Sample 3

Three samples of contaminated (con.) and three samples of cleaned (cl.) soil were taken from the running conveyor belt on Kanalstraße on June 05, 1987 and analyzed.

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
Lead		11.0			5.0	
Cadmium		< 0.1			< 0.1	
Phenole	1.5	2.2	2.3	0.1	0.1	0.1
AHC		< 0.1	for all samples			
MOHC	436	449	472	34	23	42
org. Cl		< 0.1	for all samples			
PAHC:						
Naphtaline	2.5	12.0	1.5	1.9	1.1	0.8
Acenaphtene	2.0	23.7	2.6	1.1	1.5	1.4
Fluorene	1.7	23.5	2.1	1.1	1.6	1.3
Phenanthrene	6.2	47.9	6.2	2.9	4.3	3.2
Anthracene	1.8	20.6	1.8	1.4	1.7	1.6
Fluoranthene	12.0	62.2	28.7	4.0	5.6	5.2
Pyrene	21.9	46.5	44.5	3.2	4.0	3.7
Benzo(a)anthracene	6.9	22.0	9.0	1.6	2.2	2.0
Chrysene	7.0	15.8	9.8	1.3	1.7	1.5
Benzo(b+k)fluoranthene	30.3	33.9	34.7	2.4	2.8	2.6
Benzo(e)pyrene	14.3	16.4	16.7	1.1	1.3	1.3
Benzo(a)pyrene	20.0	20.8	20.7	1.4	1.8	1.7
Perylen	4.4	3.7	3.9	0.2	0.3	0.2
Indeno(1,2,3-cd)pyrene	9.2	9.9	9.1	0.6	0.7	0.6
Benzo(ghi)perylen	8.1	9.8	8.0	0.6	0.6	0.6
Sum of all PAHCs:	148.3	368.7	199.3	24.8	31.2	27.7

PCB (in µg/kg = ppb)

No. 28	7	6	2	1	1	1
No. 52	5	2	4	1	1	1
No. 101	3	3	1	1	1	1
No. 153	4	5	2	1	1	1
No. 138	6	5	3	1	1	2
No. 180	3	3	2	1	1	1
Sum of all PCBs:	28	24	14	6	6	7

The samples of cleaned soil rank 'Class I', while the samples of contaminated soil are 'Class II'. The cleaning ratio is better than 90%. Referring to the 15 different PAHC that were analyzed, the average content in the contaminated soil is 230 mg/kg; in cleaned samples it is 31 mg/kg. The cleaning ratio for PAHCs is almost 90%. The desired results are achieved.

Sample 4

Three samples of flotation concentrate (flo.) in which the pollutants should be concentrated and three samples of cleaned (cl.) soil were taken from the running conveyor belt on Kanalstraße on June 10, 1987 and analyzed.

	^{1}cl.	^{2}cl.	^{3}cl.	^{1}flo.	^{2}flo.	^{3}flo.
Lead		12.4			94.5	
Cadmium		0.1			0.5	
Phenole	0.1	0.3	0.1	6.0	4.7	7.4
AHC:						
Benzene		0.1 for all samples				
Toluene		0.1 for all samples				
Xylene	0.1	0.1	0.1	0.2	0.3	0.2
MOHC	17	24	46	2350	870	2110
org. Cl	1.0	1.0	1.0	1.0	1.0	1.0

	^{1}flo.	^{2}flo.	^{3}flo.	^{1}cl.	^{2}cl.	^{3}cl.
PAHC:						
Naphtaline	21	44	31	< 0,1	0,9	0,1
Acenaphtene	81	104	112	< 0,1	0,1	0,1
Fluorene	77	90	100	< 0,1	0,1	0,1
Phenanthrene	146	179	181	1,0	1,4	1,6
Anthracene	75	86	95	0,1	0,2	0,2
Fluoranthene	282	267	337	1,5	1,7	2,4
Pyrene	207	201	265	1,3	1,4	2,1
Benzo(a)anthracene	97	89	112	0,8	0,9	1,3
Chrysene	83	69	83	0,7	0,6	1,0
Benzo(b+k)fluoranthene	172	140	186	1,9	2,2	3,7
Benzo(e)pyrene	78	60	81	0,9	1,0	1,7
Benzo(a)pyrene	112	90	112	1,3	1,3	2,3
Perylen	29	15	17	0,2	0,2	0,6
Indeno(1,2,3-cd)pyrene	38	34	35	0,6	0,7	1,1
Benzo(ghi)perylen	40	32	37	0,7	0,7	0,9
Sum of all PAHCs:	1538	1500	1784	11.3	13.6	19.2
PCB (in µg/kg = ppb)						
No. 28	1	1	2	39	30	32
No. 52	1	2	3	57	14	9
No. 101	1	2	2	28	32	21
No. 153	1	4	2	28	26	34
No. 138	2	5	3	28	24	48
No. 180	1	3	1	14	14	17
Sum of all PCBs:	7	17	13	194	140	159

The separation of pollutants and their concentration in the flotation concentrate have obviously been achieved. Referring to the 15 PAHCs, there are on average 15 mg contained in each kg of cleaned soil and 1200 mg contained in one kg of flotation concentrate. These hardly volatile PAHCs have been concentrated by flotation.

But not all of the pollutants do accumulate in the flotation concentrate; otherwise their overall concentration would be much higher. Therefore part of the contamination must have been removed with the exhaust air and the waste water.

Sample 5

Three samples of contaminated (con.) soil and three samples of cleaned (cl.) soil from the running conveyor belt, and three samples of flotation concentrate (flo.) were taken on Kanalstraße on June 18, 1987 and analyzed.

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
Lead		26,0			9,7	
Cadmium		0,1			< 0,1	
Phenole	< 0,1	0,6	0,2	< 0,1	< 0,1	< 0,1
AHC		bei allen Proben		0,1		
MOHC	60	63	225	9,5	7,5	10,5
org. Cl	< 0,1	< 0,1	< 0,1	-	-	-
PCB (in µg/kg = ppb)						
No. 28	1,3	2,3	1,3	0,5	-	0,5
No. 52	5,5	1,7	3,5	0,9	0,5	0,8
No. 101	7,0	7,6	5,5	1,1	1,2	1,0
No. 153	9,0	16,0	9,3	1,3	2,7	1,8
No. 138	12,0	21,7	11,5	1,9	6,1	2,7
No. 180	5,5	12,1	6,3	0,8	1,9	1,4
Sum of all PCBs:	40,3	61,4	37,4	6,5	12,4	8,2

	^{1}flo.	^{2}flo.	^{3}flo.
Phenole	4,2	4,5	12,2
Benzene	0,1	< 0,1	0,1
Toluene	< 0,1	< 0,1	0,1
Xylene	< 0,1	< 0,1	0,1
MOHC	398	486	694
org. Cl	< 1	< 1	2,6
PCB (in µg/kg = ppb)			
No. 28	35	23	100
No. 52	50	40	115
No. 101	50	35	35
No. 153	55	60	55
No. 138	113	108	90
No. 180	43	38	30
Sum of all PCBs:	346	304	425

PAHC:	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.	^{1}flo.	^{2}flo.	^{3}flo.
Naphtaline	--	--	--	--	--	--	6	16	33
Acenaphtene	0,3	0,3	0,4	<0,1	0,1	<0,1	17	40	117
Fluorene	0,3	0,3	0,4	<0,1	0,1	--	17	32	94
Phenanthrene	4,2	5,5	4,3	0,6	1,2	0,6	32	69	160
Anthracene	1,0	1,4	1,1	<0,1	0,2	<0,1	17	46	111
Fluoranthene	6,1	10,3	8,3	0,8	1,4	0,8	84	145	290
Pyrene	5,8	8,7	6,8	0,7	1,4	0,8	75	127	269
Benzo(a)anthracene	3,3	6,4	4,0	0,4	0,7	0,4	39	60	131
Chrysene	3,4	5,7	3,7	0,4	0,7	0,4	36	54	99
Benzo(b+k)fluoranthene	7,1	9,0	6,8	0,7	1,2	0,7	64	95	203
Benzo(e)pyrene	3,3	3,9	3,7	0,4	0,5	0,4	32	44	94
Benzo(a)pyrene	4,7	6,1	4,3	0,4	0,7	0,5	41	60	138
Perylen	1,3	1,2	0,7	<0,1	0,1	<0,1	8	12	27
Indeno(1,2,3-cd)pyrene	1,8	2,2	2,0	0,2	0,4	0,2	19	24	45
Benzo(ghi)perylen	2,3	2,6	2,3	0,2	0,4	0,2	21	26	55
Sum of all PAHCs:	45.3	63.6	48.8	5.2	9.1	5.3	508	850	1866

Comparing the concentrations of e.g. lead in contaminated soil (26 mg/kg), in cleaned soil (10 mg/kg), and in the flotation concentrate (250-2600 mg/kg), it is obvious that the accumulation of pollutants in the concentrate has been achieved.

The same result holds for the PAHCs. Before washing, the samples contain 52 mg/kg; cleaned soil contains 6 mg/kg, and the flotation concentrate 1100 mg/kg of the 15 analyzed PAHCs on average. In contrast to the easily volatile PAHCs which probably vaporize already when the contaminated soil is moved, these less volatile PAHCs have accumulated in the flotation concentrate.

The overall result for the assessment of the flotation concentrate is similar to that for the sample of June 10, 1987. There is an accumulation of pollutants but not of all of them because some are filtered from the exhaust air by the activated carbon filters. The flotation concentrate ranks 'Class II'.

Sample 6

On August 04, 1987, three samples of contaminated soil and three samples of cleaned soil were taken from the plant's input and output (30 minutes after the washing process), respectively, and analyzed.

The following concentrations of heavy metals were analyzed by plasma spectrometry with inductive coupled plasma (ICP) (two measurements: a and b):

		Lead	Copper	Chrome	Cobalt	Zinc	Nickel	Vanadium	Cadmium
^{1}con.	a)	133	158	17	4	263	20	9	2
	b)	123	163	11	4	287	26	9	2
Average		128	161	14	4	275	23	9	2
^{2}con.	a)	160	106	12	4	241	26	8	1,5
	b)	135	41	13	4	234	24	8	1,4
Average		148	74	13	4	238	25	8	1,5
^{3}con.	a)	91	34	9,5	4	204	20	8	1
	b)	101	39	12	4	210	24	8	1
Average		96	37	11	4	207	22	8	1
^{1}cl.	a)	67	48	9	5	188	23	8	1
	b)	71	84	8	6	185	25	8	1
Average		69	66	9	6	187	24	8	1
^{2}cl.	a)	98	91	10	3	134	22	8	1
	b)	106	81	9	3	135	21	7	1
Average		102	86	10	3	135	22	8	1
^{3}cl.	a)	64	37	8	4	140	22	7	1
	b)	62	32	8	4	141	22	7	1
Average		63	35	8	4	141	22	7	1

	water content (%)	cyanide (mg/kg)
mixed sample of contaminated soil	9.1	0.7
mixed sample of cleaned soil	15.8	0.2

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
MOHC	110	63	85	33	26	31

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
PAHC:						
Naphtaline	0,1	nn	nn	alle Proben kleiner als 0,1		
Acenaphtene	0,7	0,8	1,4	0,4	0,2	0,1kl.
Fluorene	0,2	0,9	0,2	<0,1	0,1	0,2
Phenanthrene	2,1	4,5	1,3	0,7	1,2	1,2
Anthracene	0,5	1,6	0,3	0,1	0,2	0,4
Fluoranthene	3,9	6,0	2,1	1,0	1,8	1,4
Pyrene	3,7	5,2	2,2	1,0	1,5	1,3
Benzo(a)anthracene	2,5	2,6	1,2	0,7	0,8	0,8
Chrysene	2,4	3,0	1,5	0,5	0,7	0,8
Benzo(b+k)fluo-ranthene	3,5	3,8	2,2	1,0	1,3	1,2
Benzo(e)pyrene	1,3	1,4	0,9	0,2	0,5	0,3
Benzo(a)pyrene	1,4	2,0	1,3	0,3	0,7	0,6
Perylen	0,4	0,3	0,3	<0,1	0,2 kl.	0,1
Indeno(1,2,3-cd)-pyrene	1,4	1,7	0,8	0,3	0,5	0,5
Benzo(ghi)perylen	1,3	1,1	0,8	0,2	0,4	0,4
Sum of all PAHCs:	25.4	24.9	16.5	6.6	10.1	9.3

From the three samples of contaminated and the three samples of cleaned soil, mixed samples were taken and analyzed for PCBs. The following concentrations were found:

PCB (in mg/kg)	contaminated	cleaned
No. 28	0,014 4	0,004 3
No. 52	0,020 7	0,005 3
No. 101	0,021 7	0,012 2
No. 153	0,025 4	0,011 4
No. 138	0,034 1	0,019 1
No. 180	0,016 8	0,010 1
Sum of all PCBs:	0,133	0,062 5

In general, the soil had not been very heavily polluted prior to washing. Only referring to its content of mineral oil, lead, and copper they belong to 'Class II'. The samples of cleaned soil are ranking 'Class I'. Therefore the cleaning has been successful. With respect to the soil's low initial contamination, the calculation of a cleaning ratio would not be meaningful.

Sample 7

On August 26, 1987, three samples each of contaminated and cleaned soil from the Probethain site were taken and analyzed.

		Lead	Copper	Chrome	Cobalt	Zinc	Nickel	Vanadium
^{1}con.	a)	249	68	14	7	207	13	14
	b)	251	77	14	7	214	14	14
Average		250	73	14	7	211	14	14
^{2}con.	a)	188	76	16	6	204	16	14
	b)	189	68	14	6	205	16	15
Average		189	72	15	6	205	16	15
^{3}con.	a)	201	86	15	8	211	8	12
	b)	201	71	15	8	213	9	12
Average		201	79	15	8	212	9	12
^{1}cl.	a)	80	26	7	3	108	4	6
	b)	81	25	6	3	108	4	6
Average		81	26	7	3	108	4	6
^{2}cl.	a)	65	24	11	2	110	9	6
	b)	66	29	6	2	114	7	6
Average		66	27	9	2	112	8	6
^{3}cl.	a)	78	50	9	3	115	8	6
	b)							
Average		78	50	9	3	115	8	6

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
MOHC	140	210	214	42	31	31
PAHC:						
Naphtaline	n.n.	n.n.	n.n.	< 0,1	<0,1	<0,1
Acenaphtene	2,0	0,7	1,0	< 0,1	n.n.	0,4
Fluorene	2,0	0,2	0,6	< 0,1	0,1	0,1
Phenanthrene	1,1	1,7	2,7	0,6	1,2	1,0
Anthracene	0,7	0,5	0,7	0,1	0,2	0,1
Fluoranthene	3,6	3,5	4,8	1,1	1,7	1,4
Pyrene	3,6	3,1	4,6	0,8	1,3	1,2
Benzo(a)anthracene	2,0	2,2	3,0	0,5	0,8	0,6
Chrysene	1,7	1,7	2,7	0,5	0,6	0,5
Benzo(b+k)fluoranthene	3,3	3,5	4,1	0,8	1,2	1,1
Benzo(e)pyrene	1,9	1,1	1,8	0,4	0,5	0,4
Benzo(a)pyrene	2,3	1,8	2,1	0,4	0,6	0,5
Perylen	0,6	0,6	0,7	0,1	0,1	0,1
Indeno(1,2,3-cd)pyrene	1,7	1,1	2,0	0,5	0,5	0,4
Benzo(ghi)perylen	1,8	1,1	1,4	0,2	0,4	0,2
Sum of all PAHCs:	28.3	22.8	32.3	6.3	9.3	8.1

Although the initial pollution of the contaminated soil is relatively low, it has to be classified 'Class II' referring to its content of lead and MOHCs. The cleaned soil is of 'Class I' quality. The target has been met with a cleaning ratio of 70-80 %.

Sample 8

Three samples each of contaminated and cleaned soil from the Air France/Garbage Dump No. 1 Marienfelde were taken before and 20 minutes after the washing, respectively, on October 08, 1987.

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
MOHC	123	84	110	12	10	28
PAHC:						
Naphtaline	0,2	0,1	0,6	<0,1	0,1	<0,1
Acenaphtene	0,3	0,3	1,0	<0,1	0,1	<0,1
Fluorene	0,3	0,2	0,6	0,1	0,3	0,1
Phenanthrene	2,8	1,5	4,8	0,6	1,8	1,0
Anthracene	0,7	0,6	1,5	0,1	0,7	0,2
Fluoranthene	4,6	2,9	6,6	0,8	2,2	1,2
Pyrene	4,4	2,9	6,3	0,7	1,8	1,2
Benzo(a)anthracene	3,8	1,5	3,7	0,3	1,0	0,6
Chrysene	2,8	1,8	3,5	0,5	0,9	0,5
Benzo(b+k)fluo-ranthene	4,1	2,3	4,8	0,6	1,2	0,9
Benzo(e)pyrene	1,4	1,1	2,1	0,2	0,5	0,2
Benzo(a)pyrene	2,1	1,4	2,4	0,2	0,6	0,3
Perylen	0,4	0,3	0,4	<0,1	0,1	n.n.
Indeno(1,2,3-cd)-pyrene	1,7	0,8	1,5	0,1	0,5	0,2
Benzo(ghi)perylen	1,4	0,7	1,7	0,1	0,2	0,3
Sum of all PAHCs:	33.0	18.4	41.5	4.6	12.0	6.9

These samples are also relatively low in their initial contamination. Except for the mineral oil content they could be classified 'Class I'. The cleaned soil definitely is of 'Class I' quality. A cleaning ratio of about 70 % has been reached.

Sample 9

Three samples each of contaminated and cleaned soil - origin "Eisstadion Wilmersdorf/HKW Moabit" (containing light oil) - were taken before and 20 minutes after the washing, respectively, on November 10, 1987.

Mixed samples, one of contaminated and one of cleaned soil, were created and analyzed for their content of water and cyanides:

	contaminated	cleaned
Water content	6.7 %	13.9 %
Total content of cyanides	53.4 mg/kg	6.5 mg/kg

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
MOHC	214	147	179	47	42	69
PAHC:						
Naphtaline	0,3	0,3	0,3	0,2	0,1	0,2
Acenaphtene	0,2	0,5	0,3	0,3	0,2	0,5
Fluorene	1,3	0,9	1,2	0,8	1,2	1,7
Phenanthrene	5,5	3,4	2,8	5,0	5,6	7,1
Anthracene	1,4	0,8	0,5	1,2	1,4	1,3
Fluoranthene	7,7	5,0	5,3	6,6	5,9	7,5
Pyrene	8,7	5,7	5,7	5,5	5,2	6,4
Benzo(a)anthracene	4,8	3,3	2,7	2,9	3,0	3,6
Chrysene	3,3	3,6	3,3	2,1	2,0	2,6
Benzo(b+k)fluoranthene	6,2	5,0	5,0	3,4	3,3	4,2
Benzo(e)pyrene	3,0	2,5	2,5	1,4	1,5	1,9
Benzo(a)pyrene	3,5	2,6	2,6	1,5	1,6	2,2
Perylen	0,9	1,0	0,5	0,3	0,6	0,6
Indeno(1,2,3-cd)-pyrene	3,0	2,2	2,3	1,9	1,8	1,9
Benzo(ghi)perylen	2,2	1,8	2,1	0,9	1,2	1,2
Sum of all PAHCs:	51.8	38.6	37.1	34.0	34.9	42.9

Referring to its mineral oil content, the contaminated soil belongs to 'Class II', referring to the total content of cyanides even to 'Class IV' (heavily polluted, to be disposed of). The washing significantly reduced the MOHC content.

In the case of cyanides this result does not apply. Although there is an overall reduction of pollutants of approximately 50 %, the soil still has to be classified 'Class IV' referring to its total content of cyanides. Except for the highly toxic 'free' cyanides, the total content of cyanides also includes relatively innocuous cyanides, though, so that no statement can be given on the actual menace emanating from the soil.

Sample 10

On November 27, 1987, three samples of contaminated and cleaned soil originating from Körtestraße, Berlin 61, were taken from the running conveyor belt and analyzed.

Mixed samples	Water content	Total cyanides	Phenole
contaminated soil	6.4 %	0.5 mg/kg	< 0.1
cleaned soil	14.5 %	0.3 mg/kg	---

	^{1}con.	^{2}con.	^{3}con.	^{1}cl.	^{2}cl.	^{3}cl.
MOHC (mg/kg)	1,090	2,390	3,850	121	112	113

Referring to their mineral oil content the contaminated as well as the cleaned soil are ranking 'Class II' although the cleaning ratio for MOHCs is 80-90 %. In this case the target ratio has not been met.

3.3 Summary of the Results

Samples of contaminated soil prior to the washing process and of cleaned soil after the washing process in the plant on Treidelweg were chemically analyzed for their content of pollutants. The soil originated from several locations within the city of Berlin.

The results show that the goal of receiving 'Class I' soil has been achieved in most cases. The cleaning ratios reached from 70 up to 95 %, depending on the initial degree of contamination.

In very few cases, the total content of cyanides could not sufficiently be reduced. The total content of cyanides comprised some relatively innocuous cyanides, though. A threat from 'free' cyanide could not be stated.

The pollutants accumulate in the residual concentrate of the plant as it is intended. This residue usually belongs to 'Class II', i.e. it has to be disposed of but can be deposited in a toxic waste dump without problem.

This shows that the easily volatile substances must have - at least partly - vaporized, and that the water-solvent pollutants most likely have been carried away by the waste water. As long as the exhaust air and the waste water are duly treated, the high-pressure soil washing process is appropriate for soil which is mainly contaminated with mineral oil hydrocarbons, organic solvents, polycyclic aromates, and - with reservation - heavy metals.

Finally, the main advantage of the method is the possibility to adjust its parameters according to the soil's structure and the kind and degree of contamination given. If there is only a low degree of initial contamination, an experienced operator will be able to run the plant in a way that the actual cleaning ratios do not exceed the target ratios too much. Therefore the efficiency of the plant can constantly be ensured.

4. Conclusion and Prospects

The expertises by order of AFU as well as those by the independent experts show that the pilot project on the cleaning of contaminated soil in a high-pressure soil washing plant on Treidelweg has met the goals in almost all cases. During the entire project, there have not been any problems occuring with the treatment of the exhaust air and the waste water. The actual values for the remaining pollution in air and water have always been significantly lower than the permitted limits.

Since April 1989, a third-generation high-pressure soil washing plant is running in Düsseldorf-Lierenfeld. Within six months, 70,000 tons of contaminated soil are going to be cleaned on the site of a former tube rolling mill. Compared with the previous generation, its efficiency has been raised by additional aggregates. In detail,

- an enclosed coarse screening machine,
- a steam injection,
- two additional stages in the jet pipe,
- large-scale scavenging technology for the soil,
- process water treatment by flotation and separation,
- regenerable activated carbon filters with attached solvent regeneration

have been added to the plant.

At the moment, the project in Düsseldorf-Lierenfeld is the largest environmental rehabilitation project carried out with this innovative technology in the Federal Republic of Germany.

OECOTEC High-Pressure Soil Washing Plant 2000

Cleaning efficiency at the former NRW site in Düsseldorf-Lierenfeld

Treatment period: 11/5/1989 - 30/6/1989

Summary of the analysis data (Petrolab) from 18.9.94

		Washed soil			Unwashed soil		
Type of pollutant	Required limit value mg/kg	Minimum value mg/kg	Mean value mg/kg	Maximum value mg/kg	Minimum value mg/kg	Mean value mg/kg	Maximum value mg/kg
Mineral oil hydrocarbons	< 1,00	110	440	980	1,230	2,100	9,040
Polyaromatic hydrocarbons	< 10	1.	68	8.2	6.8	14.5	5.3
Benzene, toluene, xylene	< 3.5		< 66			2.8	
Chlorinated hydrocarbons	< 0.1	< 0.06	.009	0.087	85	113	130

Appendix 5-B

Physical/Chemical Extraction Technology Case Studies

Vibration (Harbauer), Germany

EXPERIENCE GAINED WITH A SOIL-DECONTAMINATION SYSTEM IN BERLIN

H.-D. Sonnen, S. Klingebiel

1. Summary

What is being presented is an extractive soil-decontamination system developed in Berlin, the HARBAUER PB 2, which has been working on the contaminated grounds of Pintsch-Öl GmbH (in liquidation) since the summer of 1987 and has already cleaned more than 11,000 tons of contaminated soil at various locations. The experience and knowledge gained with the operation of this system are described, the state of the art explained and future perspectives outlined.

2. Introduction

Between 1925 and 1984 used oil was processed on the grounds of the Pitsch-Öl GmbH, now in liquidation. A distillation facility and CP facility, amongst others, were useed for this purpose. Some of the production residue leaked into the soil. Leaky tanks, production breakdowns and careless work led to considerable contamination of buildings, soil and ground water (Woltmann, 1985).

3. Location

The building of Pitsch-Öl GmbH, now in liquidation, is located in a typical Berlin industrial area in the south of the city, in the district of Neukölln. It is approx. 16,000 sq.m. in size. The soil consists of filled and faulted layers of soil that contained sandy, clayish silts (drift clay) to a depth of about 6 m followed by fine- to medium-grained sand down to a depth of 12.0 m. Between 12.0 and 14.8 m there are very sandy, gravelly and clayish silts (drift marl). Underlying this drift marl are medium-grained and coarse sands with gravelly supplements. These very pervious sands are the gound-water carrier proper. Layers of soil and the ground water are thoroughly contaminated with mineral oils, phenols, CHC, PCBs and PAHs

Table 1 provides a survey of the values determined at the time the clean-up began.

Since 1924 Pintsch-Öl Berlin GmbH had been collecting and processing used oil from all over Berlin on the aforementioned property. The management of the company allowed all the residue and waste products resulting from the processing of the used oil leak to away in unsealed pits in the southern part of the premises. Since used oil containing PCBs was also treated during the reraffination process, PCBs made their way into the production cycle, and thus into the soil as well. Today's contamination

of the soil, ground water and buildings was caused by this type of waste disposal, by leaks in tanks and storage receptacles as well as by several fires in the production buildings.

In March of 1982 the Senator for Urban Development and Environmental Protection commissioned a report to determine the soil and ground-water contamination on the company's premises. The report was submitted in March 1983.
From this report it can be seen that 12,000 sq.m., i.e. some 75 % of the property, are badly contaminated with mineral-oil products, chlorinated hydrocarbons. Oil in phase was discovered on the ground water at a depth of approx. 8.5 m under the ground over an area of 6,000 sq.m. As later measurements showed, the oil floating on the ground water had local layers up to 3 m thick and was contaminated with biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), chlorinated hydrocarbons CHC) as well as phenols. Moreover, polychlorinated dibenzodioxins and dibenzofuranes were detected at several places.

Contaminant	Ground water mg/l	Soil mg/kg
Non-polar aliphates (oils)	1400	37,843
Non-polar aromates		5,620
Misc. aromates		
Benzene		133
Phenols	226	80
PCB		
Clophen A 60		270
CHC		
Dichloromethane	40.5	
1.1.1 trichloroethylene	7.2	1,370
Trichloroethane	4.3	210
Tetrachloroethylene	22.8	5,209
Inorganic compounds		
Cyanides	0.135	0.5
Sulphides	-	58.5
Lead	0.44	14,418.6
Cadmium	0.0325	0.229
Chromium	0.022	70.48

Table 1: Main groups of pollutants on the Pintsch grounds (Jan. 1986)

4. General Description of the Decontamination Technology

The original clean-up concept was limited to decontamination of the ground water and directly related measures, in keeping with the legal latitude. The buildings were to be demolished only to the extent necessary to sink wells with which to pump the ground water.

A total of nine wells were planned, of which wells Br 1, Br 4 and Br 7 are in the area of former building 6. This building, which housed the distilling furnaces, therefore had to be torn down. Since the masonry of the building and, especially, the plaster were contaminated with highly toxic substances, the building was surrounded with a protective hall before its demolition to prevent hazardous dust from escaping into the surrounding area. After all the production installations and the building had been torn down the protective hall was used to accommodate the soil decontamination system and related research equipment. A biological in-situ decontamination of the soil was not possible due to the heterogenous subterranean conditions and the sometimes unknown chemical compounds. The use of thermal methods was ruled out because they were not adequately developed and because of the permit procedures to be expected. Thus, the use of an extractive soil-washing process based on the HARBAUER PB 1 system was decided on.

5. The HARBAUER Soil Decontamination System

For the simultaneous cleaning of contaminated ground water and soil as well as the contaminated soil from other locations in Berlin (utilization of the system's capacity) the HARBAUER Engineering Office for Environmental Technology, Berlin has developed a system with which it is possible to clean soil with a grain size of 15 µm to 15 mm so that the soil can be refilled again and the ground and process water can be fed to the drainage ditch with drinking-water quality.
At the centre of the HARBAUER solution is the already tested HARBAUER PB 2 soil-washing system with which contaminated soil can be treated and cleaned by washing and/or extraction with chemicals, depending on the type and quantity of the pollution and structure of the initial material (grain-size distribution).
The efficency with which harmful substances are separated from the soil particles is largely determined by the introduction of energy. In the case of the HARBAUER process, which was described by SONNEN and ORTWEIN (1986), mechanical kinetic and vibrational energy is introduced with the help of mixing, stirring, vibrating and hydrocyclone equipment.
The introduction of energy neutralizes the various bonding forces between the harmful substances and the soil particle and is supported by the extractive effect of the washing or extraction agent. The energy density required depends mainly on the type of contaminated material, less on the harmful substance.
Thus, gravelly soil requires the introduction of only a small amount of energy to wash the harmful substances off the surface of the material. In the case of very silty soil with a high percentage of clay, loam or marl

as well as fine building rubbish (e.g. contaminated plaster) the amount of energy introduced must be increased to 1 kW/t.
In the last analysis, however, it is the individual combination of energy and extraction agents that results in the cleaning success aimed for. In the selection of the extraction agent, however, there are ecological and economic restrictions, for the agent used must be either absolutely harmless and biologically degradable or completely regeneratable so that the cleaning of the process water, which is obligatory with washing or extractive processes, is technically and economicaly feasible.
Therefore, efforts are always made to work with clean water or aqueous solutions as long as the chemical and physical properties of the contaminants permit.
In individual cases it may be necessary to use organic solvents, complexing agents or other reactive substances. For reasons of emission laws and accident prevention, however, these systems belong more in the category of chemical facilities than cleaning systems for contaminated soil.
However, in the case of extractive methods a system solution does not involve only the decontamination system proper, and the related treatment of the exhaust process air, but must also deal with the question of how to treat the substances left over.
With the HARBAUER process all soil particles greater than or equal to 15 µm in size are cleaned in such a way that they can be used again as building material (screening bottom) at the original location. Fine substances less than 15 µm in size are to be found in various types of washing and rinsing water. This water undergoes preliminary dessication in settling facilities, is separated from remaining sludge on a belt screen and cleaned to nearly drinking-water quality during the treatment of the process water.
The remaining sludge is still polluted to a low to medium extent and requires further treatment (thermal treatment, disposal, compaction, pyrolysis). This waste product is still being disposed of in the GDR for the time being.
Further degradation products are concentrated mixtures of solvents and separated oil fractions, which can be disposed of by burning at high temperatures. A mobile plasma facility is presently being tested in a joint project by WESTINGHOUSE and KEMMER/HARBAUER to determine whether it is basically suited for such products.
This leaves, finally, only the substances adsorbed by the activated charcoal of the process-water conditioning system. These substances are decomposed during the thermal/chemical regeneration of the activated charcoal at the manufacturer's and are turned into ash or acids.
The complete process flow chart for the soil-washing system is shown in Fig. 1.

6. Results

After the soil-washing system had been put to several months of successful use treating the contaminated soil of the Pintsch grounds, cleaning tests were begun in October 1987 with contaminated soil excavated from two Berlin gas-works locations in Mariendorf and Wilmersdorf.
The following cleaning results with the material from Mariendorf are exemplary of the two soils.
The grain-size distribution (Fig. 2) shows that the soil is extremely fine-grained with 37 % of the particles being less than 100 µm in size.

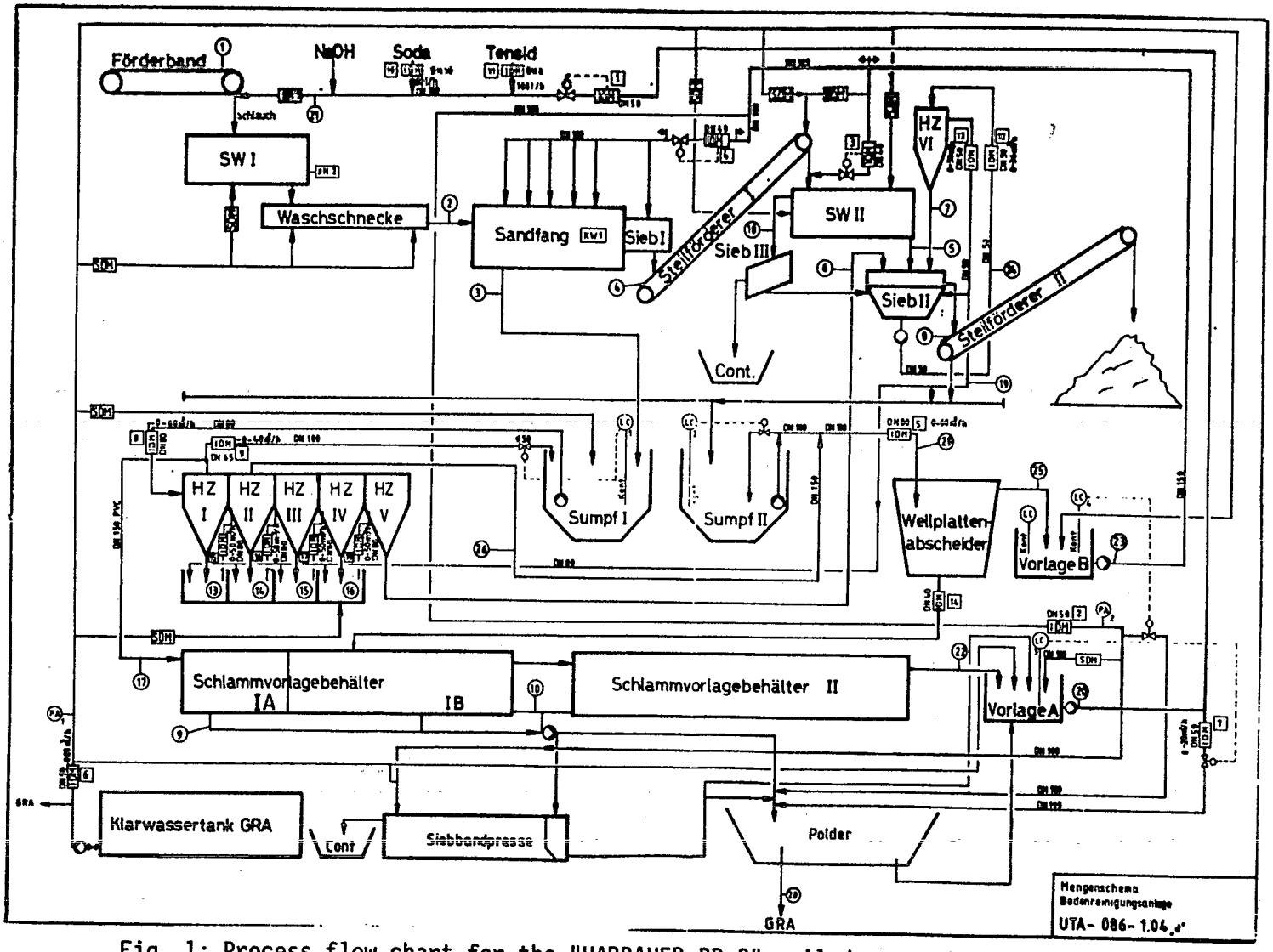

Fig. 1: Process flow chart for the "HARBAUER PB 2" soil-decontamination system

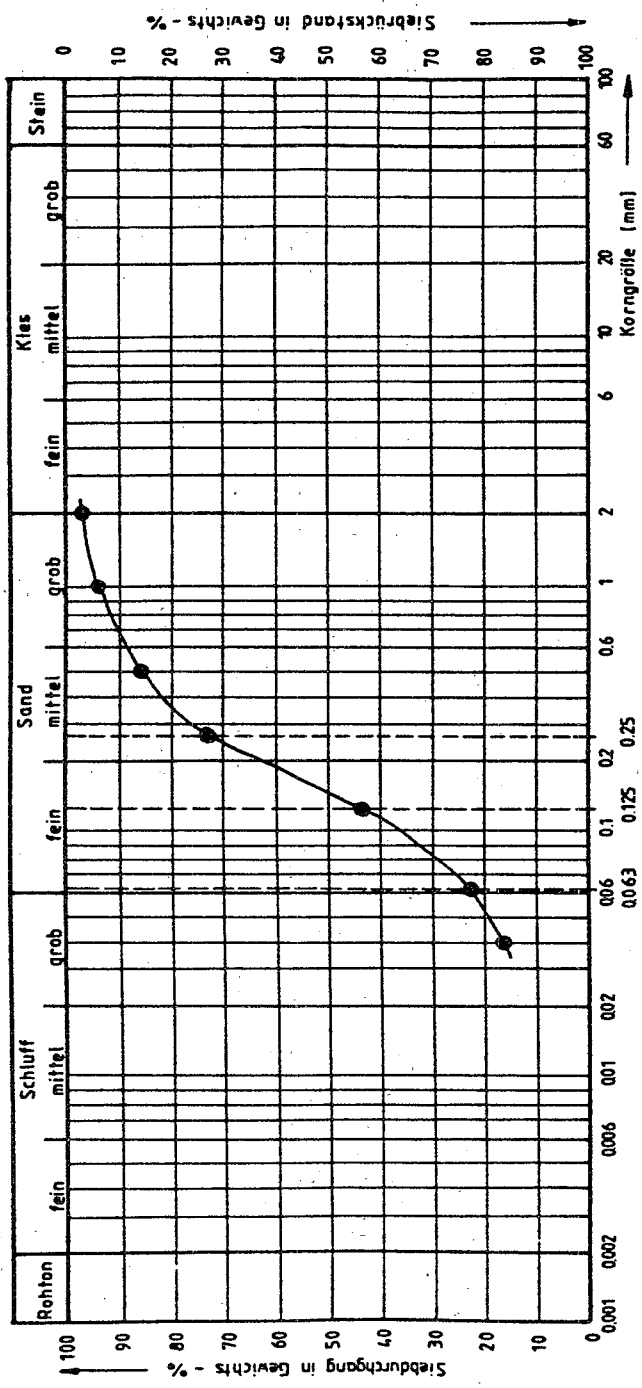

Fig. 2: Grain-size distribution of the soil at the "Berlin-Mariendorf gas works"

Such soil cannot be processed by conventional soil-washing systems since, on the one hand, the high percentage of extremely fine grains can no longer be effectively separated from the harmful substance and, on the other, they lead to complete silting-up of the system.
In comparison, during some eight weeks of tests with this material it was seen that the system is capable of effectively cleaning soil with a problematically high content of silt and clay without significant modifications or conversions.
The results of the analysis (Table 2) substantiate the high cleaning efficiency in relation to all the relevant parameters of the harmful substances. The pollution remaining in the decontaminated soil was nearly always lower than reference category A of the guideline for soil decontamination, but in general clearly beneath the B values.
The cut of the system, as related to the grain size to be processed, was determined to be approx. 15 µm within the scope of a balance sheet drawn up for the complete system.
On the average, the amount of residue to be disposed of during the test period lasting more than 6 months amounted to approximately 2 % of the initial material.

In general these statements also apply to the soil from Wilmersdorf. But since the balance sheet for the system was not yet finished for this material by the copy deadline, reference is made in this connexion to the authors' paper.

	Initial values	Remaining pollution	Washing success (%)
Petroleum ether extract: (index for mineral-oil contents)	476,000 µg/kg	67,000 µg/kg	86
PAH's	752,000 µg/kg	2,000 µg/kg	99.7
Phenol index:	60,500 µg/kg	n.n.	appr. 100
Total cyanide: (as per DIN 38 405)	5,300 µg/kg	59 µg/kg	98.9

Table 2: Cleaning efficiency, soil from gas works in Berlin-Mariendorf

7. Conclusions

With the system solution presented it is possible to clean contaminated soil with a complex matrix of harmful substances and problematical grain sizes by means of large-scale technology and then refill the soil. The entire system can be considered by now to have undergone large-scale testing, and the suitability of the system components for a process-engineering solution to the problem has been demonstrated. The process costs less than 200 DM/t on the average. The present potential for development of the system presented is, for one, a reduction of the cut to areas less than 10 µm in size and thus to further minimization of the resi-

due to be disposed of and, for another, further optimization of the separation of harmful substances from the soil. These two areas are the focal points of the R&D work being done by HARBAUER at the present and, among others, the subject of a research project sponsored by the Federal Ministry of Research and Technology and the Senator for Science and Research.

8. Literatur

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Appendix 5-C

Jet Cutting Followed by Oxidation (Keller), Germany

No final text available.

Appendix 5-D

Physical/Chemical Extraction Technology Case Studies

Electro-reclamation (Geokinetics), The Netherlands

NATO/CCMS Pilot Study

Demonstration of Remedial Action Technologies
for Contaminated Land and Groundwater

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Electro-Reclamation : State-of-the-Art

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Electrokinetical phenomena

During the last 4 years Geokinetics has been developing a method to remove heavy metals and other contaminants from soil and groundwater. The method is based on electrokinetical phenomena, which in one way or another have been made use of since the end of last century. These phenomena occur when the soil is electrically charged with direct current by means of one or several electrode arrays :

1. **Electro-osmosis** : Movement of soil moisture or groundwater from the anode to the kathode.
2. **Electrophoresis** : Movement of soil particles within the soil moisture or groundwater.
3. **Electrolysis** : Movement of ions and ioncomplexes within the soil moisture or groundwater.

Electro-osmosis

the electro-osmotic transport depends on the following factors :

- the mobility of the ions and charged particles within the soil moisture or groundwater;
- the hydratation of the ions and the charged particles;
- the charge and direction of the ions and charged particles, which cause a net water movement;
- the ion concentration;
- the viscosity of the pore solution, depending on the capillary size;
- the dielectrical constant, depending on the amount of organic and inorganic particles in the pore solution;
- the temperature.

From existing literature and own experiments the average electro-osmotic mobility has been calculated to be in the order of 5.10^{-9} $m^2/U.s$, where U = potential drop (V).

To drain 1 m^3 of soil by electro-osmosis, the following parameters should be known :

- the porosity;
- the moisture content of the soil to be treated;
- the conductivity of the pore solution;

Apart from these, other factors like the desired time period, the use of the soil after treatment and safety requirements regards maximum voltage and current are also of importance.

Electrophoresis

Electrophoresis (cataphoresis) involves the movement of particles under the influence of an electrical field. This definition includes all electrically charged particles like colloids, clay particles floating in the pore solution, organic particles, droplets etc.

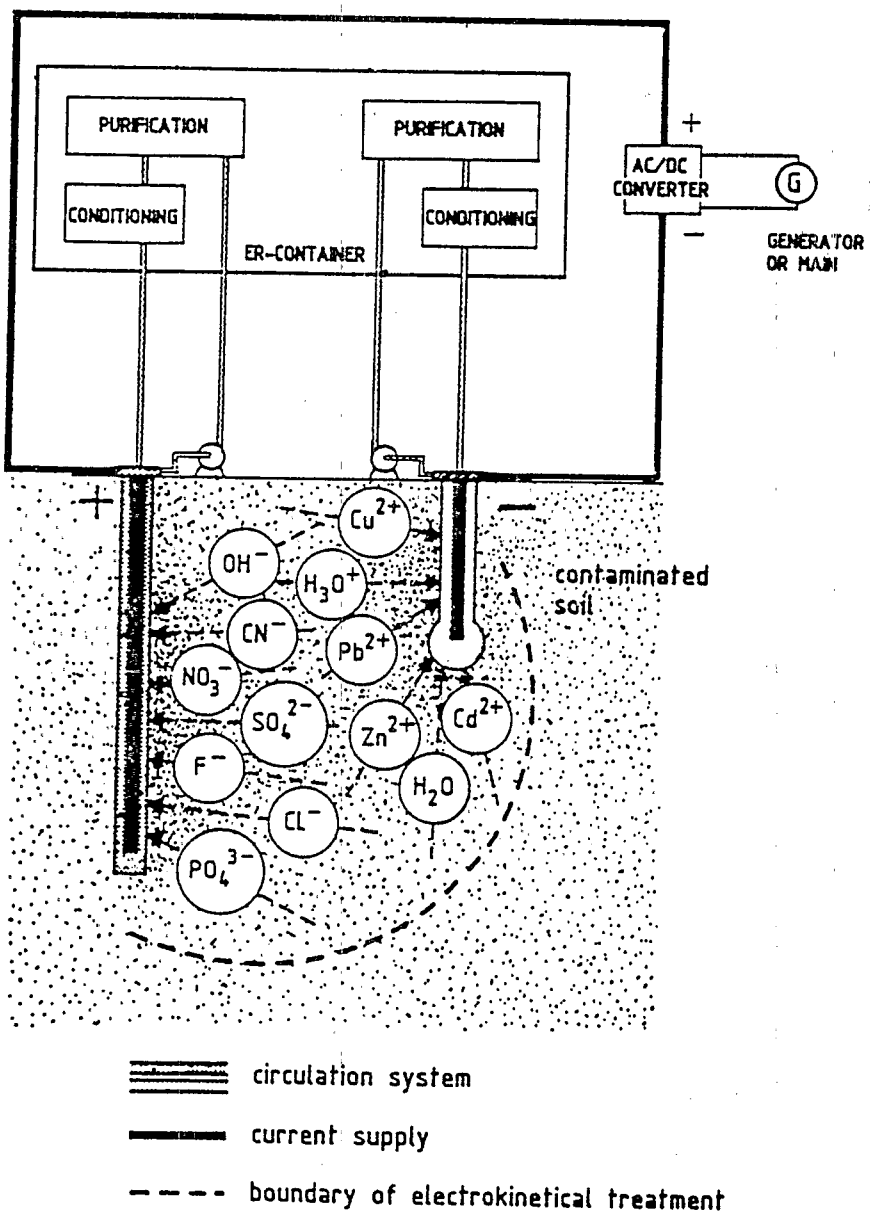


Fig. 1 : Schematic representation of ER-field unit and electrokinetical transport in the soil

The mobility of these particles corresponds with that of ions. Within the pore solution these particles transfer the electrical charges and affect the electrical conductivity and the electro-osmotic current. Clay minerals as such have 2 electrical polarity possibilities. One consists of the stucture based dipole moment, which depends on the atomic masses and has an orientation parallel to the longest axis of the clay particle. The second polarity stands at right angles to the first and is caused by the external electrical field. It depends on the way of polarization of the electrical double layer. The mobility of clay particles is an interplay between these two moments and is, therfore, less than the electro-osmotic mobility. It varies between 1.10^{-10} and 3.10^{-9} $m^2/U.s$.

Electrolysis

In the case of electro-osmosis and electrophoresis one considers only water transport or particle transport respectively; with electrolysis only the movement of ions and ioncomplexes is taken into consideration. The average mobility of ions lies around 5.10^{-8} $m^2/U.s$, which is ten times greater than that of the electro-osmotic mobility. Therefore, the energy necessary to move all ions over an average distance of 1 m through a crosssectional area of 1 m^2 of soil is ten times less than with electro-osmosis.

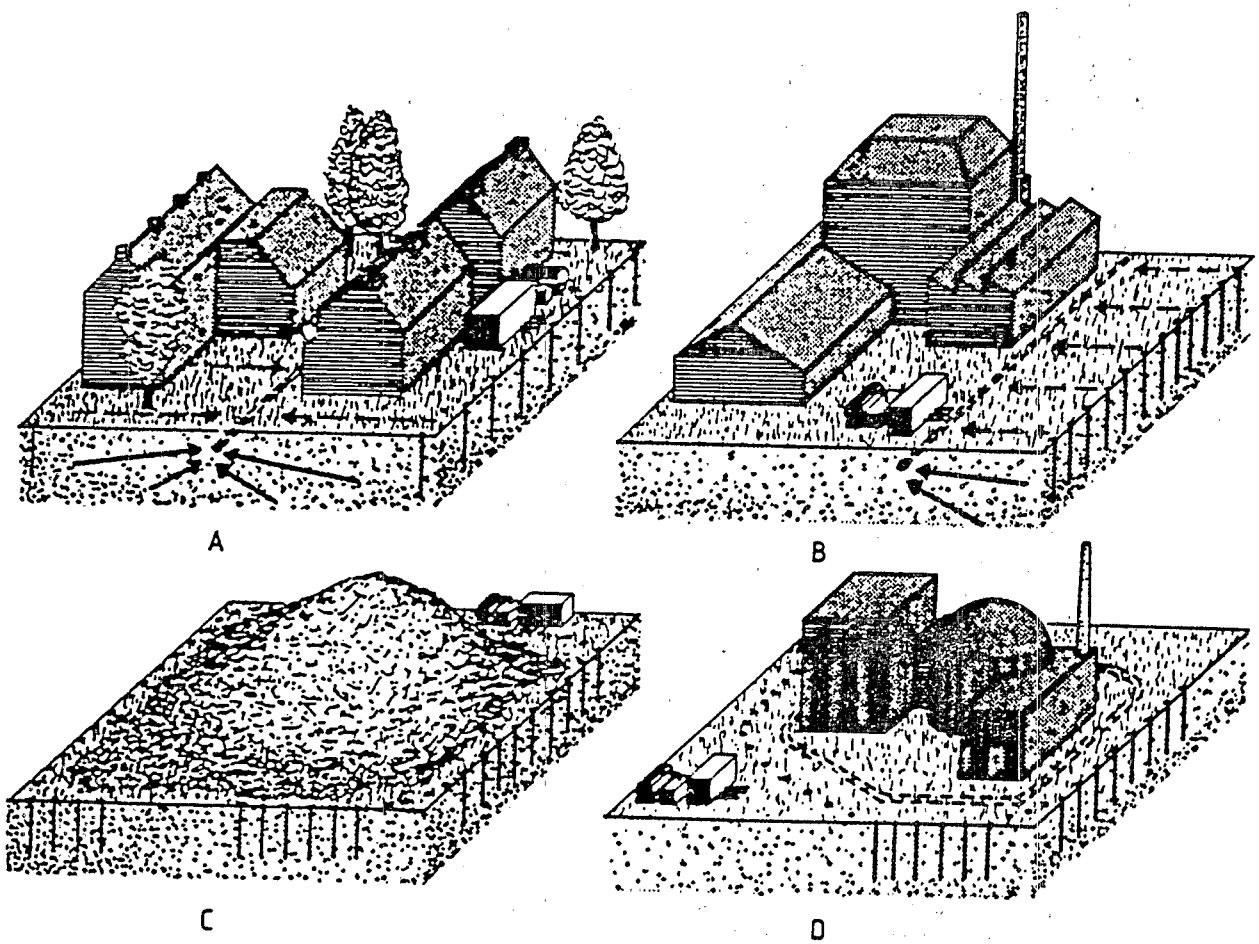
To calculate the energy necessary to dispose of the contaminants within 1 m^3 of soil, the following factors are of importance :

- chemical form of the contaminants;
- concentration of the contaminants;
- required concentrations of the contaminants;
- behaviour of the contaminants at different pH levels;
- pH control around the electrodes within the soil;
- removal of the contaminants and particles at the respective electrodes;
- supply of a conditioning solution to replace the removed contaminants and other particles at the electrodes;
- processing of the contaminated solution removed at the electrodes.

<u>The application of electrokinetical phenomena in practice</u>

The effectiveness of electro-reclamation is largely determined by the chemical composition of soil and groundwater. In marly soils for example it depends mostly on the kind of clay minerals and the calcium and magnesium bearing minerals like carbonate (e.g. lime) and sulphate (e.g. gypsum).
Another important element is iron, whose concentration in groundwater depends a.o. upon pH.
Generally speaking, the concentrations of the different metal ions depend on the CO_3^{2-} content and pH, while the following chemical equilibria are of importance :

$$Me^- \text{ (Clay-mineral)} \rightleftharpoons Me^{n+} + \text{Clay-mineral}^{n-}$$
$$Me(OH)_n \rightleftharpoons Me^{n+} + n(OH)^-$$
$$Me_n(CO_3)_m \rightleftharpoons n(Me) + m(CO_3)^{2-}$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$



A) Remediation of residential areas
B) Remediation of industrial areas
C) Remediation/fencing of hazardous waste sites
D) Preventive electrokinetical fence around potentially hazardous industrial complexes

Fig. 2 : Some applications of in situ Electro-Reclamation

The element Me can be any metal element like sodium, potassium, calcium, magnesium, iron etc, but also heavy metals like copper, nickel, lead, chromium, cadmium etc.

The concentration of the different metal ions in the groundwater depend on the solubility-products of the hydoxides and carbonates of the metals concerned and the pH (H^+ concentration) of the solution. At lower pH levels (higher H^+ concentrations) metal concentrations will increase.

When groundwater is contaminated with salts of heavy metals like lead, copper, nickel, chromium, zinc etc., the metal ions will influence the original chemical equilibrium. At the newly formed chemical equilibria part of the heavy metal ions will exchange with the original metal ions in the mineral phase (like carbonate, hydroxide, clay mineral), whereby one heavy metal ion will exchange more easily with the original metal ions than the other. The mobility or the displacement of a heavy metal ion in the groundwater or the soil depends on its exchange capacity with the original exchangable ions.

When soil is electrically charged, the following processes can a.o. be observed :

<u>At or near the anode</u>

- The positively charged particles move into the direction of the negatively charged cathode. As a consequence the concentration of the metal ions in the liquid phase (soil moisture or groundwater) will decrease. The decrease in concentration of the displaced ions in the groundwater will be restored by exchange with the solid phase (mineral phase). This ion displacement and ion-exchange will continue as long as the electrical field is maintained. The final concentration of a certain heavy metal thus depends on the initial concentrations in the liquid and solid phase, the electrokinetic mobility and the mutual exchange capacity with the other metal ions.

- At the anode moreover, H^+ ions are being formed through electrolysis of water. These positively charged ions move via soil moisture or groundwater into the direction of the cathode. As the H^+ ions exchange rather easily with the (heavy) metal ions of the mineral phase and lower pH of the groundwater, the concentrations of (heavy) metals will increase, thus accelerating the processes of exchange and displacement.

<u>At or near the cathode</u>

- At a certain point near the cathode, the (heavy) metal ions move into the direction of the cathode, but total concentration of the (heavy) metal ions will stay the same, because an equal amount of ions is being supplied from the point situated at the anode side. Total concentration of (heavy) metals will decrease when supply from the anode side is less than transport to the cathode side.

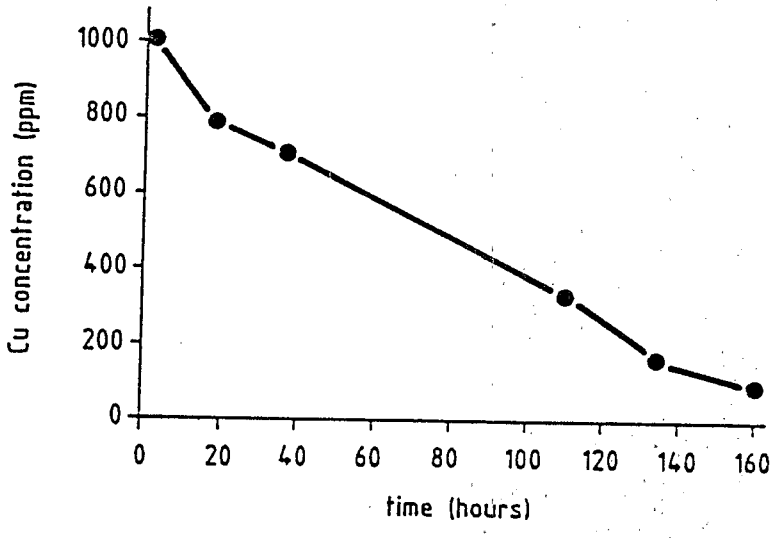


Fig. 3a : Decrease of Copper during electrokinetical treatment of contaminated pottery clay

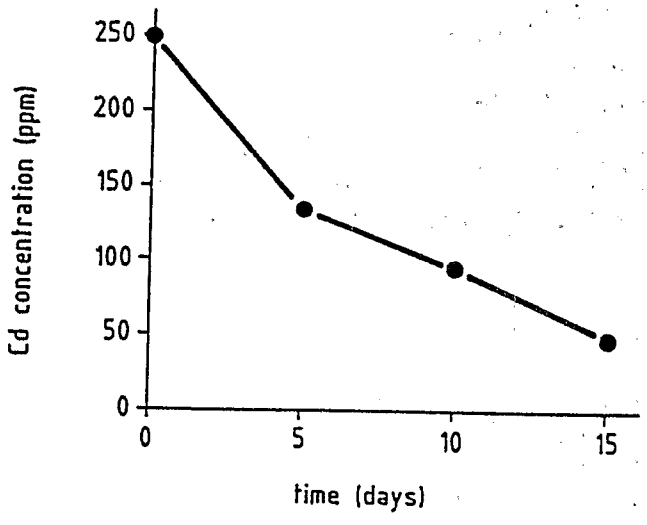


Fig. 3b : Decrease of Cadmium during electrokinetical treatment of contaminated fine argillaceous sand

The efficiency of electro-reclamation is less for soils with a high cation or metal ion exchange capacity and an acid buffering capacity (like marls). If feasible the efficiency of in situ remediation can be increased by irrigating the soil with slightly acidified (pH : 3-4) water .

When treating the soil on or off site, the soil material can be mixed with a slightly acidified solution after it is being excavated. The amount of acid to be added depends mainly on the cation exchange capacity of the soil.

Electrokinetical Installation

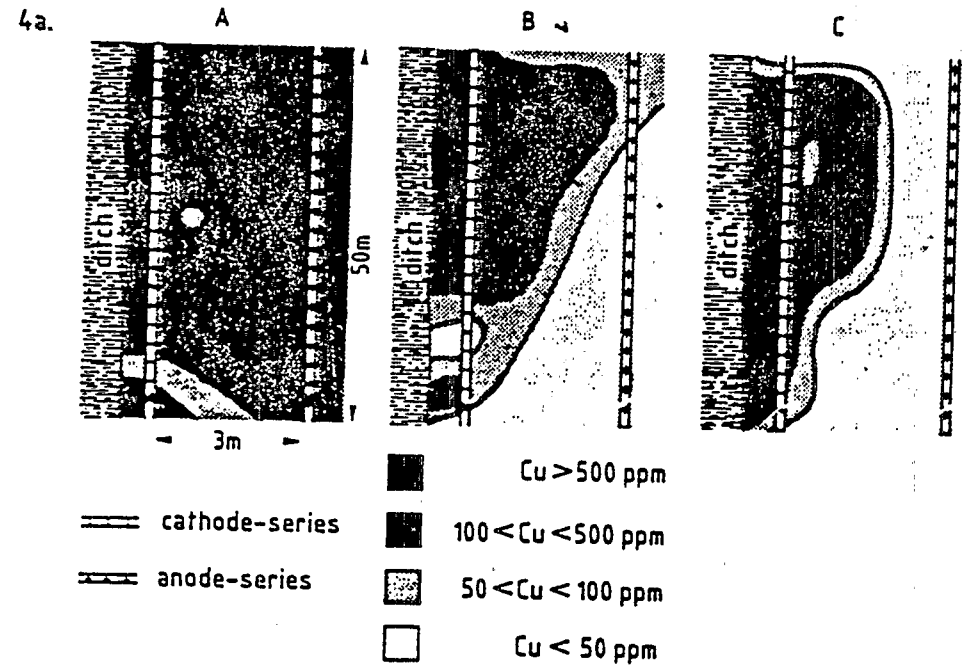
The core of an electrokinetical installation (fig. 1) consists of the electrode series and their housing. These can be installed in principle at any depth, either vertically or horizontally. The cathode and anode housings are interconnected but form two seperate circulation systems (one for the cathode, one for the anode), filled with different chemical solutions. In these solutions the contaminants are captured and brought to a connected treatment system, installed in a container together with the solution tanks and measuring and monitoring devices. The energy is supplied by a generating set or taken from the main.

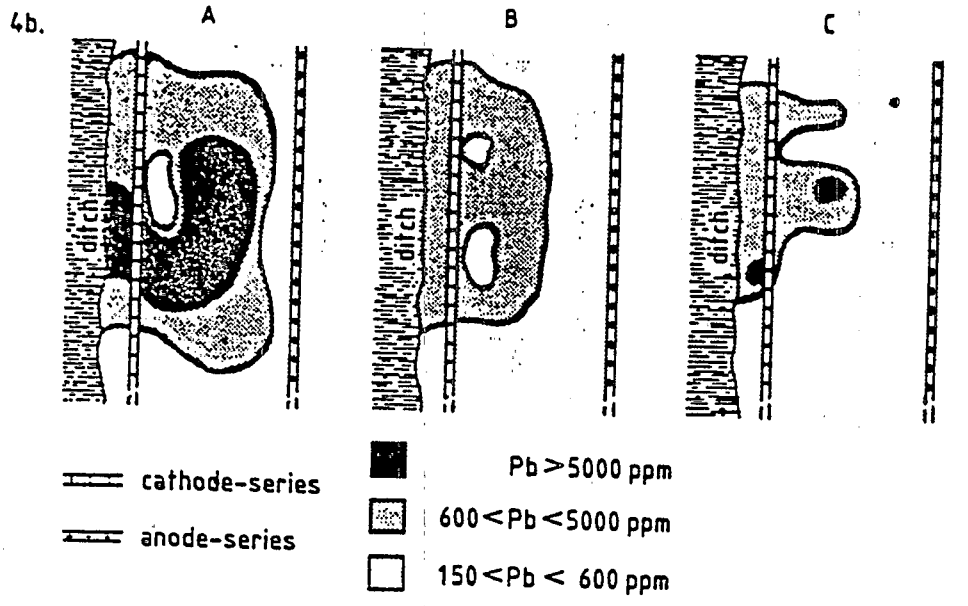
As explained before, electro-reclamation can be applied both for in situ remediation of contaminated soil (fig. 2) and for on or off site remediation of excavated polluted soil or river and/or industrial and sewage sludges. For the latter application a (semi)permanent installation would be most effective.

Laboratory experiments

The method of electro-reclamtion has been tested on the basis of numerous laboratory experiments. They focussed on important parameters like kind of current, strength of current, voltage, moisture content, chemical additives and the like. Besides, the effectiviness of the method as regards certain soil and heavy metal types has been examined with the help of several simulation experiments (clay, peat, fine argillaceous sand polluted with As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn).

These experiments also provided good insight into the energy demand and the time duration. Some results are presented in table 1 and figures 3a and 3b.





A) Sampling at 17-04-87
B) Sampling at 22-05-87
C) Sampling at 25-06-87

Fig. 4 : Results of fieldtest 1
4a. Decrease of Cu
4b. Decrease of Pb

Soil type	Metal	Conc. before (ppm)	Conc. after (ppm)	Decrease (per cent)
Peat	Pb	9000	2400	73
	Cu	500	200	60
Pottery clay	Cu	1000	100	90
Fine argillaceous sand	Cd	275	40	85
Clay	As	300	30	89
Fine argillaceous sand	Cd	319	< 1	99
	Cr	221	20	91
	Ni	227	34	85
	Pb	638	230	64
	Hg	334	110	67
	Cu	570	50	91
	Zn	937	180	81
			Average :	83
River sludge	Cd	10	5	50
	Cu	143	41	71
	Pb	173	80	54
	Ni	56	5	91
	Zn	901	54	94
	Cr	72	26	64
	Hg	0.5	0.2	60
	As	13	4.4	66
			Average :	69

Table 1 : Some results of laboratory electro-reclamation.

Field experiments

Site 1

The first field experiment took place alongside part of a waterbearing ditch, on one side bordered by a former paint factory and on the other side by open grassland. The bank on the latter part was heightened by sediment dredged from the ditch. This sediment was heavily polluted with metals in the form of paint residuary. The raised sediment layer, height 20 - 50 cm, length 70 m and width 3 m, contained Pb and Cu concentrations up to 10,000 ppm and 5,000 ppm respectively. The original peat soil underneath was contaminated by leaching of this overlying layer with Pb concentrations ranging from 300 ppm to more than 5,000 ppm, while Cu concentrations were in the order of 500 to 1,000 ppm.

A preceding electrokinetic laboratory test with a sample of the sediment reduced the concentration of Pb from ≈ 9,000 ppm to ≈ 5,000 ppm and that of Cu from ≈ 4,500 ppm to ≈ 1,600 ppm, all within a time period of 320 hours.
For the field experiment one cathode and one anode array were installed both with a length of 70 m and a mutual distance of 3 m.

The cathode was installed horizontally, while the anodes were implaced vertically into the soil about 2 m apart. On the basis of the energy consumption during the laboratory test the field experiment was confined to 430 hours.
The changes in Pb and Cu concentrations were monitored at 26 sampling locations, sampled at regular intervals at several depths (10,20,30,40 and 50 cm below ground surface). The following table lists part of the results for Cu and Pb within the peat at a depth of 30 to 40 cm below ground surface. The spatial distribution of the pollutants at the beginning and at the end of the test are shown in figs. 4a and 4b).

Sample point (30-40 cm)	Metal	Conc. before (ppm)	Conc. after (ppm)	Decrease (per cent
1	Pb	440	110	75
	Cu	185	35	81
2	Pb	3900	700	82
	Cu	540	220	59
3	Pb	> 5000	560	89
	Cu	1150	580	50
4	Pb	> 5000	2450	51
	Cu	475	250	47
5	Pb	> 5000	610	88
	Cu	1170	230	80
6	Pb	> 5000	300	94
	Cu	580	45	92
7	Pb	3780	285	92
	Cu	410	30	93
8	Pb	380	180	53
	Cu	35	15	57
9	Pb	340	90	74
	Cu	50	15	70
			Average :	74

Table 2. Electro-reclamation, field results, site 1

Site 2

The second field experiment was carried out on the site of a galvanizing plant. According to preceding investigations the soil (sandy clay) around the plant was contaminated with Zn to a depth of 40 cm below groundsurface. In the upper 10 cm Zn concentrations were reported to have a maximum of 3,000 ppm. At greater depths Zn concentrations were indicated as being in the order of 500 ppm.

For the experiment an area was selected with dimensions of 15 m x 6 m x 1 m. Two cathode drains were installed at a depth of 50 cm below groundsurface, while 33 anodes, divided along 3 rows were implaced in holes of 1 m depth with a mutual distance of 1.5 m. The distance between the cathode and anode series was also 1.5 m.

Energy was supplied by a 100 kVA generating set. The resistivity of the soil was 5 Ωm. The installation was calculated for a DC supply of 8 Amps/m² of soil, which should result in a potential drop of 40 V/m. This potential drop could not be maintained during the whole period. As a result of some material problems it was neither possible to maintain a 24 hour energy supply to the soil.

Within 2 weeks temperature rose from 12 °C to an average of 40 °C. As a consequence soil resistivity decreased to 2.5 Ωm and the potential drop to 20 V/m with an average strength of current of 8 Amps/m². The effective energysupply per 1000 kg of soil amounted to 160 kWh during the 8 week period.

Changes in Zn concentration were monitored at 12 sampling locations, which were sampled at 3 different depth intervals (10, 30 and 50 cm). Changes in groundwater concentration were monitored in 2 observation wells. In table 5 and fig. 5 the results are given for the depth interval of 30 cm.

Sample point (30 cm detpth)	Metal	Conc. before (ppm)	Conc. after (ppm)	decrease (per cent)
1	> Zn	5120	4470	13
2		2030	1960	3
3		1600	800	50
4		2320	2320	0
5		2450	2450	0
6		4390	2360	48
7		1960	940	52
8		3250	1960	40
9		2400	2000	17
10		70	30	57
11		150	120	20
			Average :	20

Table 5 : Electro-reclamation, field results site 2

The energy demand for this test amounted to 160 kWh/ton. At the beginning of the test the highest Zn concentration amounted to 7,010 ppm with an average of 2,410 ppm over the whole area. At the end of the test the highest Zn concentration was 5,300 ppm and the average had been decreased to 1,620. The concentrations of Zn, Pb and Cd in the groundwater and the filtercake are presented in the tables 6 to 8.

A total of some 1000 kg of filtercake was produced with an average Zn content of 117 g/kg. This comes to a total removal of some 50 kg of zinc, assuming an average moisture content of the filtercake of 60 % .

A rough mass balans can be summarized as follows :

- treated volume of soil : 15 x 6 x 0.5 x 3/4 = 34 m^3 (1/4 of the area did not show increased Zn concentrations).
- weight : 34 m^3 x 1.8 = 61 tons.
- weight of filtercake : 1000 kg.
- average moisture content : 60 %
- total dry matter : 400 kg.
- average Zn concentration : 117 g/kg.
- amount of zinc removed : 47 kg
- removed per 1000 kg of soil : $47 \times 10^4 / 61 \times 10^3$ = 770 ppm.

The last value is in the same order of magnitude as the average decrease in Zn concentration (2410 ppm -1620 ppm = 790 ppm).

An important outcome of the test was the relatively high energy consumption against a rather low Zn-mobility. This was the result of the high buffering capacity of the soil, caused by the presence of NH_3 and NH_4Cl (as was established later), which is used during the galvanizing process. During a following laboratory test with a soil sample from the area it was found that the energy necessary to reduce Zn-concentrations below the 200 ppm level would amount to 500 kWh/ton of soil. With an unchanged power-suplly of 100 kVA this would mean tripling the time period of 8 weeks to 24 weeks.

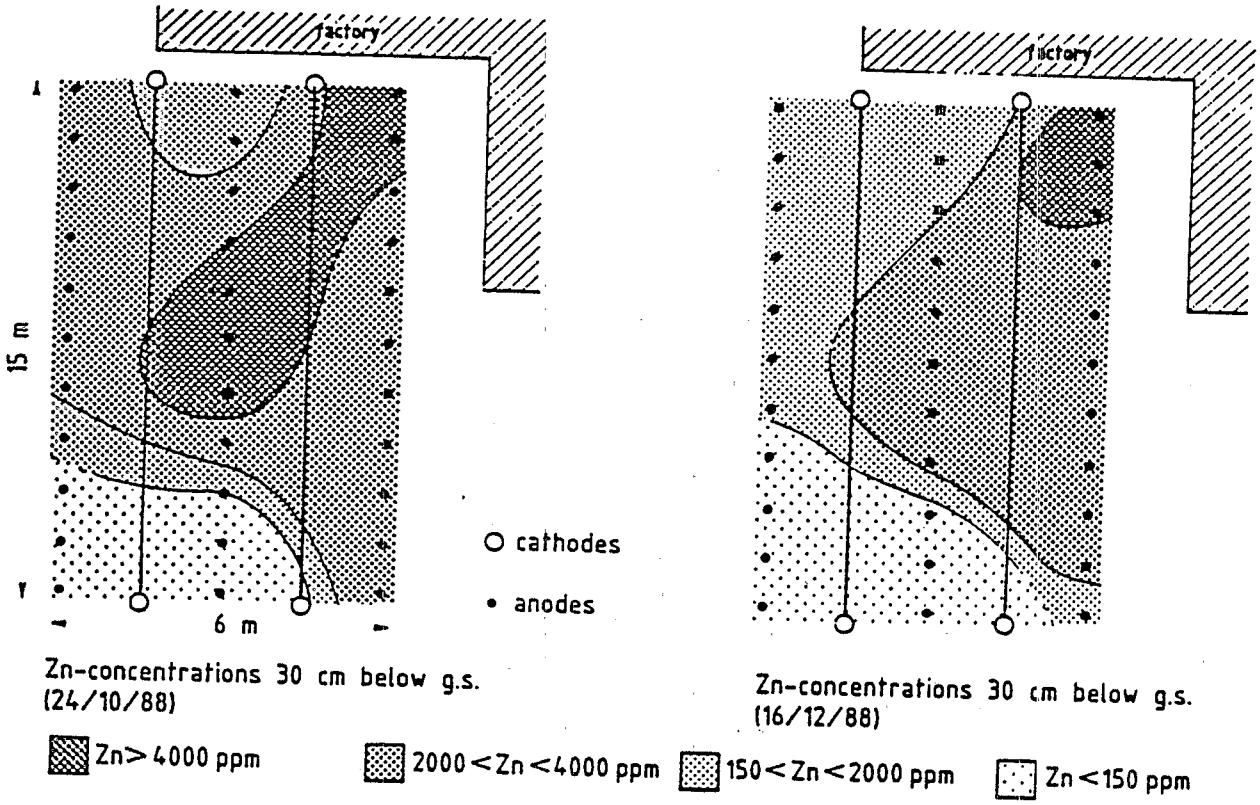


Fig. 5 : Results of fieldtest 2

Metal	:	Zn	Pb	Cd	Zn	Pb	Cd
sample treatment	:	not acidified			acidified		
date	obs. well	ppm					
24-10-88	1	200	0.09	0.06	270	1.4	0.07
01-11-88	1	120	0.07	0.00	140	0.09	0
09-11-88	1	130	0.06	0.02	160	0.17	0.02
17-11-88	1	172	0.07	0.03	198	0.11	0.04
25-11-88	1	130	0.17	0.03	180	0.22	0.03
30-11-88	1	120	0.13	0.03	150	0.16	0.03
24-10-88	2	10	0.17	0.02	40	0.34	0.02
01-11-88	2	1.5	0.09	0.09	2	0.15	0
09-11-88	2	2.5	0.06	0	3	0.15	0
17-11-88	2	6	0.03	0	8	0.07	0.01
25-11-88	2	2.8	0.03	0.01	5.8	0.18	0.01
30-11-88	2	4	0.09	0	5.5	0.14	0

Table 6. Zn-content (ppm) of the groundwater in observation wells 1 and 2.

Metal	:	Zn	Pb	Cd	moisture cnt
date		g/kg			in %
24-10-88		136.9	1.9	0.34	
09-11-88		199	1.1	0.18	
17-11-88		99	2	0.12	
25-11-88		89	1.5	0.16	78
30-11-88		61	0.58	0.11	

Table 7. Zn-content (g/kg) of the filtercake during Electro-Reclamation.

Metal	:	Zn	Pb	Cd
date		ppm		
30-11-88		30	0.6	0

Table 8. Zn-content (ppm) of the solution in the anode-circulation system.

Remedial action

The first 'official' electro-reclamation project started at the end of January 1989. It involved a site of a former timber impregnation plant, containing arsenic levels up to 400 - 500 ppm. After a fire in 1984, which destroyed a large part of the plant, it was decided not to re-build the plant. After dismantling the same a 'statement of unpolluted soil' was needed in order to allocate the land to building plots. A following investigation established the presence of As concentrations up to several 100 ppm in part of the heavy clay soil to a maximum depth of 2 m. Cause of the pollution was attributed to 'Superwolmansalt D'($Na_2HAsO_4.7H_2O$), used for impregnation.

In April 1988 Geokinetics was requested to investigate the possibility of remediating the soil by Electro-Reclamation. A following laboratory test with a soil sample reduced the As concentration of 300 ppm to 30 ppm against an energy consumption of 115 kWh/ton. An additional field investigation delineated the pollution to an area of 10 m x 10 m, contaminated to a depth of 2 m and an adjoining area of 10 m x 5 m, contaminated to a depth of 1 m. Total volume of polluted soil : 250 m^3 (= 450 tons).

The project started in January 1989. Along the length of the polluted area 4 x 2 cathode drains were installed : one at a depth of 1.5 m and the other at 0.5 m. The cathode arrays had a mutual distance of 3 m. In between 36 anodes were implaced in the soil, divided along 2 rows of 14 and 1 row of 8 pieces. Within the area of 10 m x 10 m the anodes were installed to a depth of 2 m below ground surface. In the other area of 10 m x 5 m the depth of the anodes was limited to 1 m depth. All anodes were placed at a mutual distance of 1.5 m.

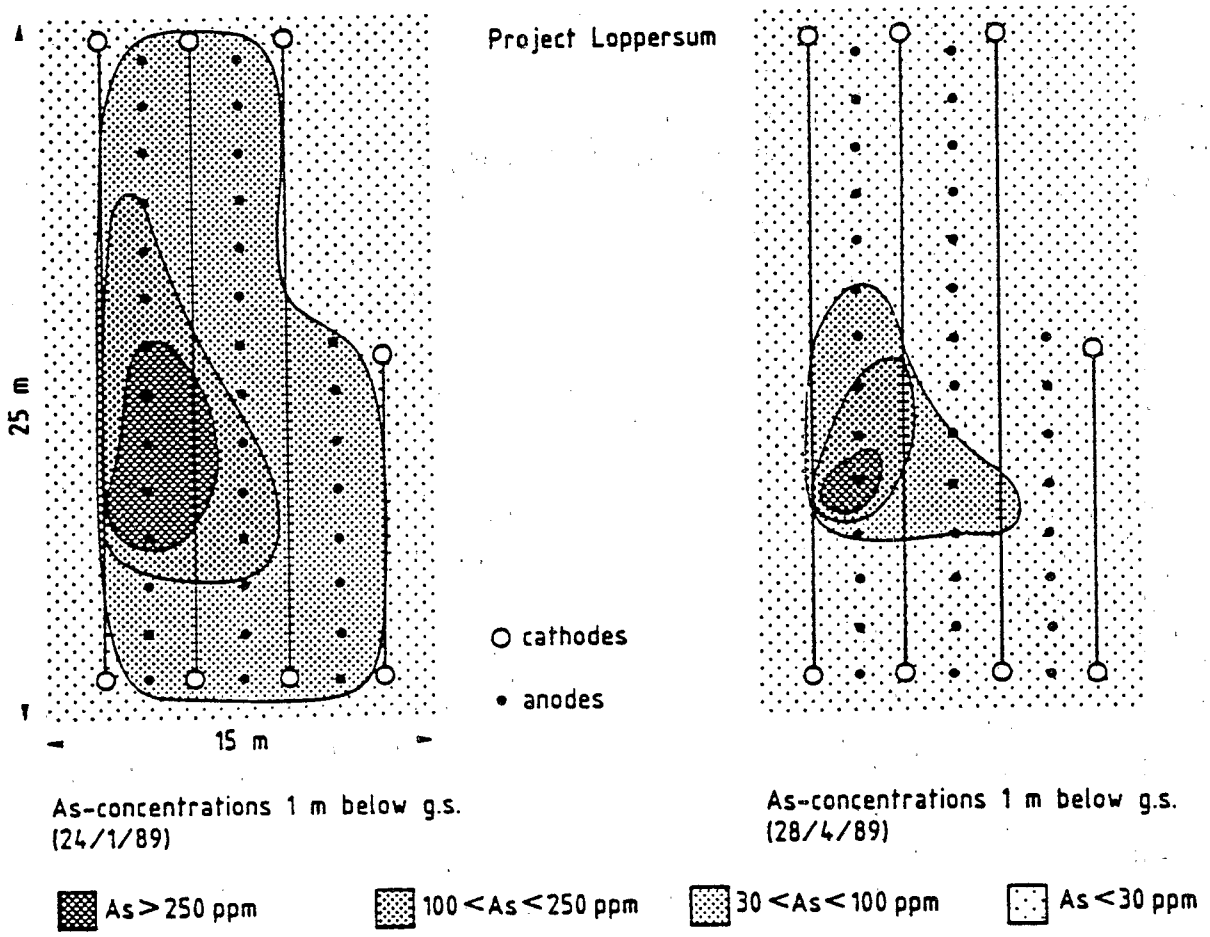
On the basis of both the laboratory test and the field investigation the duration of the Electro-Reclamation period was calculated to last 50 (24 hour) days, using an energy supply of 200 kVA (= 44 kW effective into the soil.

At the beginning the resistivity of the clay was 10 Ωm and soil temperature at a depth of 0.5 m was 7 °C. After 3 to 4 weeks temperature had risen to an average of 50 °C, while the resistivity decreased to 5 Ωm. The original potential drop of 40 V/m decreased accordingly to 20 V/m with an average current strength of 4 Amps/m^2 (total crosssectional area being 110 m^2).

Changes in As concentrations were monitored at 10 fixed sampling locations and numerous randomly distributed sampling points. Of the fixed locations, 2 were sampled at 0, 0.5, 1, 1.5 and 2 m depth. The others at 0, 0.5 and 1 m depth. The analysis results from samples taken at the beginning and on 30 April at a depth of 1 m below ground surface are listed in table 9 and fig. 6.

When starting the project, the average As concentration over the whole area amounted to 115 ppm, which comes to a total As content of an ample 50 kg.

During the remediation process it was observed that at one particular area the decrease in As concentration proceeded much more slowly than at other locations. After April 30th there was almost no reduction observed anymore.



Because of time constraints, it was decided to stop the electro-reclamation process on May 12th and excavate the remainder of the soil, which showed too high As concentrations. During excavation many metal objects like tins, barrels, concrete iron etc. were found, shining and without any rust.

The discrepancy, therefore, between estimated and real energy demand (and thus elapsed time) was caused by these metal objects, left behind in the soil. These objects function as preferential flow paths for the electrical current thereby delaying the movement of the pollutants in their vicinity, as all the iron objects will go into solution first.

Sample-point	Metal	Concentration	Concentration	Energy
1		385	250	
2		40	< 20	
3		250	< 20	
4		310	190	
5	> As	50	< 20	> 150
6		75	30	
7		40	< 20	
8		175	< 20	
9		40	< 20	
10		60	< 20	

Table 9 : Results of remedial action project.

A total of some 40 m³ of soil had to be excavated. Periodical treatment of the electrode solutions resulted in some 800 kg of filtrate. A rough mass balans can be summarized as follows :

- treated volume of soil	: 250 m³
- weight of soil	: 450 tons
- average As concentration	: 115 ppm
- amount of As before remediation	: 52 kg
- weight of excavated soil	: 71 tons
- average As concentration of excavated soil	: 200 ppm
- amount of As in excavated soil	: 14 kg
- amount of filtrate	: 800 kg
- average moisture content	: 70 %
- total dry matter	: 240 kg
- total amount of As removed by electro-reclamation	: 34 kg
- total amount of As removed after remediation	: 48 kg
- amount of As remaining in the soil	: 4 kg
- average As concentration of remediated soil	: 10 ppm

Other applications / future developments

Electrokinetical fencing

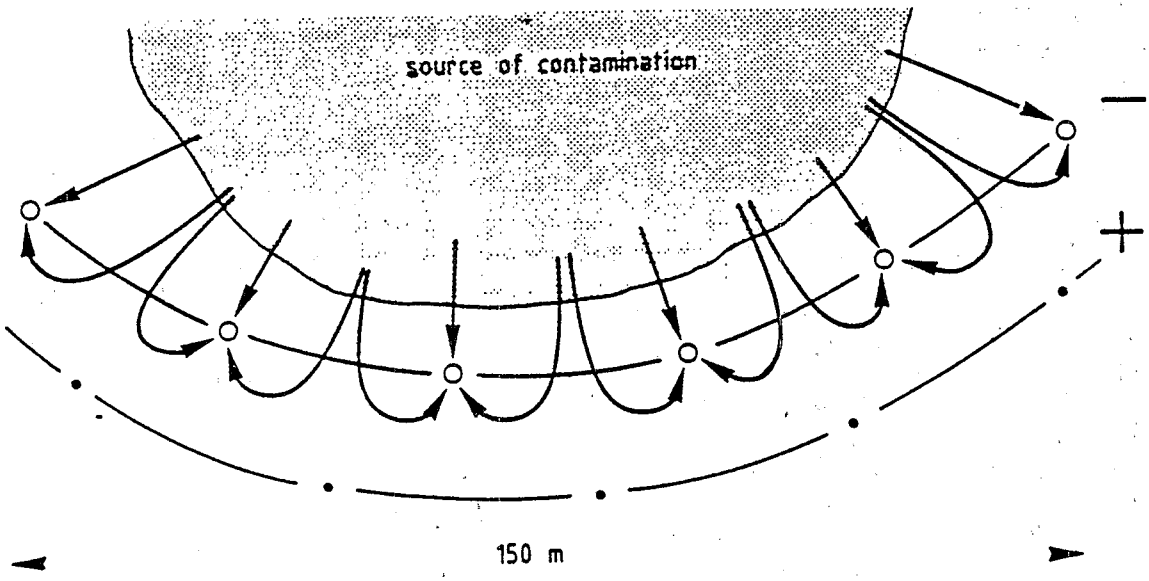
The electrokinetical phenomena occurring when the soil is electrically charged, can also be used for fencing purposes. These so-called electrokinetic fences can be installed either at refuse sites/factory complexes, where soil pollution has already been ascertained, or where soil pollution is likely to occur. Depending on the local geohydrological situation and the character of the soil, the elctrode configuration can be such that :

- the electrokinetical transport is directed towards the source of the pollution (fig. 7a). The cathode series is situated nearest to the source of pollution. Such a set-up should be applied in less permable soils without substantial groundwaterflow (< 1 m/year).

- the contaminants, which are carried along with the groundwater flow are diverted, collected around the electrodes and periodically removed. In this case the cathode series is farthest away from the source of pollution and cathode and anode series are installed perpendicular to the direction of groundwater flow (fig. 7b). Such a set-up should be applied when the soil and/or subsoil is relatively permeable (groundwaterflow velocity > 1 m/year).

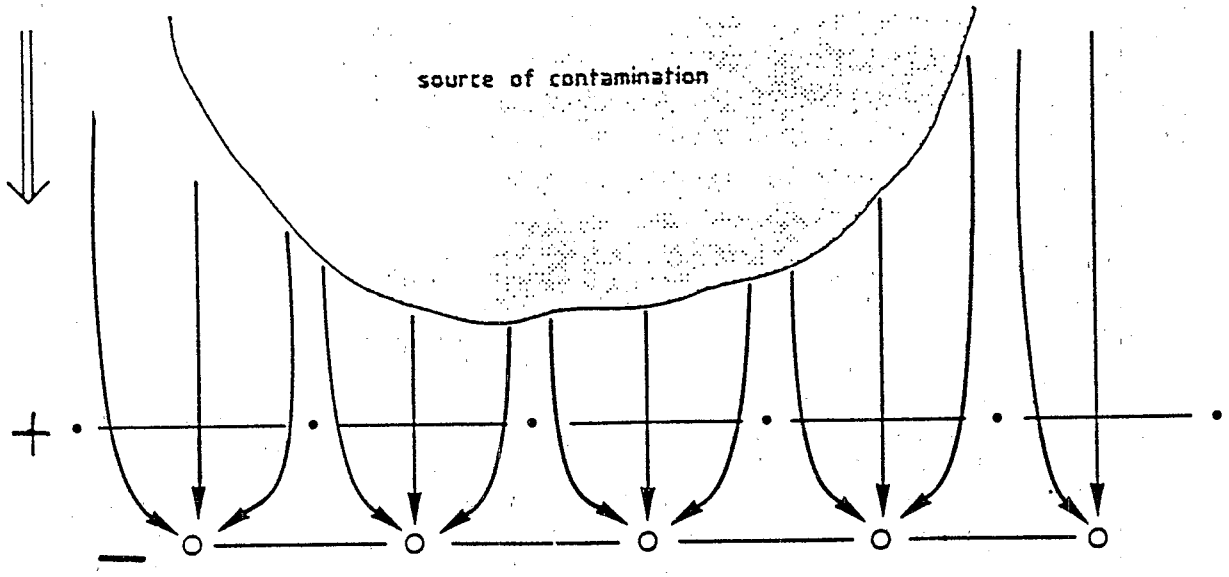
Desalination of arable land

Salination of arable land is a common problem in those countries, where precipitation is generally low and evapotranspiration high. In combination with relatively high groundwater levels (coastal areas and river lowlands), soils of low permeability and irrigation water with high total dissolved solids, the accumulation of salts in the top layers prohibits further agriculture.



anode-series (vertical)
cathode-series (vertical)
flow paths of positively charged contaminants

Fig 7a. : Set-up of electrokinetical fence in soil with low permeability



anode-series (vertical)
cathode-series (vertical)
flow paths of positively charged contaminants
direction of groundwater flow

Fig. 7b : Set-up of electrokinetical fence in soil with moderate to high permeability

The most common technique for landreclamation consists of the lowering of the groundwatertable and/or drainage of the soil by means of wells and/or horizontal drains. The soil is then frequently irrigated with relatively fresh water, thus leaching the salts from the soil. However the low permeability of the soil hampers more often than not the percolation of the leachate to the deeper layers.

By applying electrokinetical processes these problems can be overcome, as clay and argillaceous soils are specifically suited for electro-reclamation.

The As remediation project mentioned earlier showed, that after electrokinetical treatment, the permeability of the heavy clay soil had increased significantly. When furthermore gypsum is added at the anode solution, the soil structure will be improved even more and higher crop production will be obtained (Collopy, 1958).

Removal of organic contaminants

An R & D project investigating the possibilities of removal of organic pollutants like PCA's and PCB's from soils and sludges is currently in preparation. The first research objective is to examine wether extension and/or adaptation of the electrical parameters will result in the removal of organic contaminants.
The second research objective is to examine the possibilities of combining electrokinetical techniques with biodegradation, more specifically :

- can micro-organisms be distributed more evenly in the soil, or can micro-organisms be added to the soil,
- can pH and soil temperature be maintained at preferential levels (pH : 6 - 7, and T : ≈ 30 °C),
- can addtional oxygen and nutrients be brought into the soil ?

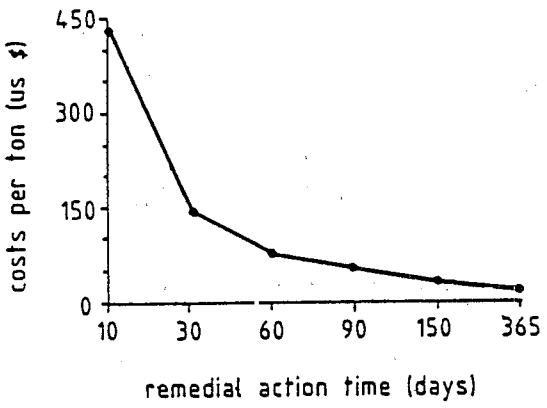
Cost estimates

Electro-Recalamation

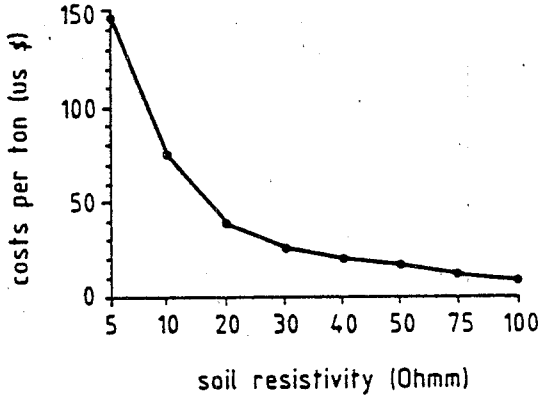
Fig. 8 shows a set of graphs depicting remediation cost per ton of soil as a function of remedial action time (fig. 8a) and as a function of the measure of contamination (fig. 8b), assuming a polluted area with dimensions of 500 m x 100 m x 1 m. From the graphs it is evident that short remediation periods and highly polluted soil (low resistivity) require a high amount of energy, having the greatest effect on the costs.

In practice, however, there is a limit to the electrical current which can be put into the soil. For every specific case, therefore, an optimum must be calaculated for energy supply and time duration.

a.



b.



Assumptions:
- Area dimensions: 500 m x 100 m x 1 m
- Weigth of soil: 90,000 ton
- Distance between C- and A-series: 10 m
- Mutual distance anodes: 10 m
- Soil resistivity: 10 Ohmm
- Duration of ER-proces: 60 days

Fig. 8 : Cost estimate of electro-reclamation
a. costs per time-period
b. costs versus grade of pollution

Electrokinetical fencing

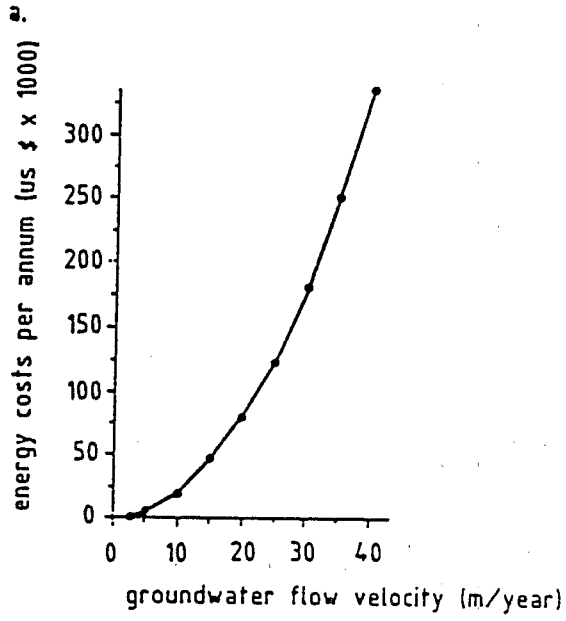
In fig. 9 the energy costs per year are given as a function of groundwater flow velocity (fig. 9a) and as a function of the rate of pollution (fig. 9b), assuming an electrokinetical fence of 500 m length and 10 m depth.

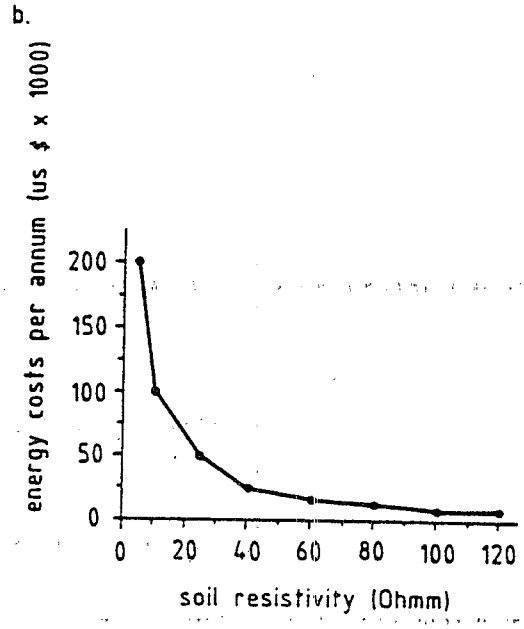
In areas of low groundwater flow velocity (clay, argillaceous sand) and low soil pollution, the yearly energy costs of an electrokinetical fence are insignificant. This changes rather quickly, when the soil becomes more permeable (sandy formations) and the groundwater flow velocity increases together with the concentration of the contaminants.

For relatively high groundwater flow velocities a combination of hydrological measures and electrokinetical techniques will render the most economic results.

Desalination of arable land

Preliminary cost estimations amount to US $ 1000 to 2000 per ha.





Assumptions:
- Length of fence: 500 m
- Depth of fence: 10 m
- Average ion mobility: 1.56 $m^2/V.year$
- Soil resistivity: 50 Ohmm
- Groundwater flow velocity: 10 m/year

Fig. 9 : Cost estimate of electrokinetical fencing
a. energy costs versus groundwater flow velocity
b. energy costs versus grade of pollution

October 1989

Geokinetics
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the Netherlands

Appendix 5-E

Physical/Chemical Extraction Technology Case Studies

In Situ Acid Extraction (TAUW/Mourik), The Netherlands

In situ cadmium removal
- full-scale remedial action of contaminated soil -

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1. INTRODUCTION

A photopaper producing plant discharged Cd containing wastewater into two infiltration ponds in the years 1935-1955. Periodical flooding of these ponds caused a soil pollution with Cd in the adjacent dune plot. In the vicinity of the polluted area a groundwater-pumping station is siuated.
This paper deals with the set up and the results of the in situ Cd "remedial action". There are three contributors to the project: province of Utrecht as principal, Mourik as contractor and TAUW Infra Consult as consultant. The calculated total costs of the in situ remedial action amounts to only 80% of the conventional sanitation costs. The costs of the whole project are approximately 4 million DM.

Figure 1 gives an outline of the cadmium pollution in the dune plot (horizontal profile) and the plant grounds (vertical profile). The total Cd content of the soil was estimated 725 kg.

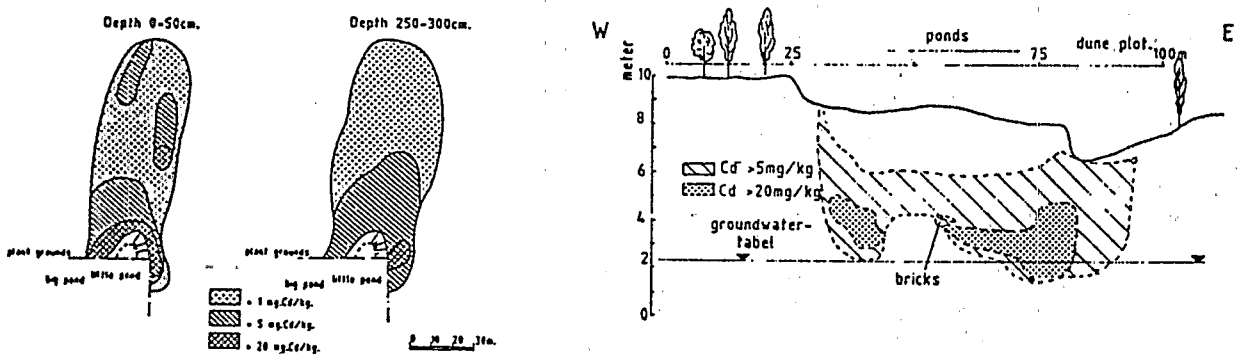

figure 1. Cadmium pollution in horizontal en vertical profile

In table 1 a few soil characteristics of the contaminated soil are presented. The analyses are carried out on more or less representative samples.

Table 1. Soil-characteristics for three soil-layers

sieve size	top layer	layer above groundwatertable	layer below groundwatertable
< 16 um	0.6	3.7	2.4
16 - 63	1.3	1.7	1.6
63 - 90	3.0	7.0	7.6
90 - 125	10.1	14.6	16.1
125 - 180	29.1	26.3	28.1
180 - 250	27.4	19.7	20.3
250 - 355	18.9	13.6	13.0
355 - 500	6.8	6.1	5.1
500 -1000	2.6	5.0	3.9
1000-2000	0.3	1.5	1.1
> 2000 um	<0.1	0.7	0.7
pH	4.9	4.7	7.4
CEC meq/100 g	3	2.5	1.8
org. carbon %	0.3	<0.1	<0.1
$CaCO_3$-content %	0.4	0.6	0.6
Fe(oxalate exactractable) mmol/kg dm	5	6	3
Al(oxalate extractable) mmol/kg dm	10	7	5
dry matter %	98.1	96.7	90.4

The soil can be characterised as middle fine to middle coarse sandy soil. The adsorption capacity of the soil in general is very low.

The whole in situ treatment involves approximately 30,000 m^3 soil within an area of 6,000 m^2. For the authorities a priority for remedial action was given because of the expected additional pollution of the ground water and the possibility of direct contact for recreants with contaminated topsoil. The groundwater is used for the preparation of drinkingwater.

2. DEVELOPMENT AND INSTALLATION OF THE REMEDIAL ACTION TECHNIQUE

Removal of the cadmium pollution out off the environment can be obtained by remedial action on the solid soil on location of the former ponds and the dune plot and by remedial actions of the deep groundwater downstreams of the plant (upstreams of the groundwater resource). In this presentation, only the remedial action of the solid soil is outlined.

Concerning in situ remedial action three aspects need special attention, because there is no or very little experience available in this matter:
- the Cd-desorption of the polluted soil (soil chemistry)
- the hydrological system of infiltration and withdrawal of water (hydrology)
- the purification of Cd-containing groundwater (watertreatment).

According to the three topics mentioned above, laboratory experiments, designs and/or installations are outlined underneath.

2.1. Desorption of cadmium

A desorption liquid was selected by batch-experiments with polluted soil. By calculation of the Cd-distribution coefficients ($K_d = C_{soil}/C_{water}$) from the batch-experiments a selection was made for column-leaching experiments.
Hydrochloric acid (10^{-3} mol) turned out to be useful; in figure 2 the results of the column-leaching experiments are compiled.

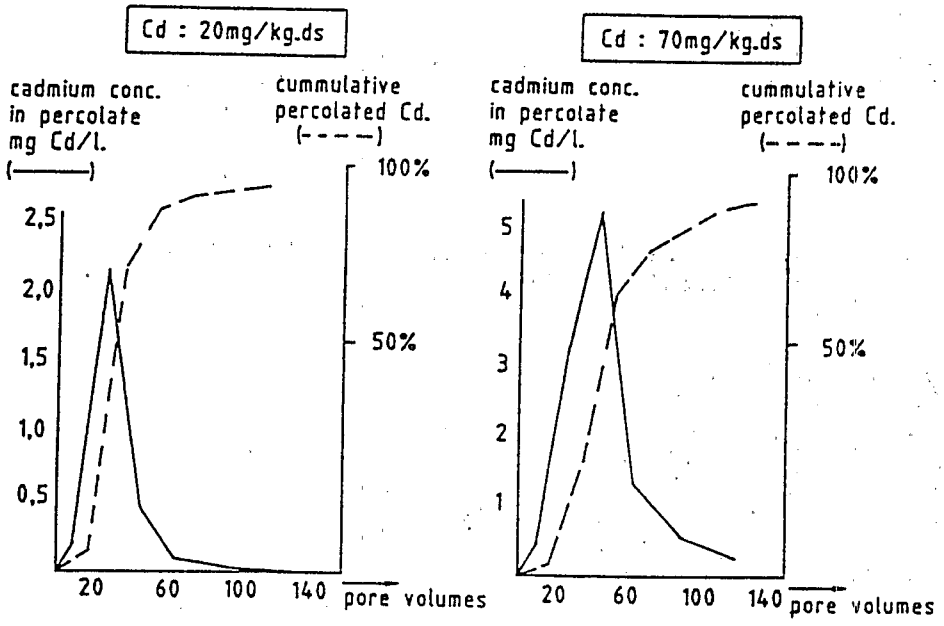

figure 2. Leaching of Cd-polluted soil by 10^{-3} mol HCH (pH = 3.5)

The K_d-value for the batch experiments range between 1.6 and 7.8 dm^3/kg and for the column experiments between approximately 2 and 3 dm^3/kg.
Results of the batch experiments can indicate an overestimation of the K_d-value due to buffer capacity of the sandy soil. The column experiments give a more accurate value for the K_d because the Liquid Solid ratio is much higher.
The expected quality of the percolate, calculated for a K_d-value of 4 (dm^3/kg) with the assumption of lineair desorption behaviour of Cd, is shown in figure 3. The hydraulic permeability of the soil used for the calculation is 1 m/day.

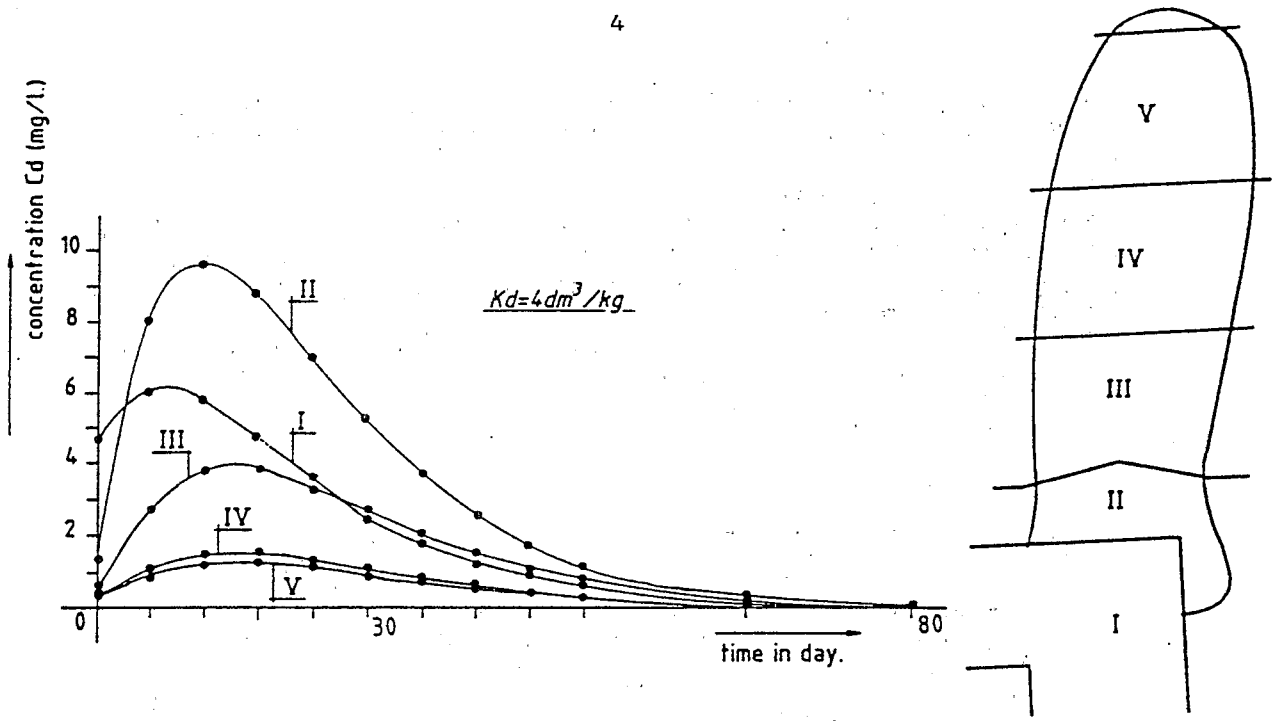

figure 3. Calculated cadmium concentration in the percolate of five separate compartments

2.2. Hydrologic system

The total area for remedial action amounts to 6,000 m^2 (see figure 1). The capacity of the groundwater treatment installation was limited to approximately 250 m^3/h, so the at one time treatable polluted area is dependent on the hydraulic properties of the soil. Horizontal drains are preferable to vertical deepwells in order to get straight groundwaterflow lines. A cross section of infiltration and withdrawal systems is outlined in figure 4.

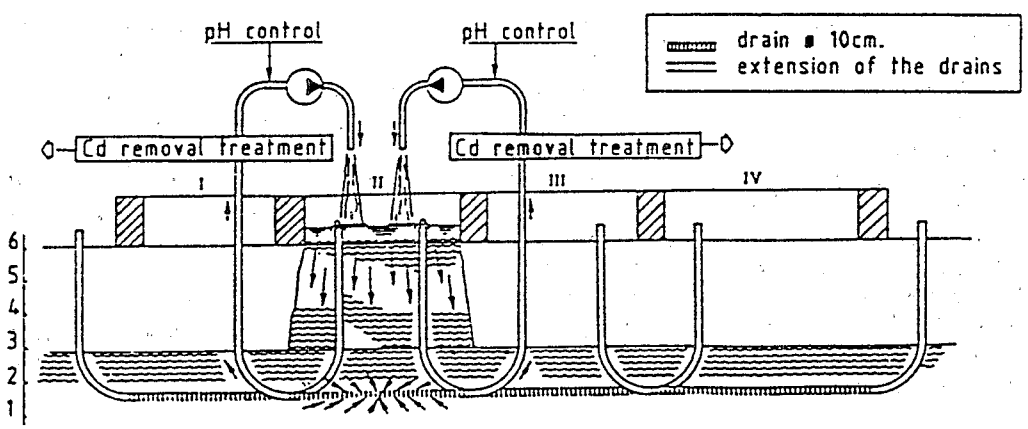

figure 4. Cross section of the infiltration and withdrawal systems

Design and dimension of the infiltration/withdrawal system was carried out by a two-dimensional (vertical) computer model. The calculated results are converted into the three-dimensional space. Full recirculation of the infiltrated water can be guaranteed when only a slight quantitity of aquifer water is discharged additionally.
For one compartment the groundwater flow pattern is represented in figure 5.

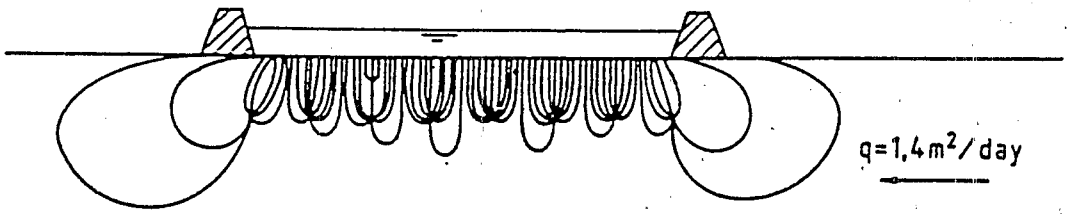

figure 5. Two-dimensional flow pattern of the infiltration water

The end of the remedial action will also be determined by the Cd-concentration in the pumped percolate for each separate compartment: in principal, infiltration with acified water should be continued untill the Cd-concentration reaches a constant low value (approximately 20 ug/l). The installed infiltration and withdrawal-system for the whole contaminated area is outlined in figure 6. The compartmentsize is bases on practical experience during the proceedings of the remedial action.

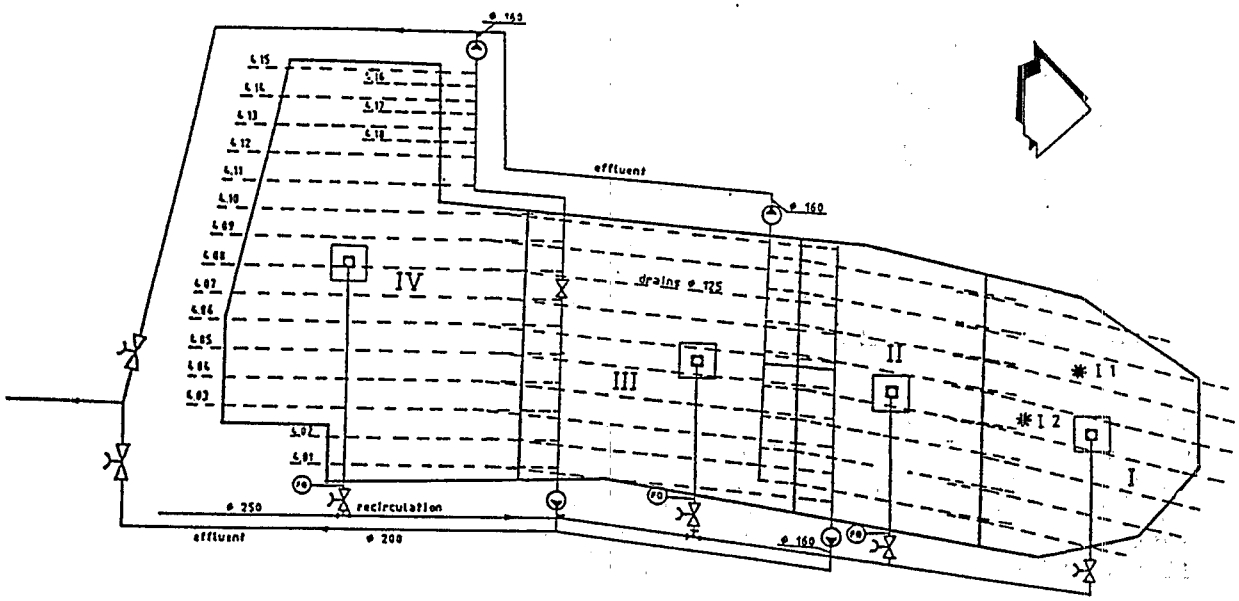

figure 6. Overview of the horizontal drains in the four compartments

2.3. Watertreatment system

A literature survey was conducted on the removal of Cd from waste water.
The three most important treatment techniques are:
. precipitation
. biosorption
. ion-exchange
Because the treated acid percolate is infiltrated again in the polluted soil and the waterflow is quite high, viz 250 m^3, sorption on resins is preferred.

First in the laboratory batch experiments were carried out. The main goal was to select a resin with a high specific Cd-adsorption in presence of a high iron-, aluminium- and calcium-concentration and a pH of 3.5.
The IMAC GT-73 turned out to be the most selective for Cd.
After the batch experiments a column experiment was set up to test the IMAC GT-73 resin of Rohm and Haas. The experimental set up is shown in figure 7.

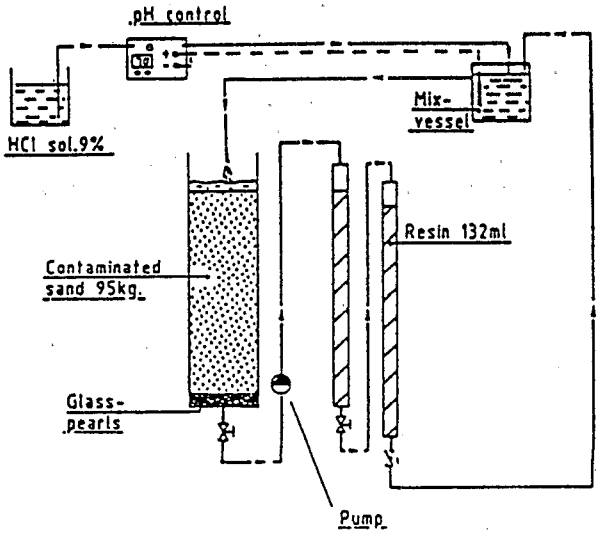

figure 7. Laboratory testunit for the resin column

The load of the first resin column is 6.7 g Cd/l resin while the effluent of the second resin column contains no Cd (<1 ug/l). Loads as high as 34 g Cd/l resin were found in previous experiments with high Cd-influent concentrations.
Regeneration of the Cd-loaded resin is more or less complete when flushed with 4 bedvolumes of 5% HCl.

Based on the laboratory results the dimensions of the full scale installation are designed. Due to the relative short operation time (approximately one year) there were made some modifications in the original design so the contractor was able to instale smaller resin filters.

The installed water treatment system is represented in figure 8.

The ion-exchange system consists of 5 filters with 3 m^3 resin IMAC GT 73 each. Two parallel streets of each two filters have been installed with one filter stand-by used during regeneration.

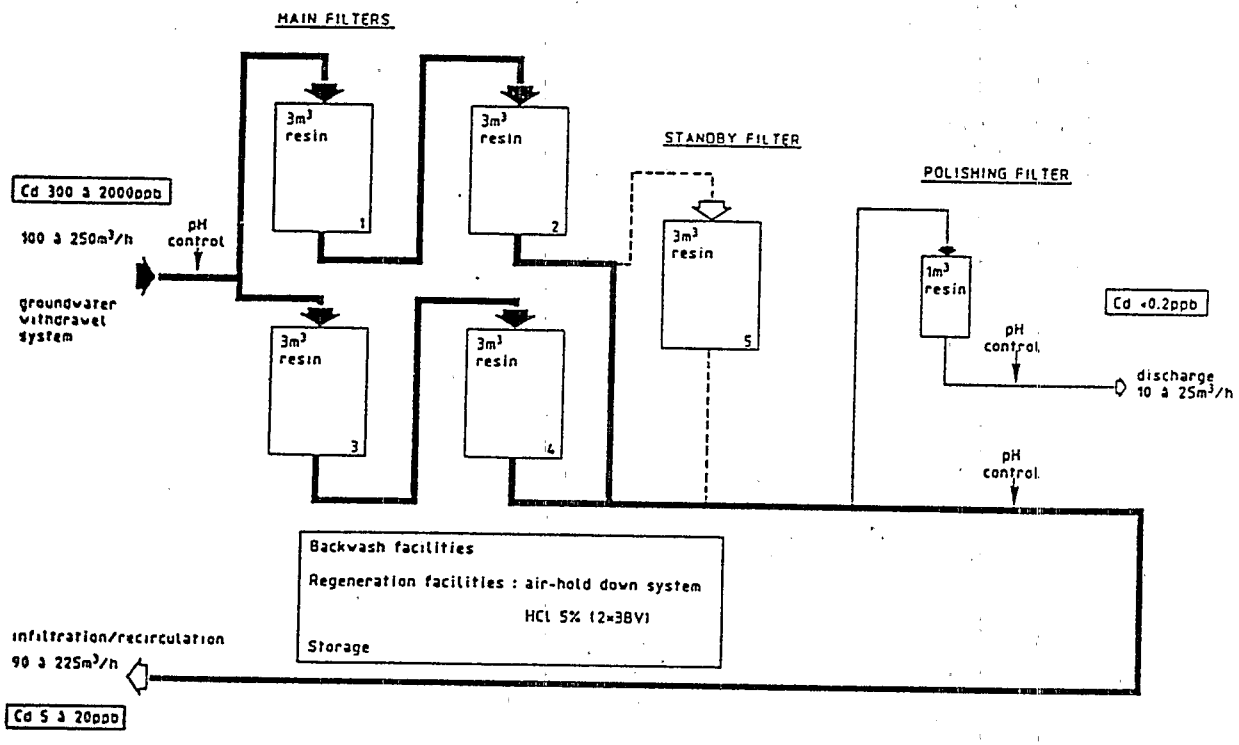

figure 8. Scheme of the water treatment plant

The regeneration is upflow by an air-hold down system to reduce the production of eluate. The step-by-step regeneration is performed with two times 3 bedvolumes hydrochloric acid of 5% upflow flushing and proceeded by 2.5 bedvolmes fresh water upflow- and 2.5 bedvolumes fresh water downflow flushing. The first 3 bedvolumes hydrochloric acid are discharged to an industrial cleaner (precipitation and ion-exchange); the sludge is conditioned and discharged to a controlled waste dump.

3. THE RESULTS OF THE REMEDIAL ACTION OF COMPARTMENT I

In August 1987 the in situ remedial action started with the less contaminated compartment I. Compartment I is the most distant compartment from the formal discharge pounds on the plantground. The compartment I remedial action forms a testcase and the results will be applied for the treating device for the rest of the contaminated soil.

3.1. Hydrologic system

First infiltration was carried out with neutral water to test hydrological permeability of the soil. The permeability of the 6 m soil layer above the horizontal withdrawal drains was much lower than was measured in the topsoil. Extrapolation of the granulair composition of the different soil layers as pointed out in table 1 and application of the results of cone penetration tests indicate also higher permeability.
The inclusion of air in the pores was expected but no complete evidence could be gained. The delivery of the drainage system was between 50 and 55 m^3/h for compartment I during the remedial action.

The flow direction of the groundwater was observed by 6 shallow piezometers around the pound and 7 deep piezometers in the pound. The deep piezometers have filters at the depth of 5, 10 and 15 m below surface.

During the remedial action of compartment I only slight changes in flow direction have taken place. The system was adjustable to change the flow in the good direction.

3.2. Desorption of cadmium

The Cd-concentration of the influent (percolate) and effluent of the first resin filter are represented in figure 9.
In figure 10 the cumulative quantity of Cd removed is outlined as well as the pH of the percolate.
In the begin of August after the soil was saturated the percolated water beared higher Cd-concentration than was measured during the normal unsaturated circumstances in 1985. Probably the little pores of the soil, which are not flushed under unsaturated conditions, are responsable for the additional Cd release. The course of the measured Cd concentrations in the influent is comparable with the calculated concentrations as represented in figure 4. In order to give a more complete impression of the percolate composition some data from chemical analyses of September 1 1987 are outlined in table 2.

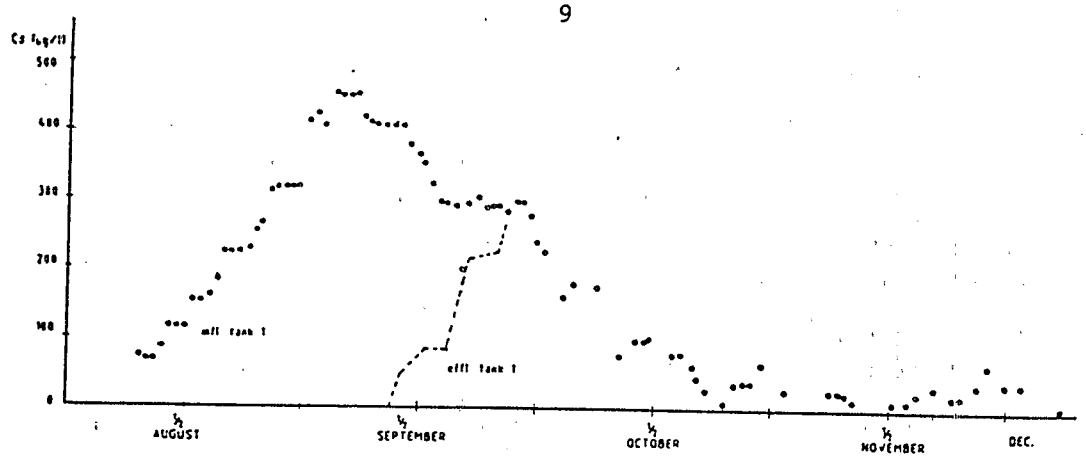

figure 9. Cd-concentration of influent (percolate) and effluent of the first resinfilter

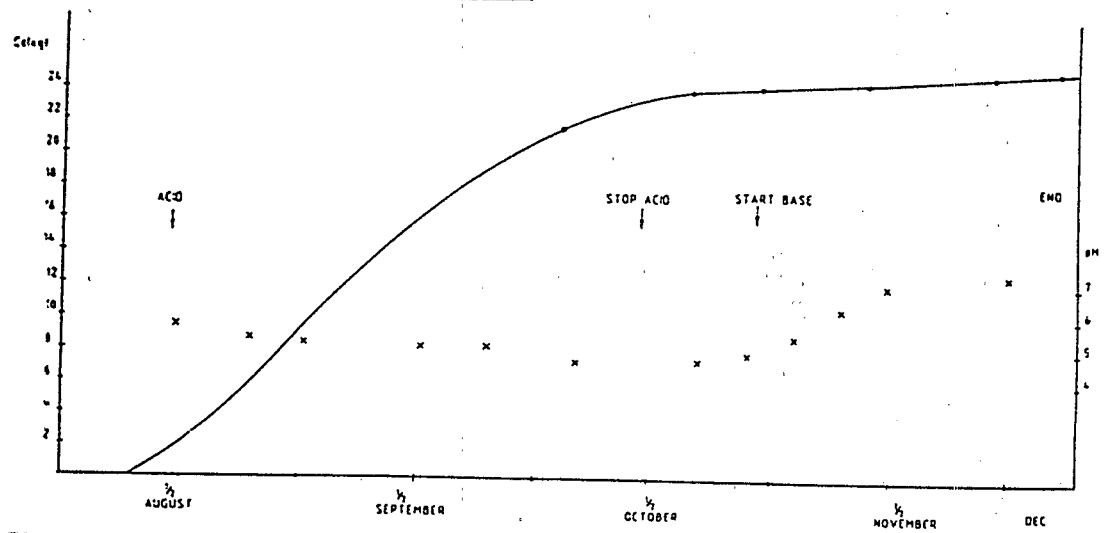

figure 10. Cumulative quantity of Cd removed and pH of the percolate

Table 2. Influent analysis, September 1

pH		5.0
E.C.	us/cm	276
Cl^-	mg/l	66
HCO_3^-	meq/l	0.09
CO_3^-	meq/l	<0.01
Cd	ug/l	440
Ca	ug/l	26000
Fe	ug/l	<15
Al	ug/l	160
Mn	ug/l	145

Table 3. Cd- and pH-values for groundwater from filters of 2 piezometers on 9th September 1987

	Piezometer I1		Piezometer I2	
filter	Cd (ug/l)	pH	Cd (ug/l)	pH
1m	16	4.1	8	3.8
2m	80	4.6	48	4.3
3m	383	4.75	2370	5.3
4m	1150	5.9	7580	5.7
5m			70	6.6

The piezometers I1 and I2 (see figure 6) with filters on 1, 2, 3, 4 and 5 m were of great value to controll and predict the process of the remedial action. In table 3 a moment survey of the Cd concentration and pH is given for the piezometers I1 and I2.
The effectiveness of the remedial action is controlled by soil analyses. The 12th October the Cd concentration in the percolate was less than 10 ug/l so acidification of the infiltrate was stopped. The 26th October neutralization of the acid soil was started with NAOH pH 8.5.
The neutralization stopped when the percolate Cd concentration of every seperate drain was not detectable (< 10 ug/l) anymore.

3.3 Water treatment system

The performance of two resin filters in series is excellent. By the end of September the first filter was totally loaded (6.7 g/l resin), while the second filter operated correctly. Due to low influent concentration the Cd load was relatively low.

The first resin regeneration pointed out a recovery of more than 98% of the adsorbed cadmium. The main metals found in this eluate are pointed out in table 4.

Table 4: Eluate composition after resin regeneration

. cadmium	2600 mg/l	. zinc	23 mg/l
. calcium	940 mg/l	. silver	15 mg/l
. aluminium	170 mg/l	. iron	12 mg/l

The conclusion can be drawn that the resin IMAC GT 73 is very selective for cadmium.

3.4 Conclusions and recommendations

The experiences with the full scale in situ remedial action of the first compartment showed that:
- the desorption of cadmium is good comparable with the laboratory studies. However neutralization takes a long time;
- the permeability of the whole soil layer is rather different from what was measured in the topsoil;
- the watertreatment system operates according to the design criteria.

Hence the remaining contaminated area, 5000 m^2, would be remediated in situ. Due to the low end values of Cd in soil for compartment I, the remedial action limit was lowered from 5 mg Cd/kg d.m. to 2,5 mg/kg dm.

The experiences of the remedial action of compartment I resulted in the following recommendations:
- enlargements of the compartment size;
- 3 m instead of 4,5 m distance between the deep horizontal withdrawal drains (5,5 m below surface);
- instale additional drains on a depth of 2.25 m below surface to accelerate the remedial action.

4. THE RESULTS OF THE REMEDIAL ACTION OF COMPARTMENTS II, III AND IV

4.2 Desorption of cadmium

The compartment configuration is outlined in figure 6. In October and November the infiltration/withdrawal of compartment IV (2000 m^2), III (1500 m^2), and II (1000 m^2) started.
From the beginning of December acid water has been supplied to the compartments.
The Cd-concentrations in the withdrawed percolate form the compartments II and III is given in the figures 11 and 13.
Concerning compartment IV two withdrawal pumps were used; at the eastside pump 2 and at the westside pump 3.
The Cd-concentrations of the pumped percolate are given in figure 15 (pump 2) and figure 17 (pump 3). The corresponding cumulative quantity Cd pumped from each compartment are shown in the figures 12, 14, 16 and 18.

Compartment IV, figures 15 and 17 indicate lower Cd concentrations than calculated (see figure 3, part I and II). Especially for the eastside of compartment IV the initial Cd concentrations without acid infiltration was quite high (figure 15).

The cumulative quantity Cd pumped from each compartment is given in table 5. While the Cd removal by the watertreatmentinstallation for the whole remedial action period was not compete, see chapter 4.3, the Cd quantity removed from the soil is less than stated in table 5.

Table 5 Cumulative quantity Cd pumped per compartment

Compartment	II	77 kg Cd
Compartment	III	154 kg Cd
Compartment	IV east	143 kg Cd
Compartment	IV west	45 kg Cd
Compartment	I	24 kg Cd
Total		443 kg Cd

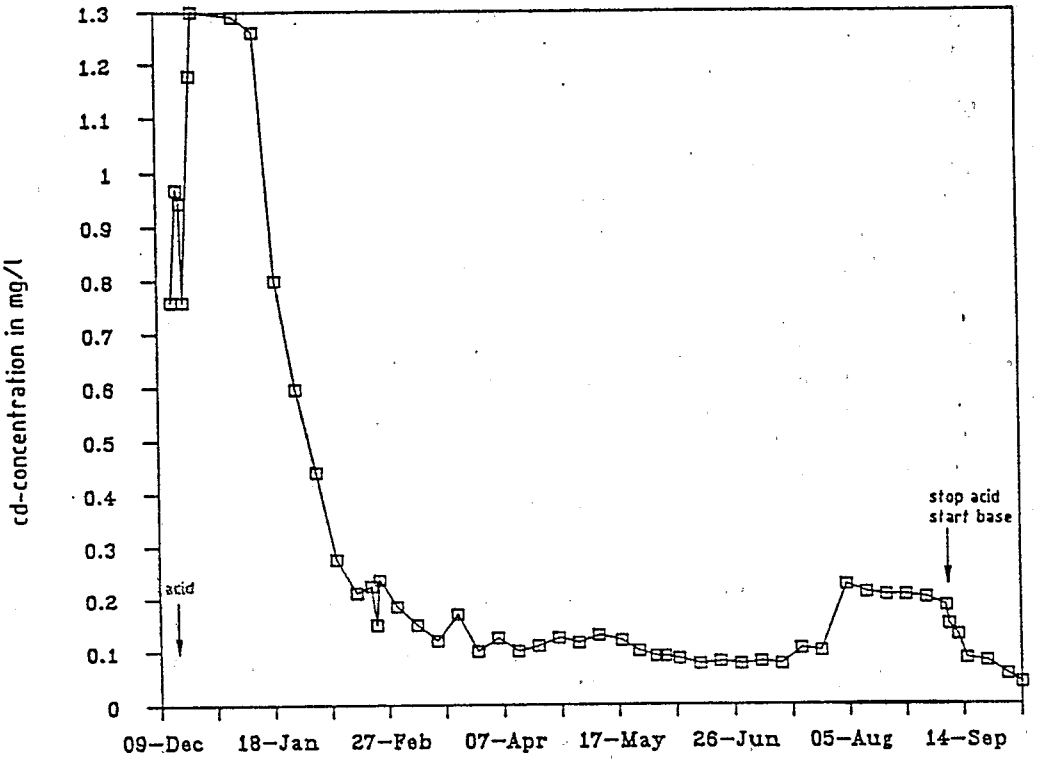

figure 11. Cd-concentration in pumped percolate of compartment II

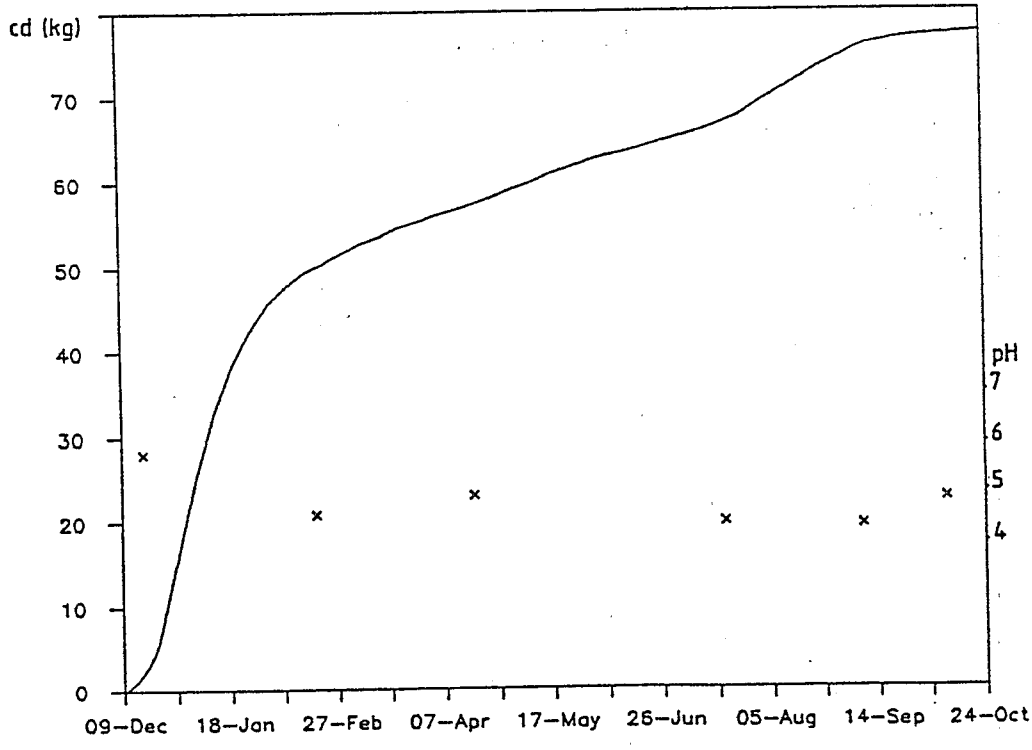

figure 12. Cumulative quantity Cd removed and pH of the percolate (compartment II)

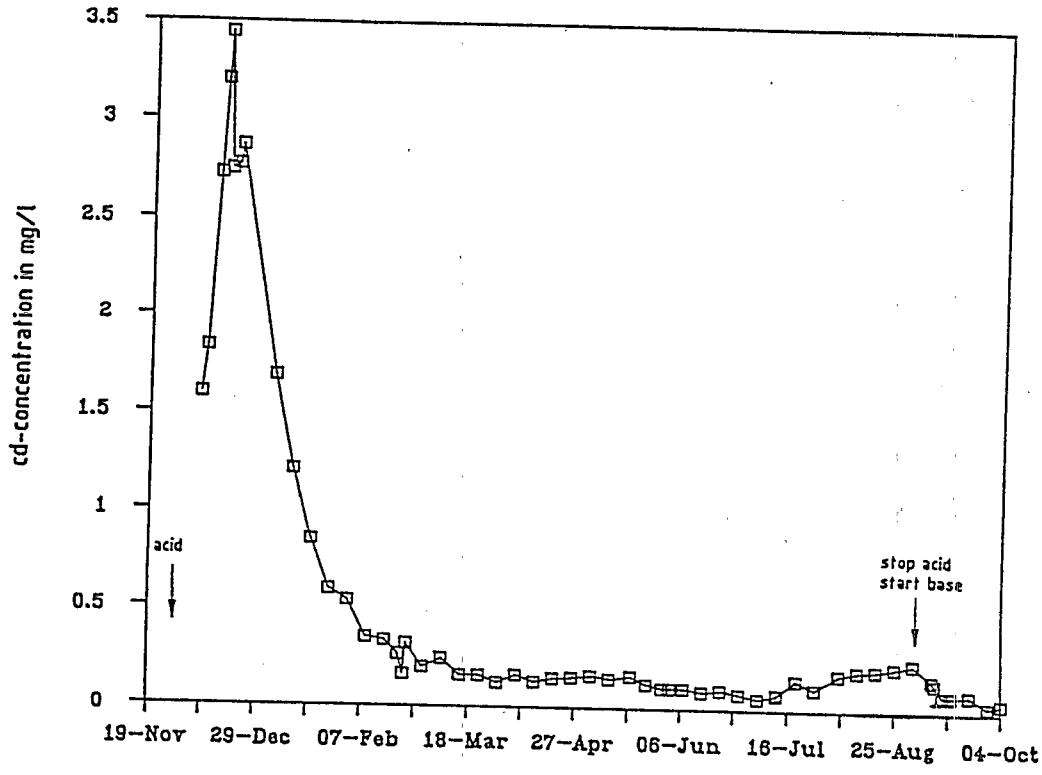

figure 13. Cd-concentration in pumped percolate of compartment III (eastside)

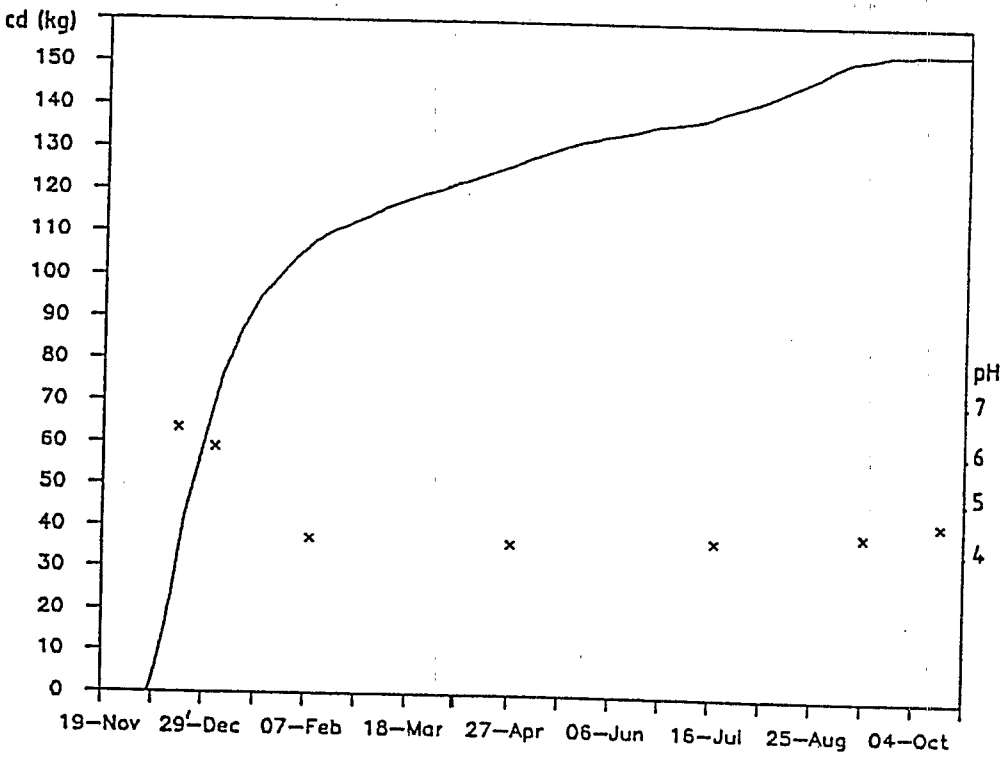

figure 14. Cumulative quantity Cd removed and pH of the percolate (compartment III)

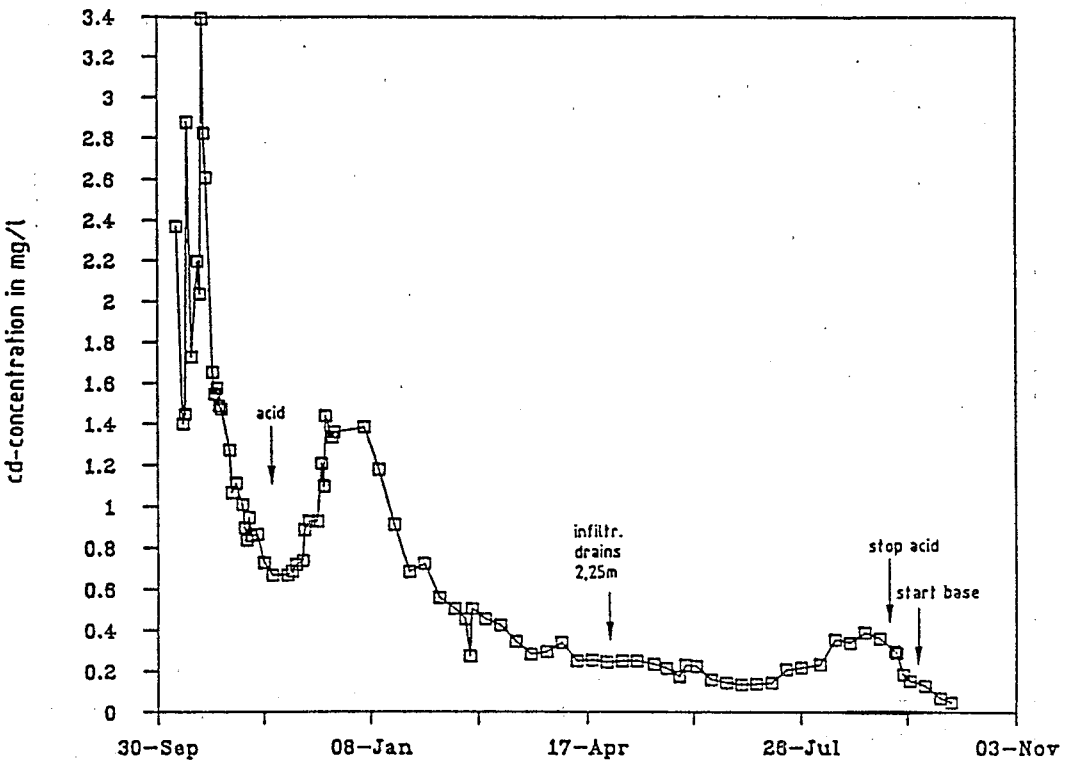

figure 15. Cd -concentration in pumped percolate of compartment IV eastside

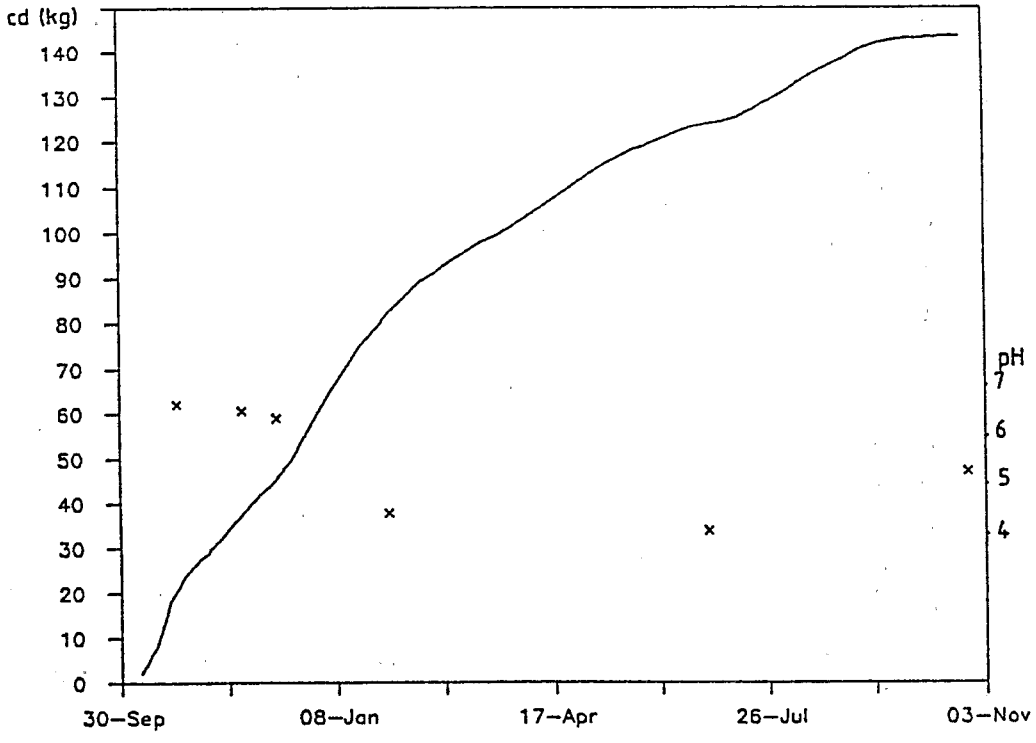

figure 16. Cumulative quantity Cd removed and pH of the percolate (compartment IV)

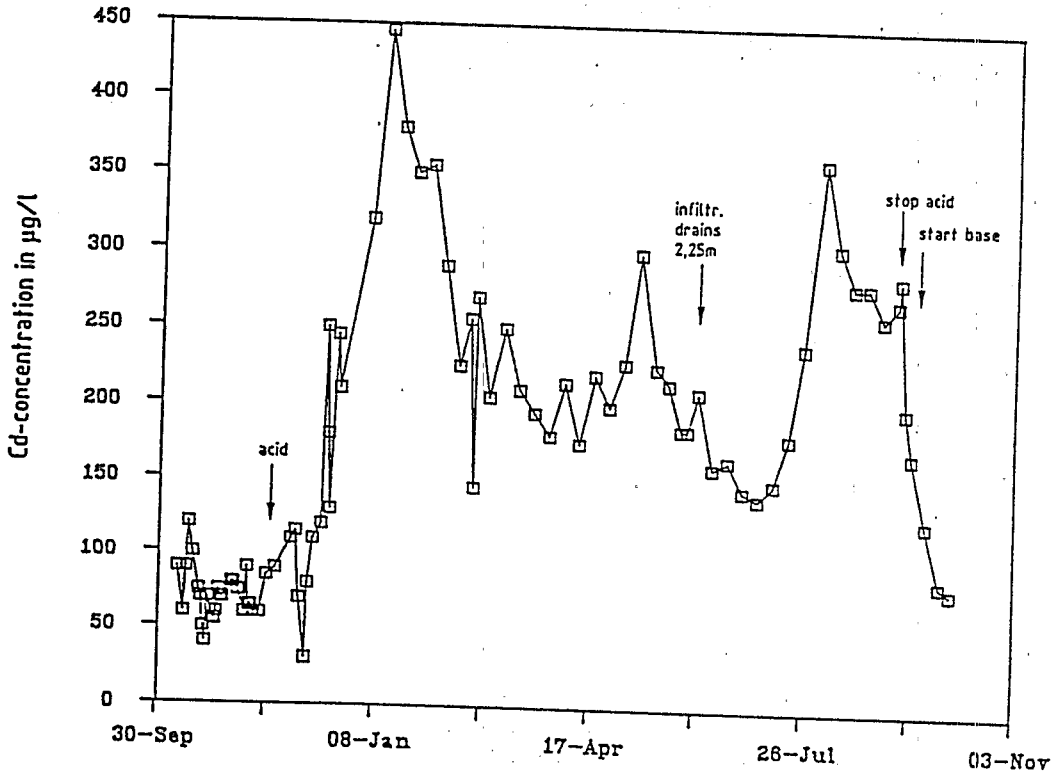

figure 17. Cd-concentration in pumped percolate of compartment IV, westside

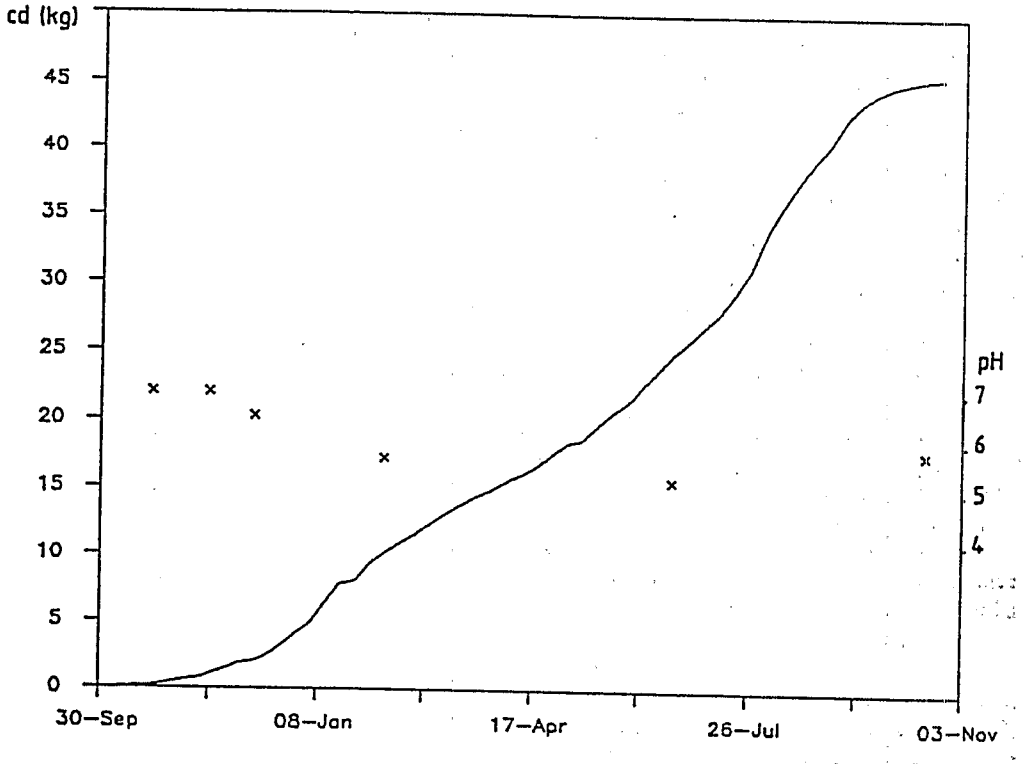

figure 18. Cummulative quantity Cd removed and pH of the percolate (compartment IV, westside)

The Cd-concentrations in the percolate water showed large differences (see for example table 3 difference of 5000 ug/l within 1 m). Figure 19 gives an impression how Cd scattered in the deep horizontal drains of compartment IV. Drain length is about 20 m.

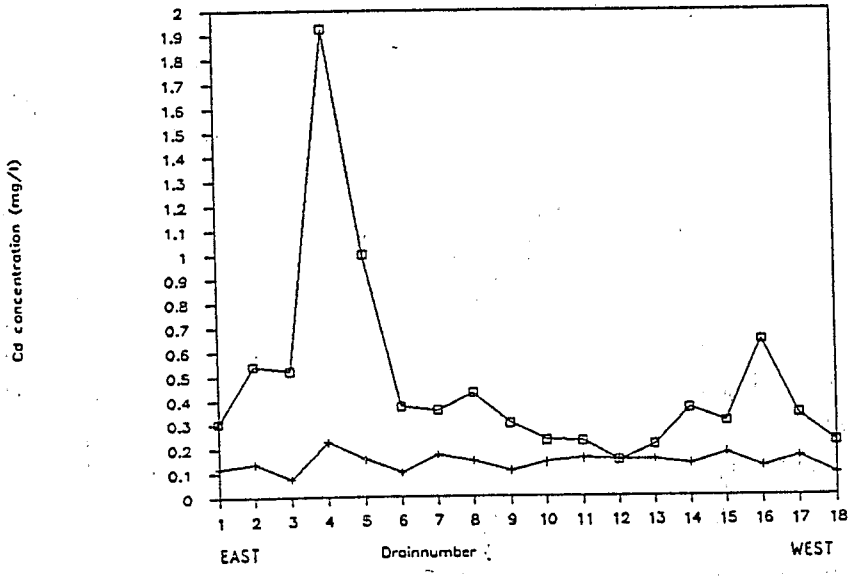

Figure 19. Cd concentrations in deep horizontal withdrawal drains compartment IV (draindistance 3 m)

The progress of the in situ remedial action is judged on the Cd concentration of soil samples. In table 6 the end values of Cd content in soil samples are given.

Table 6. The distribution of Cd-concentrations (mg Cd/kg d.m) in soil analyses

	<1	>1 and <2.5	>2.5 and <5	>5
Compartment II	39	4	2	0
Compartment III	40	1	1	0
Compartment IV	88	6	2	3*

* The origin of the Cd contamination is probably different. The natural soil layers are disturbed by antropogenic activities; incineration stags are observed.

The latest samples of table 6 were taken in the beginning of October 1988. Hence at the end of October when infiltration stopped the remedial action goal of 2,5 mg Cd/kg dm was reached, with the exception of the 3 samples taken in this middle off compartment IV west. Further investigation are carried out to determine the origin of this immobile Cd contamination. Additional excavation of the small area is probably the most suitable remediation technique.

4.2 Hydrologic system

The start up procedure took, as in compartment I quite a long time. In all compartments the escape of air could be observed. The maintenance of the desired discharge flow rate was difficult, mostly the discharge was too low.

The low permeability of the soil is due to the high resistance of a rather thin soil layer. The infiltration increased by making use of the infiltration drains on 2.25 below surface. Especially in the heavily contaminated area of compartment IV, the shallow drains are used succesfully.
The withdrawal capacities for the compartments were:

compartment I	25-50 m^3/h
compartment III	20-40 m^3/h
compartment IV east	45-65 m^3/h
compartment IV west	35-40 m^3/h

The maximal withdrawal flow was approximately 200 m^3/h, and the average flow was about 145 m^3/h. The discharge flow was only 8,3% of the infiltration water flow.

In table 7 the calculated infiltration capacity of the different compartments is stressed. During the first period discharge took place in compartment I, and for the second period the sewer was used.

Table 7. Infiltration capacity during 2 periods

compartment	period 1 dec.-may	period 2 may-aug.
	(m/d)	(m/d)
II	0.81	1.02
III	0.77	0.81
IV	0.60	0.91 (influence shallow drain)

In figures 20 and 21 computed infiltration/groundwater stream line patterns are presented for respectively discharge of surplus water onto compartment I or the sewer.
During discharge on compartment I (figure 20) there is a stream off of infiltrated water from compartment II. The streamline pattern showed in figure 21 indicate that discharge on the sewer is preferable. Still there is a little stream off, this must be related to the discharge quantity of 8.3% instead of 10% of the infiltrated water.
For the two periods it was calculated that 70% of the compartment areas are flushed more than 75 times.

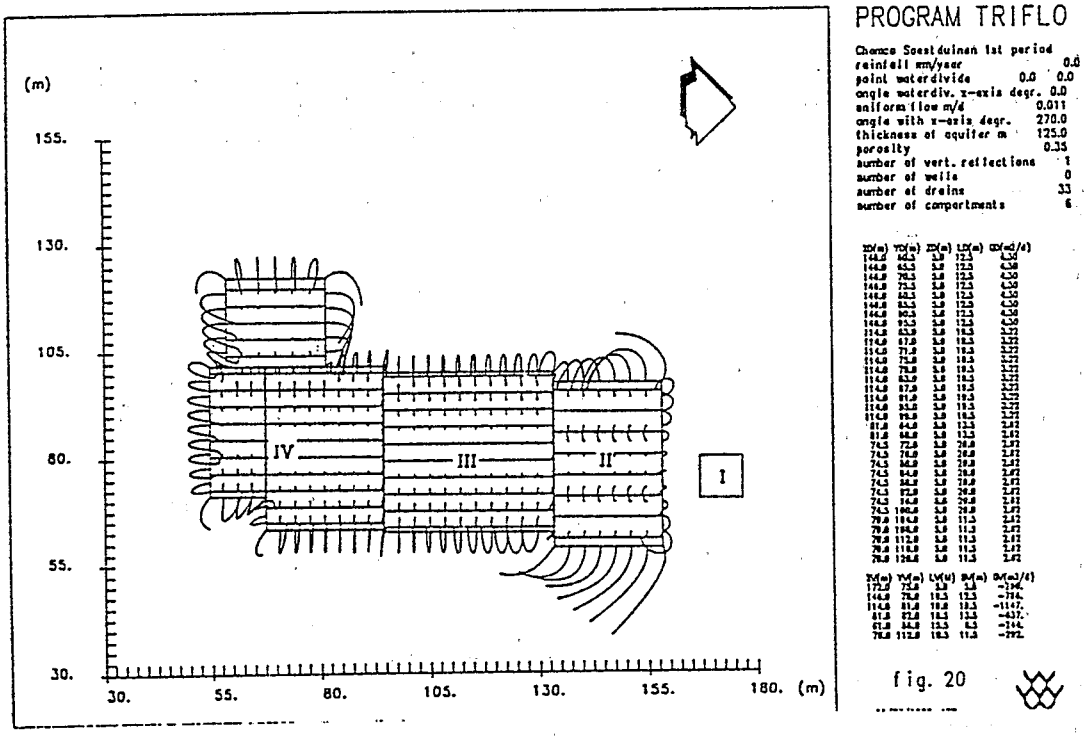

figure 20. Streamline pattern, discharge surplus water on compartment I

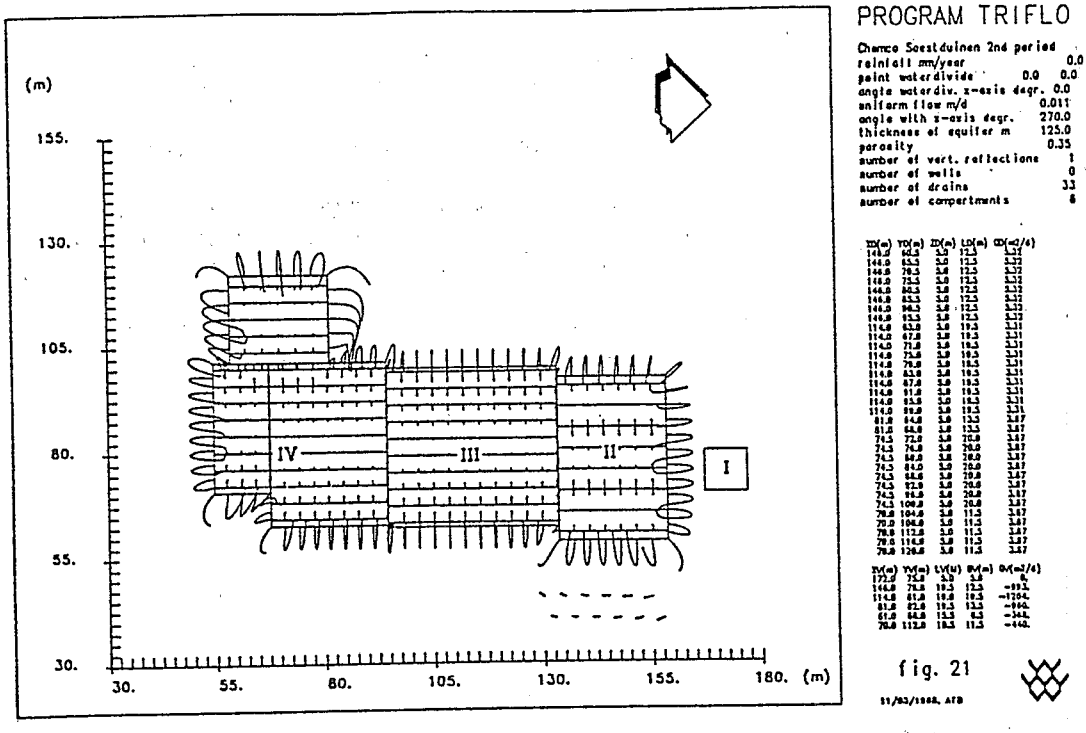

figure 21. Streamline pattern, discharge surplus water in sewer

Downstreams of the compartment (east) an additional groundwater-withdrawal system is installed to minimize the stream off. In September the system started with groundwater extraction at a flowrate of approximately 60 m^3/h, and probably it will be continued till the end of November 1988. The Cd concentration was approximately 120 ug/l in the beginning of November 1988.

4.3 Watertreatment system

-Flow

The average hydraulic loading of a resin tank was almost 24 Bedvolumes/h. The design flow was 33 Bedvolumes/h. The average influent flow rate was 143 m^3/h while the maximum measured flow rate was 206 m^3/h (27 th july 1988).

-pH-influent

The percolates from the separate compartments differed from pH and ionic composition (Al, Ca). An accurate pH adjustment was necessary to prevent flocculation in the resin tank at high pH (>5.5). While at low pH (<5.0) the Cd-adsorption of the resin decreased.

-Cd loading of the resin

The Cd loading of the resin varied between 7 to 0.5 g Cd/l resin and the disign value was 6 g Cd/l resin. No effect of hydraulic loading rate could be found on the Cd loading of the resin. To the resin only slight mechanical demage was observed, the resistance for a clean resin bed increased from 0.3 till 0.5 bar. Although humic acid substances are adsorbed to the resin no significant effect on Cd loading of the resin was found during normal operation.

-Removal efficiency

Under "normal" circumstances the Cd-concentration of the discharge flow is <1 ug/l and for the recirculation water (infiltration water) < 10 ug/l. The average removal efficiency can be estimated 96%. During two periods the performance of the watertreatment installation was poor. From 25th of December 1987 till January 1988 the pH of the influent was 4 instead of 5 as shown on the pH meter display. Hence the necessary pH adjustment of the influent did not take place. High Cd influent concentrations caused short hold out times for the resin tanks in that period.
In the period 4th of Augustus till 6th of September 1988 the steady increase of Al- and Ca-concentrations in the influent together with low Cd-concentration resulted in low Cd-loading of the resin. In table 8 four influent-analyses are shown.

Table 8. Cation concentrations of the influent (percolate)

Cation	date		
	5 jan '88	21 june '88	9 aug. '88
Cd (ug/l)	1550	125	310
Cu (ug/l)	3	3	20
Ni (ug/l)	10	10	40
Zn (ug/l)	720	360	1400
Ca (ug/l)	135000	96000	160000
Ag (ug/l)			20
Al (ug/l)	1450	840	7600
Fe (ug/l)	15	15	
pH (ug/l)	5	5.2	

At start of the neutralization of compartment II and III Al and Ca concentrations dropped strongly due to flocculation.

Taking the two above mentioned periods of poor removal efficiency in account the average removal efficiency drops from 96% to 88%. The total amount of Cd removed from the influent is 385 kg. The pumped cumulative quantity Cd should be around 440 kg, as mentioned in 4.2.

-Regeneration of the resin
The regeneration caused less trouble. The applied air hold down procedure worked out well. Additional regeneration in laboratory experiments with a NaOH/NACl mixture and with cyanide had only slight influence on the Cd adsorption.

Conclusions

Desorption of cadmium
* the Cd desorption from the soil was almost complete; 90% of the soil samples gave Cd values of 1mg/kg d.m;
* the desorption of Cd is good comparable with the laboratory studies especially the column leaching experiments;
* approximately 400 kg Cd is removed from the soil;
* change of soil pH took quite a long time.

Hydrologic system
* start up took a long time due to air inclusion in the soil;
* the permeability of the soil layer was rather low, not withstanding the greater part middle to course sand present in the soil;
* the hydrological system reacts slowly to flowrate changes. The discharge flow was mostly too low according to the design criteria.

Water treatment system
* the watertreatment system operated according to the design criteria;
* for proper operation special attention has to be given to influent pH, and Ca-, Al-concentration in the influent.

Application

* The remedial action continued the whole winterperiod, 1987-1988. Temperatures of less than minus 10 C cause no difficulties. The water treatment plant was roofed and kept free of frost.

Costs

* The total costs of the in situ remedial action are comparable with the estimated costs.
* The resin will be sold after this remedial action. The commercial value is quite high.

Recommendation

* Apply more in situ remedial actions for the extraction of contaminants from the soil;
* laboratory experiments can reasonably predict the full scale soil desorption performance of the contaminant;
* additional attention should be given to the hydrological charactaristics of the contaminated site.

From the carried out in situ remedial action it is clear that several specialists are required viz. hydrologists, environmental engineers, watertreatment engineers and soil scientists. To make in situ treatment a success they have to co-operate very close.

november 1988

Appendix 5-F

Physical/Chemical Extraction Technology Case Studies

Debris Washing, United States

The attached article has been used by permission of Air and Waste Management Association, Pittsburgh, PA. A full report of this study has been issued by U.S. Environmental Protection Agency: EPA 540/5-91/006a "Technology Evaluation Report: Design and Development of a Pilot-Scale Debris Decontamination System."

Development and Demonstration of a Pilot-Scale Debris Washing System

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Metallic, masonry, and other solid debris that may be contaminated with hazardous chemicals litter numerous hazardous waste sites in the United States. Polychlorinated biphenyls (PCBs), pesticides, lead or other metals are some of the contaminants of concern. In some cases, cleanup standards have been established (e.g., 10 μg PCBs/100 cm² for surfaces to which humans may be frequently exposed). Decontaminated debris could be either returned to the site as "clean" fill or, in the case of metallic debris, sold to a metal smelter.

This project involves the development and demonstration of a technology specifically for performing on-site decontamination of debris. Both bench-scale and pilot-scale versions of a debris washing system (DWS) have been designed, constructed, and demonstrated. The DWS entails the application of an aqueous solution during a high-pressure spray cycle, followed by turbulent wash and rinse cycles. The aqueous cleaning solution is recovered and reconditioned for reuse concurrently with the debris-cleaning process, which minimizes the quantity of process water required to clean the debris.

More than 1,200 sites are included on the U.S. EPA's National Priority List (NPL), and numerous other sites have been proposed for inclusion. Many hazardous waste sites contain toxic organic and/or inorganic chemical residues which are intermingled with remnants of razed structures (wood, steel, concrete block, bricks) as well as contaminated soil, gravel, concrete, and metallic debris (e.g., machinery and equipment, transformer casings, and miscellaneous scrap metal). Decontamination of these materials is important in preventing contamination offsite and in facilitating debris disposal in an environmentally safe manner. Since the majority of contaminated debris at Superfund and other hazardous waste sites has no potential for reuse, the purpose of a debris decontamination system would be to decontaminate the material sufficiently to permit its return to the site as "clean" fill or to allow its disposal as a non-hazardous rather than a hazardous waste.

After hazardous waste sites suitable for demonstration of the on-site DWS technology were located and evaluated, two versions were developed; the Experimental Debris Decontamination Module (EDDM) and the DWS. The EDDM was demonstrated at a Region V Superfund site and the DWS at two Region IV Superfund sites, under the Innovative portion of the EPA SITE Program which includes EPA-developed technologies.

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Study Objectives

The design goal for the DWS was to produce a transportable, hydromechanical, self-contained cleaning system consisting of an enclosure for washing debris (with an aqueous cleaning solution) and a closed-looped cleaning solution purification system. An aqueous cleaning solution was deliberately sought rather than a cleaning system which utilizes an organic solvent. Organic solvents tend to be more costly, more difficult to handle, and are often perceived (if not actually so) to be more toxic than aqueous cleaning solutions. Field-testing of the system at actual hazardous waste sites and with various contaminants was the primary objective.

Development and demonstration of a system that achieves these objectives has proceeded as follows:

(1) Bench-scale testing of a 10 gallon "off-the-shelf" debris washing system.
(2) Design, development, and field trial of a pilot-scale, 300 gallon, EDDM system at the Carter Industrial Site, Detroit, Michigan.
(3) Additional bench-scale testing of a 20 gallon version of the EDDM, to identify the most effective wash solutions.
(4) Design, fabrication, and preliminary testing of a transportable DWS demonstration unit that could be field-ready in all weather conditions.
(5) Demonstration of the DWS to decontaminate PCB-contaminated transformers at the Gray Superfund site, Hopkinsville, Kentucky.
(6) Treatment of process water used during cleaning operation to allowable discharge levels.

TABLE 1. SUMMARY OF RESULTS FOR OIL/GREASE AND TOTAL SUSPENDED SOLIDS ANALYSIS

Experimental Run No.	Sample Type[a]	Analysis	Cleaning Solution			
			Water	Sulfuric Acid Conc. 10%, wt./vol.	BB-100 Conc. 15%, v/v	Power Clean Conc. 1:6 Ratio
1	Cleaning solution	Oil and grease, mg/liter	42	161	7	1670
2	Cleaning solution	Oil and grease, mg/liter	151	143	182	1470
3	Cleaning solution	Oil and grease, mg/liter	241	138	319	2440
1	Cleaning solution	Total suspended solids, mg/liter	5	128	600	206
2	Cleaning solution	Total suspended solids, mg/liter	7	255	904	576
3	Cleaning solution	Total suspended solids, mg/liter	15	146	1000	484
1	Wipe No. 1	Oil and grease, mg/cm^2	1.77	1.48	0.32	0.50
1	Wipe No. 2	Oil and grease, mg/cm^2	1.82	1.75	0.25	0.49
2	Wipe No. 1	Oil and grease, mg/cm^2	10.54	0.7	0.15	0.43
2	Wipe No. 2	Oil and grease, mg/cm^2	4.40	4.8	0.42	0.48
3	Wipe No. 1	Oil and grease, mg/cm^2	2.43	3.81	0.26	0.34
3	Wipe No. 2	Oil and grease, mg/cm^2	NA[b]	3.27	0.33	0.61
Total of 1, 2, & 3	Oil from skimmer	Oil and grease, mg/liter	NA	1540	3380	3900

[a] All samples are posttreatment samples.
[b] Not Analyzed.

(7) Demonstration with herbicide (Dicamba) and benzonitrile contaminated drums at the Shaver's Farm Superfund site, Chickamauga, Georgia.
(8) Design, fabrication and shakedown of the full-scale DWS followed by field tests at selected Superfund sites.

Bench-Scale Tests

The bench-scale version of a Turbo-Washer (Bowden Industries) served as the debris washer for initial studies. Experiments were performed in a 10 gallon hydromechanical cleaning unit which incorporated an axial flow pump, propeller shaft, propeller, pressure chamber (all housed in a heated tank with a rotating disc for removing oil), and a cleaning solution reservoir. Measured (the same weight was added to each piece) quantities of used motor oil, grease, and soil were applied to rusted iron parts to simulate the kind of grime that is likely to be encountered on oily, PCB-contaminated metal parts and debris in the field.

Four cleaning solutions—(1) tap water, (2) 10 percent sulfuric acid solution, and (3 & 4) aqueous dilutions of two proprietary detergents [BB-100 (Bowden Industries) and Power Clean (Penetone Corporation)] were evaluated. Three tests were performed with each cleaning solution. The oil and grease contaminated metal parts were used for each test. For consistency, each set of contaminated parts was matched closely in size, shape, and type of metal. The parts were arranged similarly in the washer basket and lowered into the heated tank where they were exposed to the turbulent cleaning solution for 30 minutes.

At the completion of each test, the cleaning solution was analyzed for oil and grease and total suspended solids. Two surface wipe samples from selected metal parts were analyzed for oil and grease to determine the level remaining on the metal surfaces after treatment in the parts washer.

Results of the oil/grease and total suspended solids analyses are summarized in Table 1. Analytical results obtained for the wipe samples indicated that relatively large amounts of oil and grease remained on the metal surfaces after cleaning with water or sulfuric acid. Clearly more oil/grease was removed after cleaning with BB-100 and Power Clean. Moreover, handling 10 percent sulfuric acid was difficult, and had a corroding effect on the hydromechanical cleaning equipment. Water and sulfuric acid were eliminated as potential cleaning solutions for oily PCB-contaminated debris. Based on the results of surface wipe testing listed in Table 1, the BB-100 solution was judged to be a better cleaning solution than the Power Clean solution.

Pilot-Scale Field Tests at Carter Industrial Site

A 300 gallon-capacity pilot scale system, the EDDM, was designed, assembled, installed (on a 48-foot semitrailer) and tested at the Carter Industrial Superfund Site in Detroit, Michigan. The process flow diagram for the sys-

TABLE 2. CONCENTRATION OF PCBs FOUND IN SURFACE WIPES AND BLANKS (µg/100cm^2)

Batch Number	Sample Number	Pretreatment	Posttreatment	% Reduction
1	1	134	50	63
	2	490	178	64
	3	1280	856	33
	4	73	43	41
	5	203	23	87
		Field Blank: <1.0		Avg. 58
2	1	8.0	13.0	63
	2	6090	1800	70
	3	374	128	66
	4	96	10	90
	5	1690	18	99
		Field Blank: 1.0		Avg. 81

tem is illustrated in Figure 1. Two 200-lb. batches of metallic debris were cleaned with the system. BB-100 surfactant solution was used as the cleaning agent. Before cleaning, five individual pieces of metal from each batch were sampled for PCBs by a surface wipe technique in which hexane-soaked cotton gauze pads were used to wipe a 100 cm^2 area on the surface of the object being sampled.[1] The metal items in Batch 1 were then placed in a basket, transferred to the EDDM, and cleaned for two hours. In Batch 2, the metallic debris was rearranged after one hour, then cleaned for an additional hour. A portion of the cleaning solution in the Turbo-Washer was pumped through a closed-looped particulate filter into the oil/water separator. The effluent from the oil/water separator was recycled into the module. After the cleaning process, five additional wipe samples were taken from the same pieces of metallic debris, at a location directly adjacent to that of the pretreatment samples, to determine the post decontamination PCB levels.

The quantity of PCBs on each metal surface before and after cleaning is summarized in Table 2. The average percentage reduction of PCBs was 58 percent for Batch 1 with a range from 33–87 percent. Batch 2 had a range from 66–99 percent and an average reduction of 81 percent. Better cleaning results for Batch 2 may be the result of removing the debris basket from the EDDM after one hour and manually rearranging the debris so that all sides of the debris were exposed to the cleaning solution with the same force of the Turbo-Washer. It was then placed back into the washer for the second hour. In Batch 1 the cleaning process was for two hours without disturbing debris placement.

The surfactant solution in the Turbo-Washer was sampled once during each of the two cleaning operations. PCB values were 420 and 928 μg/L. After the debris experiment, the cleaning solution was pumped through a series of particulate filters and activated carbon. The PCB concentration of the surfactant solution was reduced to 5.4 μg/L following this treatment. The cleaning solution was passed through the activated carbon a second time and the PCB level was reduced to less than 1.0 μg/L. Subsequently, under the direct supervision of EPA's On-Scene Coordinator for the site, the water was discharged to the PCB-contaminated soil located on site.

Bench-Scale Testing of Surfactant

Based on experience gained during the Carter site field test, a bench-scale (20 gallon surfactant solution capacity) hydromechanical cleaning apparatus was designed, constructed, and assembled. This system consisted of a spray tank, ash tank, oil-water separator, and ancillary equipment (i.e., heater, pumps, strainers, metal tray, etc.). Development of a bench-scale DWS allowed assessment of the system's ability to remove contaminants from debris and to facilitate selection of the most efficient surfactant solution.

A survey of surfactant products identified five nonionic surfactants (BG-5, MC-2000, LF-330, BB-100, and L-422) for an experimental evaluation to determine their capacity to solubilize and remove contaminants from the debris surface. Unlike anionic and cationic surfactants, nonionic surfactants perform adequately during moderate pH changes and in the presence of electrolytes.*

Prior to each bench-scale experiment, six pieces of debris, including three rusted metal plates, a brick, a concrete block and a piece of plastic, were "contaminated" by dipping each piece into a spiking material consisting of a known amount of used motor oil, grease, topsoil, and sand. The pieces of contaminated debris were then arranged on a metal tray, inserted in the spray tank and subjected to a high-pressure spray of surfactant solution for 15 minutes. At the end of the spray cycle, the tray was transferred to the high turbulence wash tank, where the debris was washed for 30 minutes with a solution of the same surfactant as that in the spray tank. After the wash cycle was completed, the tray was removed from the wash tank and the debris was allowed to air-dry.

Before and after treatment with surfactant solutions, surface wipe samples were obtained from the six pieces of debris. These wipe samples were analyzed for oil and grease. The results are summarized in Table 3. Based on the results of the wipe testing, L-422 was selected as the surfactant best suited for cleaning oily metal parts and debris.

To evaluate the ability of the bench-scale system to remove specific contaminants from debris, DDT, lindane, PCB and lead sulfate were mixed into the spiking material. The six pieces of debris were spiked with this mixture, then washed using L-422. Three trials were performed. Surface wipe samples from debris from the first two trials were analyzed for PCB, lindane, and DDT. The surface wipe samples from the third trial were analyzed for total lead.

The average overall percentage reduction of PCBs and pesticides achieved during Trials 1 and 2 were greater than 99 and 98 percent, respectively. The overall percentage reduction of lead was greater than 98 percent. The results are summarized in Tables 4 through 6. It is recognized that actual debris, especially porous material such as concrete blocks or bricks, is often permeated by PCB-containing oils. Testing of these surrogate materials, while important, is not necessarily representative of a worst case scenario, although testing did provide

* Manufacturers of these surfactants are: BB-100, Bowden Industries, Huntsville, AL; BG-5, Modern Chemical, Jacksonville, AR; MC-2000, Alcolac, Baltimore, MD; LF-330, GAF Chemicals Corporation, Wayne, NJ; and L-422, DuBois Chemicals, Cincinnati, OH.

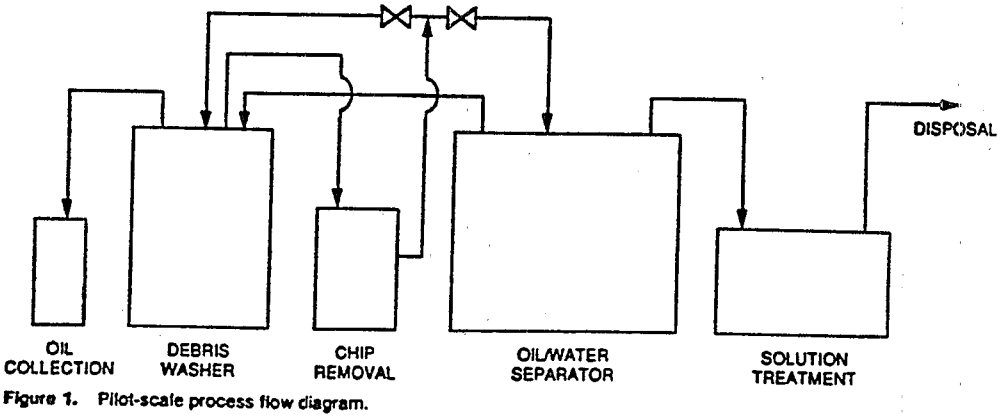

Figure 1. Pilot-scale process flow diagram.

TABLE 3. A COMPARISON OF THE CLEANING CAPABILITIES OF SURFACTANT SOLUTIONS BASED ON REMOVAL OF OIL AND GREASE

	Sample ID Number	Pretreatment (g/100 cm²)	Posttreatment (g/100 cm²)	Percent Change	Avg. Percent Change
BG-5	C1-1-6/20	6.7131	0.0071	99.89	99.82
	C2-1-6/20	5.2936	0.0171	99.68	
	C3-1-6/20	5.5088	0.0111	99.80	
	C4-1-6/20	5.4138	0.0060	99.89	
	C5-1-6/20	4.7310	0.0074	99.84	
	C6-1-6/20	5.4689	0.0107	99.80	
MC-2000	C1-2-6/22	4.1462	0.0313	99.25	99.62
	C2-2-6/22	4.0274	0.0155	99.61	
	C3-2-6/22	4.0025	0.0322	99.19	
	C4-2-6/22	6.7795	0.0057	99.91	
	C5-2-6/22	7.3356	0.0162	99.78	
	C6-2-6/22	4.2899	0.0144	99.66	
LF-330	C1-5-6/30	5.2878	0.0686	98.70	98.74
	C2-5-6/30	5.0433	0.0878	98.26	
	C3-5-6/30	5.8143	0.0811	98.61	
	C4-5-6/30	6.0277	0.0533	99.11	
	C5-5-6/30	4.1388	0.0262	99.37	
	C6-5-6/30	4.1278	0.0667	98.38	
BB-100	C1-6-6/30	4.5929	0.0221	99.52	98.64
	C2-6-6/30	4.9409	0.0349	99.29	
	C3-6-6/30	5.3973	0.1315	97.56	
	C4-6-6/30	4.9976	0.1498	97.00	
	C5-6-6/30	3.9820	0.0067	99.83	
	C6-6-6/30	4.9440	0.0477	99.03	
L-42	C1-7-7/6	5.1850	0.0017	99.97	99.96
	C2-7-7/6	4.8263	0.0028	99.94	
	C3-7-7/6	5.1807	0.0011	99.98	
	C4-7-7/6	5.6047	0.0023	99.96	
	C5-7-7/6	5.0469	0.0015	99.97	
	C6-7-7/6	4.7127	0.0019	99.96	

TABLE 4. SUMMARY OF BENCH-SCALE RESULTS OF CONTROLLED DEBRIS ANALYZED FOR PCBs AND PESTICIDES (TRIAL 1)

	Contaminant	Pretreatment (µg/100 cm²)	Posttreatment[a] (µg/100 cm²)	Percent Reduction	Average Performance
Metal	Lindane	13,800	0.75	99.99	≥99.87
	4, 4' DDD	1010	3.8 U	≥99.62	
	4, 4' DDT	6710	5.0 U	≥99.93	
	PCB-1260	3550	2.0 U	≥99.94	
	Lindane	12,500	0.7	99.99	
	4, 4' DDD	1020	3.8 U	≥99.63	
	4, 4' DDT	7610	5.67	99.93	
	PCB-1260	3230	2.0 U	≥99.94	
	Lindane	12,300	0.7	99.99	
	4, 4' DDD	1020	3.8 U	≥99.63	
	4, 4' DDT	7600	5.0 U	≥99.93	
	PCB-1260	2990	2.0 U	≥99.93	
Brick	Lindane	14,600	5.8	99.96	≥98.88
	4, 4' DDD	1220	3.8 U	≥99.69	
	4, 4' DDT	7840	11.6	99.85	
	PCB-1260	2570	20.3	99.21	
	Lindane	12,900	130	98.99	
	4, 4' DDD	1170	4.9	99.58	
	4, 4' DDT	10,100	360	96.43	
	PCB-1260	3360	90.4	97.31	
Concrete Block	Lindane	14,000	11.1	99.92	≥99.72
	4, 4' DDD	1240	3.8 U	≥99.69	
	4, 4' DDT	10,200	28.3	99.72	
	PCB-1260	3410	15.3	99.55	
Plastic	Lindane	9370	1.1	99.99	≥99.62
	4, 4' DDD	952	3.8 U	≥99.60	
	4, 4' DDT	7120	12.6	99.82	
	PCB-1260	2500	23.4	99.06	
				Average Overall Performance	≥99.39

[a]U indicates that the target compound was not detected at this level.

data that indicated the cleaning process was efficacious for removing contaminants from the surface of the debris. Whether or not removal of surface contamination is sufficient for a particular situation would depend on clean-up guidelines.

After the completion of the bench-scale debris washing experiments, the cleaning solution was neutralized to a pH of 8 and then pumped through a series of particulate filters and finally through activated carbon. During this treatment, the PCB, lindane, and DDT concentrations were reduced to <2.0, 0.03, and 0.33 μg/L, respectively. The concentration of lead was reduced to 0.2 mg/L after treatment. During this process, it was noticed that a gel-like precipitate was formed when the L-422 cleaning solution was neutralized, which quickly plugged the particulate filters and had the potential of clogging the activated-carbon drums. As a result, BG-5, which performed almost as well as L-422 in removing oil and grease and formed only a fine precipitate when neutralized, was selected as the surfactant to be used for the subsequent pilot-scale DWS study.

Design, Fabrication, and Initial Testing of the Pilot-Scale DWS

Based on results obtained from bench-scale studies, a transportable, pilot-scale debris washing system was designed and constructed. The pilot-scale system consists of a 300-gallon spray tank; a 300-gallon wash tank; a surfactant holding tank; a rinse water holding tank; an oil/water separator; and a solution-treatment system with a diatomaceous earth filter, an activated carbon column, and an ion-exchange column. Ancillary equipment includes a spray tank heater, pumps, particulate filters, a metal basket, and a stirrer motor. The process flow diagram for the DWS is illustrated in Figure 2.

The pilot-scale system was assembled in a Cincinnati, Ohio warehouse. Several tests were conducted using pieces of oil/grease-coated objects found in the warehouse. Surface wipe samples were obtained before and after washing in the pilot-scale system and analyzed for oil and grease. In three trials using five objects in each trial, oil and grease removed ranged from 19 to 91 percent and averaged 76 percent. The warehouse testing also involved optimization of several test parameters, including spray and wash cycle durations, and cleaning solution temperature. Based on these results and a visual inspection of the washed debris, the system was judged to be effective in removing oil and grease from the surface of these objects.

TABLE 5. SUMMARY OF BENCH-SCALE RESULTS OF CONTROLLED DEBRIS ANALYZED FOR PCBs AND PESTICIDES (TRIAL 2)

	Contaminant	Pretreatment (μg/100 cm²)	Posttreatment[a] (μg/100 cm²)	Percent Reduction	Average Performance
Metal	Lindane	11,800	0.13 U	100	≥99.91
	4, 4' DDT	9320	2.32	99.97	
	PCB-1260	1770	2.0 U	≥99.89	
Metal	Lindane	8180	0.31 U	100	
	4, 4' DDT	7540	4.8	99.94	
	PCB-1260	1780	2.79	99.84	
Metal	Lindane	6150	0.41	99.99	
	4, 4' DDT	5840	2.61	99.95	
	PCB-1260	1450	2.0 U	≥99.86	
Brick	Lindane	5810	3.49	99.94	99.80
	4, 4' DDT	5660	10.5	99.81	
	PCB-1260	1220	4.1	99.66	
Concrete Block	Lindane	6440	397	93.83	94.39
	4, 4' DDT	6610	389	94.11	
	PCB-1260	1390	66.1	95.24	
Plastic	Lindane	10,300	52	99.49	98.22
	4, 4' DDT	8400	223	97.34	
	PCB-1260	1620	35	97.84	
			Average Overall Performance		≥98.08

[a]U indicates that the target compound was not detected at this level.

Demonstration at the Gray PCB Site

The Ned Gray Superfund site was selected for the first demonstration of the upgraded pilot-scale debris washing system. The twenty-five acre site is located in Hopkinsville, Kentucky. From 1968 to 1987, a metal reclaiming facility which conducted open burning of electrical transformers to recover copper for resale was operated at the site. Soil, where the transformers were burned, was contaminated with lead and PCBs. The demonstration took place during December 1989. Ambient temperatures were at or below freezing during the entire operation.

Subsequent to the warehouse testing, the system was disassembled and loaded onto a 48-foot semitrailer. The system and the ancillary equipment was transported to the Gray PCB site. The entire system was reassembled on a 25 ft × 25 ft concrete pad that was

TABLE 6. SUMMARY OF BENCH-SCALE RESULTS OF CONTROLLED DEBRIS ANALYZED FOR LEAD (TRIAL 3)

	Contaminant	Pretreatment (μg/100 cm²)	Posttreatment (μg/100 cm²)	Percent Reduction	Average Performance
Metal	Lead	876	6.0	99.31	>99.06
Metal	Lead	414	6.0	98.55	
Metal	Lead	450	<3.0	>99.33	
Brick	Lead	508	<3.0	>99.41	>99.34
Concrete Block	Lead	414	<3.0	>99.27	
Plastic	Lead	446	<3.0	>99.33	
			Average Performance on All Materials Tested		>99.20

poured on site prior to the arrival of the equipment. A temporary enclosure was also built on the concrete pad (approximately 25 ft. high) to enclose the system and to protect it and the surfactant solution from rain and cold weather.

Before initiation of the cleaning process, 75 transformer casings, with sizes ranging from 5 to 100 gallons, were cut in half with a partner saw. Pretreatment samples were obtained from one half of each of the transformer casings by using the surface wipe technique previously described.[1]

The transformer halves were placed in the wash basket and lowered into the spray tank, equipped with multiple water jets that blast loosely adhered contaminants and dirt from the debris. After the spray cycle, the basket was removed and transferred to the wash tank, where the debris was washed with a high-turbulence wash. Each batch of debris was cleaned for a period of 1 hour in the spray tank and 1 hour in the wash tank. During both the spray and wash cycles, a portion of the cleaning solution was cycled through a closed-loop system where the oil/PCB-contaminated cleaning solution was passed through an oil/water separator, and the cleaned solution was then recycled. After the wash cycle, the debris

TABLE 7. RESULTS OBTAINED DURING FIELD DEMONSTRATION OF DWS AT GRAY PCB SITE

Batch Number	Average PCB Concentration on Surfaces (µg/100 cm²)				Average Percentage Removed
	Before Cleaning		After Cleaning		
	Average	Range	Average	Range	
1	19.7 (N[a] = 10)	<0.1 – 94.0	1.5 (N = 10)	<0.1 – 9.7	92
2	9.9 (N = 6)	4.8 – 17.0	1.5 (N = 6)	<0.1 – 4.7	85
3	6.6 (N = 4)	5.0 – 9.9	1.4 (N = 4)	<0.1 – 3.3	79
4	4.1 (N = 6)	<0.1 – 12.0	0.8 (N = 6)	<0.1 – 4.1	80
5	4.0 (N = 8)	<0.1 – 28.0	<0.1 (N = 8)	<0.1 – <0.1	>98
6	2.0 (N = 4)	<0.1 – 7.8	2.9 (N = 4)	<0.1 – 10.0	b
7	2.8 (N = 2)	1.4 – 4.3	3.9 (N = 2)	<0.1 – 7.7	b
8	23.5 (N = 5)	<0.1 – 70.0	1.3 (N = 5)	<0.1 – 3.8	94
9	8.3 (N = 4)	2.9 – 23.0	3.1 (N = 4)	1.5 – 4.9	63
10	5.2 (N = 4)	<0.1 – 9.7	1.9 (N = 4)	<0.1 – 2.8	63
11	9.4 (N = 4)	<0.1 – 17.0	3.0 (N = 4)	<0.1 – 9.5	67
12	48.8 (N = 4)	2.3 – 98.0	1.1 (N = 4)	<0.1 – 3.2	98
13	12.3 (N = 2)	9.6 – 15.0	5.1 (N = 2)	<0.1 – 10.0	59
14	16.7 (N = 2)	8.7 – 25.0	<0.1 (N = 2)	<0.1 – <0.1	>99
15	18.5 (N = 4)	8.1 – 27.0	<0.1 (N = 4)	<0.1 – <0.1	>99
16	11.3 (N = 2)	8.6 – 14.0	2.0 (N = 2)	1.5 – 2.5	82
17	24.8 (N = 4)	1.1 – 80.0	2.2 (N = 4)	<0.1 – 8.4	91
18	8.4 (N = 5)	<0.1 – 19.0	3.4 (N = 5)	<0.1 – 7.4	60
19	8.3 (N = 4)	<0.1 – 18.0	3.2 (N = 4)	<0.1 – 5.3	61
20	24.0 (N = 3)	13.0 – 45.0	3.3 (N = 3)	<0.1 – 9.8	86
21	18.6 (N = 8)	<0.1 – 44.0	0.4 (N = 8)	<0.1 – 2.1	98
22	25.0 (N = 4)	12.0 – 35.0	<0.1 (N = 4)	<0.1 – <0.1	>99
23	8.6 (N = 4)	1.5 – 18.0	<0.1 (N = 4)	<0.1 – <0.1	>99
24	6.8 (N = 8)	<0.1 – 31.0	0.3 (N = 8)	<0.1 – 1.4	96

[a] N indicates the number of samples.

[b] The distribution of PCB contamination on the surfaces of these transformers is obviously not uniform and therefore in some cases a meaningful comparison of post-treatment PCB levels with pre-treatment levels cannot be achieved.

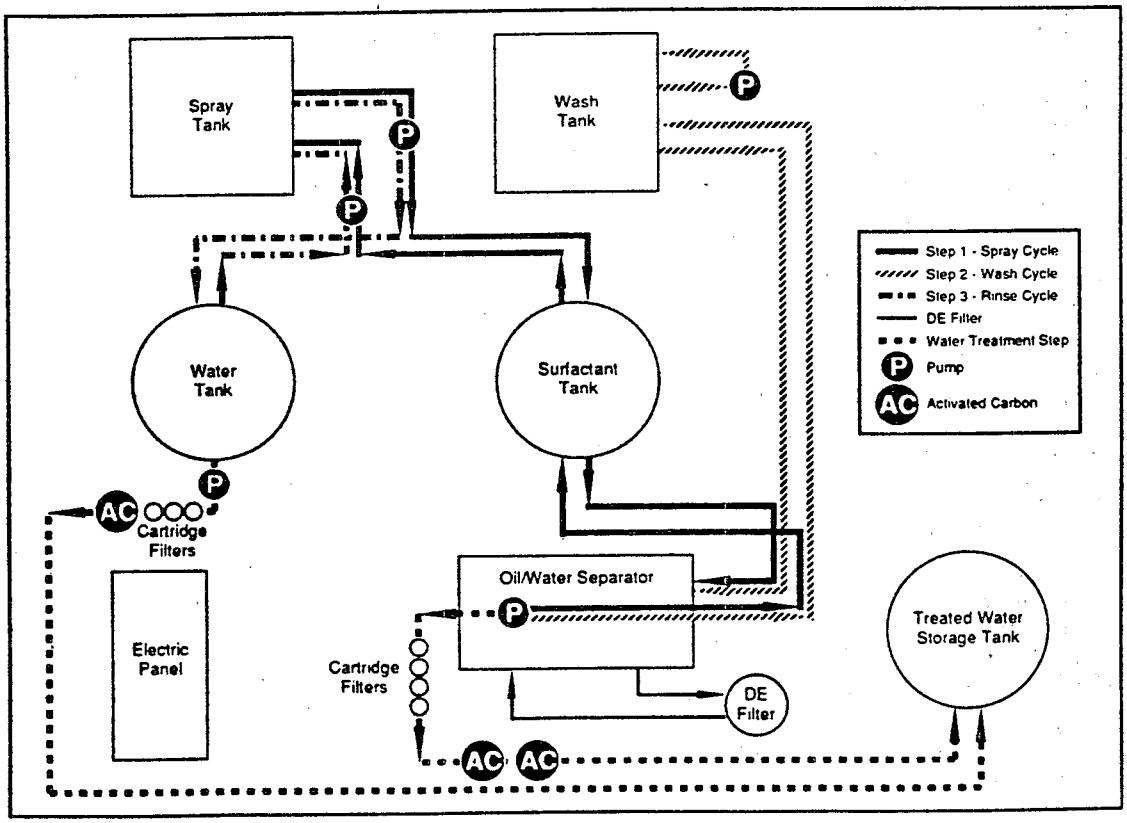

Figure 2. Schematic of pilot-scale debris washing system.

TABLE 8. RESULTS OF SURFACE WIPE SAMPLES ANALYZED FOR BENZONITRILE, 2,4-DICHLOROPHENOL, 2,6-DICHLOROPHENOL, 1,2,4-TRICHLOROBENZENE ($\mu g/100 cm^2$)

Batch Number	Sample Number	Benzonitrile		2,4-Dichlorophenol		2,6-Dichlorophenol		1,2,4-Trichlorobenzene	
		Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment
1	1	180[a] (50)	ND[b]	ND (50)	ND	ND (50)	ND	ND (50)	ND
	2	130[a] (50)	ND	ND (50)	ND	ND (50)	ND	ND (50)	ND
2	1	125	117	34	ND	ND	ND	ND	ND
	2	90	7.8[a] (5)	43	ND	ND	ND	ND	ND
3	1	43	ND	ND	16[a] (5)	ND	ND	ND	ND
	2	28	ND	ND	14[a] (5)	ND	ND	ND	ND
4	1	4400	ND	NA[c]	NA	NA	NA	NA	NA
	2	2700	ND	NA	NA	NA	NA	NA	NA
5	1	47000	10[a] (5)	ND	ND	ND	ND	ND	ND
	2	22000	7.9[a] (5)	ND	ND	ND	ND	ND	ND
6	1	10[a] (5)	ND	ND	ND	ND	ND	ND	ND
	2	8[a] (5)	ND	ND	ND	ND	ND	ND	ND
7	1	200	ND	ND	ND	ND	ND	ND	ND
	2	320	10[a] (5)	ND	ND	ND	ND	ND	ND
8	1	1400	28	ND	ND	ND	ND	ND	ND
9	1	3000	ND	ND	ND	ND	ND	ND	ND
	2	3500	7[a] (5)	ND	ND	ND	ND	ND	ND
10	1	22[a] (5)	ND	ND	ND	ND	ND	ND	ND
	2	1400	ND	ND	ND	ND	ND	ND	ND

[a] Estimated result less than 5 times detection limit.
[b] None detected in excess of the minimum detectable concentration of 5 $\mu g/100 cm^2$ unless otherwise specified in parenthesis.
[c] Not analyzed.

basket was returned to the spray tank, where it was rinsed with water.

After completion of the cleaning process, posttreatment wipe samples were obtained from each of the transformer pieces to assess the post-decontamination levels of PCBs.[2] All Superfund site activities described in this document were governed by EPA approved Health and Safety and Quality Assurance Plans.[3,4] In the case of the metallic debris sampled in this study, the posttreatment wipe sample was obtained from a location adjacent to the location of the pretreatment sample. This was necessary because wiping the surface removes the contamination and if one were to wipe the same surface after cleanup, the results obtained would be biased low.

The average concentrations of PCBs on the internal surfaces of the transformer casings before and after cleaning are summarized in Table 7. Concentrations before treatment ranged from 0.1 to 98 $\mu g/100 cm^2$. Posttreatment analyses showed that all but seven of the transformers that were cleaned had a PCB concentration less than the acceptable level of 10 $\mu g/100 cm^2$. The seven transformers with a concentration greater than the acceptable level were rewashed in the DWS, and posttreatment samples were obtained and analyzed. The concentration of PCBs in these seven samples after the second wash was below the detection limit of 0.1 $\mu g/100 cm^2$.

Treatment of the Process Water

After all transformers at the site were decontaminated, the surfactant solution (BG-5) and the rinse water were neutralized to a pH of about 8,

TABLE 9. RESULTS OF METAL STRIP SAMPLES ANALYZED FOR BENZONITRILE, 2,4-DICHLOROPHENOL, 2,6-DICHLOROPHENOL, 1,2,4-TRICHLOROBENZENE ($\mu g/g$)

Batch Number	Sample Number	Benzonitrile		2,4-Dichlorophenol		2,6-Dichlorophenol		1,2,4-Trichlorobenzene	
		Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment
1	1	4.9	0.89	0.33[a] (0.33)	ND[b] (0.15)	ND (0.15)	ND (0.15)	ND (0.15)	ND (0.15)
2	1	5.4[a] (1.2)	0.31[a] (0.12)	5.0[a] (1.2)	ND (0.12)	ND (1.2)	ND (0.12)	ND (1.2)	ND (0.15)
3	1	ND (0.15)	ND (0.10)	26	1.9	ND (0.15)	ND (0.10)	ND (0.15)	ND (0.10)
4	1	ND	ND	NA[c]	NA	NA	NA	NA	NA
5	1	190	0.6[a] (0.22)	ND (0.28)	ND (0.22)	ND (0.28)	ND (0.22)	ND (0.28)	ND (0.22)
6	1	1.0	ND (0.08)	ND (0.085)	ND (0.08)	ND (0.085)	ND (0.08)	0.13[a] (0.085)	ND (0.080)
7	1	140	0.28[a] (0.16)	ND (0.19)	ND (0.16)	ND (0.19)	ND (0.16)	ND (0.19)	ND (0.16)
8	1	16	0.41[a] (0.15)	ND (0.14)	ND (0.15)	ND (0.14)	ND (0.15)	ND (0.14)	ND (0.15)
9	1	61	0.81[a] (0.17)	ND (0.10)	ND (0.17)	ND (0.10)	ND (0.17)	ND (0.10)	ND (0.17)
10	1	ND (1.2)	ND (0.11)	ND (0.12)	ND (0.11)	ND (0.12)	ND (0.11)	ND (0.12)	ND (0.11)

[a] Estimated result less than 5 times detection limit. Detection limits are indicated in parenthesis.
[b] None detected at specified detection limit.
[c] Not analyzed.

TABLE 10. RESULTS OF SURFACE WIPE SAMPLES ANALYZED FOR DICAMBA, 2,4-D, 2,4,5-T ($\mu g/100cm^2$)

Batch Number	Sample Number	Dicamba		2,4-D		2,4,5-T	
		Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment
4	1	1.9	0.63[a] (0.27)	ND[b]	ND	ND	ND
	2	3.4	ND	NA[c]	NA	NA	NA
5	1	ND	ND	ND	ND	ND	ND
	2	ND	2.6	ND	ND	ND	ND
6	1	ND (2.7)	ND	ND (12)	ND	ND (2.0)	ND
	2	ND (2.7)	ND (2.7)	ND (12)	ND (12)	ND (2.0)	ND (2.0)
7	1	7.3[a] (2.7)	1.8	ND	ND	ND	ND
	2	15	2.3	ND (12)	ND	ND (2.0)	ND
8	1	55	5.7[a] (2.7)	ND (12)	ND (12)	ND (2.0)	ND (2.0)
	2	13	0.62[a] (0.27)	ND	ND	ND	ND
9	1	1.7	0.63[a] (0.27)	ND	ND	ND	ND
	2	ND (2.7)	ND	ND (12)	ND	ND (2.0)	ND
10	1	41	0.30[a] (0.27)	ND (12)	ND	ND (2.0)	ND
	2	180	0.34[a] (0.27)	ND (12)	ND	ND (2.0)	ND

[a] Estimated result less than 5 times detection limit. Detection limits are indicated in parenthesis.
[b] None detected in excess of minimum detectable concentration of Dicamba at 0.27; 2,4-D at 1.2; and 2,4,5-T at 0.20 unless otherwise specified.
[c] Not analyzed.

TABLE 11. RESULTS OF METAL STRIP SAMPLES ANALYZED FOR DICAMBA, 2,4-D, AND 2,4,5-T ($\mu g/g$)

Batch Number	Sample Number	Dicamba		2,4-D		2,4,5-T	
		Pretreatment	Posttreatment	Pretreatment	Posttreatment	Pretreatment	Posttreatment
2	1	0.37	0.030[a] (0.0097)	ND[b] (0.34)	ND (0.043)	ND (0.0056)	ND (0.0072)
3	1	82	13	ND (0.36)	ND (0.38)	ND (0.060)	ND (0.064)
4	1	0.057	0.020[a] (0.0065)	ND (0.029)	ND (0.029)	ND (0.0048)	ND (0.0048)
6	1	25	ND (0.059)	ND (0.26)	ND (0.26)	ND (0.044)	ND (0.044)
7	1	2.3	0.023[a] (0.062)	ND (0.50)	ND (0.28)	ND (0.084)	ND (0.046)
9	1	2.3	0.11	ND (0.32)	ND (0.040)	ND (0.054)	ND (0.0066)
10	1	0.40	0.017[a] (0.0062)	ND (0.24)	ND (0.028)	ND (0.040)	ND (0.0046)

[a] Estimated result less than 5 times detection limit. Detection limits are indicated in parenthesis.
[b] None detected at specified detection limit.

TABLE 12. RESULTS OF METAL STRIP SAMPLES ANALYZED FOR DIOXINS AND FURANS (ng/g)

Analyses	Sample Number 1		Sample Number 2	
	Pretreatment	Posttreatment	Pretreatment	Posttreatment
HpCDD	1.2	ND[b] (0.30)	ND (0.22)	ND (0.31)
HpCDF	ND (0.16)	ND (0.23)	ND (0.17)	ND (0.23)
HxCDD	2.8	ND (0.24)	ND (0.18)	0.71[a] (0.27)
HxCDF	ND (0.12)	ND (0.11)	ND (0.11)	ND (0.17)
OCDD	4.1	ND (0.66)	1.6[a] (0.45)	5.5
OCDF	ND (0.19)	ND (0.36)	ND (0.22)	ND (0.34)
PeCDD	ND (0.11)	ND (0.14)	ND (0 10)	ND (0.16)
PeCDF	ND (0.066)	ND (0.085)	ND (0.065)	ND (0.092)
TCDD	ND (0.10)	ND (0.13)	ND (0.10)	ND (0.15)
2,3,7,8-TCDD	ND (0.10)	ND (0.13)	ND (0.10)	ND (0.15)
TCDF	ND (0.062)	ND (0.079)	ND (0.065)	ND (0.089)

[a] Estimated result less than 5 times detection limit.
[b] Not detected at specified detection limit. Detection limits are indicated in parenthesis.

using concentrated sulfuric acid. The neutralized surfactant solution and rinse water was treated by passing it through a series of particulate filters, an activated-carbon drum, and finally through an ion-exchange column. The treated water was stored in a 1000-gallon polyethylene tank pending analysis. The before- and after-treatment water samples were collected and analyzed for PCBs and selected metals (cadmium, copper, chromium, lead, nickel, and arsenic).

The PCB concentration in the water was reduced to below the detection limit of 0.1 μg/L. Concentrations of five of the six metals were reduced to the allowable discharge levels set by the City of Hopkinsville. Arsenic remained above the allowable level. After receipt of the analytical results for the water, the treated water, which was stored in the holding tank, was pumped into a plastic-covered, 10,000 cubic yard pile of contaminated soil at the site. An incision of about ¾ inch was made into the plastic covering at the top of the soil pile, and a rubber hose was inserted into the incision. After all of the water was pumped into the contaminated soil, the hose was pulled out and the incision was covered with tape.

Equipment was decontaminated with a high-pressure wash. Wash water generated during the decontamination process was collected and treated in the water treatment system. The DWS and the enclosure was disassembled, loaded into the semitrailer and transported to Cincinnati.

During this site cleanup, 75 PCB-contaminated transformer casings (approximately 5000 lb) were cleaned. A total of 1000 gallons of process water (surfactant solution and rinse water) was utilized in this demonstration. Additional waste generated included three activated-carbon drums and four miscellaneous drums containing safety gear, solids, and plastic. All of the transformers are now considered clean and could be sold to a scrap metal dealer or to a smelter for reuse.

Demonstration at the Shaver's Farm Drum Disposal Site

A second demonstration of the DWS was conducted at the Shaver's Farm drum disposal site in Walker County, Georgia. Fifty-five gallon drums containing varying amounts of a herbicide, Dicamba (2-methoxy-3,6-dichlorobenzoic acid), and benzonitrile, a precursor in the manufacture of Dicamba, were buried on this 5-acre site. An estimated 12,000 drums containing solid and liquid residues from the manufacture of Dicamba are thought to have been buried here from August 1973 to January 1974. EPA Region IV had excavated more than 4000 drums from one location on the site when this demonstration occurred in August 1990.

The pilot-scale system was transported to this site on a 48-foot semitrailer and assembled on a 24 ft. × 24 ft. concrete pad. The temporary enclosure, used previously at the Gray site, was reassembled to protect the equipment from rain. Ambient temperature at the site during the demonstration ranged from 75 to 105 degrees Fahrenheit.

Fifty-five gallon, pesticide-contaminated drums were cut into four sections. Pretreatment surface-wipe samples were obtained from each section and two metal strips (approximately 6 cm by 3 cm) were taken from one of the sections with a nibble. The latter were analyzed in an attempt to obtain data which would corroborate surface-wipe test results and to determine if contaminants were imbedded in the metallic surfaces. The drum pieces were placed in the spray tank of the DWS for one hour of surfactant spraying, then placed in the wash tank for an additional hour of surfactant washing, followed by 30 minutes of water rinsing in the spray tank. The drum pieces were then allowed to air-dry prior to obtaining the posttreatment surface-wipe and metal strip samples. Ten batches of one to two drums per batch were treated during this demonstration.

Data in Tables 8 to 12 provide an indication of the effectiveness of the DWS technology for removing pesticide and related contaminants (other than PCBs) from the surfaces of excavated drums. Pretreatment concentrations of benzonitrile in surface wipe samples ranged from 8 to 47,000 μg/100 cm^2 (average: 4556 μg/100 cm^2) while post treatment samples averaged 10 μg/100 cm^2 with a range from below the detection limit to 117 μg/100 cm^2. Pretreatment Dicamba values averaged 23 μg/100 cm^2 (range: below detection limit to 180 μg/100 cm^2) while posttreatment concentrations ranged from below detection limit to 5.2 μg/100 cm^2 and averaged 1 μg/100 cm^2.

Conclusions

Field-test results obtained using the upgraded pilot-scale DWS in demonstrations at two Region IV Superfund sites showed the unit to be both transportable and rugged. Extreme high and low temperatures had little effect on the operation of the equipment. The system was successfully used to remove PCBs from transformer casing surfaces and certain pesticides, dioxins and furan residues from drum surfaces. While the system has not been proven effective for removal of all types of organic contaminants from surfaces of debris, results obtained to date are considered promising.

The cleaning solution was recovered, reconditioned and reused during the actual debris-cleaning process which minimized the quantity of process water required for the decontamination procedure. The water treatment system was effective in reducing contaminant concentrations, with the exception of arsenic and Dicamba, to below the detection limit.

Planned progression of this U.S. EPA-developed technology includes design, development, and demonstration of a full-scale, transportable version of the DWS unit. Commercialization of the technology will be handled by IT Environmental Programs, Inc. (formerly PEI Associates, Inc.)

Acknowledgments

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Appendix 6-A

Ground Water Pump and Treat Technology Case Studies

Decontamination of Ville Mercier Aquifer for Toxic Organics, Ville Mercier, Quebec, Canada

ASSESSMENT OF CONTAMINATED GROUNDWATER TREATMENT AT VILLE MERCIER, QUÉBEC

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1.0 INTRODUCTION

In Canada, the first large, full scale aquifer restoration effort was initiated in Ville Mercier, Québec, by the Québec Ministry of the Environment (MENVIQ), in July 1984. Due to the nature of this large scale remediation project, a unique opportunity existed to collect and analyze operational data in order to assess the performance of the remediation effort.

Consequently, a Canadian consortium consisting of The SNC Group, the University of Sherbrooke and Laval University, was awarded, under the scientific authority of the Wastewater Technology Centre (WTC), in July 1988, a research, development and pilot demonstration contract, as a result of an unsolicited project proposal submitted to the Department of Supply and Services Canada (DSS) in June 1988, entitled "Aquifer Decontamination for Toxic Organics: The Case Study of Ville Mercier, Québec".

The aim of the study (1988-89) was to determine the impact of the existing restoration program on the rehabilitation of the aquifer and to establish the best strategy to complete the requirements of the remediation program.

The project focused on the following two (2) areas of research:

a) assessment of the hydrogeological impact of the existing restoration program on the contaminated aquifer.
b) performance evaluation of the groundwater treatment plant, and the conduct of bench and pilot scale treatability studies to improve the plant's performance. The treatment study dealt exclusively with physical chemical technologies similar to those used in the full scale groundwater treatment plant of Ville Mercier.

1.1 Historical Background[1,2,3,4]

The Ville Mercier site is located on the south shore of the St. Lawrence River, 20 km southwest of Montréal, Québec (Figure 1).

In 1968, the "Régie des Eaux du Québec", a Québec government agency, authorized an oil carrier to temporarily store oily liquid wastes, mainly from petro-chemical industries, in a former sand and gravel pit located in an esker formation near Ville Mercier, with the intention of recovering the hydrocarbons at a later date.

From 1968 to 1972, an estimated 40 000 m^3 of organic liquid wastes were stored in an abandoned pit (lagoon) located on a ridge composed mainly of sand and gravel overlying an extensive fractured dolomitic sandstone aquifer. Contaminants were soon noticed in nearby farm wells and disposal of liquid waste was discontinued. Shortly after, clean-up of the lagoon was conducted and incineration of the organic waste was performed at a liquid waste incinerator built nearby for the purpose.

Ten years after the disposal of liquid wastes had ceased, a plume of contaminated groundwater (Table 1) extending over 30 km^2 was mapped south and west of the lagoon affecting local municipal water supplies.

In 1982, studies to understand the migration of the contaminated groundwater, suggested that a pumping and treatment system, which would consist of three (3) purge wells with an operating hydraulic capacity of 0.076 m^3/s, would create a hydraulic barrier sufficient to control the progression of the contaminated plume, and restore the aquifer within a five-year period.

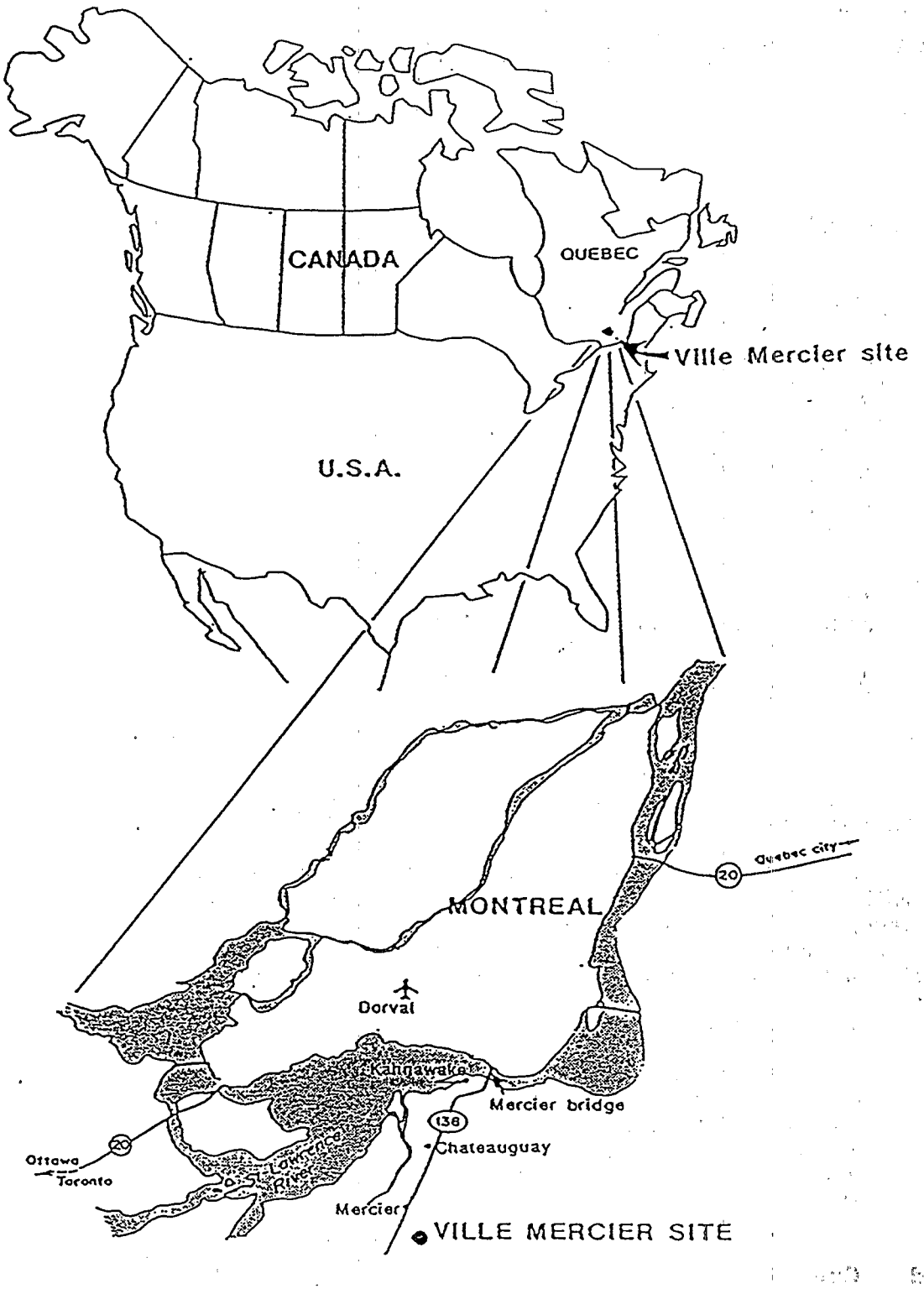

FIGURE 1 LOCATION MAP OF THE VILLE MERCIER SITE (REF 2)

TABLE 1 DETECTED GROUNDWATER CONTAMINANTS AND PLANT EFFLUENT QUALITY OBJECTIVES

Contaminant	Concentration (µg/L)			
	Minimum	Maximum	Mean	Effluent Objective
Total Phenol	167	1 000	507	2.0
1,2 Dichloroethane (1,2 DCA)	76	517	187	50
1,1,1 Trichloroethane (1,1,1 TCA)	23	326	127	33
1,1,2 Trichloroethane (1,1,2 TCA)	16	326	-	-
Trichloroethene (TCE)	19	349	114	4.5
Chloroform (CCl_3)	1	165	-	-
Chlorobenzene (-)	2	16	-	-
Trans 1,2 Dichloroethene (Trans 1,2 DCE)	6	139	-	-
PCBs: Arochlor 1242, 1254, 1260	0.01	0.08	0.05	0.01
Iron (mg/L)	0.84	12.00	8.19	0.30
Manganese (mg/L)	0.06	0.82	0.18	0.05

Based on this information, the first large scale Canadian program to remediate an aquifer was commissioned in 1983 by the MENVIQ in Ville Mercier, Québec.

The MENVIQ allocated, at the time, $5.7 million to restore the site, as follows: $3.0 million to build the treatment facility, and $2.7 million to cover its 5-year operation by The SNC Group/Hydro-Mécanique Inc. (SNC/HMI). In 1986, an additional $1.7 million supplemented the original operating cost estimate in order to continue the remediation work until July 1989. Since then (1989), the MENVIQ has assumed the responsibility for the operation of the groundwater treatment plant.

The treatment train incorporated the following physical chemical unit operations:

a) air stripping, to partially remove the volatile organics (VOCs) of concern, and to aerate the groundwater for iron and manganese oxygenation;
b) alum and polymer additions;
c) clarification and rapid sand filtration; and
d) granular activated carbon adsorption, to remove the remaining VOCs and other organics of concern.

1.2 Operational Difficulties and Modifications Implemented

The original treatment train incorporated the following elements: three groundwater purge

wells, an air stripper, a flash-mixer, a pulsating clarifier, two rapid sand filters, three activated carbon absorbers, and a sludge dewatering chamber.

During the first year of operation, serious operational difficulties were encountered. These were:

a) biological fouling throughout the plant;
b) a surge of Dense Non-Aqueous Phase Liquids (DNAPLs) in the pumped groundwater, and ensuing fouling of the treatment train;
c) excessive iron precipitation in the air stripper;
d) incomplete removal of iron;
e) substantial granular activated carbon loss during the frequent backwashes required to minimize plugging of the GAC adsorbers;
f) reduced capacity of the wells due to fouling of the strainers;
g) incompatibility of flocculating and dewatering polymers; and
h) increased load of organic contaminants in the pumped groundwater.

1.3 Existing Treatment Train

This section briefly presents the treatment train since its last modification in January 1987. It should also be noted that the remediation effort to decontaminate the aquifer has been extended by the MENVIQ beyond its 5-year program, originally scheduled to terminate in July 1989. The plant is still in operation today (January 1992).

The presently operating treatment train incorporates the following process elements: three groundwater purge wells, hydrogen peroxide addition, chlorine addition, an air stripper, a flash-mixer, chlorine dioxide addition, a pulsating clarifier, two rapid sand filters, three activated carbon adsorbers, and a sludge dewatering chamber.

The existing treatment plant's process diagram and characteristics are summarized in Figure 2 and Table 2, respectively.

2.0 FULL SCALE PLANT PERFORMANCE ASSESSMENT

SNC/HMI, was mandated by the MENVIQ to sample, on a semi-monthly basis, raw and treated groundwater. Starting in the second year of operation, sampling was extended to include selected locations along the treatment train, and in the fifth year of operation, the original list of organics to monitor was expanded. The data were collected and analyzed, and are presented in Section 2.1, entitled *"Historical Performance"*.

Two (2) full scale plant sampling monitoring campaigns (1989) were undertaken in the context of this study. The intent of these campaigns was to evaluate the impact that each unit process had on the contaminants found in the groundwater. The list of targeted contaminants was expanded, solely for the purpose of this performance evaluation. The data were subsequently analyzed, and are presented in Section 2.2, entitled *"Full Scale Plant Sampling Monitoring Campaigns"*.

2.1 Historical Performance

In order to gain a better understanding of the operation of the treatment train, and to better assess the impact of the modifications implemented to the train, the historical performance data were sub-divided into three (3) populations:

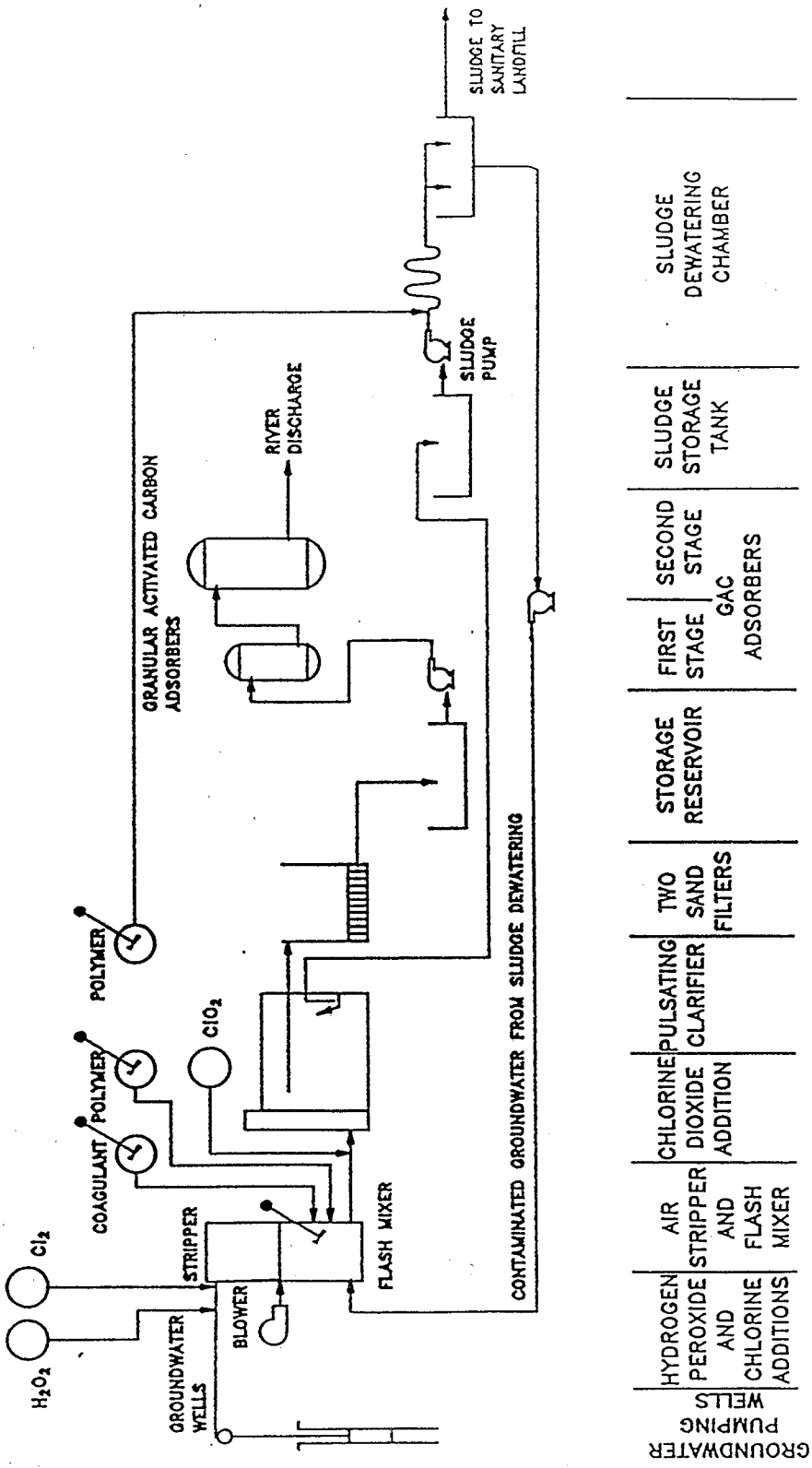

FIGURE 2 VILLE MERCIER GROUNDWATER TREATMENT PLANT PROCESS DIAGRAM

TABLE 2 VILLE MERCIER GROUNDWATER TREATMENT PLANT CHARACTERISTICS

SUBMERSIBLE PUMPS AND WELLS

Number	3
Flow Rate per Unit	0.038 m^3/s
Total Head	58 m
Motor Input Rating	30 kW

HYDROGEN PEROXIDE

On-Line Addition	11 mg/L

CHLORINE

On-Line Addition	20 mg/L

AIR STRIPPER

Packing Height	2.1 m
Diameter	2.7 m
Packing Media	Pall Rings
Packing Size	0.051 m
Stripping Air Flow Rate	2.83 m^3/s

FLASH-MIXER

Volume of Chamber	6 m^3
Alum Addition	50-85 mg/L
Aquafloc 464 Addition (Dearborn Co.)	0.7-1.2 mg/L
350 RPM Fast Mixer	

CHLORINE DIOXIDE

On-Line Addition	2.5 mg/L

PULSATING CLARIFIER

Type	Plate Type PULSATOR
Size	8.40 m X 8.05 m X 5.50 m
Vacuum Pump	
Capacity	0.035 m^3/s
Vacuum	75 mm Hg

RAPID SAND FILTERS

Number	2
Design Flow Rate (per filter)	0.038 m^3/s
Bed Surface Area	14.9 m^2
Filter Bed Media	
Effective Diameter	0.9 mm
Bed Depth	1.07 m
Filtration Rate	2.5 X 10^{-3} m/s

ACTIVATED CARBON ADSORBERS

Number	3
Media	CECA Type 1240
Mean Particle Diameter	0.9 - 1.2 mm
Sacrificial (1)	
Superficial Velocity	10.7 X 10^{-3} m/s
Design Flow Rate	0.076 m^3/s
Empty Bed Contact Time	55 s
Polishing (2)	
Superficial Velocity	5.4 X 10^{-3} m/s
Design Flow Rate	0.038 m^3/s
Total Empty Bed Contact Time	222 s

SLUDGE DEWATERING (VACUUM FILTRATION)

Number of Filter beds	2
Size	5.5 m X 12.2 m
Sludge conditioning: Aquafloc 464 Addition	(Dearborn Co.)
Treated Sludge Volume	12.5 X 10^{-4} m^3/s

OTHER CHARACTERISTICS

Power Input	3 Lines 400A - 600V
Laboratory facility	
Control system for automated operation	
Chemical feed system and storage tanks	

1. July 1984 to April 1985: this period corresponds to an evaluation of the original design of the treatment train, prior to any modifications.

2. May 1985 to December 1986: this period corresponds to an evaluation of the partially modified treatment train, following hydrogen peroxide and chlorine additions.

3. January 1987 to August 1989: this period corresponds to an evaluation of the presently operating treatment train, following the additions of hydrogen peroxide, chlorine and chlorine dioxide.

2.1.1 Data Analysis: Period 1 (1984-1985)

Due to the operational problems experienced during the plant's first operating year, a limited number of samplings (4) were conducted during this time period.

Table 3 presents the performance evaluation for the groundwater treatment plant for this period.

Figures 3 and 4 summarize the information presented, and display influent and effluent mean concentrations for iron and manganese, and total phenol and total chlorinated hydrocarbons monitored, respectively.

2.1.2 Data Analysis: Period 2 (1985-1986)

A more extensive and detailed data base, consisting of 35 samplings, and allowing the performance evaluation of the two following segments of the treatment train, is available for this time period:

a) hydrogen peroxide and chlorine additions, air stripper, pulsating clarifier, sand filters; and
b) sacrificial and polishing GAC adsorbers.

Table 4 presents the performance evaluation for the groundwater treatment plant for this period.

Figures 5 and 6 summarize the information presented, and display treatment profiles for iron and manganese, and total phenol and total chlorinated hydrocarbons monitored, respectively.

2.1.3 Data Analysis: Period 3 (1987-1989)

An even more extensive and detailed data base, consisting of 65 samplings, and allowing the performance evaluation of the following segments of the treatment train, is available for this time period:

a) hydrogen peroxide and chlorine additions; air stripper;
b) pulsating clarifier; sand filters;
c) sacrificial GAC adsorber (GAC1); and
d) polishing GAC adsorbers (GAC2).

Table 5 presents the performance evaluation for the groundwater treatment plant for this period.

TABLE 3 SUMMARY TABLE - HISTORICAL DATA PERIOD 1 (1984-1985)

PARAMETER	IRON		MANGANESE		1,2 DCA		1,1,1 TCA		TCE		TOTAL PHENOL		PCBs	
	Mean Conc (mg/L)	Mean Removal (%)	Mean Conc (mg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)
RAW	3.88	-	0.10	-	2597	-	0.4	-	61	-	394	-	<0.01	-
POST-GAC2	0.20	95	0.01	94	1476	43	0.4	0	3	96	65	84	<0.01	n.a.
MENVIQ OBJECTIVE	0.30	-	0.05	-	50	-	33	-	4.5	-	2	-	0.01	-
OBJECTIVE MET	yes		yes		no		yes		yes		no		yes	

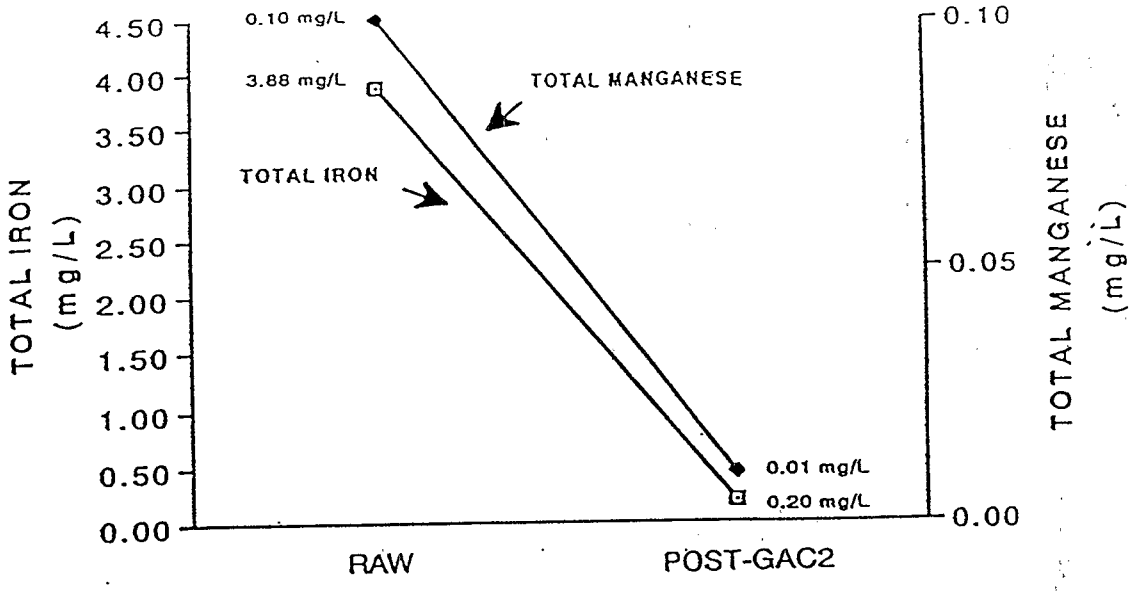

FIGURE 3 HISTORICAL DATA 1984-85: INORGANICS

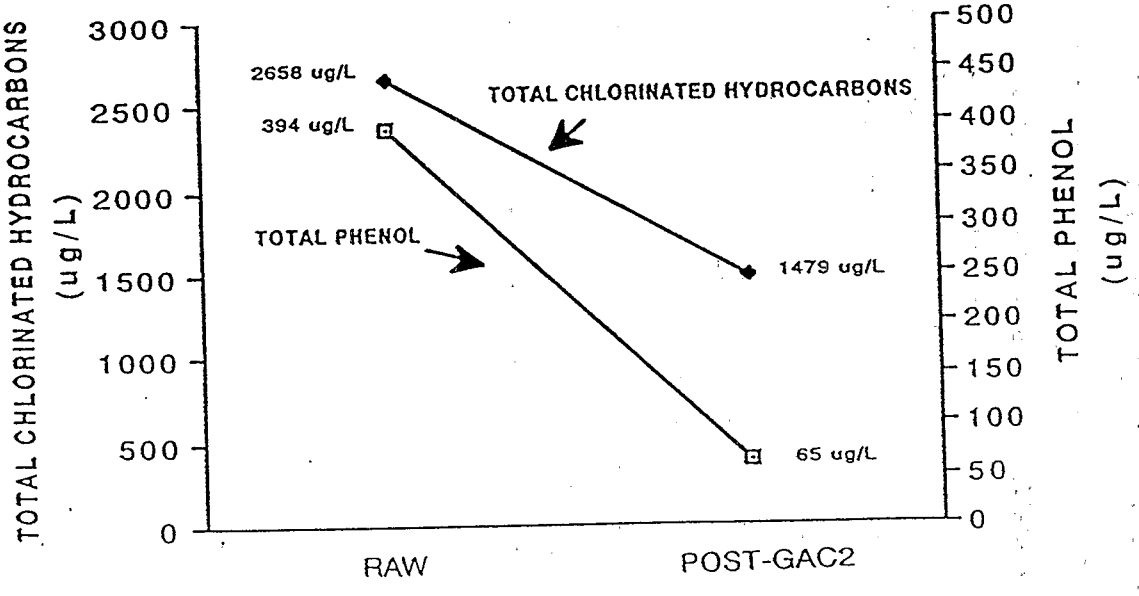

FIGURE 4 HISTORICAL DATA 1984-85: ORGANICS

TABLE 4 SUMMARY TABLE - HISTORICAL DATA PERIOD 2 (1985-1986)

PARAMETER	IRON		MANGANESE		1,2 DCA		1,1,1 TCA		TCE		TOTAL PHENOL		PCBs	
	Mean Conc (mg/L)	Mean Remo-val (%)	Mean Conc (mg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)
RAW	2.18	-	0.14	-	1314	-	6	-	54	-	90	-	<0.01	-
POST-FILT	0.36	84	0.08	46	925	30	2	62	14	73	60	33	<0.01	n.a.
POST-GAC2	0.09	96	0.07	52	873	34	2	68	4	92	4	96	<0.01	n.a.
MENVIQ OBJECTIVE	0.30	-	0.05	-	50	-	33	-	4.5	-	2	-	0.01	-
OBJECTIVE MET	yes		no		no		yes		yes		no		yes	

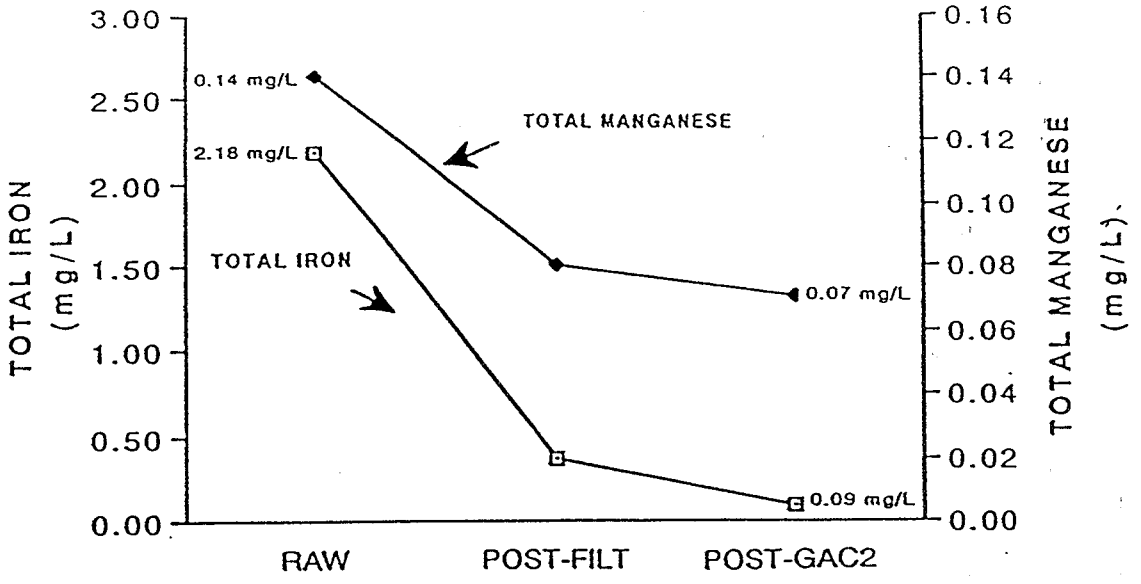

FIGURE 5 HISTORICAL DATA 1985-86: INORGANICS

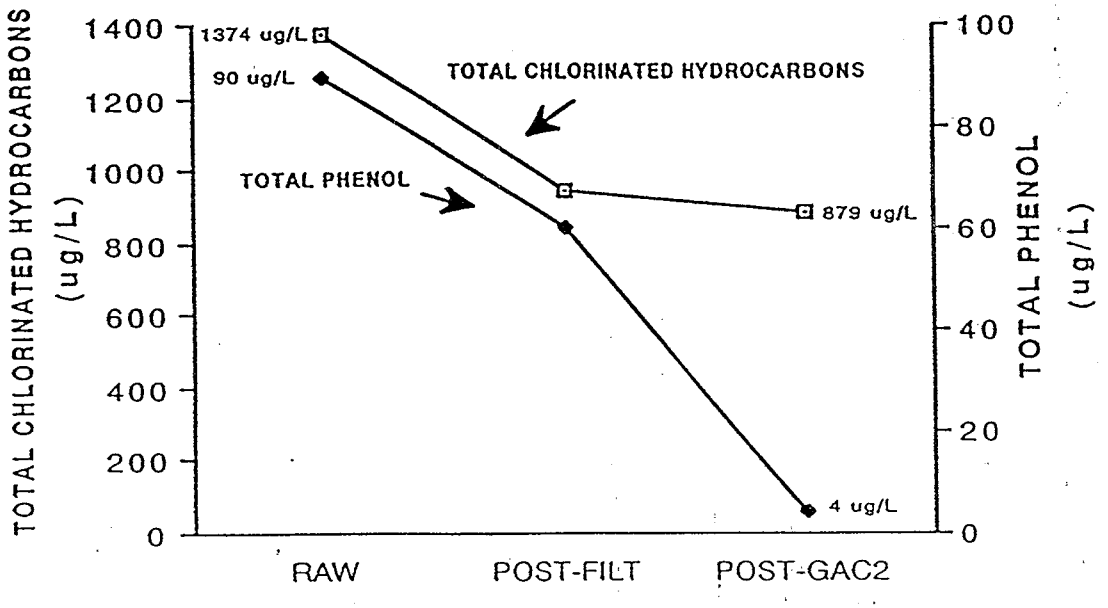

FIGURE 6 HISTORICAL DATA 1985-86: ORGANICS

TABLE 5 SUMMARY TABLE - HISTORICAL DATA PERIOD 3 (1987-1989)

PARAMETER	IRON		MANGANESE		1,2 DCA		1,1,1 TCA		TCE		TOTAL PHENOL	
	Mean Conc (mg/L)	Mean Remo-val (%)	Mean Conc (mg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)
RAW	4.09	-	0.19	-	1841	-	4	-	92	-	39	-
POST-STRIP	4.03	2	0.17	11	1304	29	1	63	32	66	19	51
POST-FILT	0.22	95	0.16	16	1394	24	n.a.	n.a.	38	59	13	66
POST-GAC1	0.16	96	0.15	21	888	52	1	73	15	84	8	79
POST-GAC2	0.12	97	0.14	32	1057	43	2	55	10	89	4	91
MENVIQ OBJECTIVE	0.30	-	0.05	-	50	-	33	-	4.5	-	2	-
OBJECTIVE MET	yes		no		no		yes		no		no	

Figures 7 and 8 summarize the information presented, and display treatment profiles for iron and manganese, and total phenol and total chlorinated hydrocarbons monitored, respectively.

During the last year of operation (1989), a series of 18 samples of influent, post sand filters and effluent waters were collected and analyzed for the following additional parameters: 1,1,2 Trichloroethane (1,1,2 TCA); 1,2 Dichloroethene (1,1 DCE); 1,1 Dichloroethane (1,1 DCA); Tetrachloroethene (PCE); Chloroform (CCl_3); Toluene; and Benzene.

Table 6 presents the performance evaluation for the groundwater treatment plant for this period.

Figure 9 summarizes the information presented, and displays treatment profiles for the aromatics and for some of the additional chlorinated hydrocarbons monitored.

2.1.4 Observations

The following observations can be made, based on the analyses of the data collected by SNC/HMI:

1. 1,2 DCA and phenolic compounds did not meet their respective effluent objectives during the first period (1984-1985).

2. Manganese, 1,2 DCA and phenolic compounds did not meet their respective effluent objectives during the second period (1985-1986).

3. Manganese, 1,2 DCA, phenolic compounds and TCE did not meet their respective effluent objectives during the third time period (1987-1989).

4. Although a combination of chemical oxidants were added to the train during the second and third period, manganese was more effectively removed during the first period.

5. The addition of chemical oxidants during the second and third period allowed the groundwater treatment plant to operate more effectively than during the first period, by minimizing all operational problems associated with the presence of iron and manganese, and with the growth of microorganisms, e.g. Iron bacteria, *Pseudomonads*. However, the addition of chemical oxidants had little impact in abating the concentration of the organic contaminants monitored. Removal efficiencies for each targeted organic contaminant were comparable during all three (3) periods.

6. 1,2 DCA and 1,1,2 TCA amounted to approximately 90% (w/w) of the concentration of chlorinated organics monitored in the groundwater (1989), with 1,1,2 TCA accounting for 28%. The concentration profile for this contaminant was monitored solely in 1989. Also of interest, is that a large percentage of the removal observed took place prior to the GAC adsorption step, i.e. 89% of the 1,2 DCA removed by the train was eliminated prior to the GAC adsorbers.

2.2 Full Scale Plant Sampling Monitoring Campaigns

The data presented in Section 2.1 has confirmed the existence of problems encountered in achieving an effective treatment of Ville Mercier's groundwater. Performance data were provided solely on selected segments of the treatment train, and only for selected parameters. For these reasons, a study program was initiated in order to carry out an in-depth performance evaluation of the treatment train.

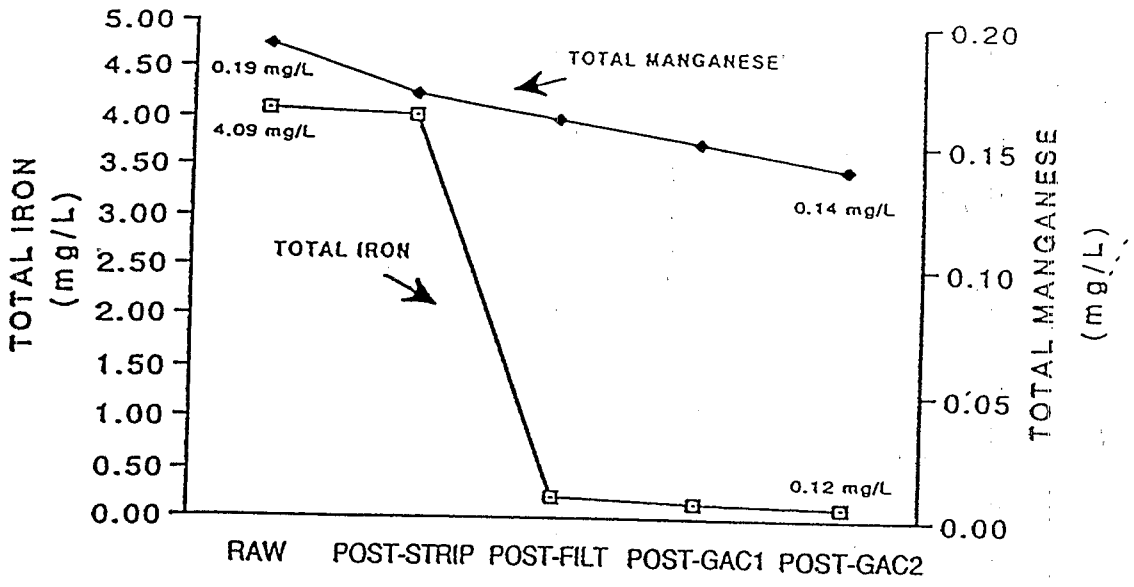

FIGURE 7 HISTORICAL DATA 1987-89: INORGANICS

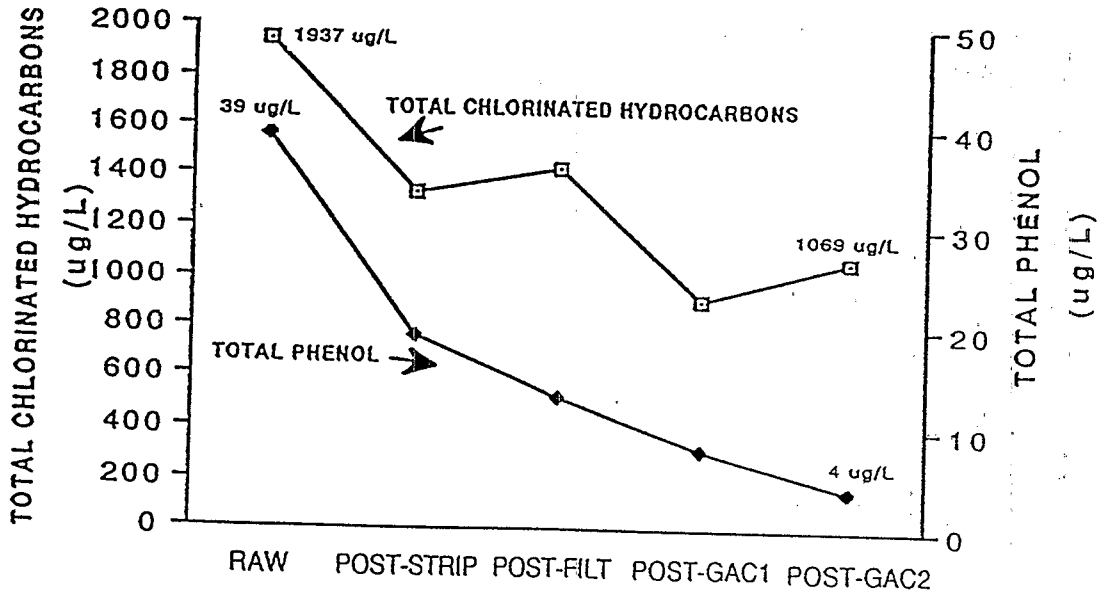

FIGURE 8 HISTORICAL DATA 1987-89: ORGANICS

TABLE 6 SUMMARY TABLE - HISTORICAL DATA 1989: ADDITIONAL PARAMETERS

PARAMETER	1,1,2 TCA		1,2 DCE		1,1 DCE		1,1 DCA		PCE		CCl_4		TOLUENE		BENZENE	
	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val(%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)
RAW	856	-	53	-	41	-	66	-	58	-	21	-	39	-	147	-
POST-FILT	611	29	20	63	20	51	28	57	31	46	11	47	18	53	49	67
POST-GAC2	586	32	19	65	19	53	15	78	11	80	5	78	4	89	4	97

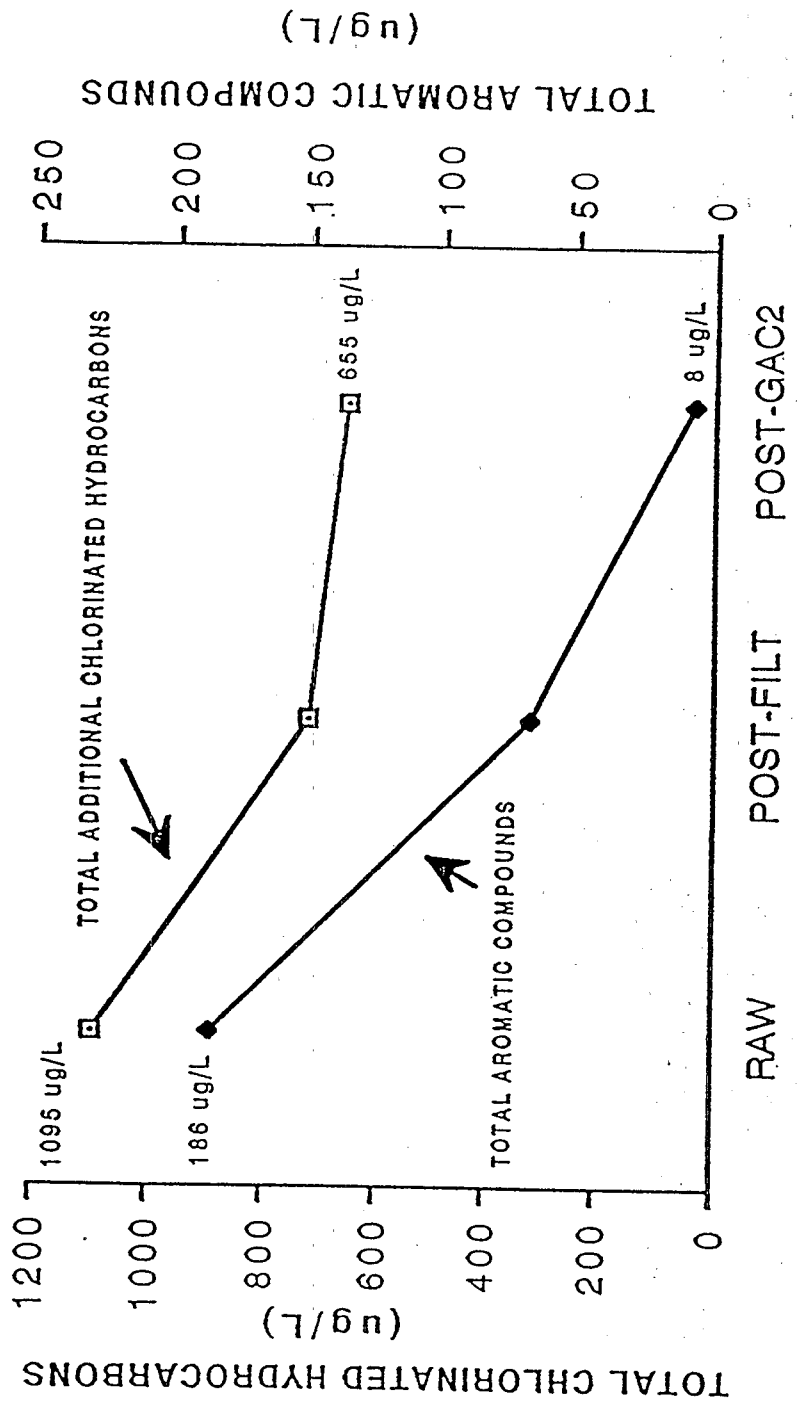

FIGURE 9 HISTORICAL DATA 1989: ADDITIONAL ORGANICS

Scans for organic and inorganic contaminants were carried out separately by the MENVIQ and by WTC. Good correlation was obtained. The data showed that 61 organic compounds were detected in the groundwater, amounting to a total concentration of 2 500 µg/L, 97% (w/w) of which were volatiles. The 3% remainder consisted of non-volatile organic compounds. Of these volatiles, 1,2 DCA and 1,1,2 TCA accounted for more than 60% (w/w) of the total VOC count. The inorganics scan showed iron and manganese above the drinking water objectives set by the MENVIQ. The organic and inorganic contaminants, shown in Table 7, were selected as target compounds. The organic parameters selected, amounted to 84% (w/w) and 81% (w/w) of the total organic count, determined by the MENVIQ and WTC laboratories' analyses (GC-MS), respectively.

TABLE 7 LIST OF ORGANIC AND INORGANIC PARAMETERS MONITORED

Organic Contaminants	Inorganic/Parameters
Cis- 1,2 Dichloroethene (1,2 DCE)	Iron (Total/Dissolved)
1,2 Dichloroethane (1,2 DCA)	Alkalinity
1,1,1 Trichloroethane (1,1,1 TCA)	Hardness
1,1,2 Trichloroethane (1,1,2 TCA)	Dissolved Oxygen/Temperature
Trichloroethene (TCE)	pH/Temperature
Tetrachloroethene (PCE)	Turbidity
	Suspended Solids
Benzene	
Toluene	
meta-Xylene	
ortho-Xylene	
para-Xylene	

Two (2) monitoring campaigns were carried out on the plant. The first campaign was conducted four (4) months after the last GAC replacement, in March 1989, in order to gather a performance profile of the adsorbers, once in operation for some time. Samples of raw and treated groundwater along the treatment train were drawn daily for a period of two (2) weeks. The second campaign began immediately following a GAC replacement, in July-August 1989, in order to specifically assess the performance of the GAC adsorbers. Samples of raw and treated groundwater along the treatment train were drawn regularly for a period of six (6) weeks in order to compile the necessary data required to assess the performance of the GAC adsorbers (breakthrough), and of the train in removing the organic contaminants of concern.

Furthermore, the concentration of the following parameters were occasionally monitored throughout the treatment train by an outside laboratory, i.e. Montréal-based Lab Elite Ltée and/or WTC, since the field groundwater laboratory trailer was not equipped to conduct these analytical determinations: Manganese; Metal Scan: Ag, Al, As, B, Ba, Ca, Cd, Co, Cr^{+3}, Cr^{+6}, Cu, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Si, V and Zn; and Total Organic Carbon (TOC).

These data are presented in the body of the text under the sub-heading "Other Analyses". Tabulated data are presented together with the data for the full scale sampling monitoring campaigns.

2.2.1 First Full Scale Plant Sampling Monitoring Campaign: Data and Results

Table 8 presents the performance evaluation for the groundwater treatment plant during this sampling monitoring campaign.

TABLE 8 SUMMARY TABLE - FIRST FULL SCALE PLANT SAMPLING MONITORING CAMPAIGN

PARAMETER	IRON		BENZENE		TOLUENE		m+p-XYLENES		o- XYLENE		1,2 DCA		1,1,1 TCA		1,1,2 TCA		TCE		PCE	
	Mean Conc (mg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)	Mean Conc (µg/L)	Mean Removal (%)
RAW	6.73	-	109	-	77	-	26	-	12	-	752	-	1	-	547	-	135	-	95	-
POST-H_2O_2	6.76	0	90	17	57	26	20	23	12	5	715	5	1	15	524	4	106	22	79	17
POST-CL_2	6.72	0	89	18	55	29	17	35	10	16	757	-1	1	15	621	-14	108	20	90	5
POST-STRIP	6.30	6	59	46	37	51	12	54	7	44	652	13	1	15	508	7	64	52	41	57
POST-CLAR	0.51	92	67	39	36	53	12	54	n.a.	n.a.	642	15	1	31	501	8	61	55	41	57
POST-FILT	0.04	99	53	51	36	53	11	58	7	41	641	15	1	45	500	9	61	55	36	62
POST-STOR	0.04	99	55	50	31	60	12	54	7	42	643	15	1	46	499	9	59	57	35	63
POST-GAC1	0.00	100	39	64	13	83	6	78	0	99	635	16	0	92	484	11	51	62	23	76
POST-GAC2	0.02	100	78	30	0	100	0	100	0	100	620	18	0	100	441	19	11	92	1	99
MENVIQ OBJECTIVE	0.30		-		-		-		-		50		33		-		4.5		-	
OBJECTIVE MET	yes										no		yes				no			

Figures 10 and 11 summarize the information presented and display treatment profiles for iron, the aromatics and for the chlorinated hydrocarbons monitored, respectively.

Other Inorganic Parameters

The pH of the groundwater remained fairly constant throughout the train. Mean influent and effluent pH values were 7.0 and 7.2, respectively.

The hardness of the groundwater remained fairly constant throughout the train. Mean influent and effluent hardness values were 576 mg $CaCO_3$/L and 588 mg $CaCO_3$/L, respectively.

The alkalinity of the groundwater showed a slight decrease throughout the train. Mean influent and effluent alkalinity values were 306 mg $CaCO_3$/L and 252 mg $CaCO_3$/L, respectively.

The dissolved oxygen content of the groundwater increased to saturation level following air stripping, and remained saturated throughout the train. Mean influent and effluent dissolved oxygen values were 2.7 mg/L and 8.4 mg/L, respectively.

Suspended solids values increased immediately after H_2O_2 addition and decreased following clarification and sand filtration. Mean influent and effluent values were 0.3 mg/L and 0.9 mg/L, respectively.

Other Analyses

Manganese: Manganese was poorly removed by the train (52%). Removal was essentially observed in the pulsating clarifier, i.e. 25% of that unit's influent concentration, and in the GAC2 adsorbers, i.e. 35% of that unit's influent concentration. Influent and effluent concentrations for manganese were 0.23 mg/L and 0.11 mg/L, respectively, and therefore the effluent objective of 0.05 mg/L was not met.

Metals: The following metals were below the detection limit of the analytical method used: Al, Ag, Ba, Cd, Cr^{+3}, Cr^{+6}, Hg, Ni, Pb, Se, Sb and Si. The concentrations of the following metals remained essentially constant throughout the train: As, Ca, Cu, K, Mg and Na.

Indicator Organic Parameters

TOC values were generally low. Influent and effluent TOC values were 15.4 mg/L and 11.6 mg/L.

2.2.2 First Full Scale Plant Sampling Monitoring Campaign: Discussion

Throughout this sampling monitoring campaign, both 1,2 DCA and TCE did not meet their respective effluent objectives. The same conclusions were drawn during the historical performance data analyses.

Aside from benzene which consistently showed signs of desorption from the polishing GAC2 adsorbers, all ring compounds and double-bond compounds monitored were still adsorbing effectively. In addition, it should be noted that benzene was the only compound desorbing from the GAC2 adsorbers. Furthermore, it also desorbed from the sludge bed of the pulsating clarifier. Analysis of the historical data indicated that benzene would still be adsorbing on the GAC when the chlorinated hydrocarbons would start desorbing (Section 2.1.3). A possible explanation for this observation might reside in a higher concentration of benzene in the raw groundwater prior to the start of the sampling monitoring campaign. This would explain the desorption observed for this contaminant from the

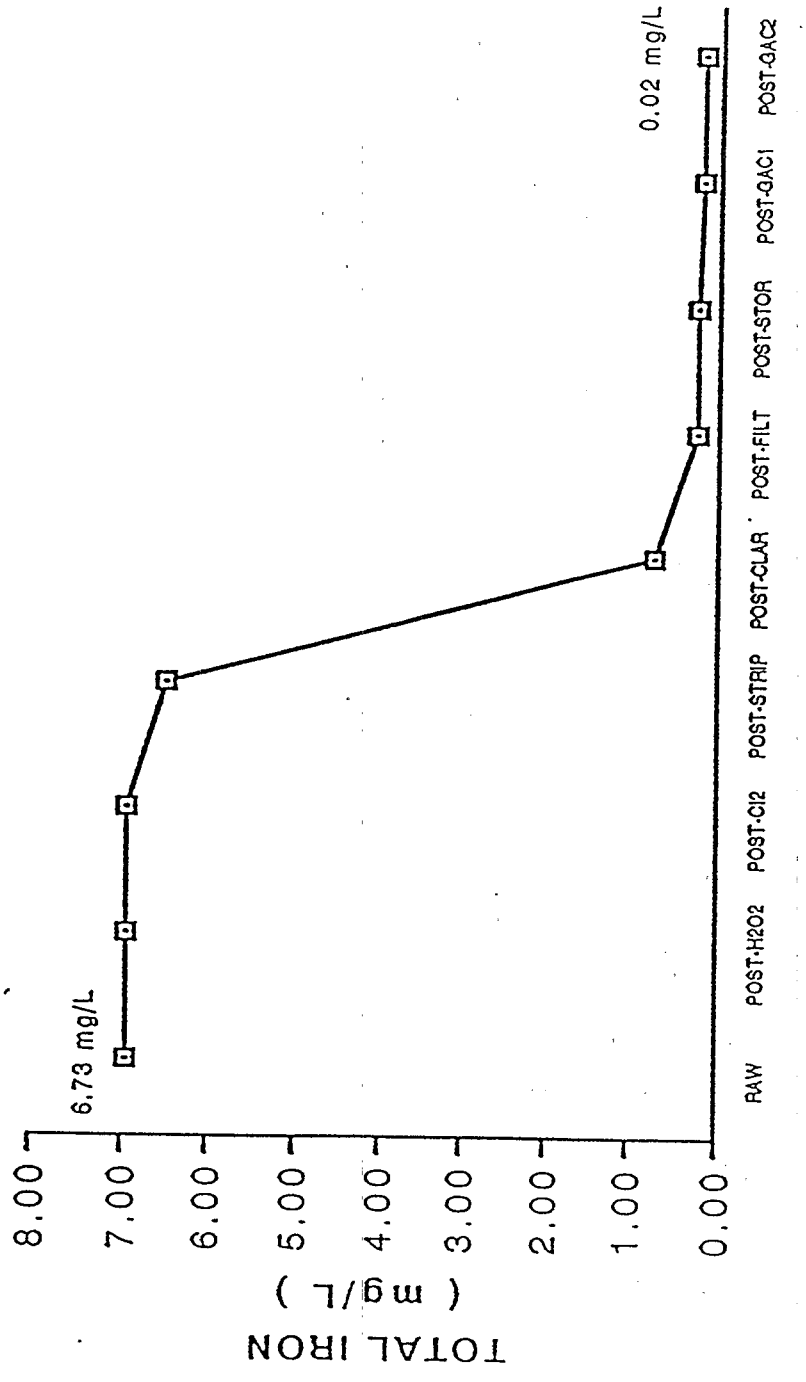

FIGURE 10 FIRST MONITORING CAMPAIGN: IRON

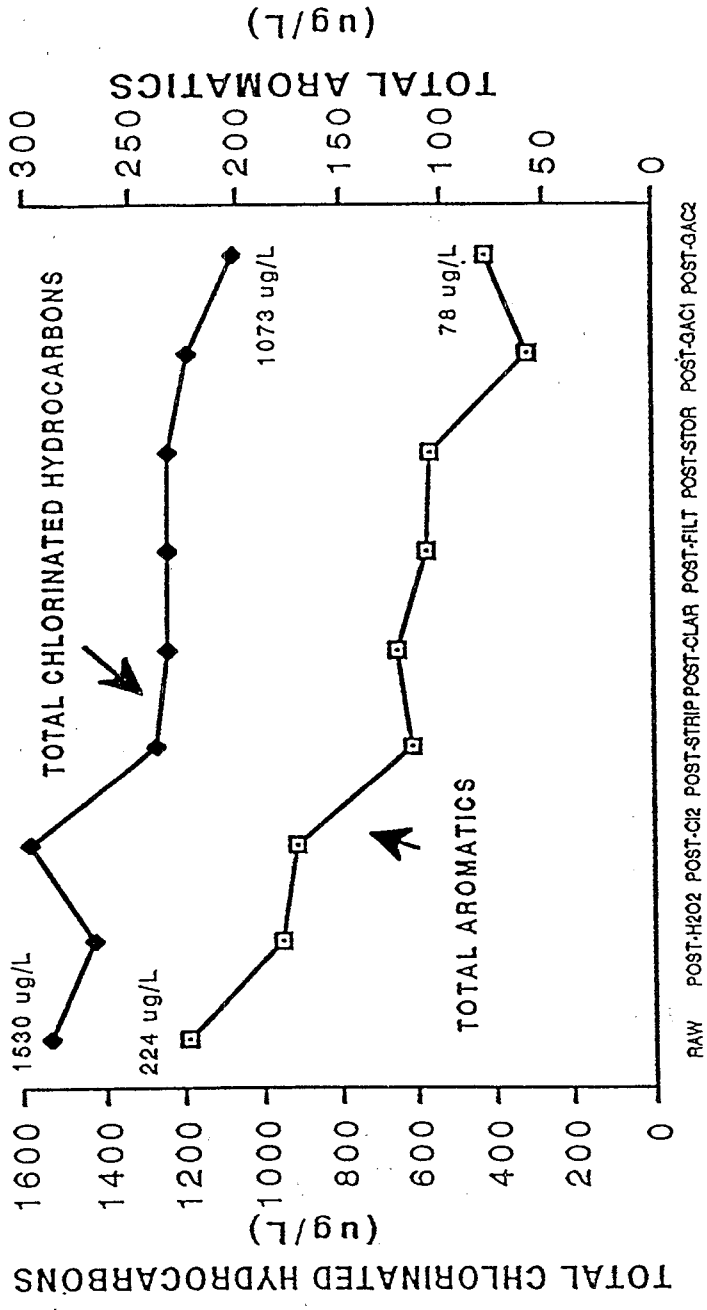

FIGURE 11 FIRST MONITORING CAMPAIGN: ORGANICS

sludge bed during the first few days, following the start of the campaign, and the subsequent shift to lower equilibrium values on a relatively exhausted GAC bed, resulting in the observed steady desorption. Furthermore, evidence of sensitivity to such swings in incoming benzene concentration only adds to the reality that the GAC2 adsorbers are evidently close to exhaustion.

Looking at the removal efficiency of each process unit with respect to the chlorinated hydrocarbons and aromatic compounds monitored, the following is noted:

H_2O_2 Addition: The weighted oxidation rates for the chlorinated hydrocarbons and aromatics were 7% and 20%, respectively. One should note that the oxidation of all unsaturated molecules was higher than for saturated ones, e.g. TCE (22%), PCE (17%). Hence, in addition to oxidizing iron, H_2O_2 addition contributed to a partial removal of the organic contaminants monitored.

Cl_2 Addition: The overall oxidation rates, following Cl_2 addition, for the hydrocarbons studied was nil. Instead, Cl_2 addition added to the load of chlorinated organics to be air stripped, by a weighted increase of 11%. This halogenation was more pronounced for some of the chlorinated organics monitored, i.e. 18% increase for 1,1,2 TCA, than for others, i.e. no increase for TCE. The sole beneficial impact, therefore, of Cl_2 addition is to control biological growth in the air stripper.

Air Stripper: The weighted stripping rate for the hydrocarbons studied was 21%. Of particular interest, the weighted stripping efficiency for 1,2 DCA and 1,1,2 TCA, which accounted for 75% w/w of the hydrocarbons studied, was 16%.

Pulsating Clarifier/Sand Filters/Storage Reservoir: Some removal, i.e. 3%, of the hydrocarbons monitored was observed, either together with the removal of the inorganic sludges generated, i.e. adsorption, or by volatilization/evaporation.

Granular Activated Carbon Adsorbers: The GAC is evidently saturated after four (4) months of operation. The chlorinated hydrocarbons, with the exception of the two (2) unsaturated compounds, TCE and PCE, did not adsorb any longer onto the media. Aromatics still adsorbed well, however, with the exception of benzene which showed signs of desorption.

The main focus of the first sampling monitoring campaign was to assess the performance of each unit process of the train since this information was lacking from the historical data collected during the five years of operation of the plant. The behaviour of a series of inorganic and organic parameters was assessed, and was found to correlate very well with the "overall picture" presented during the historical performance analyses of the plant.

2.2.3 Second Full Scale Plant Sampling Monitoring Campaign: Data, Results and Discussion

A second full scale sampling monitoring campaign commenced immediately following the replenishment of the adsorbers with fresh GAC (July 1989). The focus of that campaign was put on the breakthrough behaviour of the organic contaminants monitored from the GAC adsorbers. For that reason, Section 2.2.4 has been devoted exclusively to the presentation of the analytical data collected on GAC adsorption.

The performance data collected on the inorganics monitored, and on the organics from the first segment of the train (H_2O_2 addition $\rightarrow$ sand filtration) are presented together below.

Iron: Iron was almost completely oxidized (91%) following H_2O_2 addition. Chlorine addition did result in completely oxidizing (99%) the remaining iron (II). The shut-down of the plant, required to replace the GAC in the adsorbers, allowed the plant's operators to clean all unit processes of the

treatment train, including the air stripper packing. Throughout the second monitoring campaign, an extensive re-deposition of iron hydroxides took place on the stripper's packing: twenty-three percent (23%) of the incoming iron precipitated in the stripper. Iron was mainly removed (97%) by the pulsating clarifier, with the remaining 3% removed in the sand filters. Overall, 100% of the incoming iron was removed by the train. The mean influent and effluent concentrations were 8.64 mg/L and 0.01 mg/L, respectively, and therefore the 0.30 mg/L effluent objective was met (Figure 15).

Other Parameters: Similar results were observed during both sampling monitoring campaigns for the following parameters: pH, hardness, alkalinity, dissolved oxygen content, suspended solids, turbidity, manganese and all other metals monitored, COD and TOC.

Organic Contaminants: Generally, the experimental findings for the overall removal of organic contaminants from the first process element (H_2O_2 addition) to the seventh unit process (sand filtration) matched that observed during the first full scale plant sampling monitoring campaign and during the historical data analyses.

Table 9 presents the performance evaluation for the groundwater treatment plant during this sampling monitoring campaign.

Figures 12 and 13 summarize the information presented, and display treatment profiles for iron, the aromatics and chlorinated hydrocarbons monitored, respectively.

2.2.4 Second Full Scale Plant Sampling Monitoring Campaign: GAC Adsorption Study

The removal performance of the organic contaminants monitored by the GAC adsorbers was studied for a period of forty (40) days.

Breakthrough of a contaminant from a GAC adsorber was defined as the detectable appearance of that contaminant in the unit's effluent stream. The information collected has been summarized in Table 10.

2.2.5 Full Scale Plant Performance Assessment: Conclusions

Based on the information presented, the following is concluded:

a) The process elements of the treatment train, responsible for organics removal, do not perform as well as originally anticipated.
b) The capacity of the GAC adsorbers to remove the groundwater contaminants of concern to their respective effluent objectives, is exhausted only three (3) days following fresh GAC replenishment, for 1,2 DCA.
c) The process elements of the treatment train, responsible for inorganics removal, perform satisfactorily for iron but not for manganese.
d) Given the presence and the significant concentrations of the contaminants of concern still observed in the groundwater, comparable to that observed prior to the start of the remediation exercise, it can be concluded that the remediation of the aquifer is not complete after five (5) years of Pump-and-Treat.

TABLE 9 SUMMARY TABLE - SECOND FULL SCALE PLANT SAMPLING MONITORING CAMPAIGN

PARAMETER	IRON		BENZENE		TOLUENE		m+p XYLENES		o - XYLENE		1,2 DCA		1,1,1 TCA		1,1,2 TCA		TCE		PCE	
	Mean Conc (mg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)	Mean Conc (µg/L)	Mean Remo-val (%)
RAW	8.64	-	132	-	40	-	31	-	19	-	508	-	6	-	236	-	55	-	15	-
POST-H_2O_2	8.67	0	101	24	32	20	25	19	13	32	410	19	3	48	217	8	43	22	14	5
POST-CL_2	8.40	3	99	25	24	40	21	32	9	47	463	9	3	46	303	-28	29	47	12	17
POST-STRIP	6.63	23	95	28	20	50	22	29	14	26	427	16	3	47	241	-2	35	37	12	22
POST-CLAR	0.28	97	89	33	16	60	16	48	13	32	379	25	2	72	190	19	32	42	11	24
POST-FILT	0.03	100	86	35	18	55	19	39	10	47	411	19	1	80	185	22	30	46	9	39
POST-STOR	0.02	100	84	37	18	55	18	42	11	42	376	26	3	60	160	32	31	45	11	24
POST-GAC1	0.03	100	60	55	4	90	3	90	3	84	179	65	2	77	74	69	6	90	2	84
POST-GAC2	0.01	100	27	80	2	95	1	97	1	95	123	76	0	94	25	89	1	98	1	96
MENVIQ OBJECTIVE	0.30		-		-		-		-		50		33		-		4.5		-	
OBJECTIVE MET	yes										no		yes				yes			

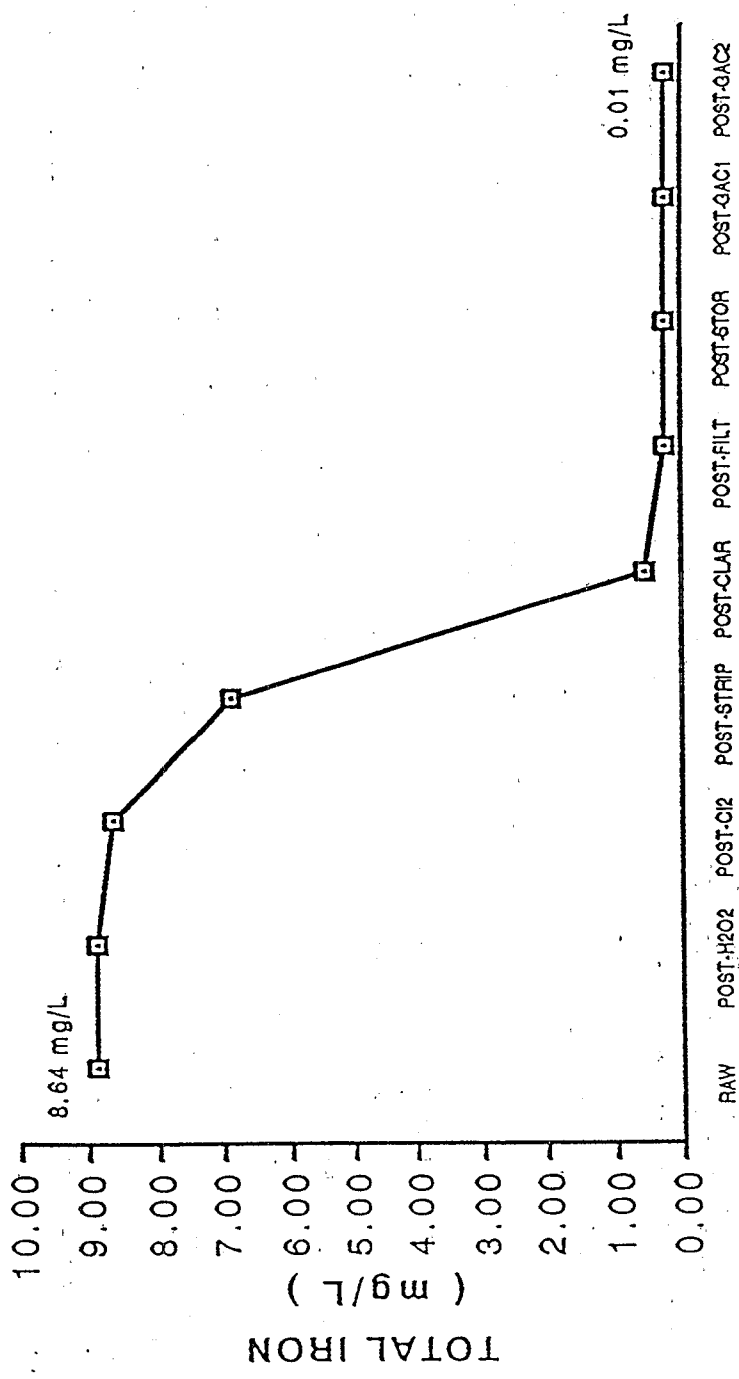

FIGURE 12 SECOND MONITORING CAMPAIGN: IRON

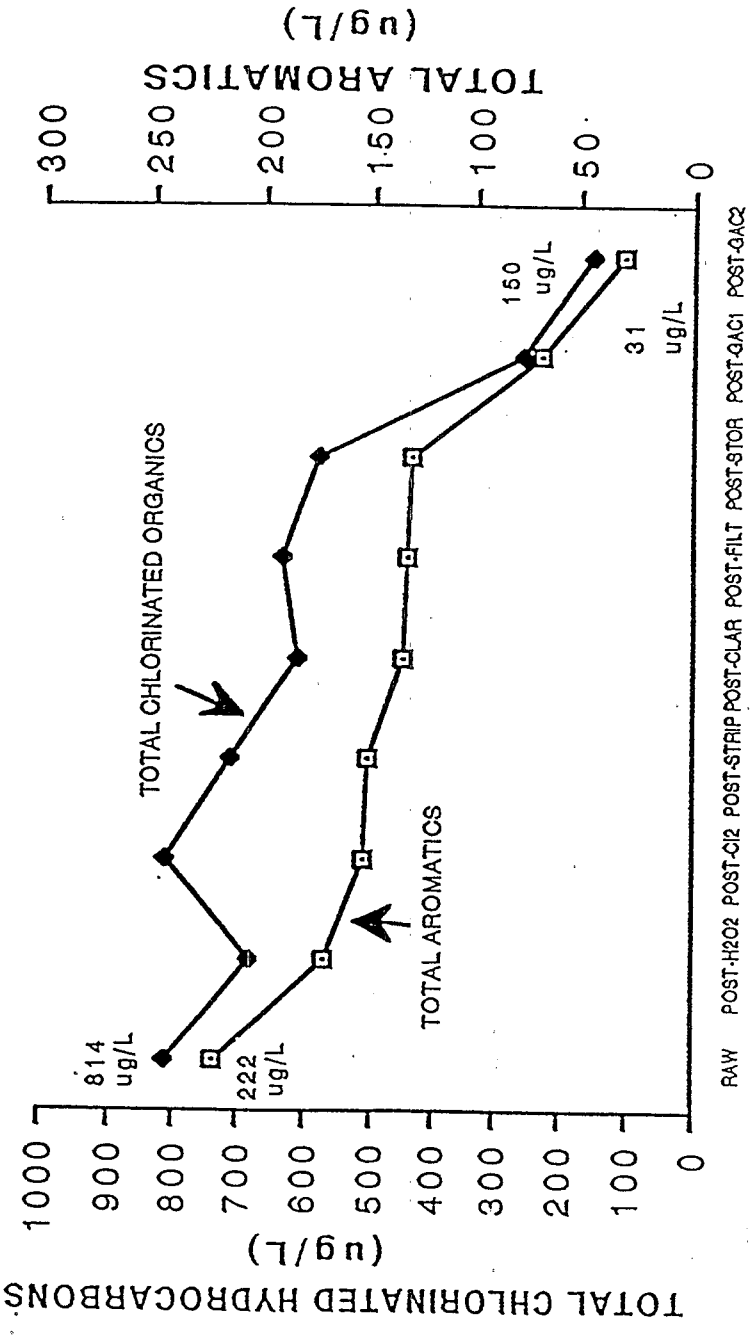

FIGURE 13 SECOND MONITORING CAMPAIGN: ORGANICS

TABLE 10 SUMMARY TABLE - SECOND FULL SCALE PLANT CAMPAIGN: GAC ADSORPTION STUDY

Parameter	Mean 1,2 DCA Conc (µg/L)	Mean 1,1,2 TCA Conc (µg/L)	Mean 1,1,1 TCA Conc (µg/L)	Mean TCE Conc (µg/L)	Mean PCE Conc (µg/L)	Mean Benzene Conc (µg/L)	Mean Toluene Conc (µg/L)	Mean m+p-Xylenes Conc (µg/L)	Mean o-Xylene Conc (µg/L)
Pre-GAC1	525	243	3	31	11	84	33	32	29
Post-GAC1	267	68	2	6	2	60	12	9	11
Post-GAC2	123	23	0	1	1	27	1	1	1
MENVIQ Objective	50	-	33	4.5	-	-	-	-	-
Objective Met Throughout Campaign	no*		yes	yes					
Occurence of Breakthrough	immediate <0.5d	immediate <0.5d	9 d	immediate <0.5d	immediate <0.5d	immediate <0.5d	immediate <0.5d	immediate <0.5d	immediate <0.5d
Occurence of Exhaustion	~10d	~21d	-	-	-	~21d	-	-	-

* Effluent objective for 1,2 DCA was met during three(3) days of operation (~ 750 bed volumes).

3.0 BENCH AND PILOT SCALE TREATABILITY STUDIES

A continuous flow pilot plant designed to integrate various combinations of physical chemical unit operations was installed in the vicinity of the full scale treatment facility. The entire pilot plant was fitted into two trailers. A third trailer was used to conduct on-site analytical determinations and preliminary bench scale treatability studies.

Figure 14 shows a schematic of the pilot plant. The pilot plant included the following unit operations:

- a diffused aeration vessel - for iron (II) and possibly manganese (II) oxygenation
- three (3) chemical oxidation reservoirs designed for use with hydrogen peroxide, sodium hypochlorite and chlorine dioxide - for iron (II) and manganese (II) oxidation and also, some oxidation of organics.
- a rapid mix chamber and a flocculation tank - to prepare groundwater for clarification/ sedimentation.
- a sedimentation tank - to remove suspended solids.
- a granular media filter - to remove suspended solids.
- an air stripping column - to remove volatile organic compounds (VOCs).
- three (3) activated carbon columns - to remove organics (volatile and others).

3.1 Pilot Scale Treatability Studies: Summarized Data and Conclusions

This work has illustrated the need, through performance data analyses of the full scale groundwater treatment plant and experimental results from the bench and pilot scale treatment studies, to remove inorganics prone to precipitation at the earliest possible stage in the physical chemical treatment of groundwater contaminated by toxic organics. This allows for the proper operation of subsequent unit processes, responsible for the removal of the organics of concern from the groundwater, by minimizing the potential for physical fouling and the ensuing biological fouling.

One of the objectives of the experimental project was the development and demonstration of an effective iron removal process train, as a pre-treatment prior to the removal of the organics of concern from the groundwater. In order to fulfil this objective, several iron removal process trains were evaluated at pilot scale for their ability to remove iron effectively (Table 11). In addition, attempts were made to minimize the number of unit processes involved, eliminate the requirement for coagulant(s), flocculant(s), chemical oxidant(s), aqueous pH conditioner(s), and also minimize sludge production.

The study resulted in the selection and subsequent optimization of a simple iron removal process train consisting of a fine pore diffused aeration vessel followed by rapid direct contact sand filtration. The hydraulic retention time of the groundwater in the aeration vessel was 22 min, and the air to water flow rates ratio was 5.5:1. The oxygenation of iron (II) was shown to be virtually complete. Direct contact sand filtration, conducted in the subsequent unit process, was shown effective in removing the majority of the iron, thereby consistently meeting the 0.30 mg/L iron effluent objective. A sand bed depth of 110 cm, effective sand diameter of 0.46 mm, and a filtration rate of 5.3×10^{-3} m/s resulted in a mass storage capacity of 2.8 kg iron/m^3 of sand, expressed as Fe.

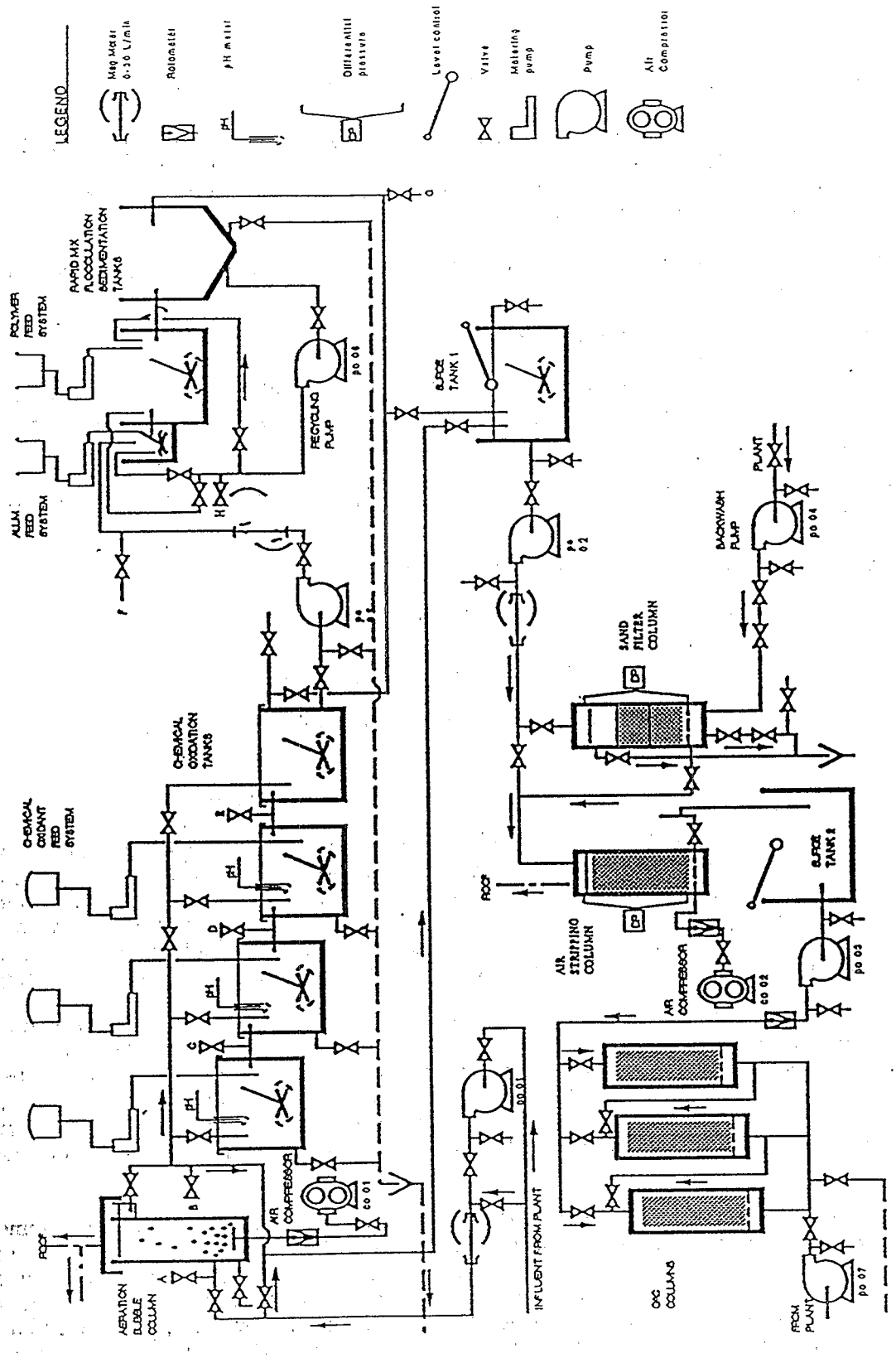

FIGURE 14 PILOT PLANT SCHEMATIC FLOW DIAGRAM

TABLE 11 IRON REMOVAL TRAINS (VILLE MERCIER, QUÉBEC)

1. Chemical Oxidation - Coagulation - Flocculation - Sedimentation - Sand Filtration
2. Chemical Oxidation - Direct Contact Sand Filtration
3. Diffused Aeration - Coagulation - Flocculation - Sedimentation - Sand Filtration
4. Diffused Aeration - Chemical Oxidation - Direct Contact Sand Filtration
5. Diffused Aeration - On-Line Coagulant Addition - Direct Contact Sand Filtration
6. Diffused Aeration - On-Line Flocculant Addition - Direct Sand Filtration
7. Diffused Aeration - Direct Contact Sand Filtration

The organics of concern were removed from the groundwater by air stripping, due to their volatile nature. An air stripper was demonstrated effective in removing 1,2 DCA and all other VOCs from the groundwater for an air to water flow rates ratio of 240:1.

Figures 15 and 16 illustrate the performance of the diffused aeration-direct contact sand filtration-air stripping process train for iron and organics removal, respectively. This performance evaluation was conducted during a three (3) month period of continuous operation.

Performance data analyses of the full scale plant, and performance data collected during the pilot scale treatment study have strongly indicated the poor removal performance offered by liquid-phase GAC adsorption for the volatile organics found in the groundwater. This was observed for high VOC concentrations (full scale plant) and for low VOC concentrations, i.e. in the evaluation of the diffused aeration-sand filtration-air stripping-GAC adsorption pilot scale process train. Hence, due to the poor removal performance offered by GAC adsorption, it was not recommended in order to remove the remaining VOCs from the groundwater.

A biological fouling control technique, developed by F.J. Dart (Ontario Ministry of the Environment), incorporating zinc granules in the sand bed, to abate and control *Pseudomonads* was shown effective.

4.0 HYDROGEOLOGICAL STUDY: DATA AND SUMMARIZED CONCLUSIONS[5]

Boreholes and monitoring instruments were installed to measure the distribution of contaminants in the area located between the former lagoon (the "source") and the purge wells (the "sink"). Monitoring procedures also included a program to sample groundwater at fifty points at different depths and location with respect to the source and the sink. Measuring points are located in unconsolidated sediments (sandy till formation) and bedrock. The depth of investigation reaches 45 m which is below the depth of the purge wells with intake screens partly in loose sediments and the fractured bedrock.

Measurements of aquifer hydraulic properties, monitoring water levels and use of numerical models were the tools used to assess the performance of the hydraulic trap created by the high performance purge wells.

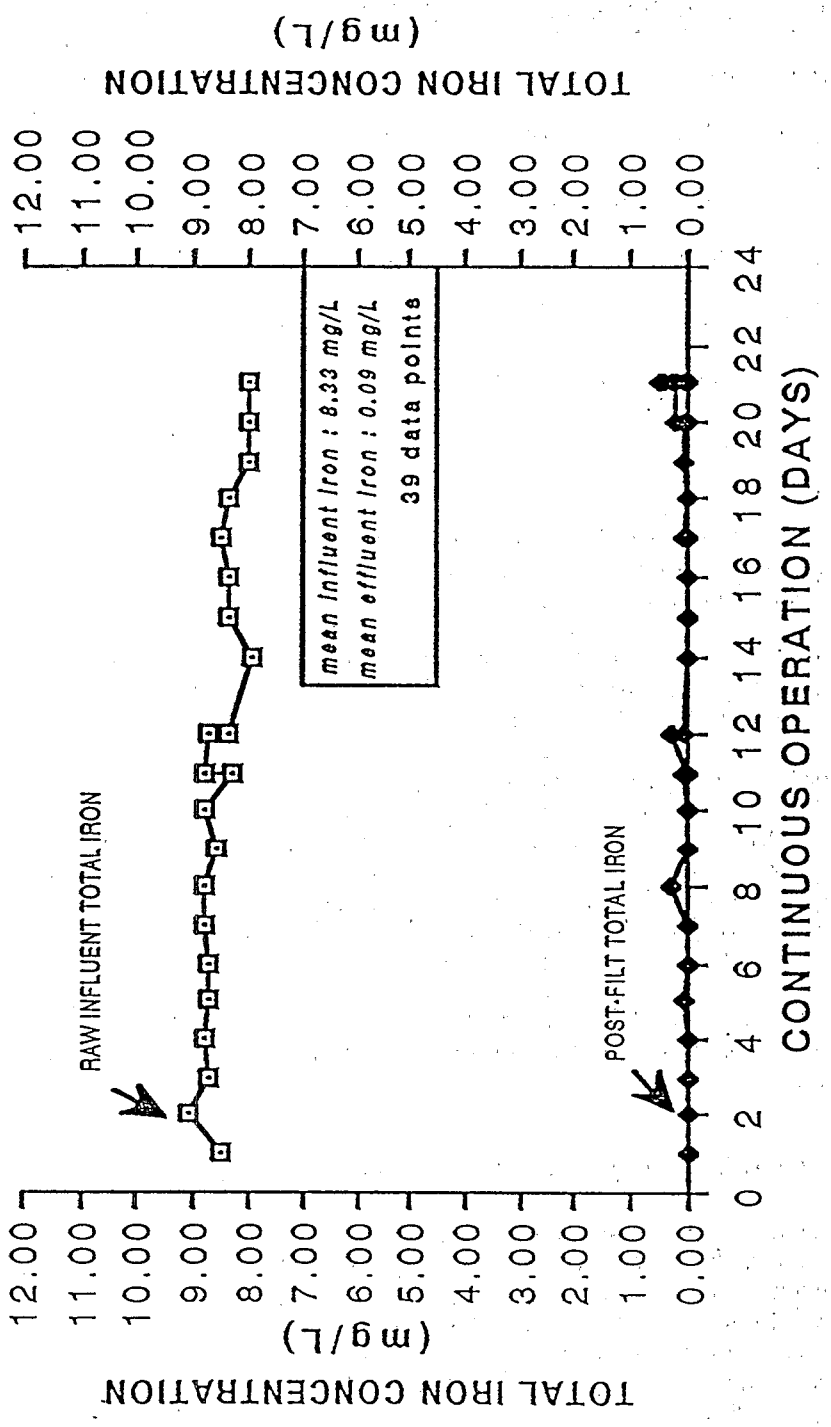

FIGURE 15 IRON REMOVAL BY A-F TRAIN: PERFORMANCE EVALUATION 2

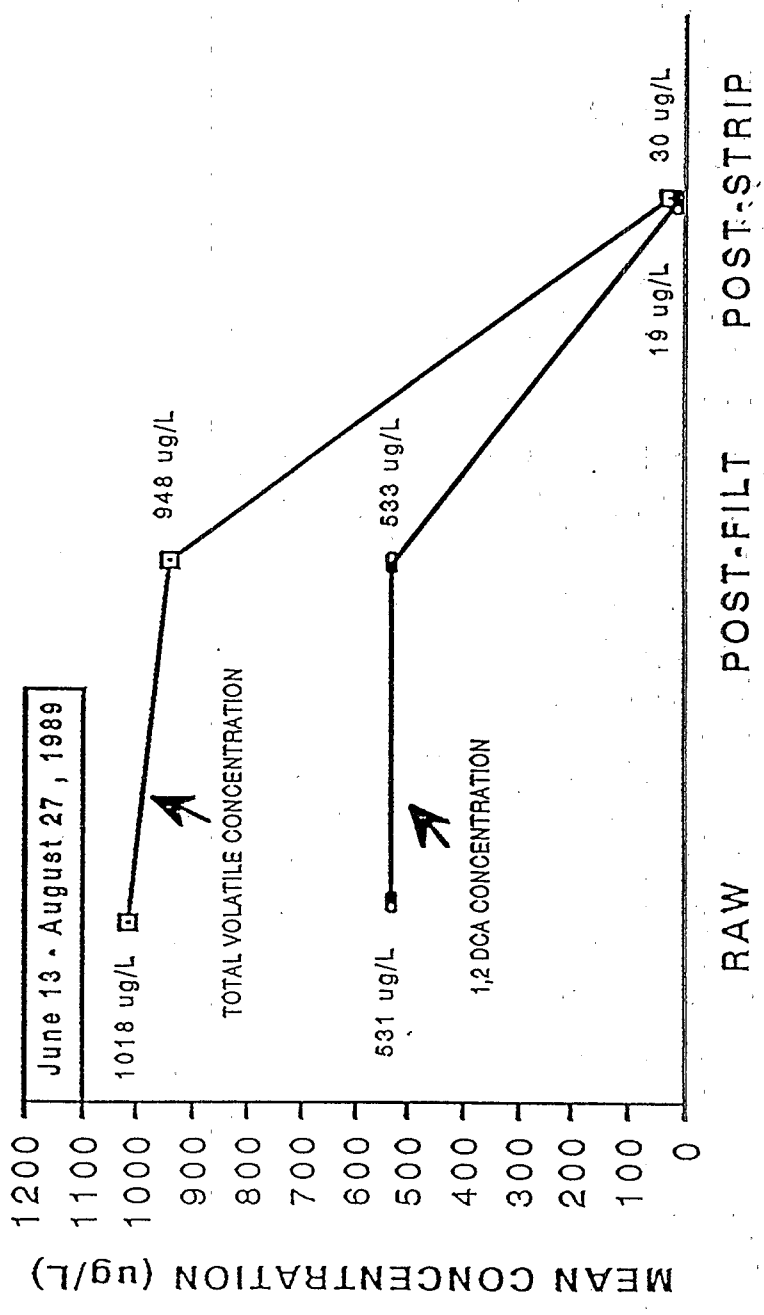

FIGURE 16 VOLATILES REMOVAL BY A-F-S TRAIN: CONTINUOUS PERFORMANCE EVALUATION

Monitoring data show that a plume of highly contaminated groundwater is still present between the lagoon and the purge wells both in unconsolidated sediments and bedrock fractures. "Oil" samples were taken in the former lagoon and in several observation wells tapping the rock fractures. The characteristics of this oil residue are unusual. The organic fluids have a density greater than water and reach the bottom of the sand aquifer to infiltrate the fracture network. Their composition shows the presence of aliphatic hydrocarbons, a proportion between 30 and 35% of polyaromatic hydrocarbons (PAH), and the presence of chlorinated hydrocarbons, solvents and pesticides.

The existence of these dense non-aqueous phase liquids (DNAPL) far from the source area is unexpected and raises several problems. Many constituents of the DNAPL are slightly soluble in water so that the movement of these fluids in the pore space of the unconsolidated sediments and in the fracture space of the rocks increases considerably their area of contact with groundwater. Solubility equilibria between the organics and groundwater will persist for a very long period of time (hundreds of years or more) if the DNAPL are not removed. The purge wells should continue to pump highly contaminated groundwater for a comparable period of time. The problem has evolved from a concentrated fixed source area to a moving and dispersing source with a large contact area with groundwater.

Poor vertical connectivity between the surface and bedrock aquifers has been documented. High upward vertical gradient from the bedrock to the sand exists but flow is small because of the presence of a low hydraulic conductivity layer at the sand/rock interface. During an interval when pumping was stopped to permit maintenance in the treatment plant, recovery of the water levels in the bedrock was extremely slow. Concentrations of volatile organics in a few samples coming from the bedrock aquifer are from 20 to 50 times higher than the water actually entering the purge wells. More data is needed before concluding that the bedrock aquifer is less affected by the restoration scheme.

Presence of DNAPL in the deepest bedrock piezometer may indicate that the hydraulic trap is of limited efficiency in controlling the movement of the organic phase. The higher density of this fluid and the poor vertical connectivity between the two aquifers may create a situation whereby some of the DNAPL can escape the trap by the overflow.

Monitoring data from observation wells located outside the study area show that the hydraulic gradients as far as 1.5 km downstream of the purge wells are oriented toward the sink. The hydraulic trap is therefore considered effective to control the spreading of the contaminant plume in the dissolved phase.

Conclusions at this stage are that:

1. the hydraulic trap must be maintained to prevent further migration and spreading of the plume of dissolved organics, and

2. that any long-term management of the plume must consider the removal of the DNAPL by a method more effective than pumping the contaminated groundwater.

5.0 CONCLUSIONS

Based on the analyses presented, the following is concluded:

- The unit operations of the groundwater treatment plant do not perform as well as originally anticipated. Hence, the treatment train of the Ville Mercier plant will require further modifications in order for the treated effluent to meet the objectives set by the MENVIQ.

- Remediation of the aquifer is not complete after five (5) years of pump-and-treat.

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Vieille-Montagne France S.A. **30.01.91**
Viviez - 12110 Aubin

1. Principles of Operation of the Treatment Facility

1.1 Sources of Water

1.1.1 Old Storage Basins for Hydrometallurgical Sludges
Infiltration water crosses three basins. The polluted water flows by gravity to the treatment plant.
Flowrate 6 to 30 m^3/h (during wet weather)
Composition Zn = 0.2 to 1.5 g/L
Cd = 10 to 30 mg/L

1.1.2 Water pumped from the aquifer
Comes from the surroundings of the old facilities for the hydrometallurgical extraction of zinc from the ore
Flowrate 4 to 10 m^3/h
Composition Zn = 0.2 to 0.8 g/L
Cd = 30 to 50 mg/L
pH = ± 5

1.1.3 Rinsewater from zinc metal finishing plant
Flowrate ± 8 m^3/h
Composition pH = 2 to 4

1.2 Process

1.2.1 The polluted waters are mixed and treated continuously in 5 reactors in series of 100 m^3 each. PH adjustment is accomplished by adding hydrated quicklime at 150 g/L (suspended solids) to 3 of the reactors. In each reactor the amount of lime is controlled by a pH feedback loop. (combination electrodes and on/off pneumatic valves)
pH reactor No. 1 = 6.5 to 7
pH reactor No. 2 = 8 to 8.5
pH reactor No. 4 = 8.8 to 9

1.2.2 The free acidity and the dissolved elements such as Zn and Cd form $CaSO_4$, hydroxides and sulphates of zinc and cadmium. This mixture of solids and liquids is separated in one gravity clarifier with a volume of 800m^3. A flocculant dosage of ±15 mg/L is necessary to ensure clarification because of:
- the effluent quality required (the effluent to the river must meet the requirements set by DRIR)
- the increase in sludge density (density 1 030 to 1 100). The sludge is dewatered by a filter press (FAURE) in order to minimize the moisture content and then it is shipped to VMF AUBY.

1.2.3 To complement the lime addition and overcome the partial solubility of Cd which would precipitate as sulphates and hydroxides, a stoichiometric quantity of sodium sulphide Na_2S is added to precipitate the cadmium as cadmium sulfide. The concentration of Na_2S in solution is 200 g/L.

1.2.4 Operation

The facility has a design maximum flowrate of 140m^3/h.
Without exception this permits an operation through an 8 hour shift each day, given the volumes to be treated and the storage capacity provided by the 800 m^3 clarifiers.

The suspended solids produced are filtered and shipped to another site of the company for recovery of zinc, the clean residue is then disposed of.

The purpose of this shipment is more to accelerate the clean up of old sites of the Viviez plant than to reclaim the solids.

2.0 Principle of Operation of the Facility

Recycled material was used for the hydrometallurgical extraction of zinc, which explains the volume of tankage installed for treatment, clarification and storage.

2.1 Preparation and distribution of lime

- 1 silo of powdered quick lime, ultra fine, 100T
- preparation in industrial water at 150 g/L
- distribution in a continuous loop

2.2 Reactors

- 5 reactors cascading (100 m^3 per reactor)
- Agitator motor: 50 HP at 750 rpm
- Turbine mixers - Ø=1.20m - 12 blades
- Construction - mild steel, rubber and bricks

2.3 Clarifiers

- 1 clarifier in use, 1 standby
- Volume 800 m^3
- Construction: mild steel, rubber and bricks
- Equipped with a rake with 4 arms; stainless steel
- Motor: 4 KW at 11 rph

2.4 Filter Press

- TITAN model 219 with recessed plates of polypropylene 1 200 x 1 200 mm for 127 chambers 30 mm
- Volume: 3 800 L
- Pressure: 15 bars
- Filter surface: 296 m^2
- Closing, opening and cake discharge mechanically
- Cake characteristics
  - Density 20 to 30% with: Zn: 25 to 35%
    Cd: 0.2 to 0.5%
    Ca: 1.5 to 6%

- For 1 shift of 7 working hours:
  - dry solids 6T
  - cycle time 1 hour 40 minutes or 4 to 5 cycles per shift

2.5 Storage capacity for the waters to be treated

$800 \times 3 = 2\,400\ m^3$

3.0 Effluent Criteria set by a Regional decree in Aveyron as of February 1989

- PH: between 5 and 9
- Temperature: less than 30°C
- Suspended Solids: less than 30 mg/L
- Phosphorus: less than 10 mg/L
- Total hydrocarbons: less than 5 mg/L
- Total metals: less then 15 mg/L
  (Zn + Cu + Ni + Al + Fe + Cr + Cd + Pb + Sn)
- Zinc: less than 5 mg/L

(a) Specific to Cadmium

Monthly effluent concentration: less than 0.2 mg/L
Daily effluent criteria: 0.4 mg/L

(b) Self-Monitoring

- Continuous effluent monitoring for flowrate and pH, prior to discharge. Flowrate values are recorded in a notebook.
- Control monthly by a representative daily sample for suspended solids, COD pH and Zn.

  Daily sample for Cd. Results communicated monthly to the inspection authority.

(c) Daily average effluent results (discharge to a river)

pH = 8.5 to 9
Zn = 0.5 to 3 mg/L
Cd = 0.03 to 0.18 mg/L

4.0 Principle of Operation of the Facility

4.1 Staffing Requirements

Treatment, clarification: filtration for one shift, each weekday:

- shift from 5:00 a.m. to 1:00 p.m. for 7 hours of effective work

From 1:00 p.m. to 5:00 a.m. the next day, the water to be treated is stored in 800 m^3 reservoirs

- Shift 5:00 a.m. to 1:00 p.m.: 2 workers
- Shift 1:00 p.m. to 9:00 p.m. and 9:00 p.m. to 5:00 a.m.: no staff
- 1 Foreman: (daytime hours)

4.2 Cost breakdown

- Material costs

(lime, filter cloth, flocculant)		2 460 F/d
• Handling		600 F/d
• Energy		2 190 F/d
• Analyses		260 F/d
• Clean up, maintenance		1 890 F/d
• Personnel Salaries		2 830 F/d
	TOTAL	10 230 F/d

Original version in French: J.M. Granier, M. Darcy
Translation: J. Schmidt

Appendix 6-B

Ground Water Pump and Treat Technology Case Studies

Evaluation of Photo-oxidation Technology (Ultrox International), Lorentz Barrel and Drum Site, San Jose, California, United States

United States
Environmental Protection
Agency

EPA/540/M5-89/012
November 1989

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

Demonstration Bulletin

Ultraviolet Radiation and Oxidation

Ultrox International

TECHNOLOGY DESCRIPTION: The ultraviolet (UV) radiation/oxidation treatment technology developed by Ultrox International uses a combination of UV radiation, ozone, and hydrogen peroxide to oxidize organic compounds in water. Various operating parameters can be adjusted in the Ultrox® system to enhance the oxidation of organic contaminants. These parameters include hydraulic retention time, oxidant dose, UV radiation intensity, and influent pH level.

A schematic of the Ultrox system is shown in Figure 1. The treatment system is delivered on four skid-mounted modules, and includes the following major components:

- UV radiation/oxidation reactor module
- Ozone generator module
- Hydrogen peroxide feed system
- Catalytic ozone decomposer (Decompozon) unit for treating reactor off-gas

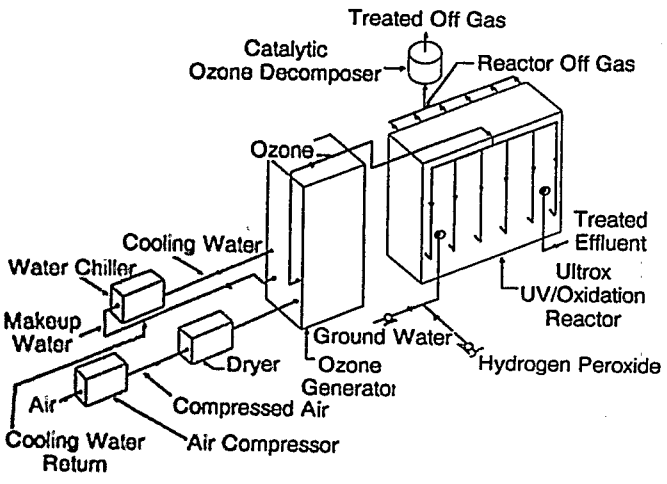

Figure 1. Isometric view of Ultrox System.

The commercial-size reactor used for the SITE Demonstration is 3 feet long by 1.5 feet wide by 5.5 feet high. The reactor is divided by five vertical baffles into six chambers. Each chamber contains four UV lamps as well as a diffuser which uniformly bubbles and distributes ozone gas into the groundwater being treated.

WASTE APPLICABILITY: This treatment technology is intended to destroy dissolved organic contaminants, including chlorinated hydrocarbons and aromatic compounds, that are present in wastewater or groundwater with low levels of suspended solids, oils, and grease.

DEMONSTRATION RESULTS: The SITE Demonstration was conducted at a former drum recycling facility in San Jose, California, over a 2-week period in February and March 1989. Approximately 13,000 gallons of groundwater contaminated with volatile organic compounds (VOC) from the site were treated in the Ultrox system during 13 test runs. During the first 11 runs, the 5 operating parameters were adjusted to evaluate the system. The last 2 runs were conducted under the same conditions as Run 9 to verify the reproducibility of the system's performance.

To evaluate the performance of each run, the concentrations of indicator VOCs in the effluent were analyzed overnight. Three of the 44 VOCs identified in the groundwater at the site were selected as indicator VOCs. These indicator VOCs were trichloroethylene (TCE); 1,1 dichloroethane (1,1-DCA); and 1,1,1-trichloroethane (1,1,1-TCA). TCE was selected because it is a major volatile contaminant at the site, and the latter two VOCs were selected because they are relatively difficult to oxidize.

Key findings from the Ultrox demonstration are summarized as follows:

- The groundwater treated by the Ultrox system met the applicable National Pollutant Discharge Elimination System (NPDES) standards at the 95 percent confidence level. Success was obtained by using a hydraulic retention time of 40 minutes; ozone dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; all 24 UV lamps operating; and influent pH at 7.2 (unadjusted).
- There were no volatile organics detected in the exhaust from the Decompozon unit.
- The Decompozon unit destroyed ozone in the reactor off-gas to levels less than 0.1 ppm (OSHA Standards). The ozone destruction efficiencies were observed to be greater than 99.99 percent.
- The Ultrox system achieved removal efficiencies as high as 90 percent for the total VOCs present in the groundwater at the site. The removal efficiencies for TCE were greater than 99 percent. However, the maximum removal efficiencies for 1,1-DCA and 1,1,1-TCA were about 65 and 85 percent, respectively (Table 1).

Table 1. Performance Data During Reproducible Runs

	Mean Influent (µg/L)	Mean Effluent (µg/L)	Percent Removal
Run Number: 9			
TCE	65	1.2	98
1,1-DCA	11	5.3	54
1,1,1-TCA	4.3	0.75	83
Total VOCs	170	16	91
Run Number: 12			
TCE	52	0.55	99
1,1-DCA	11	3.8	65
1,1,1-TCA	3.3	0.43	87
Total VOCs	150	12	92
Run Number: 13			
TCE	49	0.63	99
1,1-DCA	10	4.2	60
1,1,1-TCA	3.2	0.49	85
Total VOCs	120	20	83

- Within the treatment system, the removals of 1,1-DCA and 1,1,1-TCA appear to be due to both chemical oxidation and stripping. Specifically, stripping accounted for 12 to 75 percent of the total removals for 1,1,1-TCA, vinyl chloride, and other VOCs.
- No semivolatiles, PCBs, or pesticides were found in the groundwater at the site. Among the VOCs, the contaminant present at the highest concentration range (48 to 85 µg/L) was TCE. The groundwater also had contaminants such as 1,1-DCA and 1,1,1-TCA in the concentration ranges of 10 to 13 µg/L and 3 to 5 µg/L, respectively.
- The organics analyzed by Gas Chromatography (GC) methods represent less than 2 percent of the total organic carbon (TOC) present in the water. Very low TOC removal occurred, which implies that partial oxidation of organics (and not complete conversion to carbon dioxide and water) took place in the system.

A Technology Evaluation Report and an Application Analysis Report describing the complete demonstration will be available in the Spring of 1990.

FOR FURTHER INFORMATION:

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Environmental Protection
Agency

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Appendix 6-C

Ground Water Pump and Treat Technology Case Studies

Zinc Smelting Wastes and the Lot River, Viviez, Averyon, France

VIEILLE MONTAGNE

The origin of zinc production in VIVIEZ goes back to the years 1870. Until 1930, the process was thermic, and all the wastes were thrown near to the plant, on the hill slope. Such is the origin of this waste heap. Afterwards, the Vieille Montagne company shot hydrometallurgic refuse coming from the electrometallurgic process.

The total amount of wastes stored in the heap is evaluated to 700000 tons.

Natural lixiviation by rainfall takes metallic ions to the ground water located at the hill-foot then to surface water which are contaminated.

The amount of cadmium thrown in the environment amounted to a mean 36 kg/day up to 1987.

When this permanent pollution was proved,studies were carried out in order to understand the circulation phenomena of metallic ions to the superficial hydraulic system and, then decide which means had to be put into operation so as to eliminate this pollution.

1) Hydrogeological study :

The aim of this study was to evaluate:

- the hydrodynamic behaviour of the alluvial aquifer,
- the hydraulic relations aquifer/heap,
- the surface water regime.

At the same time,the qualitative aspect, based on water analysis, had to be taken into account.

Analysis of boreholes and water have led to collect a certain amount of information which can be summed up as follows:

- initial geological scheme showing various overlaid structures,

- drawing of a piezometric map on which a mathematical model was set up in order to localize flow repartition,

- detailed analysis of data taken from all the control equipment, including cadmium content in surface and ground waters leading to a global balance.

In this general context, the first actions, brought up in 1988, were taken so as to cover ponds containing muds and to relocate the smallest storages.

The impact on natural environment was in a very short time effective since the day cadmium content went down from a 36 kg/day (1987) to a 2 kg/day early in 1989.

2) P2 point

P2 is a special point highly polluted in cadmium (1250 mg/l) which was due to a temporary storage of ore. P2 is an important element of cadmium re-emission (about a third of the pollution).

Tests carried out in July 1988 have led to a better knowledge of the "P2 point" which had been located before and to locate cadmium concentrations around this point.

It was possible to locate a zone of cadmium dissolved content higher than 300 mg/l around boreholes P2, P3, S7 and S5. Maximal contents are surrounded by concentric circles: a 200-300 mg/l circle and another one at 100-200 mg/l, both 10-20 m wide are limited by boreholes S6, S1, S2 and S3 ; further around, cadmium contents are similar to that measured elsewhere, particularly in the waste heap in the THR zone.

Hydraulic values have been fairly evaluated : mean transmissivity is $T = 5,0 \cdot 10^{-4}\ m^2/s$ and storage coefficient $S = 3,0 \cdot 10^{-2}$

These values have been used to test in a mathematical model three hypotheses of decontamination by pumping/injection : it has been decided to decontaminate putting into operation two pumping boreholes (P2 and S5) at 8 m^3/h and four injecting boreholes (S2, S4, S6 and S7) at 4 m^3/h.

Tests carried out during the spring season in 1989 have led to the idea that this solution was feasible and efficient. In addition, leaching has been carried out by injecting in three points and pumping in two others. Nowadays, cadmium content as controlled in two boreholes under

permanent pumping at 2 m^3/h does not exceed 50 mg/l, same value as in the rest of the plant.

3) General balance at "Laboratory" point.

A permanent control located on the surface network (Riou Mort) on a point considered as perfectly representative ("Laboratory" point), is used in order to follow the impact of the installation.

Although hydrological conditions have been exceptionnally dry for two years, il is confirmed that cadmium emission has been drawn down and that, even when flow rates are high due to important rainfall, the maximum cadmium content approved by the authorities (500 g/h) is respected.

Thus, in general, actions carried out on the site have led to a cadmium lowering of 90%.

But this control leads the Vieille Montagne company to spend each year about 5 MF (1 M$) to maintain in order the station in which pumped waters are decontaminated.

The Company staff is of course eager to reduce, or even to cut off this operating costs, leading to a special study which has been launched in THR zone (Traitement humide des résidus = waste processing by humid way).

Dewatering of the THR zone.

Based on 10 boreholes, cadmium content analysis of water and of driling cuttings, an interpreted log has been drawn up, which confirms the interpretations which had been previously done:

- phreatic ground water does not flow in a normal way due to building fondations
- there exists a continuous and homogeneous clay layer
- ground water in porous medium flows under the buildings and goes to the P2 zone.

Generally speaking, from a zone in borehole F1 (1 mg/l Cd), there is a progressive enrichment of waters up to a mean value of 50 mg/l.

Two options can be taken to solve this problem:

- a "methodologic" way aimed at understand all the mecanisms involved,specially the role played by the clay layer (resorption)
- a pragmatig "field" way aimed at dewatering the downstream part of the heap (THR) where the clay layer - which is supposed to enrich the upper part of the aquifer in Cd - is located.

This second option has been chosen and includes three steps :

1) construction of a derivation system of surface waters coming from the upstream part of an old river bed covered by the heap

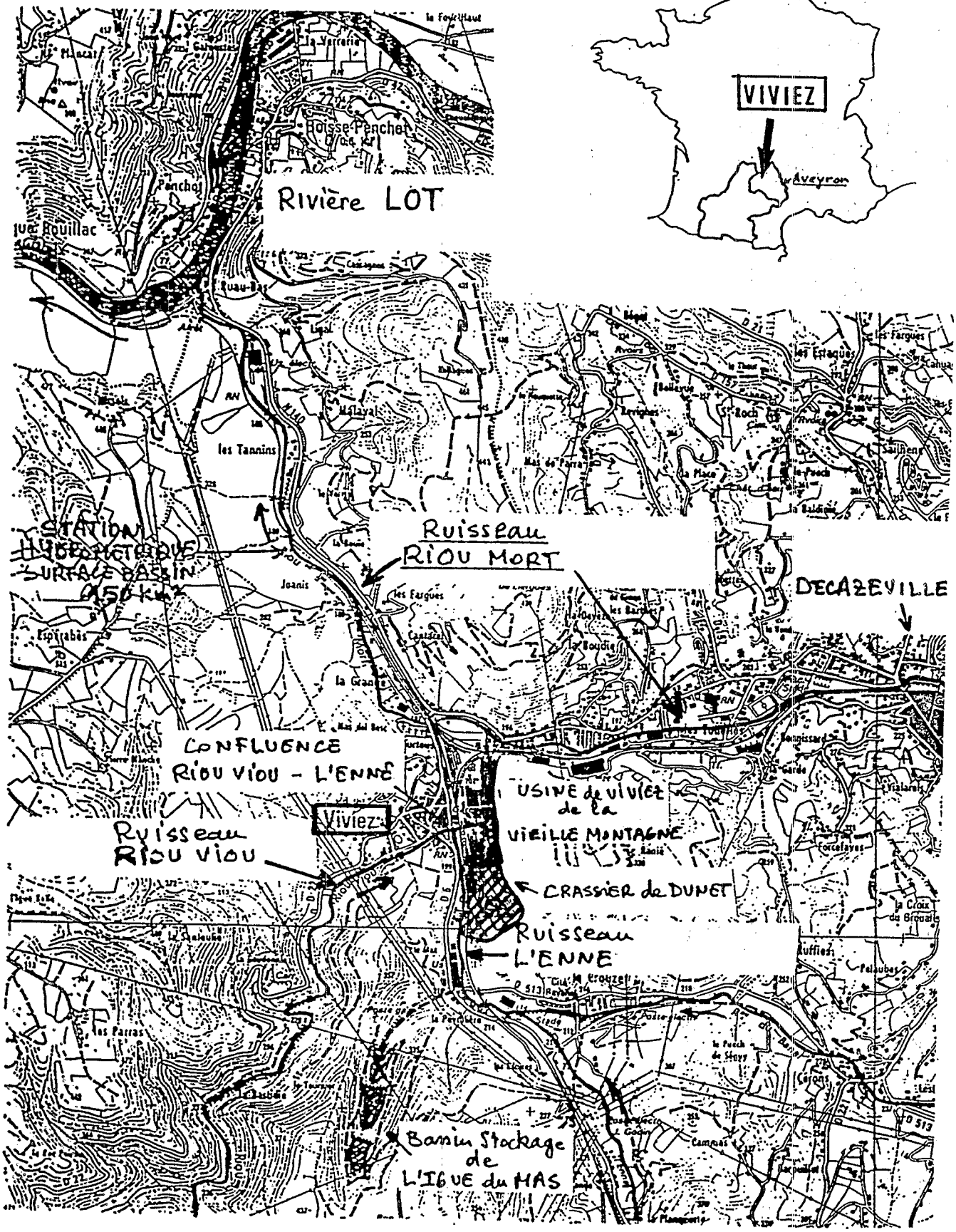
2) evaluation phase : it is supposed that waters infiltrated in the heap do not dissolv Cadmium, due to the high permeability of the "thermic" part of the wastes and to the protective impervious layer of the basins. If this hypothesis is confirmed, waters can directly be evacuated in the environment without flowing through the THR zone
Controls will be achieved through water analysis on F1 on a complete hydrological cycle.

3) Water recovery : in this case, it has been decided to dig a collecting system including a trench, an acces gallery and a final drain.

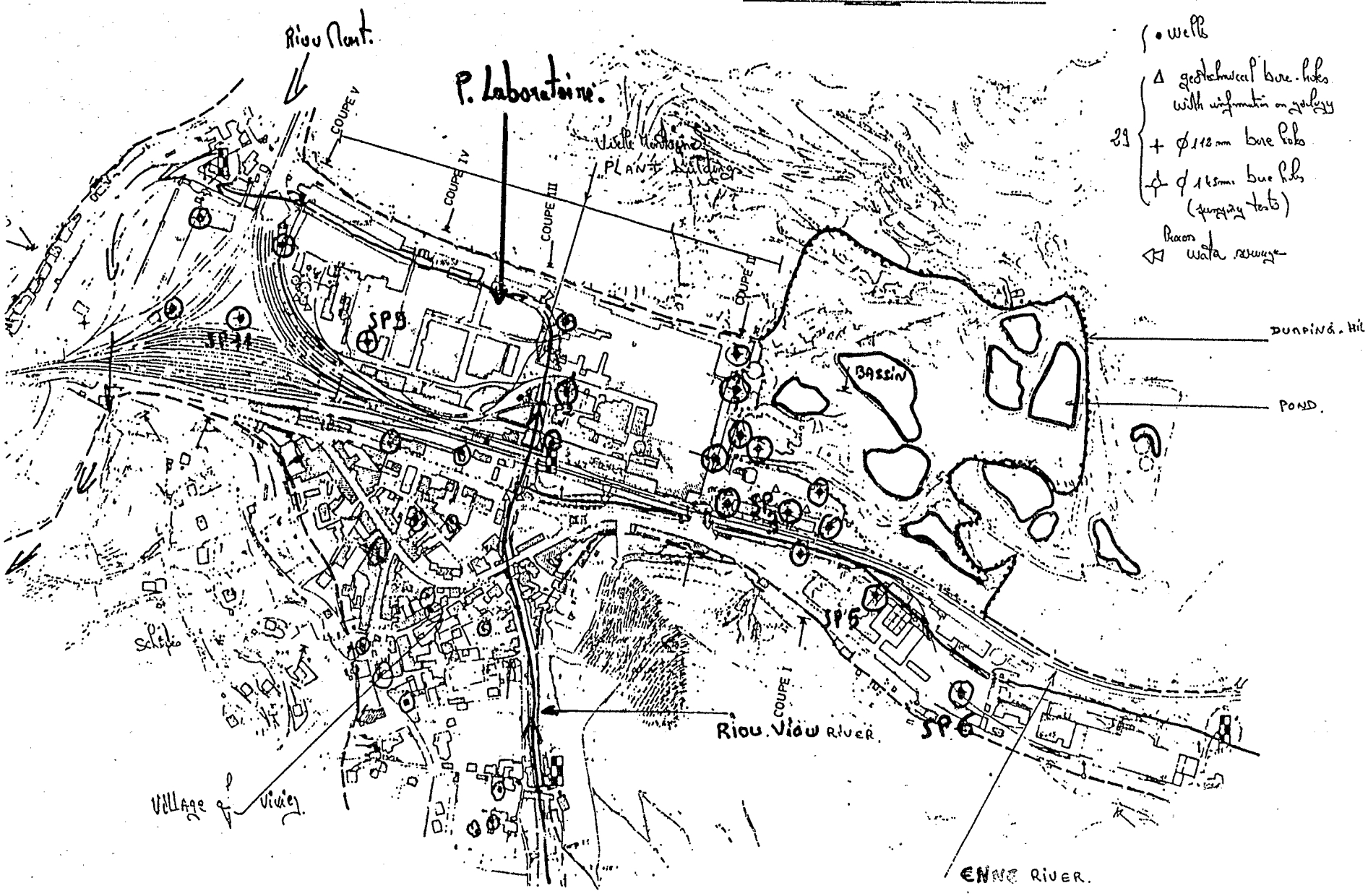
Calendar : decision to be taken in 1991 (if the hypothesis n°2 appears not to be ascertained,waters will have to be decontaminated); works to start in 1992.

Estimated cost : 2 MF.

PLAN de SITUATION



Ionlagne Usine de Viviez



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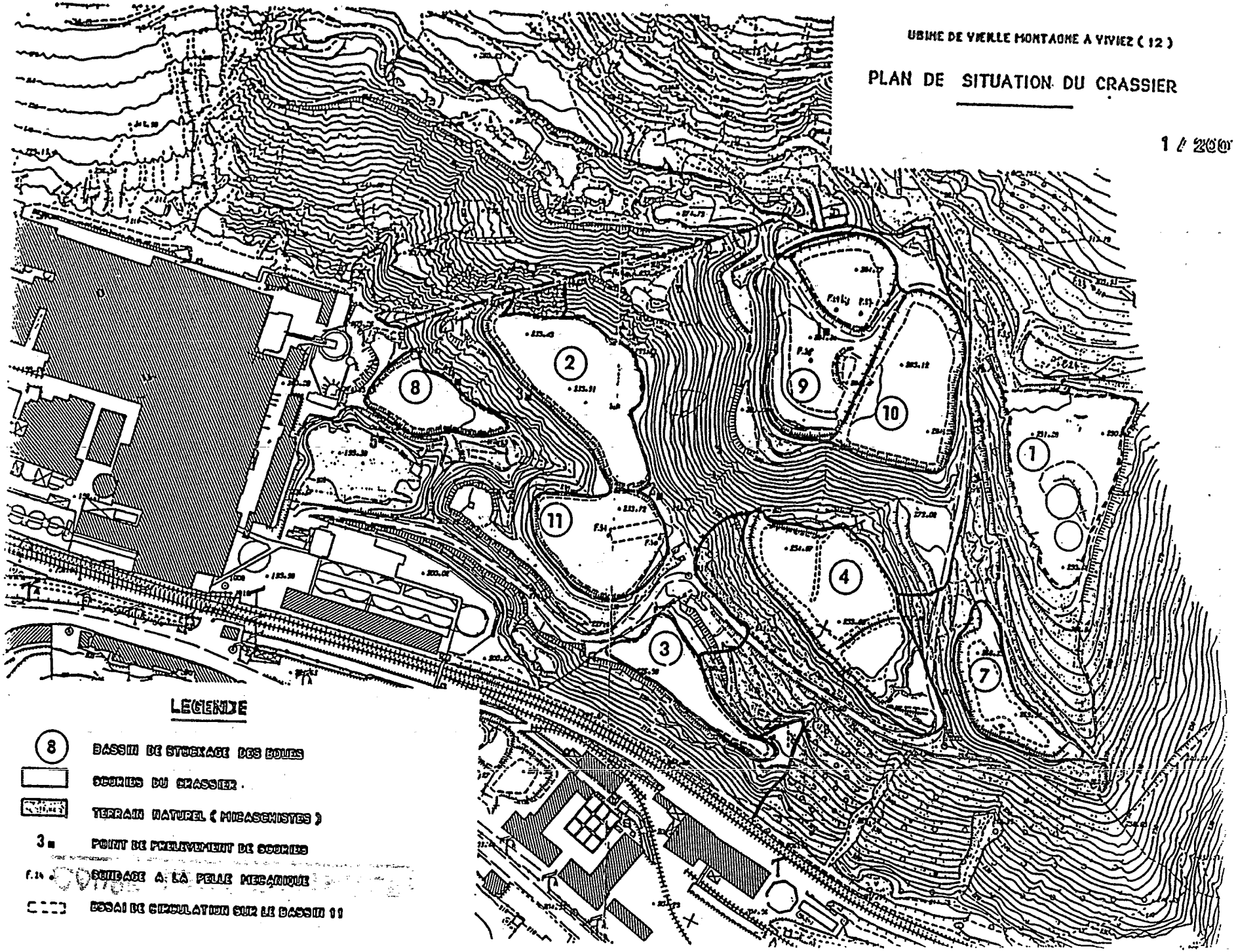
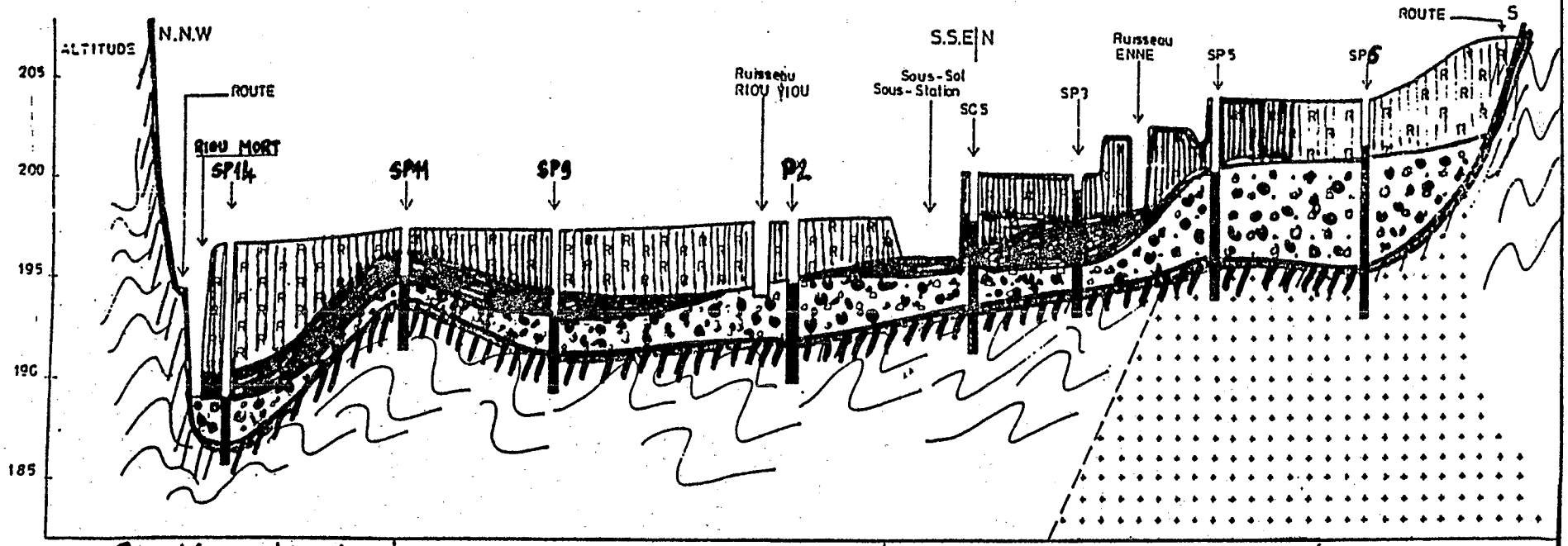
USINE DE VIEILLE MONTAGNE A VIVIEZ (12)

PLAN DE SITUATION DU CRASSIER

1 / 2000



COUPE LONGITUDINALE:



1219

P2 = désignation du SONDAGE
niveau d'eau.

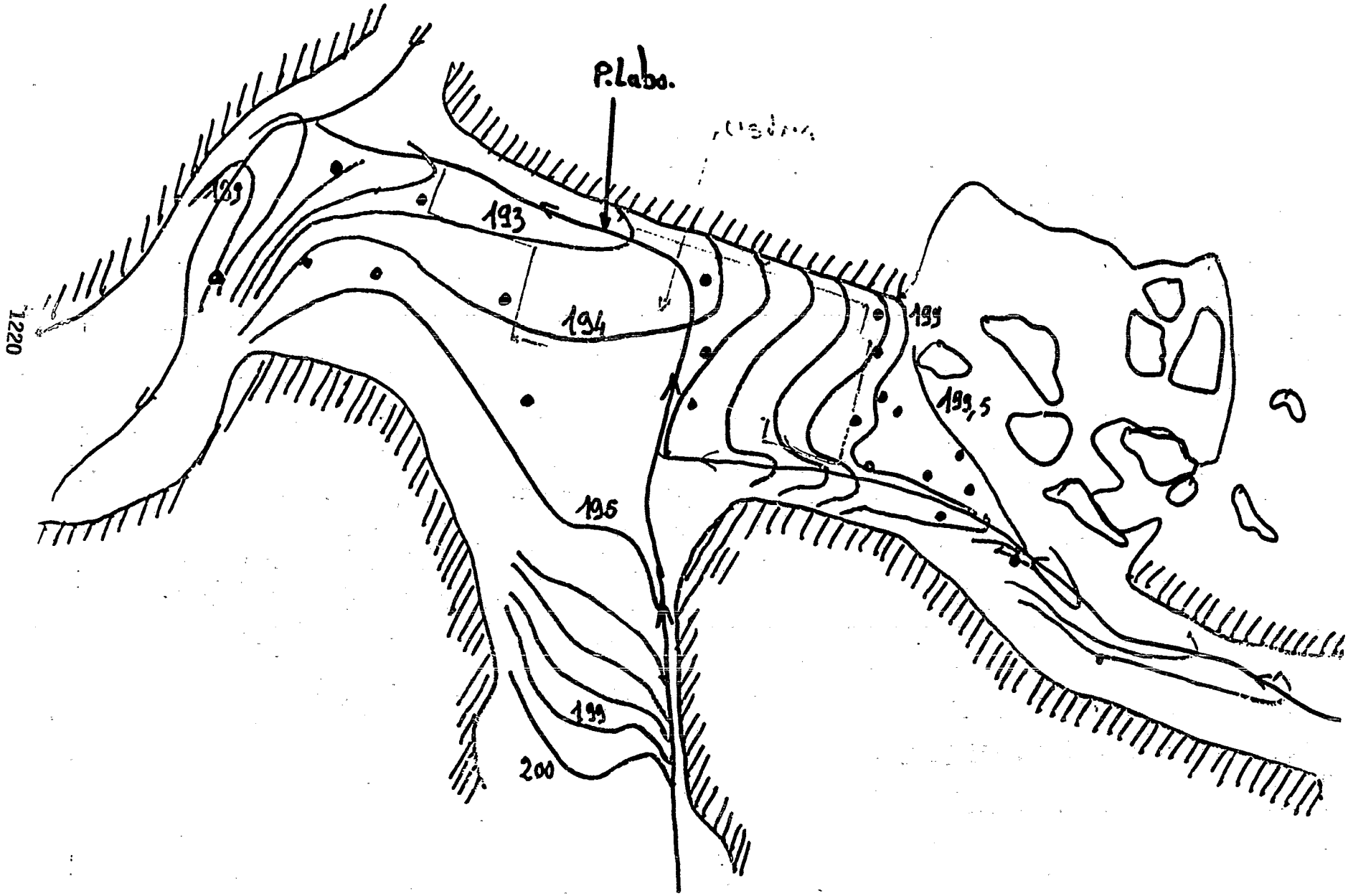
REMBLAIS CRASSIER

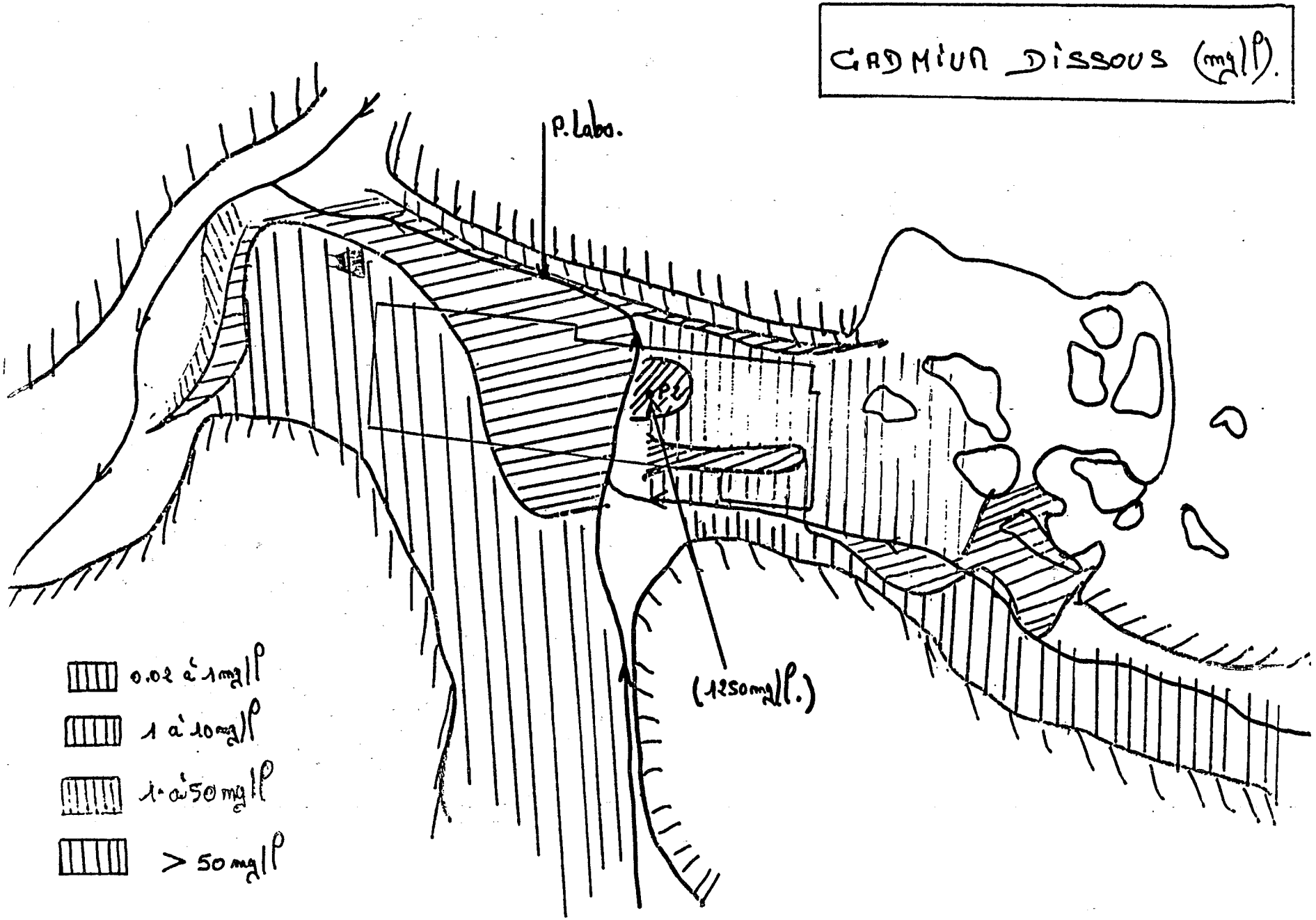
REMBLAIS TOUTVENANT

LENTILLE ARGILEUSE

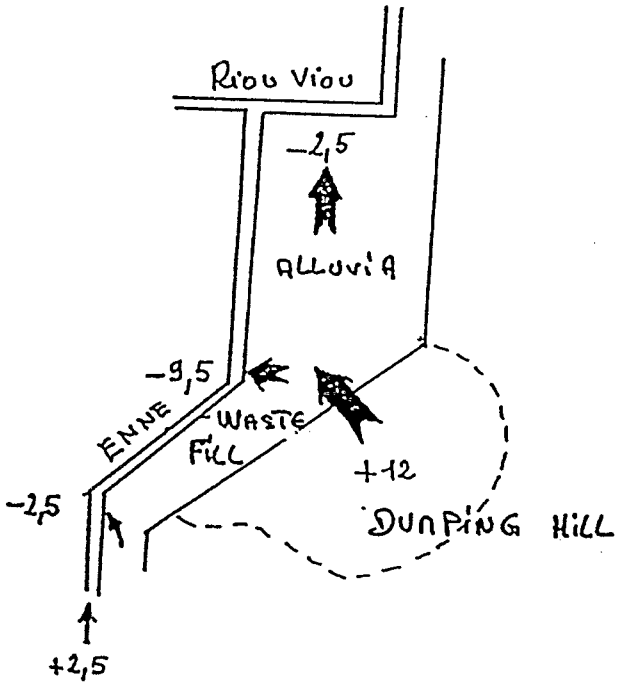
NAPPE ALLUVIALE
SUBSTRATUM SCHISTEUX

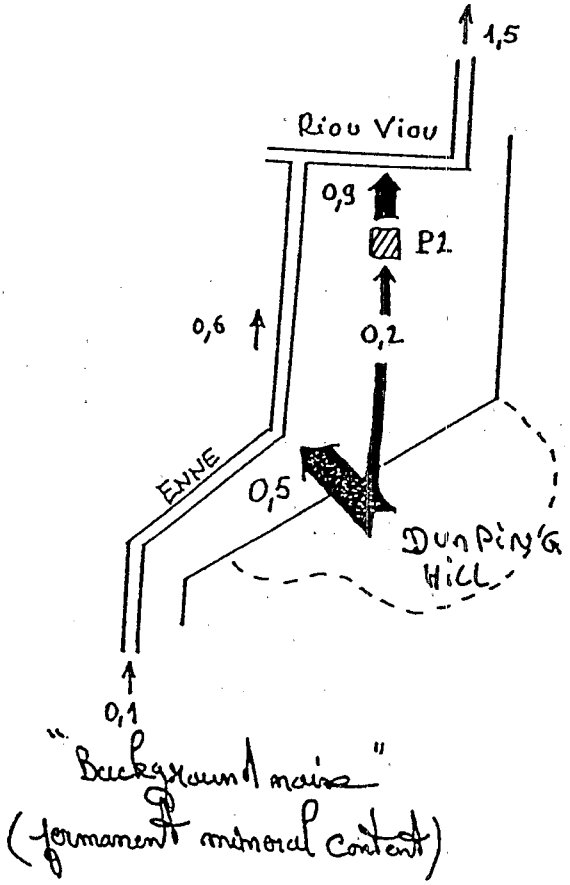
CARTE PIEZOMETRIQUE (AVRIL 1987)




CADMIUN DISSOUS (mg/l).
P. Labo.
(1250 mg/l.)
0.02 à 1 mg/l
1 à 10 mg/l
10 à 50 mg/l
> 50 mg/l

Schematic Balance of Discharges and Mineral Contents.





Schematic Balance of discharges (in m^3/h)

Schematic balance of Cadmium content (in kg/h) (out of dumping)

VIEILLE-MONTAGNE

Usine de Viviez - 12110 AUBIN

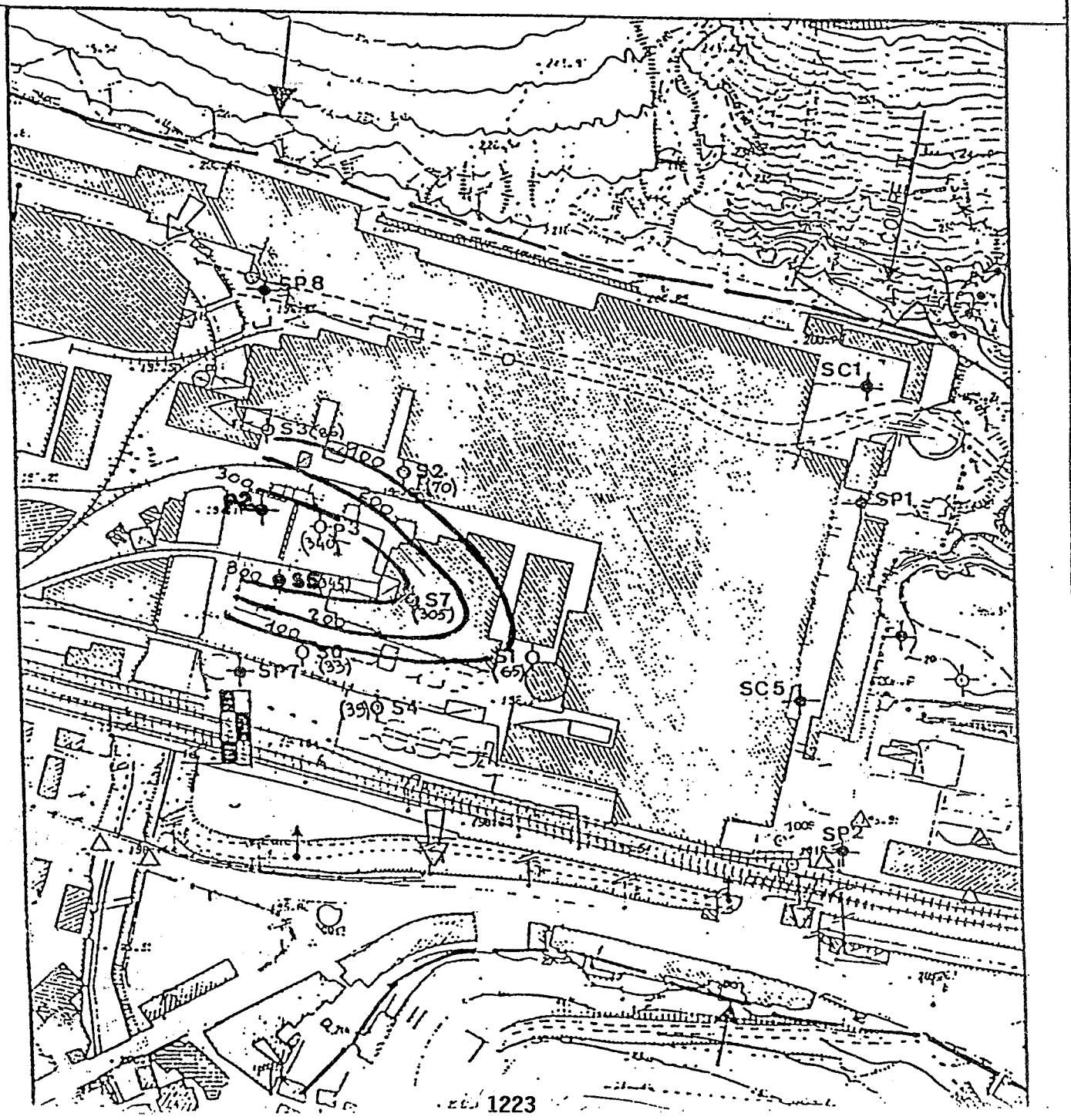
ETUDE HYDROGEOLOGIQUE et HYDROCHIMIQUE
de la PLAINE ALLUVIALE du RIOU VIOU

LEGENDE GENERALE

• P2.S5 POMPAGE DU 26/07/88 sur S5 : REPARTITION DES CONCENTRATIONS EN CADMIUM DE L'EAU DE LA NAPPE DANS LE SECTEUR DU P2

• S2.S4.S6.S7

Concentration en mg/l



CONCENTRATION MOYENNE EN CADMIUM DES EAUX AU POINT "LABORATOIRE"

ANNEES	x(mg/l)	Qm3/h	FLUX g/h	REMARQUES
89				
-				
-				
10	0.17	445	74	
11	0.16	683	106	
12	-	-	-	
90				
01	0.14	515	72	
02	-	-		
03	0.17	1 000	116	(pointe à 2 260 m3/h -> 0.10 mg/h)
04	0.14	1 120	123	(pointe à 1 850 m3/h -> 0.08 mg/h)
05	0.10	2 243	206	(pointe à 3 230 m3/h -> 0.10 mg/h)
06	0.10	720	26	(pointe à 1 130 m3/h -> 0.15 mg/h)
07	0.11	270	28	
08	0.14	180	30	
09				
10				
11				

12, VIVIEZ, VIEILLE MONTAGNE

PLANCHE 2

RECONNAISSANCE HYDROGEOLOGIQUE DU CRASSIER ET DU T.H.R

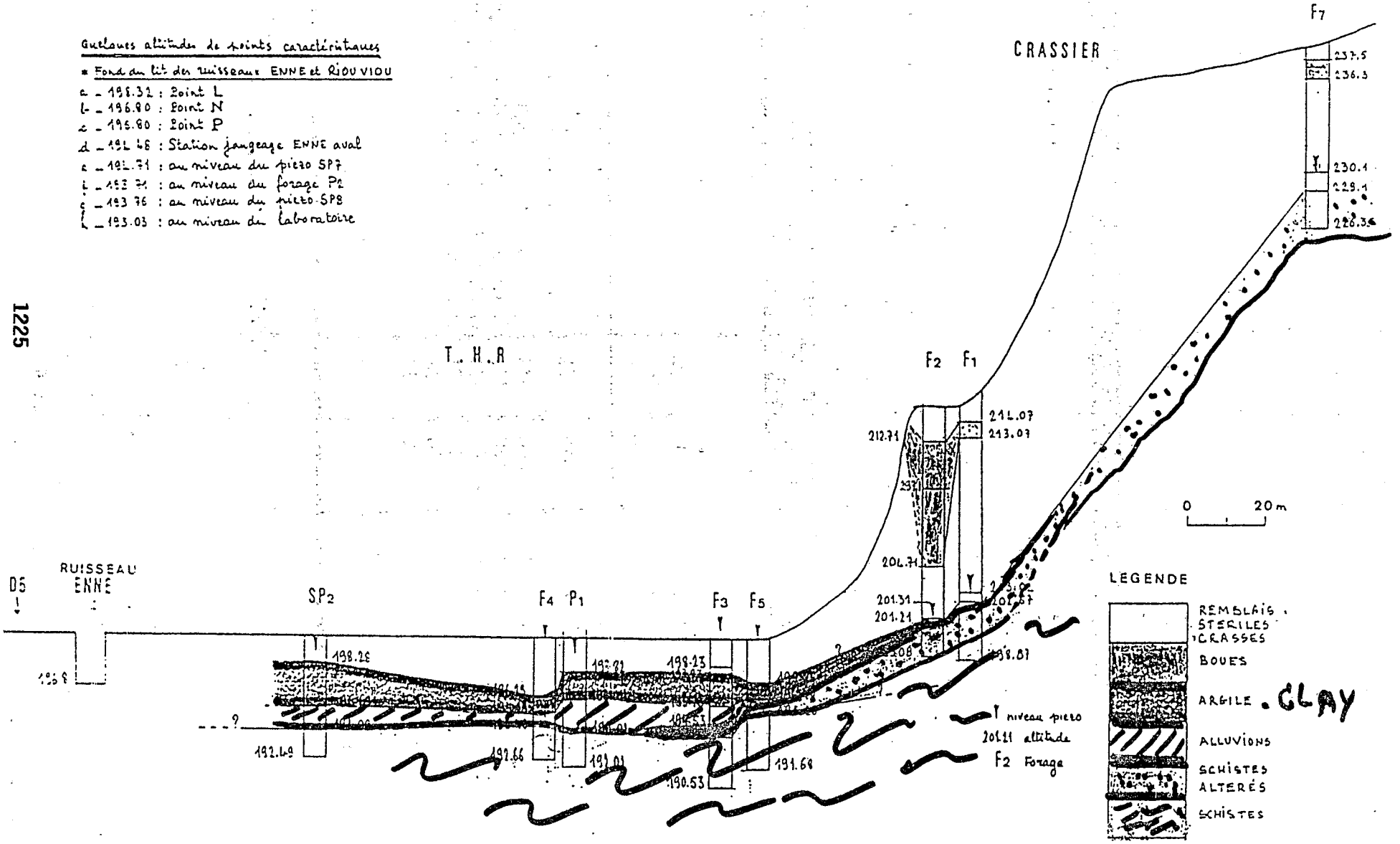
COUPE AU NIVEAU DU T.H.R ET DU CRASSIER

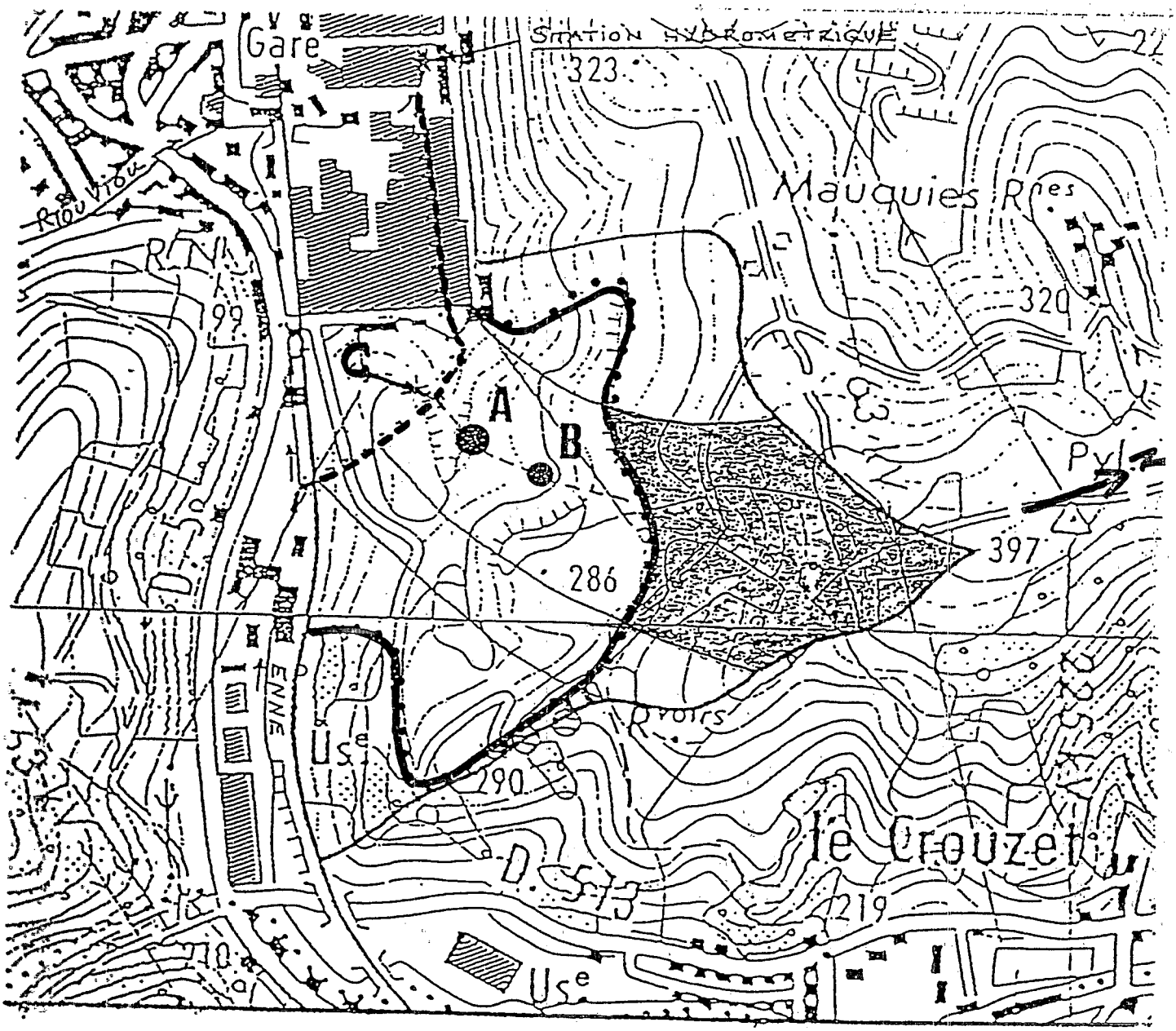
Quelques altitudes de points caractéristiques

* Fond du lit des ruisseaux ENNE et RIOU VIOU

a _ 198.32 : Point L
b _ 196.80 : Point N
c _ 196.80 : Point P
d _ 192.48 : Station jaugeage ENNE aval
e _ 192.71 : au niveau du piezo SP7
f _ 193.71 : au niveau du forage P2
g _ 193.76 : au niveau du piezo SP8
h _ 193.03 : au niveau du laboratoire

1225





LEGENDE

Bassin versant crassier

Limite d'extension maximale crassier

Fraien lit de l'Enne

Ravin Dunet

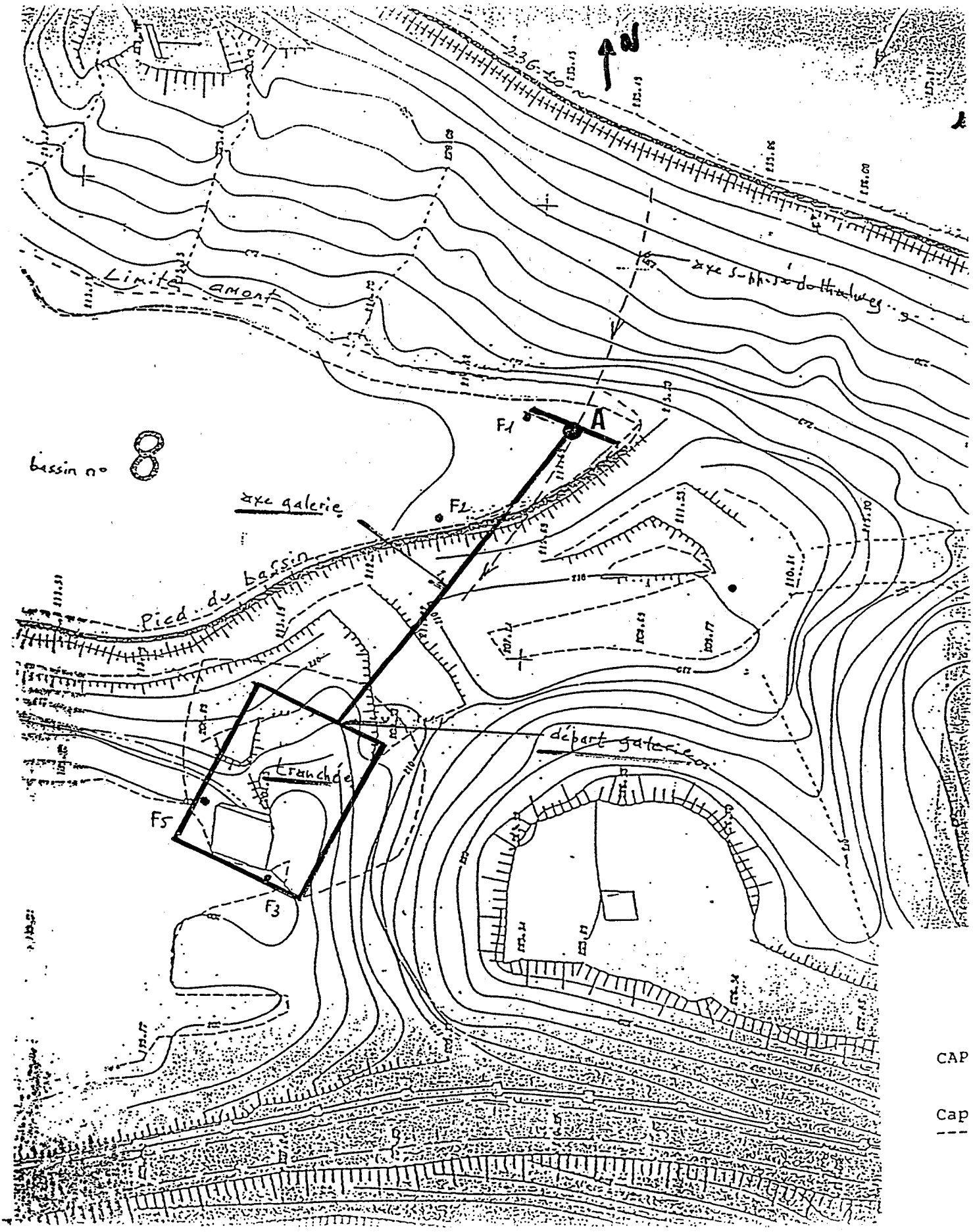
Confluence ancien lit Enne-Ravin Dunet, sous le crassier

Bassin versant amont cras. influençant le secteur d'é T.H.R, eau de ruissellement Surface = 67.180 m²

Bassin versant sous cr influençant le secteur d'é T.H.R eau d'infiltration Surface = 48.600 m²

★ Station hydrométrique "La

0 m


Limite amont
axe galerie
Pied de bassin
tranchée
départ galerie
F1
F2
F3
F5
A
bassin n° 8

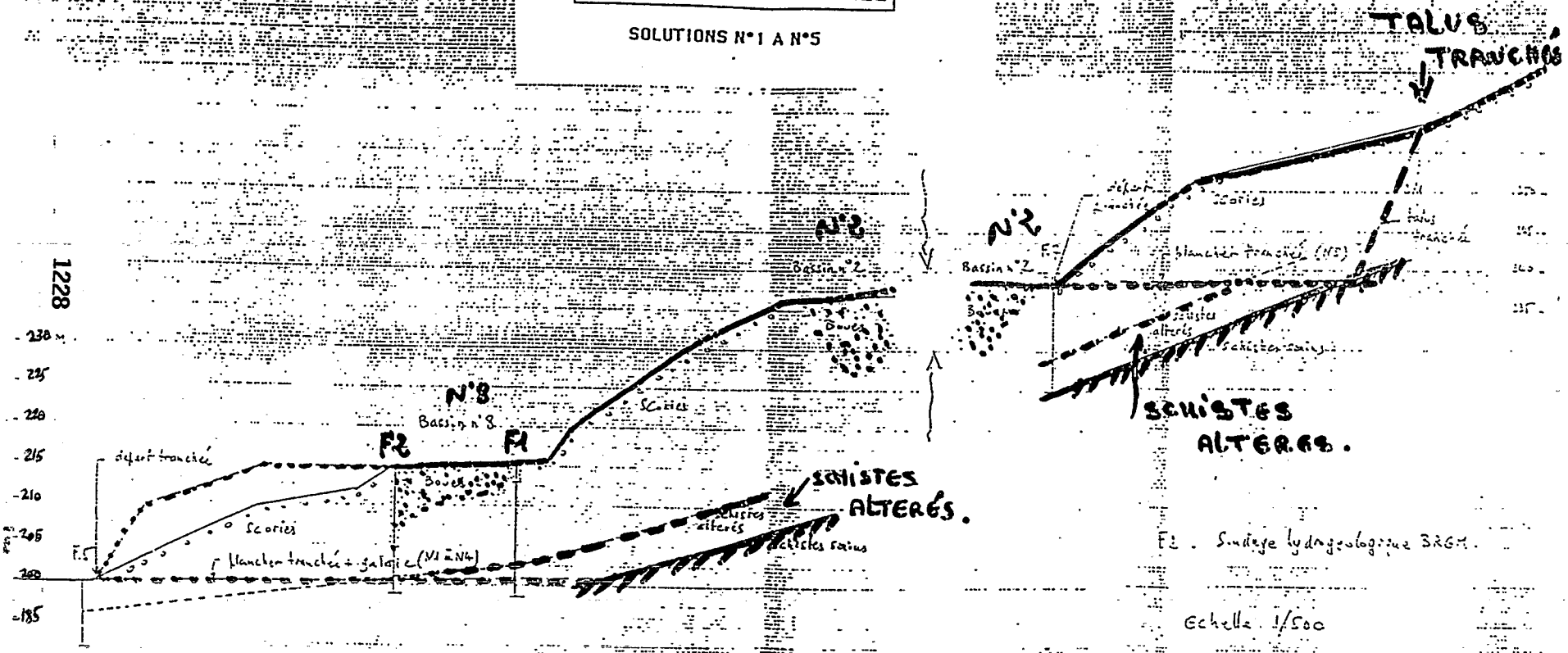
CAP

Cap

CAPTAGE DU RUISSEAU DU CRASSIER DE DUNET

COUPE LONGITUDINALE

SOLUTIONS N°1 A N°5



F2 . Sondage hydrogéologique BRGM.

Echelle 1/500

DEPENSES ENGAGEES POUR LE TRAITEMENT DES CRASSIERS

(exprimées en Francs français)

PRINCIPAUX POSTES	1987	1988	1989	1990	Sous-Totaux
1. Campagnes de forages analyses, suivis, aménagements transferts de boues...	1 325 000	1 665 000 1 550 000	1 020 000	300 000	
2. Station de traitement des eaux		860 000			
3. Aménagements du point de mesure (point laboratoire)	45 000	130 000			
4. Etude des mécanismes de fixation des ions dans le sol	250 000				
5. Mise en place d'un filtre presse				1 600 000	
SOUS-TOTAUX	1 620 000	4 205 000	1 020 000	1 900 000	8 745 000
6. Frais de fonctionnement : (traitement des eaux)		7 500 000	5 000 000	4 000 000	16 500 000
7. Aménagements des bassins de l'Igue du Mas			1 420 000	1 900 000	3 320 000
TOTAL GENERAL					28 565 000

Appendix 6-D

Ground Water Pump and Treat Technology Case Studies

Separation Pumping, Skrydstrup, Denmark

The NATO/CCMS Pilot Study on
Demonstration of Remedial Action
Technologies for Contaminated
Land and Groundwater

Fourth International Conference
5-9 November 1990
Angers
France

THE SEPARATION PUMPING TECHNIQUE

by
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Rasmus Jakobsen

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Denmark

0. Abstract

Demonstration tests of the separation pumping technique has been performed at several sites in Denmark. The separation pumping technique relies on simultaneous pumping from top and bottom of a fully penetrating well, through the polluted section of the aquifer. Separation pumping is developed from the concept of scavenge pumping. The method can optimize remedial action pumping by minimizing the volume of polluted water to be treated. Furthermore the inflow distribution and transmissivity of selected sections of a well can be determined. Moreover the method can be used for collection of level-accurate samples. Finally, changes in the vertical distribution of pollutants in the aquifer as a function of pumping time can be monitored.

Results from two different sites, a sand and gravel aquifer, and a limestone aquifer show that separation of polluted groundwater from slightly polluted or non-polluted groundwater was possible, and for the sand and gravel aquifer the amount of water to be treated was initially reduced to 40%. Tests with separation pumping as an investigation tool at a third site, showed that the influx distribution could be determined with high precision, and very high vertical concentration gradients could be discerned with separation pumping used as a level-accurate sampling method.

3. Methodology

3.1. Separation pumping

The water well is simultaneously pumped by two pumps at the top and bottom, respectively, Fig. 1. A water divide is created in the borehole between the two pumps. Water from above the water divide will move towards the top pump and water below the water divide towards the bottom pump.

By adjusting the pumping rates of the two pumps the water divide can be established at any position in the borehole according to the ratio between the pump rates and the hydraulic conductivity above and below the divide. These position are unknown but can be found indirectly by a separation injection test (SIT), see section 3.2, by conventional flow-logs or by direct measurement with a Heat-Pulse-Flow-Meter (HPFM), see section 3.3.

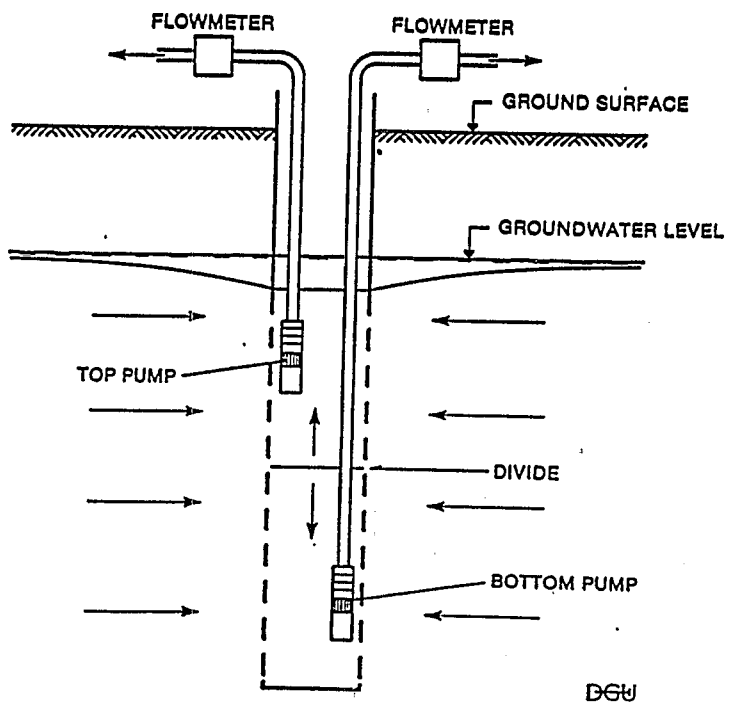

Fig. 1.: Schematic illustration of separation pumping by simultaneous pumping from top and bottom of a well. From Andersen (1990).

The following parameters are measured during separation pumping for every "steady state" situation (step), the total capacity is kept constant for all steps.

a) The pumping rates for the top and bottom pumps.
b) The chemical composition of the water from the top and bottom pumps.
c) The water level in the borehole.

The water samples from the top and bottom pumps are taken when these parameters are stabilized at each pumping ratio (step). The vertical distribution of a pollutant within the penetrated part of the aquifer can be calculated.

The principles of a 9 step separation pumping is shown in Fig. 2. Nine different combinations of pumping rates (step 1 - 9) divides the screened part of the well in 10 inflow intervals.

The flow pattern shown on the sketch corresponds to step 3, where intervals I1-I3 supply the top pump and intervals I4-I10 the bottom pump.

For steady state conditions the total flux of each pollutant leaving the well $((Q \cdot C)^t + (Q \cdot C)^b)$ should be constant.

The influx of the pollutants from the ten intervals: $q_i \cdot c_i$ $(i=1,2,.....,10)$ can be calculated from the following equations:

$$
\begin{aligned}
q_1 \cdot c_1 &= (Q_1 \cdot C_1)^t \\
q_2 \cdot c_2 &= (Q_2 \cdot C_2)^t - (Q_1 \cdot C_1)^t \\
q_3 \cdot c_3 &= (Q_3 \cdot C_3)^t - (Q_2 \cdot C_2)^t \\
q_4 \cdot c_4 &= ((Q_4 \cdot C_4 - Q_3 \cdot C_3)^t + (Q_3 \cdot C_3 - Q_4 \cdot C_4)^b)/2 \\
q_5 \cdot c_5 &= ((Q_5 \cdot C_5 - Q_4 \cdot C_4)^t + (Q_4 \cdot C_4 - Q_5 \cdot C_5)^b)/2 \\
q_6 \cdot c_6 &= ((Q_6 \cdot C_6 - Q_5 \cdot C_5)^t + (Q_5 \cdot C_5 - Q_6 \cdot C_6)^b)/2 \\
q_7 \cdot c_7 &= ((Q_7 \cdot C_7 - Q_6 \cdot C_6)^t + (Q_6 \cdot C_6 - Q_7 \cdot C_7)^b)/2 \\
q_8 \cdot c_8 &= (Q_7 \cdot C_7)^b - (Q_8 \cdot C_8)^b \\
q_9 \cdot c_9 &= (Q_8 \cdot C_8)^b - (Q_9 \cdot C_9)^b \\
q_{10} \cdot c_{10} &= (Q_9 \cdot C_9)^b
\end{aligned}
$$

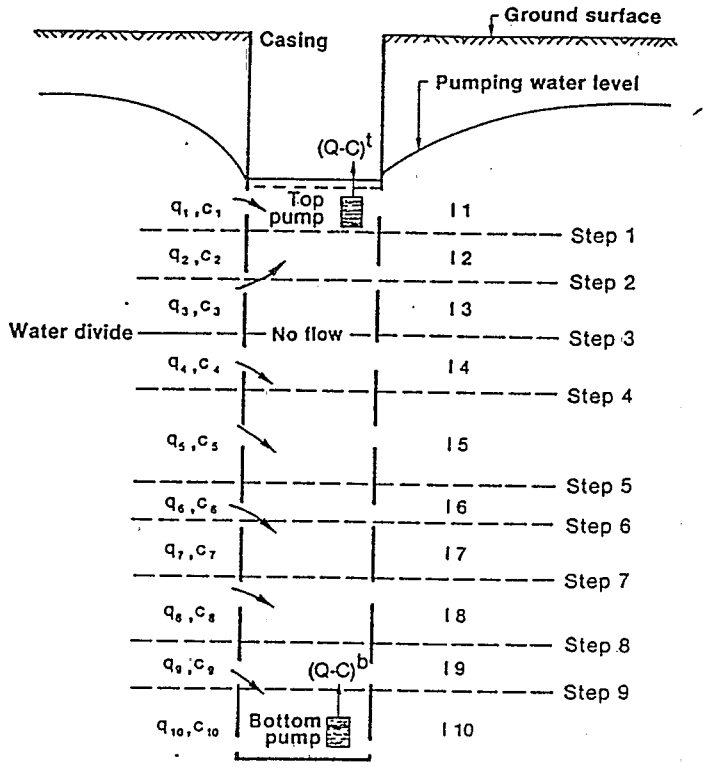

Fig. 2.: Sketch of a 9 step separation pumping. Q = measured pumping rate, C = measured concentration, b = bottom, t = top, c = calculated concentration and q = calculated inflow from the aquifer.

The q·c-fluxes for the top and the bottom intervals are given directly from the measurements, the fluxes for interval I2, I3, I8 and I9 are calculated using the top and bottom data respectively while the middle intervals I4-I7 are calculated using average values from the top and bottom pumps.

All Q-values are measured and q-values are easily calculated.

$$q_1 = (Q_1)^t$$
$$q_2 = ((Q_2 - Q_1)^t + (Q_1 - Q_2)^b)/2$$
$$q_3 = ((Q_3 - Q_2)^t + (Q_2 - Q_3)^b)/2$$
$$q_4 = ((Q_4 - Q_3)^t + (Q_3 - Q_4)^b)/2$$
$$q_5 = ((Q_5 - Q_4)^t + (Q_4 - Q_5)^b)/2$$
$$q_6 = ((Q_6 - Q_5)^t + (Q_5 - Q_6)^b)/2$$
$$q_7 = ((Q_7 - Q_6)^t + (Q_6 - Q_7)^b)/2$$
$$q_8 = ((Q_8 - Q_7)^t + (Q_7 - Q_8)^b)/2$$
$$q_9 = ((Q_9 - Q_8)^t + (Q_8 - Q_9)^b)/2$$
$$q_{10} = (Q_{10})^b$$

The principles of calculation and assumptions are described in Andersen et al. (1989) and Gosk & Bishop (1989).

3.2. Hydraulic conductivity log

3.2.1. Separation pumping test (SPT)

The object of the separation pumping test (SPT) is to determine the inflow distribution in a well. The principle is seen in Fig. 2 for a 9 step SPT. The location of the water divides is done with a Heat-Pulse-Flowmeter, described in section 3.3. The yield of each section can be calculated as shown in section 3.1.

3.2.2. Separation injection test (SIT)

The separation injection test (SIT) is an inverted (SPT). Water is injected to the top and the bottom of a well and of the measured flow rates are the recharge rates of the intervals above and below the convergence zone, the opposite of a water divide. The location of the convergence zone between top-water and bottom-water is determined by using an in-hole-detectable tracer mixed in the top- or bottom injection water. For example chloride, in a concentration sufficient enough to separate it from fresh water, can be used. The interface between the salty

and the fresh water is detected by an electric conductivity probe.

3.3. Level-accurate water sampling

The well is simultaneously pumped from top and bottom, Fig. 3. The position of the water divide is found by a Heat-Pulse-Flow-Meter (HPFM). A HPFM-probe is a directional low-velocity flowmeter. An electric energy pulse is fired through a wire grid creating a small volume of warm water and its direction and velocity, corresponding to the flow of the fluid in the borehole, is determined by the monitoring of two thermistors, one above and one below the wire grid.

A water sample is collected at the water divide by a third pump, pumping with a yield of a few percents of the total capacity with which the well is pumped.

By varying the pumping rates of the two pumps, the water divide can be placed at any depth so that a chemical profile of the penetrated sequence of the aquifer, can be made.

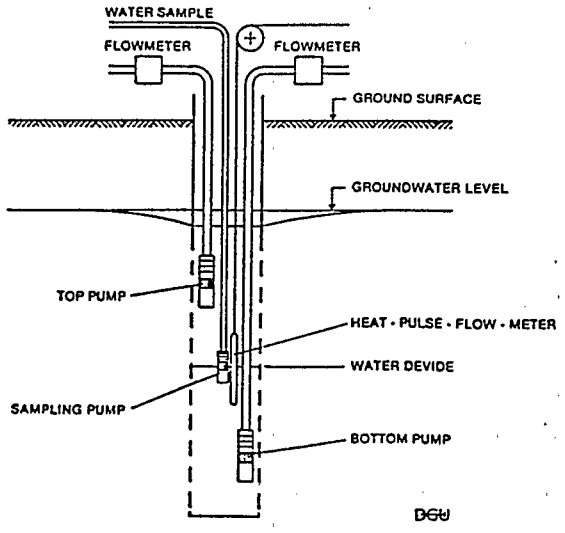

Fig. 3.: Schematic illustration for level-accurate groundwater sampling by separation pumping. From Andersen (1990).

3.4. Separation pumping as a remedial action

From the concentration profile determined in section 3.1, it is known at which yield ratio between the top and bottom pumps one of the pumps only recover water from the polluted layer and the other water from the unpolluted layer, Fig. 4. In this way the volume of polluted water is restricted to a minimum, the polluted part of the inflow to a well. The efficiency of the method is limited if the partial transmissivity of the unpolluted layer is much smaller than the one of the polluted layer.

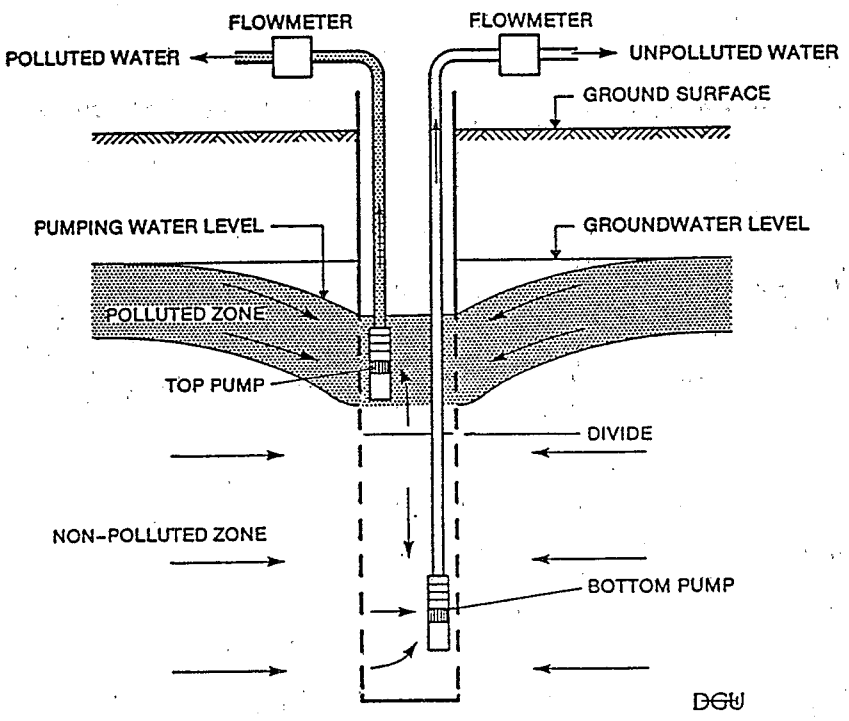

Fig. 4.: Schematic illustration of remedial action pumping by use of separation pumping technique. From Andersen (1990).

4. Results and discussion

The separation pumping technique has been tested at different sites in Denmark and has been used at a site in United Kingdom. Experiments from three sites in Denmark are presented.

4.1. Experiments of remedial action pumping in a sandy aquifer

4.1.1. Site description

The first tests have been performed at the chemical waste disposal site registered under No. 543-01, Skrydstrup, Municipality of Vojens, County of Sønderjylland. The site is located close to Skrydstrup Airport, Vojens City and approximately 2,5 km up-stream one of the water works of the Municipality of Vojens (Fig. 5).

Fig. 5.: Locations of test sites in Denmark.

In the period 1963-1974 chemical waste has been dumped in an old gravel pit near Skrydstrup by a refrigerator factory. The waste caused a considerable contamination of the groundwater by

chlorinated solvents, mainly 1,1,1-trichloroethane and organic phosphorus compounds.

The waste was excavated in 1986, the drums with chlorinated solvents were sent to destruction, and the contaminated soil was placed in a special waste disposal site with aerobic/anaerobic in-situ biodegradation of the chlorinated compounds. The latter enter into the NATO Pilot Studies.

The pollution plume has been found up to 1,5 km down-stream from the dump site. The remedial action pumping is from four wells screened to a depth of about 25 m.b.s. The pumped water is treated in a on-site groundwater cleaning plant by air-stripping, and active carbon filtration. In November 1988, at the beginning of the remedial action pumping, wells PB2, PB5, PB9 and PB10 were used, (Fig. 6). In june 1989 well PB5 was replaced by well PB16, in which the demonstration experiments with separation pumping were performed.

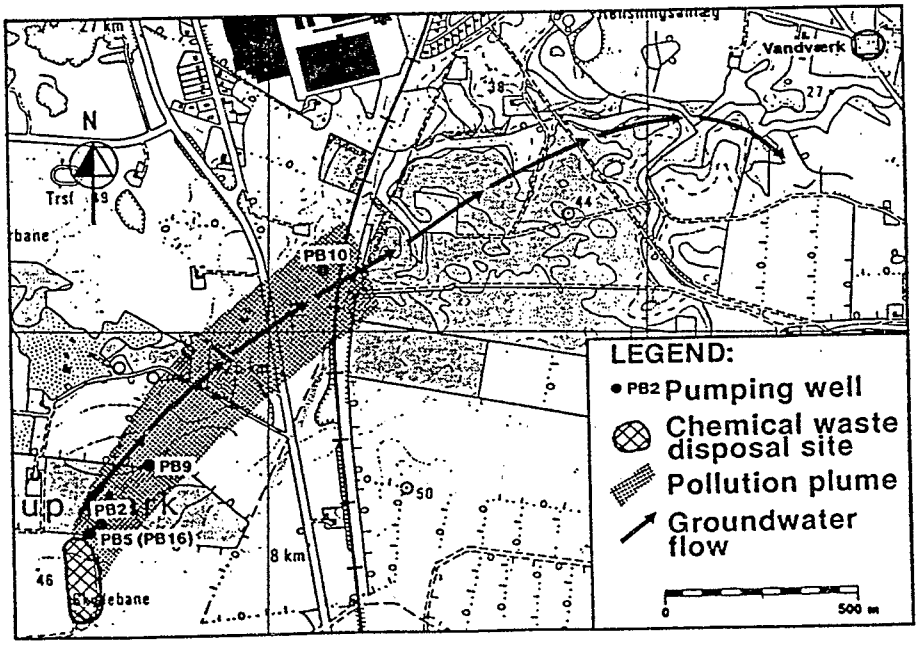

Fig. 6.: Skrydstrup chemical waste disposal site and the pollution plume. Location of the remedial action pumping wells PB2, PB5, PB9, PB10, PB16 and the direction of groundwater flow are shown.

4.1.2. Hydrogeology

The aquifer material consists of meltwater sand and gravel under water table conditions. The thickness of the aquifer is about 60 m, just below the waste disposal site, decreasing down-stream, and the water table is approximately 4-10 m.b.s. The thickness of polluted groundwater was 7-10 m at the beginning of the experiment, determined by a well drilled close to well PB16, section 4.1.4.

4.1.3. Experimental set-up

Well PB16 is 200 mm in inner diameter, 25 meter deep, and screened from 6-25 m.b.s. The set-up consists of two submersible pumps (max. capacity 11 m^3/hr) in the borehole, valves to adjust the pumping rates of the two pumps, and electromagnetic flow-meters to measure the actual flow from each pump.

4.1.4. Results and discussion

First a 9 step separation pumping was performed, dividing the inflow interval in 10 sections each contributing a flow partial of approximately a 1/10 of the total discharge of 10 m^3/hr. (Fig. 2). The positions of the water divides have been estimated indirectly from an impeller flow log, run in well PB5. Fig. 7 shows a calculated concentration profile of three chlorinated solvents (TCA, TCE and TeCE) and the electrical conductivity (EC). It is seen that the concentration of the pollutants is highest in the upper most intervals I1-I2 and the concentration decreases strongly in interval I3 and the underlying intervals. Generally 1,1,1-trichloroethane occur in a concentration about 10 times higher than trichloroethylene while tetrachloroethylene only occur in the upper most intervals I1-I2 in a concentration below 1 µg/l. The electrical conductivity is correlated to the chlorinated solvents. Furthermore it appears from Fig. 7, that approx. 30% of the total yield is coming from the inflow interval 7,5 - 17,0 m.b.s., while 40% comes from 17,0 - 20,5 m.b.s. and the last 30% from a depth of 20,5 - 25 m.b.s.

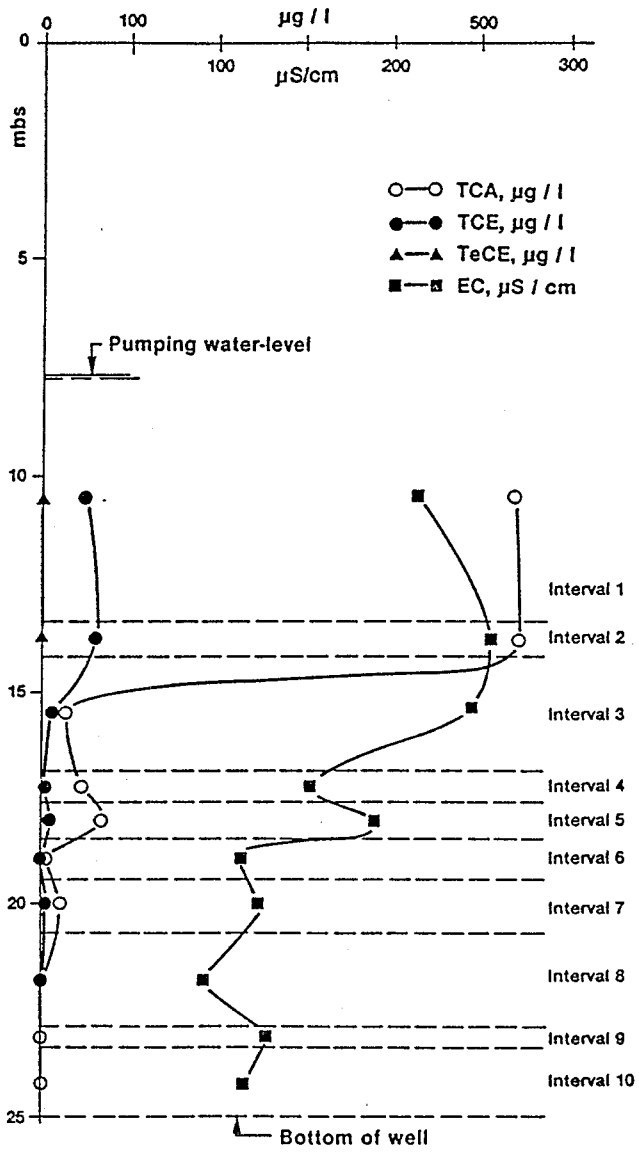

Fig. 7.: Calculated concentration profile in well PB16, Skrydstrup of the chlorinated solvents (1,1,1-trichloroethane (TCA), trichloroethylene (TCE), tetrachloroethylene (TeCE)) and the electrical conductivity (EC) compared with the interval depths.

The calculated concentration profile of the chlorinated solvents has been confirmed immediately after by drilling a BOTESAM-well (Larsen & Andersen, 1988) a few meters from the testing well, sampling groundwater for every meter (Fig. 8).

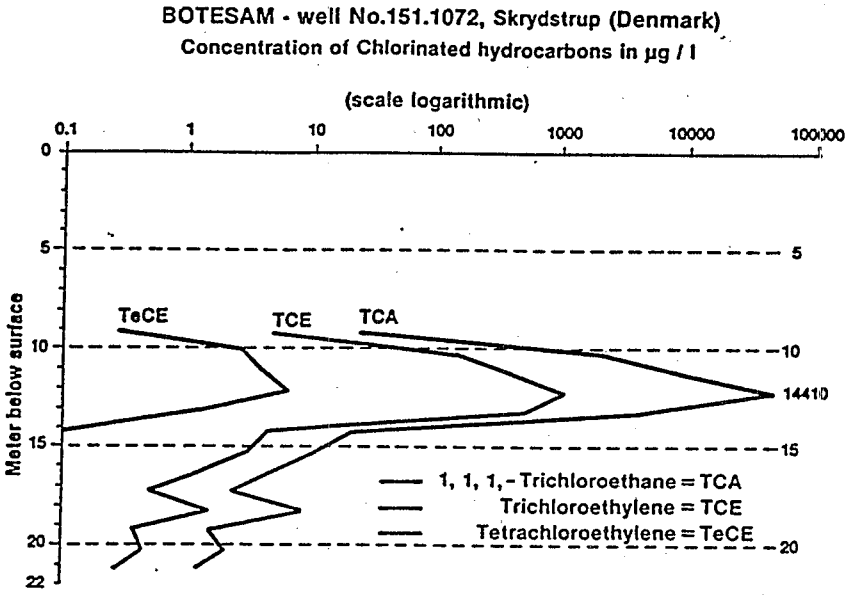

Fig. 8.: Chemical profile from the BOTESAM-well, Skrydstrup.

Based on the results of the separation pumping test it is possible to optimize the remedial action pumping by separation pumping, (section 3.4). The efficiency of the optimization has been examined as a function of the pumping time (Fig. 9). Further the optimized remedial action pumping with two pumps has been compared to the situation where, traditionally, only a single pump is used so, that water from polluted layers is mixed with water from non-polluted layers. In the period July - October 1989 the content of chlorinated solvents in the bottom water was below 1 µg/l while the concentration in the top water was 900 - 1450 µg/l when the contribution from the top pump varied from 35% - 50% of the total discharge and the bottom pump from 65% - 50%. In the subsequent period November 1989 - March 1990 the pump ratios are changed in order to keep the non-polluted bottom water free of solvents. This means that less than 10% of the total discharge is non-polluted water. This must be related to a change in vertical distribution of chlorinated solvents within the aquifer. The change is probably due to reinfiltration of the cleaned water from the treatment plant, into a pit at the

disposal site. This must cause a downwards movement in the groundwater, which appears to have forced the lower boundary of the plume, downwards by 10 meters in 9 months, at the position of the test well.

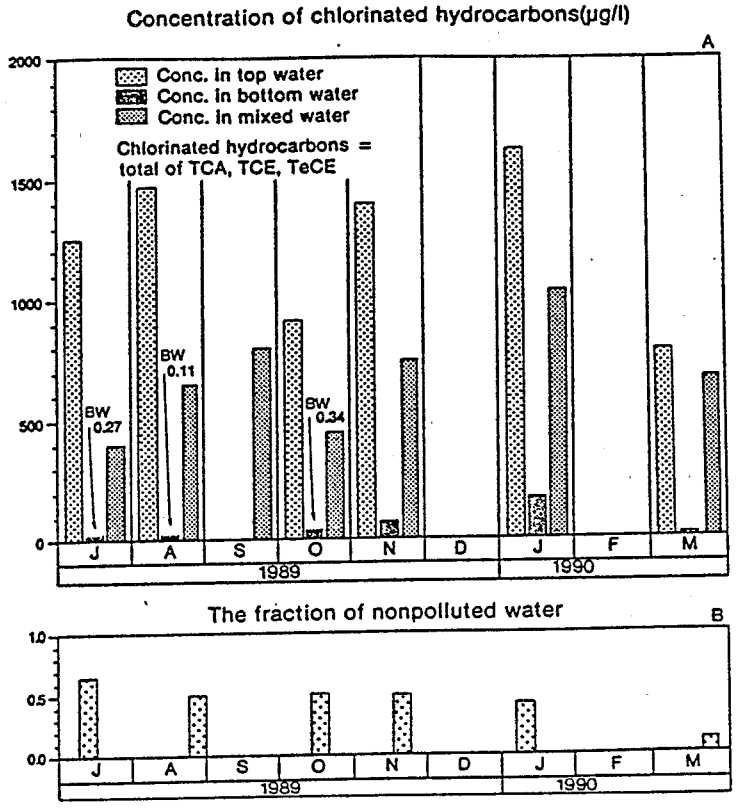

Fig. 9.: Optimized remedial action pumping by separation pumping in well PB16, Skrydstrup. Test period July 1989 - March 1990. A: The concentration of chlorinated hydrocarbons, a total of TCA, TCE and TeCE, in top, bottom and mixed pump water. B: Fraction of non-polluted water of total yield.

4.2. Experiments of remedial action pumping in a limestone aquifer

4.2.1. Site description

Tests have been performed in a Water Supply well at P. Andersens Vej Waterwork, Municipality of Frederiksberg, situated in the

Chlorinated solvents, mainly trichloroethylene (TCE), have polluted the limestone aquifer. One of the water supply wells at the test site is slightly contaminated with up to 15-20 µg/l TCE in the production water. This was chosen as the test well.

4.2.2. Hydrogeology

The confined limestone aquifer with fissure flow occurs from about 20 m.b.s. and downwards. The test well has a diameter of 300 mm, is about 71 m deep, and has an open-hole interval from 50-71 m.b.s. All the water supply wells in the municipality of Frederiksberg are situated in a 500 m wide, high yielding fault zone, named the Carlsberg Fault.

4.2.3. Experimental set-up

The experimental arrangement consists of two submersible pumps placed in the borehole, one just above the bottom of the casing with the intake approx. 47 m.b.s. and the other pump near the bottom of the well with the intake approx. 68 m.b.s. The submersible pumps each have a max. capacity of approx. 50 m^3/hr.

4.2.4. Results and discussion

Modifying the equations presented in section 3.1., and calculating, gives the distribution of concentrations of TCE and the electrical conductivity (EC) for a 7 step separation pumping presented in Fig. 10. The calculated TCE values shows higher concentrations in the upper inflow intervals I1-I3 than in the lower ones, while the EC-values are highest in the bottom of the well, inflow intervals I7-I8.

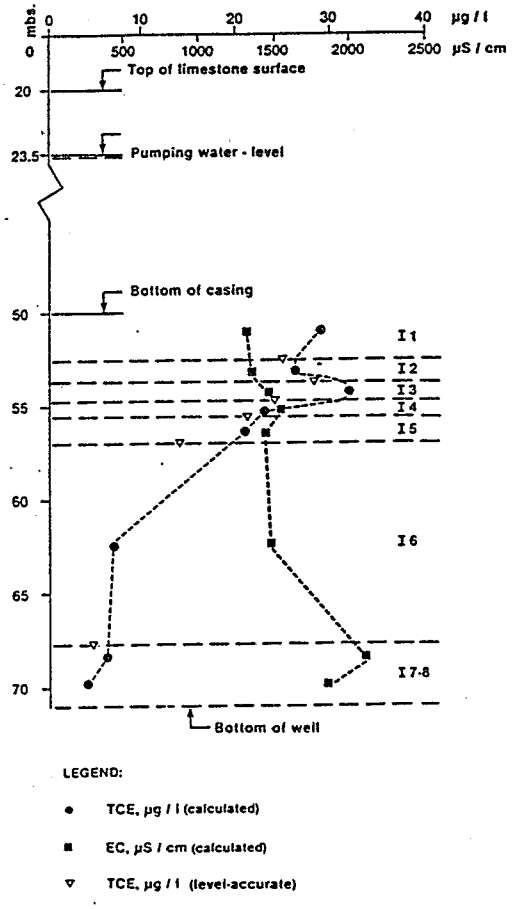

Fig. 10: Calculated concentration profile, and inflow distribution in a water supply well at P. Andersens Vej Waterwork, and a chemical profile based on level-accurate water samples collected at the water divides. TCE = trichloroethylene and EC = electrical conductivity. I = inflow interval.

The boundaries of the inflow intervals have been located by a Heat-Pulse-Flow-Meter, and level-accurate samples were taken at the boundaries (see section 3.3). The results are shown in Fig. 10. The inflow from interval I1-I8 has been determined as fractions of total yield:

$q_1 = 0,20$, $q_2 = 0,10$, $q_3 = 0,12$, $q_4 = 0,08$, $q_5 = 0,11$, $q_6 = 0,09$, $q_7 = 0,09$ and $q_8 = 0,21$.

60% of the total yield comes from a fissure system 50 - 57 m.b.s. and 30% from an other fissure system at a depth of approx. 67,5 - 71 m.b.s.

As in Skrydstrup (section 4.1.4), the optimized remedial action pumping have been examined as a function of the pump time. Fig. 11 shows that in the period 20. February 1990 - 22. May 1990, the TCE concentration has stabilized at a value of 25 µg/l TCE in the top water and 5-6 µg/l TCE in the bottom water, compared to approx. 15 µg/l TCE if only one pump was used. The pump ratio has been held constant, so the fraction of slightly polluted bottom water has been approximately 40% of the total yield through the whole period. In the period 30. April to 22. May 1990 the total discharge has been adjusted from about 45 m^3/hr to about 70 m^3/hr. This change did not influence the concentrations of TCE in top and bottom water.

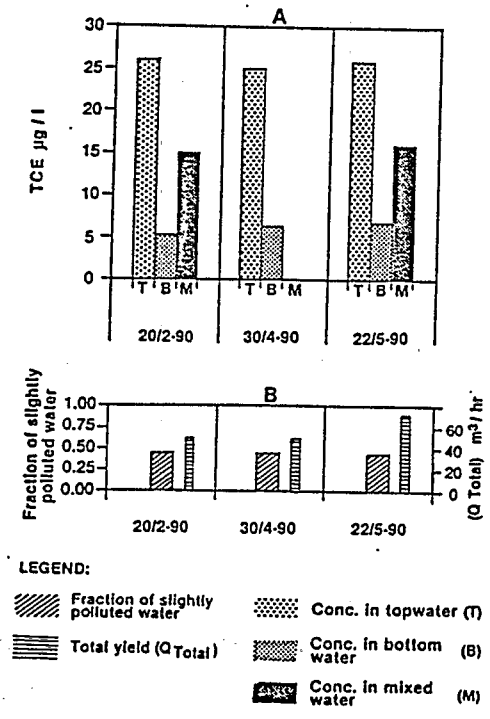

Fig. 11.: Optimized remedial action pumping by separation pumping in a Water Supply Well at P. Andersens Vej Waterwork, Frederiksberg in the period 20. February 90 - 22. May 90. A: The concentration of TCE in top (T), bottom (B) and mixed (M) pump water, B: The fraction of slightly polluted water of total discharge, and the total discharge in m^3/hr.

The ratio of yields between the top and bottom pumps must carefully be balanced, so the TCE-concentration is as high as possible in the top water. However, in this case, the situation is complicated by the high chloride content from intruding saltwater from the bottom of the well which has the low content of TCE.

This reflects an enormous water supply problem in the Copenhagen area. Chlorinated solvents of anthropogene origin infiltrates the limestone aquifer from above and saltwater intrudes the same aquifer from below, because of the large demand for water.

4.3. Localization of a pollution plume in a chalk aquifer

4.3.1. Site description

A former chalk quarry has been filled with mixed industrial and domestic wastes. The chalk is 1-4 m.b.s. and the groundwater level is approximately 4-5 m.b.s. The chalk has been quarried below the natural groundwater level, which means that the waste has been dumped below the water table.

4.3.2. Hydrogeology

The aquifer is a fractured chalk, with closely spaced fractures, with rather random orientation. The fracture porosity amounts to around 1,5% while the total porosity varies from 20-35%. Around the former quarry there are water table conditions in the aquifer, but just south of the dump site the aquifer becomes confined. The chalk is overlain by glacial till, with minor sand lenses.

4.3.3. SIT

Two open boreholes 150 mm in diameter, 25 m and 29 m deep, downstream of the disposal site were tested with the separation injection test (SIT), as described in section 3.2.2. Salt water was injected at the bottom and fresh water at the top, and the position of the interface, at the various injection rates, was determined with an EC-probe.

4.3.4. Level-accurate sampling

Knowing the flow distribution, and the positions of the boundaries between the ten, 10% flow partials, level accurate sampling at the boundaries, was just a matter of pumping with the same ratios from top and bottom as used for the SIT, and sampling at the corresponding boundaries. The pumping of the sample was done with a flow rate of approx. 2% of the total flow, and a limited volume of approx. 3 litres. It should be noted, that the position of the boundaries can only be considered equivalent, when pumping and injection takes place through the same cross-section of the aquifer. In other words the water level should in both cases be above the highest filter interval. This was the case for the well, for which the results are shown, but in the other well there was a small difference of 30 cm in the two cross-sections, because the casing did not reach the water table.

4.3.5. Results and discussion

The result of the SIT is shown in Fig. 12. It is evident that the upper part of the aquifer has a much larger permeability, as 90% of the flow takes place within the upper 25% of the tested interval. Quite narrow flow zones can be discerned, down to approx. 30 cm.

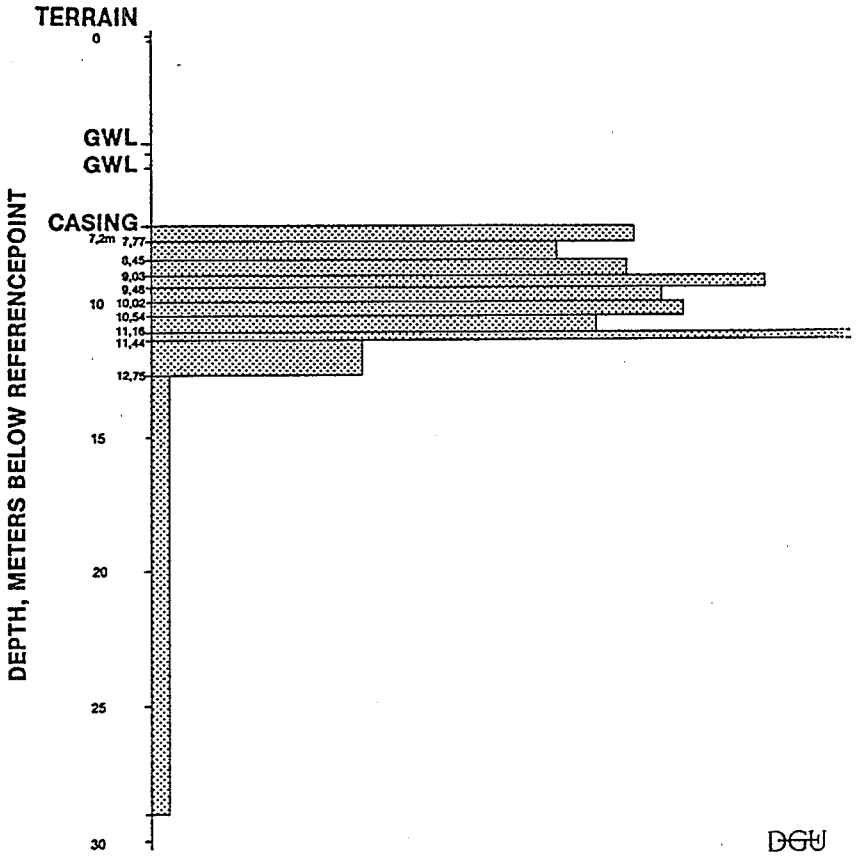

Fig. 12.: The relative influx distribution of ten 10% intervals in well 207.2802, Karlstrup, determined by a separation injection test (SIT).

The results from the sampling are seen in Fig. 13. The sampling method is clearly capable of showing very high concentration gradients. High contents of K^+, Na^+, Cl^-, NH_4^+, and relatively low contents of NO_3^- and SO_4^{--}, show the existence of a pollution plume at the top of the aquifer. This, together with the found flow distribution, makes it unfeasible to use separation pumping as a tool for optimizing remedial actions, in this case.

These investigation methods have a high potential for use in similar cases, because they can be applied in existing wells, even in the production well, where the pollution may have been discovered.

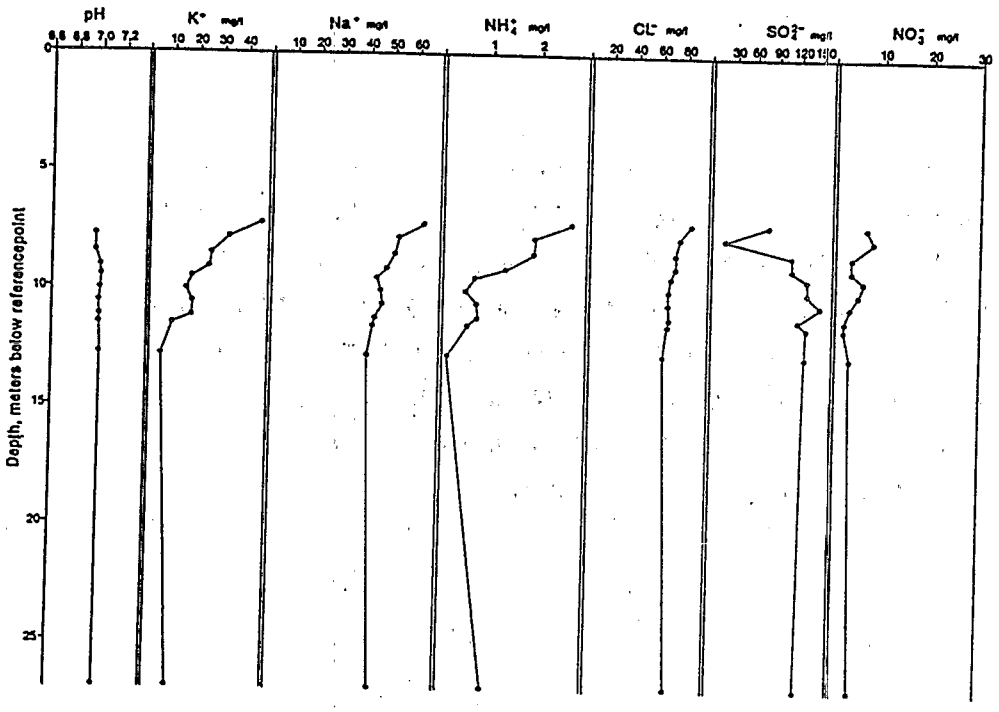

Fig. 13.: Concentration profiles from well 207.2802. The level-accurate sampling was done using separation pumping.

5. Costs

Because the technique has only been tested at pilot scale, no cost-benefit analyse has been made yet. Still comparing traditional remedial action pumping by use of one pump, to simultaneous pumping with 2 or more pumps, the installation costs are increased by using the separation pumping technique, but contemporaneously the remediation time would probably decrease and the costs for treatment decrease because the volume of polluted water is reduced.

6. Concluding remarks and perspectives

The separation pumping technique is a method applicable for locating and recovering the polluted water, from a vertically partially polluted aquifer by simultaneous pumping from top and bottom with two or more pumps in a fully penetrating well without installation of packers.

The method can be used for determination of the inflow distribution and transmissivity of selected sections of a well. The vertical distribution of pollutants can furthermore be determined and a concentration profile calculated.

Moreover the method is applicable for collecting level-accurate water samples from any levels of a fully penetrating well only by pumping from the well itself.

The method has been tested at two different sites, a polluted water table aquifer in meltwater sand and gravel with pollution down to 25 m.b.s., and a confined limestone aquifer with fissure flow. In both cases the effect of the separation of polluted groundwater from slightly or non-polluted groundwater were successful. The separation pumping can be provided in existing wells without disturbances of the pollution distribution with the aquifer. Remedial action pumping can be provided in a production well in a way, so the well continues the production of drinking water at a waterwork using the non-polluted part of the inflow to the production well.

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Appendix 7-A

Case Studies on Chemical Treatment of Contaminated Soils: APEG

Supplementary Information on the APEG Process, Wide Beach, United States

APPENDIX 7-A

SUPPLEMENTARY INFORMATION ON THE APEG PROCESS AND THE WIDE BEACH (UNITED STATES) DEMONSTRATION STUDY

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The reagent, APEG, dehalogenates pollutants to form a glycol ether and/or a hydroxylated compound and an alkali metal chloride which are water soluble. These products are regarded as nontoxic, although they may have an undesirable environmental impact if they are released in an uncontrolled manner.

SCIENTIFIC BASIS OF PROCESS

The most widely used variant of the process employs potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG) to form a polymeric alkoxide anion, referred to as KPEG. This acts as an effective nucleophile and as a phase-transfer catalyst (Kornel & Rogers 1985). Other reagents can be used (see below). The presence of oxygen is an essential requirement of the process. The polyethylene glycol typically has a molecular weight in the range 300 - 600.

The reagent, APEG, dehalogenates the pollutant to form a glycol ether and/or a hydroxylated compound and an alkali metal chloride which are water soluble. These products are regarded as nontoxic (but see below), although they may have an undesirable environmental impact if they are released in an uncontrolled manner.

The reactions involved are shown schematically in Appendix Figures. 7-1 and 7-2.

In some KPEG reagent formulations to treat chlorinated aromatics, dimethyl sulfoxide (DMSO) is added to enhance the reaction kinetics, presumably by improving rates of extraction of the haloaromatic compounds and/or overcoming inhibitory effects attributed to the formation of hydroxide anions. Sofolane (SFLN - tetrahydrothiophene) may also be used to accelerate the reaction.

Although potassium hydroxide has been the most widely used reagent, sodium hydroxide has been used in the past and may find increasing application, in part at least because of lower costs. Other possibilities include the use of combinations of potassium or sodium hydroxides with tetraethylene glycol (ATEG).

When KTEG reagent is used (i.e., potassium hydroxide with tetraethylene glycol) to treat aliphatic halogenated hydrocarbons, a dehydrohalogenation reaction occurs. Halogenated compounds with one carbon atom react to form carbon dioxide and potassium halide. Compounds containing more than one carbon react to form acetylene (Rogers and Kornel 1987, Harden & Ramsay 1986).

THE WIDE BEACH CASE STUDY (UNITED STATES)

Only one case study was included in the NATO/CCMS Pilot Study: the United States Environmental Protection Agency's (U.S. EPA's) SITE (Superfund Innovative Technology Evaluation) Demonstration at Wide Beach, New York (EPA 1989B, EPA 1991A, EPA 1991B). This involved application of a KPEG process to the treatment of PCB contaminated soils in combination with a complex four stage "thermal processor". This is a continuous process in contrast to the batch processes demonstrated or used at a number of other sites. The basic processor has wider applications where thermal, desorption or pyrolysis is required (Taciuk 1991).

Background. The Wide Beach site is located in a residential area of the town of Brant approximately 48 km (30 miles) south of Buffalo, New York.

From 1968-1978 PCB (Aroclor 1264) contaminated waste oil was used for dust control on local roads at Wide Beach. About 155,000 liters of oil were applied. During installation of a sewer in 1980 highly contaminated soil was excavated from the roadways and surrounding areas. After completion of the installation surplus soil was used as fill in residential gardens (yards) and a community recreation area. An odor complaint in 1981 led to discovery of 19 drums, some containing PCB-contaminated oil. Subsequent sampling revealed widespread PCB contamination in air, homes, private water supplies, ground water, drainage ditches and soil. About 274 residences were affected in Wide Beach community and surrounding areas. There are 60 residences in the Wide Beach community itself accommodating about 120 people in summer and 45 on a permanent basis. A detailed description of the site is available (EPA 1991B).

Pending long term remedial action, ameliorative measures were taken to limit public health and environmental impacts. Roadways, drainage areas and driveways were paved to prevent public exposure to dust and runoff. Measures to decontaminate homes included vacuuming, cleaning of carpets, etc., and replacement of air conditioner and furnace filters. Particulate filters were installed to protect individual private wells from sporadic PCB contamination.

Soil contamination ranged from 0.18 to 1026 mg/kg in samples collected from residential driveways, roadways and drainage ditches. PCB concentrations in excess of 10 mg/kg were detected at depths of up to 1 meter in drainage ditches, although in general these concentrations reached only to about 0.15 to 0.3

meters in depth. It was estimated that 21,700 tonnes (15-16,000 m^3) of soil were contaminated. In practice, however, about 43,000 tonnes of soil were processed (see below).

PCB concentrations up to 126 mg/kg were found in surface waters from adjacent wetlands.

After a review of possible remediation options, KPEG soil treatment was chosen as the most cost effective. Preliminary pilot scale studies showed that initial PCB concentrations ranging from 30 to 260 mg/kg could be reduced to less than 10 mg/kg. Final concentrations ranged from 0.7 to 1.7 mg/kg.

Accordingly, a clean up target of not more than 2 mg/kg was been set (EPA 1989B, AOSTRA 1990).

The Demonstration Project. The remedial action at Wide Beach consisted of excavation of soils with PCB concentrations greater than 10 mg/kg from all areas; excavation of contaminated asphalt material from roadways for disposal off-site, with uncontaminated material being retained for reuse; treatment of the PCB-contaminated soils using the an Anaerobic Thermal Processor (ATP) in association with a KPEG process; use of the cleaned soil as fill in excavated areas; repavement of the roadways and driveways; and treatment of perched water in the sewer trench (this water has been found to contain up to 10 μg/L PCB's).

On completion of the work the residences were subjected to a further thorough cleaning to remove any stray dust, etc.

About 43,000 tonnes (23,000 m^3) contaminated soil were treated in a continuous process. An AOSTRA (Alberta Oil Sands Technology and Research Authority) ATP (anaerobic thermal processor) unit was used under license by SoilTech Inc. to thermally desorb the organic contaminants from the soil for subsequent dechlorination (EPA 1991A, EPA 1991B). The AOSTRA "Taciuk" processor, conceived in about 1975 (Taciuk 1991) was developed in about 1985 for the continuous extraction and primary upgrading of bitumen and oil from oil sand and shale feedstocks but has been adapted to the removal of oily materials from soils (AOSTRA 1990, Taciuk 1991, Taciuk & Ritcey 1991). Development work leading to its application to treat PCB-contaminated soil has been described by Taciuk (1991).

The ATP system is designed to heat and mix contaminated soils, sludges and liquids and is heated indirectly. It has four separate, internal heating zones: the preheat, retort, combustion, and cooling zones.

The process is designed (EPA 1991A, EPA 1991B) to work as follows (see also Appendix Figures 7-3 through 7-5):

Before entering the **preheat zone** the contaminated soils are

sprayed with a diesel fuel and oil mixture containing alkaline polyethylene glycol reagents (the oil mixture acts as a carrier for the dehalogenation reagents and is also necessary to achieve optimum operation of the various stages of the process). In the **preheat zone**, water and volatile organic compounds (VOC's) vaporize. At the same time, the reagents dehalogenate or chemically break down chlorinated compounds including PCB's. The vaporized contaminants and water are removed at a temperature of 200-315 °C under a slight vacuum to a **preheat vapor cooling system** consisting of a cyclone, condenser and 3-phase preheat system. Uncondensed light organic vapors are fed by a gas blower directly into the combustion chamber of the processor. Condensed liquids are separated: the oil fraction is recycled to a reagent blending tank, and recovered water is pretreated and sent off-site for disposal.

From the preheat zone, the hot, granular solids pass through a sand seal to the **retort zone** (approximately 600 °C). Here heavy oils vaporize and thermal cracking of hydrocarbons forms coke and lower molecular weight gases. The vaporized contaminants are removed under vacuum to a **retort gas handling system.** Entrained particles are removed by a two-stage pair of cyclones (the collected dusts and fines are blended with the treated soil). After passing through the cyclones the vapor is cooled by oil circulating in two packed columns, acting as a two-stage direct contact condenser for the high boiling point compounds. Remaining uncondensed vapors are cooled in a water-cooled non-contact condenser and passed to the combustion chamber of the process. The oil phase is combined with the condensate from the packed columns. This oil condensate is then sent to the blending unit to mix with the APEG reagents. The blend is pumped at a measured rate and is applied to the untreated soils in the feed chute of the processor. Condensed water is pumped directly to the on-site treatment system.

The coked soils pass through a second sand seal into the **combustion zone** (650-815 °C), where they are combusted and either recycled to the retort zone or sent to be cooled in the **cooling zone.** Exhaust gas from the combustion zone is treated in a system consisting of a cyclone and baghouse that removes particulates; a scrubber to remove acid gases; and an absorption bed to remove trace organics. The treated gas is then discharged to atmosphere.

The combusted soils that enter the **cooling zone** are cooled in the annular space between the outside of the preheat and retort zones and the outer shell of the kiln. Treated soils leaving the cooling zone are quenched with scrubber water and then transported to a storage pile.

Residence time in the preheat and retort zones is approximately 15 to 30 minutes each, sufficiently long to ensure complete volatilization of the hydrocarbons. The heat requirements are provided by natural gas burned in the **precombustion chamber.** A fraction of the coke in the combustion chamber may also burn.

The optimal moisture content of the waste is 5 to 10 weight percent. Although wastes with a moisture content greater than 20 percent may be treated the high moisture content will affect net throughput rates. The ATP system is designed to treat wastes with a nominal hydrocarbon concentration of 10 percent. However, heavy oil contaminants have been reduced from as high as 60 percent in the feed to near detection limits in the treated solids.

The rate of contaminant desorption and dechlorination from soils and sediment is influenced by the contaminant concentration. SoilTech report that the contaminant concentration in the feed waste is generally independent of the contaminant concentration in the feed waste and will be near the detection limit of the contaminant. The processor treats wastes containing low boiling contaminants more effectively than wastes containing high boiling contaminants. However, high boiling organics such a PCBs and polycyclic hydrocarbons can be removed to concentrations below detection limits of 1 mg/kg.

Demonstration Results. The ATP technology was demonstrated under the U.S. EPA SITE program in May 1991. Three test runs were conducted, each consisting of five and one half hours of solids and liquids sampling and five hours of stack sampling. Key findings of the demonstration were:

The SoilTech ATP unit removed PCB's in the contaminated soil to levels below the desired cleanup concentration of 2 mg/kg. PCB concentrations were reduced from an average concentration of 28.2 mg/kg in the contaminated feed soil to an average concentration of 0.043 mg/kg in the treated soil.

The SoilTech ATP does not appear to create dioxins and/or furans.

No volatile or semivolatile organic degradation products were detected in the treated soil. There were also no leachable VOC's or SVOCs detected in the treated soil.

No operational problems affecting the ATP's ability to treat the contaminated soil were observed.

HEALTH AND SAFETY ISSUES

Polyethylene glycol and dimethyl sulfoxide are essentially nontoxic materials. The addition of the glycol to the aromatic PCB or dioxin ring produces a water soluble, low toxicity product. Testing by the US EPA indicates that replacement by polyethylene glycol of a single chlorine on a PCB or dioxin molecule produces a material of low toxicity (LD50 greater than 5000 mg/kg) which does not appear to bioaccumulate or cause mutagenic effects. However, the long term stability of these compounds in a soil environment where they may be subject to microbial and other degradative reactions does not appear to have been determined.

Treatment of certain chlorinated aliphatics in high concentrations with APEG may produce compounds that are potentially explosive (e.g., chloroacetylenes) and/or cause a fire hazard. The use of DMSO or similar reagents may result in the formation of highly flammable volatile organics (e.g., methyl sulphide). Alkaline reactive materials such as aluminium can result in formation of hydrogen. Vapors from, heating oily soils, which are often the matrix in which PCBs are found, can also create such potential problems as fires and noxious fumes. These potential problems can all be overcome by appropriate process design.

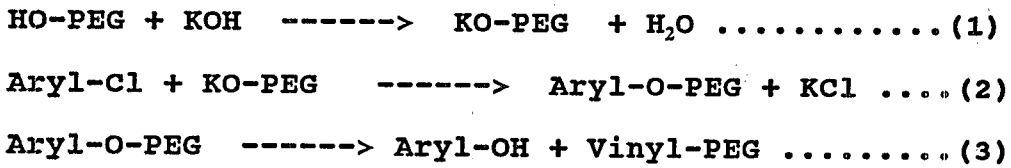
The process must also be conducted with care because of the elevated temperatures and production of steam, the use of caustics in the process, and the acids used in neutralization.

If DMSO, which is a powerful solvent and skin penetrant, is used care must be taken to prevent contact with skin as it enhances transport of PCB's through the skin, thus increasing the risk of exposure.

KTEG processes are exothermic and can produce vinyl halides as intermediate compounds. Special considerations will therefore apply in the design of plants to operate these processes (Harden and Ramsay 1986).

REFERENCE:

See References following Chapter 7, Vol. 1.



Note: *In reaction (1) the polyethylene glycol (PEG) is reacted with potassium hydroxide to form the reactive KPEG species. This preparative step may be performed directly in the contaminated matrix or externally. Reaction (2) takes place takes place over a wide temperature range from ambient to about 110C. Reaction (3) represents the conversion of the ether linked PEG/Aryl moeity to a phenolic with consequent release of a vinyl terminal polyethylene glycol.*

Equation (4) below represents this overall reaction.

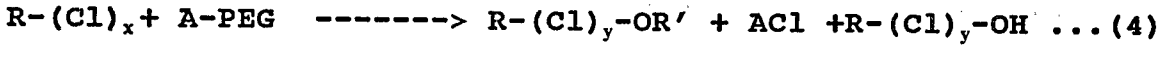


Fig 6.1 APEG REACTIONS

$$HO\text{-}PEG + KOH \xrightarrow{\text{------}} KO\text{-}PEG + H_2O \quad \text{.....(1)}$$

$$Aryl\text{-}Cl + KO\text{-}PEG \xrightarrow{\text{------}} Aryl\text{-}O\text{-}PEG + KCl \quad \text{....(2)}$$

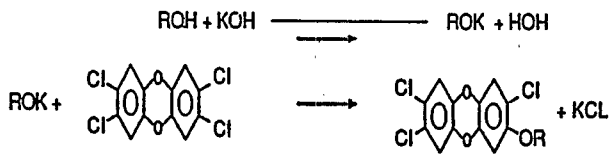
$$Aryl\text{-}O\text{-}PEG \xrightarrow{\text{------}} Aryl\text{-}OH + Vinyl\text{-}PEG \quad \text{.....(3)}$$

Note: *In reaction (1) the polyethylene glycol (PEG) is reacted with potassium hydroxide to form the reactive KPEG species. This preparative step may be performed directly in the contaminated matrix or externally. Reaction (2) takes place takes place over a wide temperature range from ambient to about 110C. Reaction (3) represents the conversion of the ether linked PEG/Aryl moeity to a phenolic with consequent release of a vinyl terminal polyethylene glycol.*

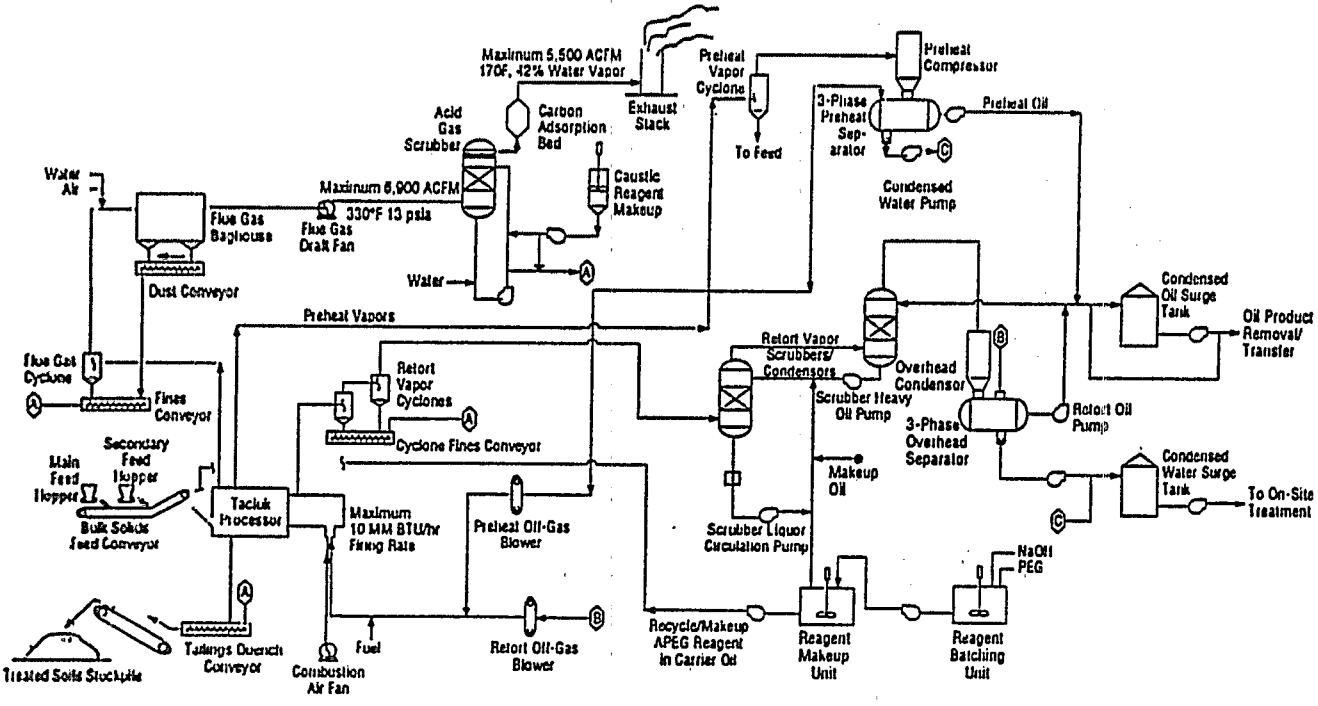
Equation (4) below represents this overall reaction.

$$R\text{-}(Cl)_x + A\text{-}PEG \xrightarrow{\text{-------}} R\text{-}(Cl)_y\text{-}OR' + ACl + R\text{-}(Cl)_y\text{-}OH \quad \text{...(4)}$$

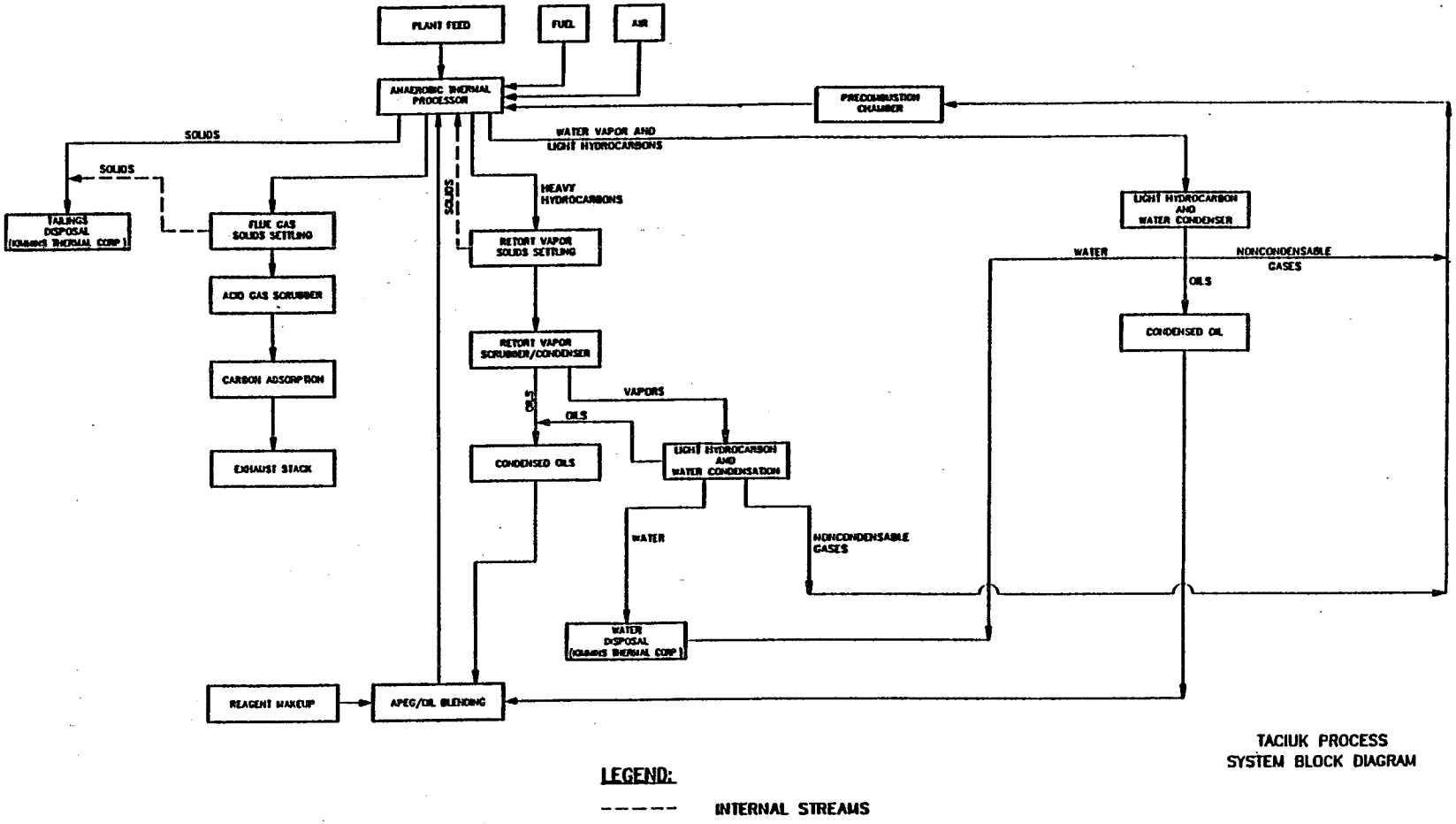
Appendix Figure 7-1. APEG reactions.



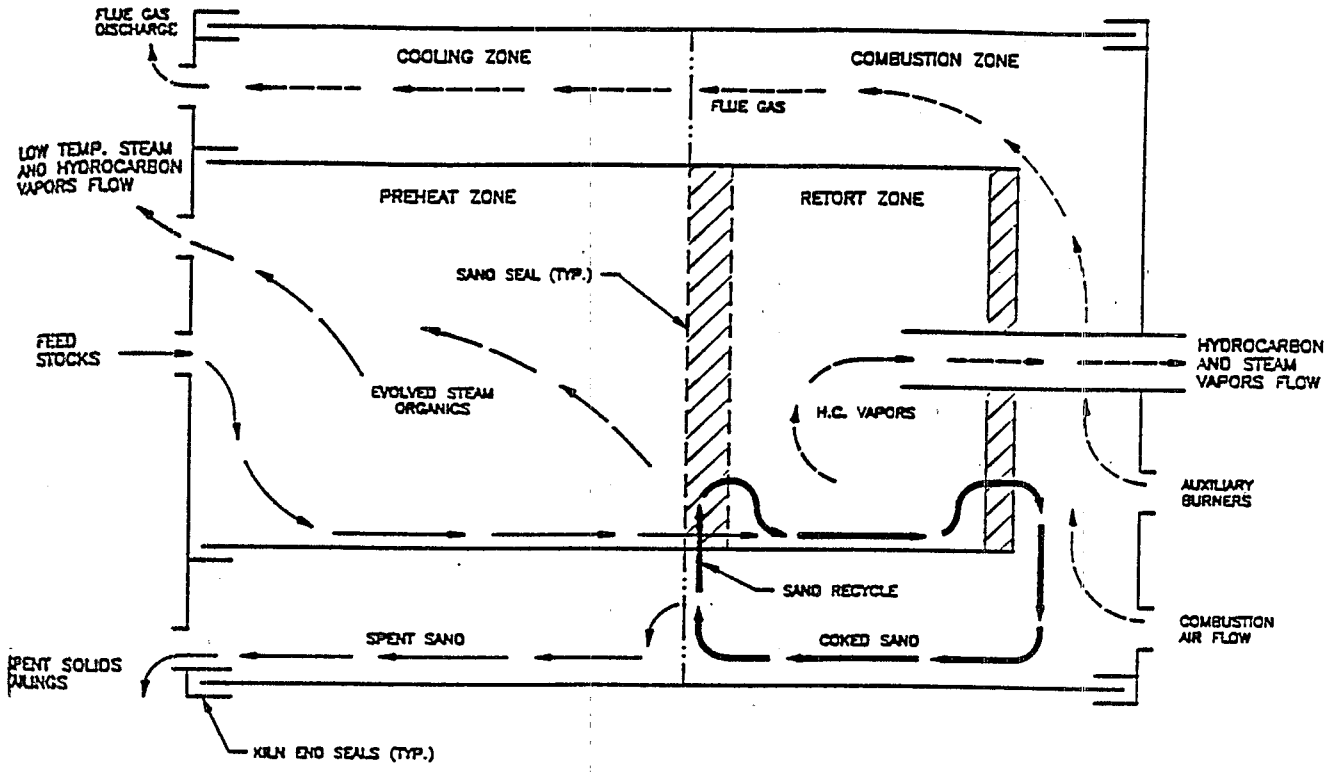
Appendix Figure 7-2. Chemical reactions during the KPEG process.



Appendix Figure 7-3. Simplified process flow diagram.



Appendix Figure 7-4. Block diagram of internal flow of materials.



Appendix Figure 7-5. Simplified sectional diagram showing the four internal zones.

Appendix 7-B

Case Studies on Chemical Treatment of Contaminated Soils: APEG

The AOSTRA-Taciuk Thermal Pyrolysis/Desorption Process, Canada

THE AOSTRA-TACIUK THERMAL PYROLYSIS/DESORPTION PROCESS

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Washington, D.C.
November 18-22, 1991

ABSTRACT

The AOSTRA-Taciuk Thermal Pyrolysis and Desorption Process, for use in contaminated waste clean-up applications, has been under development since 1986. The basic AOSTRA-Taciuk Processor machine was conceived in 1975 and was actively researched and developed for oil sands and oil shale treatment applications for oil production purposes. The patents for this technology are held by the Alberta Oil Sands Technology and Research Authority (AOSTRA) which is located in this oil-producing province in Western Canada.

UMATAC Industrial Processes, located in Calgary, Alberta, Canada, are responsible for the research, development, design and manufacturing of equipment and plants which utilize this technology. UMATAC is actively involved in oil sands and oil shale prototype projects and, in 1989, constructed a 10 ton/hour transportable waste treatment plant which has recently successfully completed at 42,000 ton clean-up project where chemical dechlorination and desorption of PCB-contaminants was combined within the unique features of the Processor machine.

Unlike incineration, the use of the Processor system provides options for recovery and reuse of separated by-products.

This paper provides a brief view of the development history, description of the Process and carries on to describe current development status and potential future development for treating other specific contaminated waste streams.

DESORPTION PYROLYSIS UTILIZING THE AOSTRA-TACIUK PROCESSOR SYSTEM

The basic design and concepts for the AOSTRA-Taciuk Processor were conceived in 1974-75 for application in the Athabasca Oil Sands located near Fort McMurray, northern Alberta. The Processor is a horizontal, rotating unit which has internal components to permit staged processing, removal and separation of product streams depending on thermal sensitivity. The internal reactor design permits thermal processing of preheated feed materials in an anaerobic atmosphere at temperatures in the range of 950° to 1100°F. Vaporized and/or thermally cracked hydrocarbons from the reactor are removed and condensed so there is potential for recycling or reuse of this concentrated energy stream. The Processor can accept a wide range of feed material sizes, water content and hydrocarbon content. Since the Processor is a basic machine consisting of a heat exchange zone, reaction zone and combustion zone, it can be used to treat any type of contaminated feed material that responds to temperature phase changes within the reactor operating range.

DEVELOPMENT HISTORY

The UMA Group, a Canadian employee-owned consulting engineering company with the head office in Vancouver, B.C., formed UMATAC Industrial Processes in 1976. UMATAC's primary function was to research, test, develop, design and market the AOSTRA-Taciuk Processor Technology. This work was carried out under funding agreements with the Alberta Oil Sands Technology and Research Authority (AOSTRA) which owns and licenses use of the technology. UMATAC retains the engineering, development, design and manufacturing rights for all proprietary equipment associated with this technology.

A 5 ton/hour Pilot Processor was constructed in Calgary in 1977 and has been operated on a wide range of feed materials to provide test data for use by UMATAC engineering involved in design, modeling, scale up and assessing suitability of the Process for handling these materials.

During the period 1976 through 1984, development of the Technology was

concentrated on Athabasca oil sands processing capability. In excess of 12,000 tons of various grade oil sands were processed in this development which verified the predicted stability, ease of operation and uniformity of oil product yield that could be obtained from use of the ATP.

In 1985, with the extreme decline in world oil prices, plans for oil sands demonstration/commercial prototype projects had to be delayed and UMATAC shifted its research efforts towards Processor applications in processing of oil shales, treatment of various hydrocarbon-contaminated wastes and separation of hazardous waste constituents from contaminated soils.

During the period 1985-1987, UMATAC successfully completed various phases of test work relating to Australian oil shales processing. These efforts included pilot testing of 1,400 tonnes of Australian oil shales in 1987, and UMATAC is currently working with the Australian lease operator towards a large-scale (6,000 tonne per day) demonstration plant.

In 1986, UMATAC began a program of research and testing for developing the AOSTRA Taciuk Process Technology for clean-up and separation of waste materials containing various hydrocarbon contaminants. A series of batch pyrolysis tests and pilot plant tests has been successfully completed since that time.

Programs relating to the waste treatment application are summarized as follows:

1. Oil Refinery Wastes such as API Separator Sludges, Emulsions and Oil-Contaminated Solids.

    a) In early 1987, a series of ATP batch tests was carried out on the typical oil refinery waste streams of API separator sludges, slop oil emulsions and DAF float sludges. Samples were received from a refinery located in Montreal. The results of these tests demonstrated that the Process could treat these materials and produce a solids reject that meets acceptable leachate criteria, produce an oil product that could be recycled, and produce a water product that could be treated to acceptable environmental standards.

This program was conducted for inclusion in the evaluation by the American Petroleum Institute (API) of available process technology applicable to clean-up treatment of these particular wastes of oil refinery operations. The UMATAC results were submitted to API and were included in the subsequent API report of its Task Force Study (API Report #4465, May, 1988).

b) A series of batch tests was carried out on samples of oil-contaminated solids from a decommissioned refinery located in Montreal. These tests were successful and were followed in December, 1986, by a pilot plant run with the Processor on a 30 ton bulk sample of oil-contaminated solids from this site. Results of this test run substantiated the environmental acceptability of the ATP System treatment.

c) In mid-1987, a series of batch tests was carried out on oily sludge and oil samples from a refinery site in the U.S.A. Results of these tests were similar to those obtained from the a) and b) programs discussed above, and confirmed Processor applicability for treatment of these wastes.

2. Heavy Oil Production Wastes

A major test program was completed in 1988 on samples of oily wastes from production of heavy oil obtained from 17 different heavy oil operations located in Alberta and Saskatchewan. This program included pilot plant test runs during which 400 tons of bulk waste samples from four representative sites were tested in the pilot plant. This program was sponsored and funded by Environment Canada, DSS, CANMET, and AOSTRA.

3. PCB Contamination Removal

In 1988, UMATAC carried out a series of batch tests on PCB material (Aroclor 1242 and 1260) to examine and demonstrate the ability of the Taciuk Processor to vaporize and extract these materials from host solids and condense them into concentrated liquid form. The concentrated PCB condensates could then be disposed by destruction in remotely located incinerators, or could be burned in a pre-combustion chamber connected to the ATP Processor combustion zone.

Two test runs on PCB-spiked soil samples were carried out in the pilot plant whereby approximately 300 Kg of Aroclor 1242 was injected into the 5 TPH Processor unit along with feed sand to simulate a contaminated sand feed. The test results verified that the PCB's could be removed and condensed with no production of dioxins and with minimal production of non-toxic furans. The tailings solids contained no trace of PCB's, dioxins or furans. In addition, dioxins or furans were not produced in the oxygen-deficient vaporizing and condensing phase of processing.

In 1989 and 1990, batch tests on PCB removal using a combination of chemical dechlorination and desorption, were successfully completed and was first utilized for commercial clean-up operation at Wide Beach in New York State, U.S.A.

4. Other Materials Tested

Following is a listing of other materials tested in UMATAC's batch pyrolysis equipment with potentially successful results:

a) Scrap Rubber Tires
b) Coal Tar Residues and Emulsions
c) Plastic Containers
d) Compacted, Shredded Garbage
e) Emulsions from Heavy Oil in the United States
f) Athabasca Bitumen/Solids/Water Mixtures

5. Processor Flexibility

The AOSTRA-Taciuk Process Technology provides a rugged, simple unit that has excellent operating stability and flexibility to deal with feedstock variations and process variations. It can produce liquid products, which have been separated, at temperatures near their vaporizing points, and oil by-products that can be recycled or transported to other locations for final treatment or reuse. These functions are achieved in an oxygen-free atmosphere in the Processor, which also incorporates heat exchange to minimize fuel requirements and flue gas treatment. The internal design of the combustion annulus provides for long

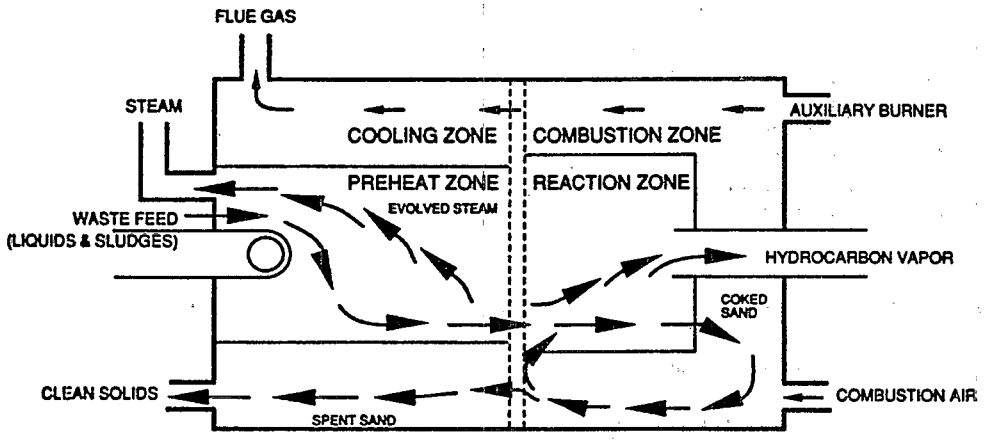
residence time and intimate mixing of gases and solids to ensure complete combustion.

During the past 10 years, the pilot plant has been operated in excess of 10,000 hours and has processed in excess of 15,000 tons of various feed materials. This operation has demonstrated the ability to provide safe, stable and consistent operation while testing a range of feed materials. These features of the Process and equipment are now being confirmed in the commercial operation of the SoilTech 10 TPH ATP waste treatment plant.

BASIC PROCESS DESCRIPTION

The AOSTRA-Taciuk Processor is a single, horizontal, rotating unit that contains several zones where specific functions are performed. Below is a diagram illustrating the major zones and flows which cooperate to achieve the following:

AOSTRA Taciuk Processor



1. High thermal efficiency by use of an internal heat exchange which cools hot flue gases and combusted solids, while preheating the incoming feed.

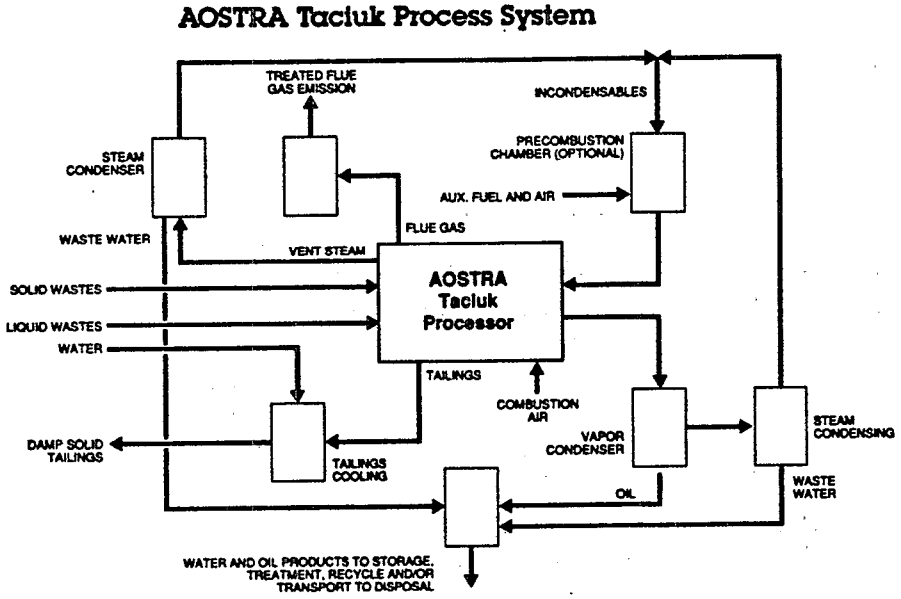
2. Anaerobic vaporizing of water and light hydrocarbons, which are extracted from the preheat zone as a separate low-temperature vapor stream.

3. Anaerobic vaporizing and/or thermal cracking of hydrocarbons, which are extracted from the reaction zone as a high-temperature vapor stream.

4. Oxidization of carbon residues deposited on inert solids during thermal cracking. This is carried out in a combustion zone which envelopes the reaction zone. This combustion provides a portion of the Processor heat requirements.

5. Thermal stability and zone separation by use of patented, unique, sand seals and a sand recycle system, which provide heat to the reactor via a "locked-in" recycle sand charge.

Auxiliary treatment and recovery systems are used to contain and process the various Processor effluents. Below is a block diagram illustrating the auxiliary systems, which can be easily altered



to suit the requirements of a specific feed material and site conditions.

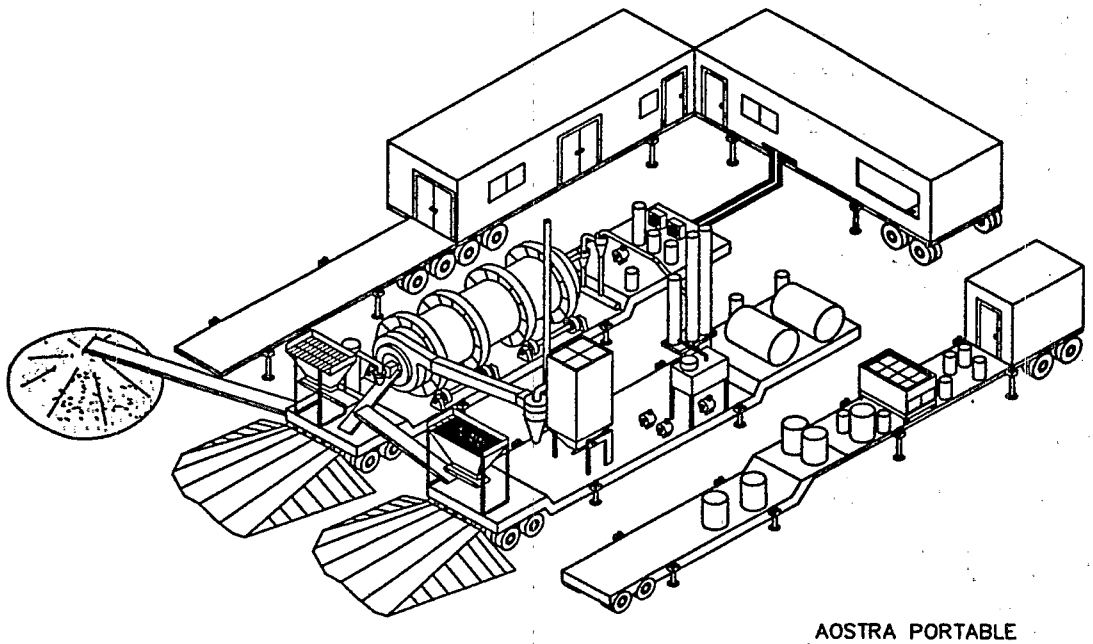
SOILTECH COMMERCIAL TRANSPORTABLE PLANT

In 1989, UMATAC designed and constructed a 10 ton/hour transportable waste treatment plant for use by SoilTech, Inc. of Porter, Indiana. This plant was designed

with parallel, full capacity, flue gas treatment trains and, where possible, standby pumps, blowers, burners, compressors, etc., were provided to maximize plant reliability. This plant has recently successfully completed treatment of 43,000 tons of PCB and oil-contaminated soils located at Wide Beach, south of Buffalo in New York state. The plant is being relocated to Waukegan Harbor, north of Chicago, where it will be used to treat 20,000 tons of dredged sediments and drainage ditch soils contaminated by PCB's and various cutting and lubricating oils. SoilTech has gained commercial acceptance for the AOSTRA-Taciuk Processor in the United States and is actively involved with UMATAC in batch testing and evaluating use of the ATP for other projects and industry problem areas in wastes treatment.

AOSTRA RESEARCH AND DEMONSTRATION PORTABLE PLANT

In early 1991, AOSTRA commissioned UMATAC to design, construct and operate a 2 to 5 ton-per-hour portable AOSTRA-Taciuk Processor plant. This plant will be completed in early 1992 and will be initially used at UMATAC's pilot plant site for developmental testing of several internal Processor configurations leading towards use of the ATP for processing of municipal solid wastes, and investigate potential for use on sulfur or phosphorous contaminants. This unit will be available for use as a demonstration facility for oil sands development and for clean-up operations in Alberta. On-site demonstration at locations outside Alberta will be available, dependent on operating schedules.



AOSTRA PORTABLE
5 TON/HR ATP TREATMENT PLANT
ISOMETRIC LAYOUT

PYROLYSIS - AN OPTION TO INCINERATION

The use of staged heating and separation of vapor phase products at the lowest possible temperature provides an efficient and flexible way of dealing with complex waste mixtures. Certain incinerator manufacturers are evolving options to their base equipment tending towards staged separation and partial pyrolysis, which is then followed by second-stage combustion.

The AOSTRA-Taciuk Processor System can provide this flexibility if a benefit can be derived as a result of its use. These benefits are accentuated if:

a) The feed contains a high water content that can be removed by vaporizing at low temperature.

b) The feed contains a high hydrocarbon content where product oils in excess to that required for Process heating can be stored and used for other purposes.

c) The feed contains other impurities, metals, etc., that concentrate in the fine solids fractions that are removed in the cyclones and baghouses.

d) The flue gas quantity remains at a low level since combustion is determined by Process heat requirements, not by total product combustion.

e) The combustion process is carried out at 1300° to 1400°F instead of 1800° to 2300°F so this reduces potential for slagging and partial oxidation of heavy metals, etc. Most contaminants are never exposed to combustion since they are stripped off in the preheat zone and the reaction zone.

f) The feed can contain minor amounts of coarse rocks and debris since the ATP unit has an internal screening and rejecting system for handling difficult materials.

The ATP system can be more complex to construct and operate than a straight incinerator so its use must be closely evaluated to determine its costs/benefits for a particular feed material.

COMPARISON OF INCINERATION VERSUS PYROLYSIS FOR HYDROCARBON SLUDGES

UMATAC carried out a series of tests and comparisons of Process parameters for a sludge feed using the ATP Process versus a portable incinerator. The key results from this comparison are as follows:

Feed Characteristics	
Water Content	35%
Hydrocarbon Content	50%
Solids Content	10%
Sulfur Content	5%
Feed Rate (assumed)	15 tons/hour

Process Parameters	Pyrolysis	Incineration
Process Combustion Heat Release (MM BTU/Hour)	28.3	270.0
Flue Gas Flow (lbs./hour)		
Inert Gases	30,000	450,000
Water Vapor	5,000	175,000
Light Oil Recovered (lbs./hour)	11,000	-0-
Reagent Consumption (lbs./hour)	250	7,000
Solids Residence Time (minutes)	15 to 20	.02 to .04

The much reduced flue gas flow requirements, cooling water requirements and the recovery of oil condensate, indicate the basic advantages of pyrolysis/desorption as compared to straight incineration.

DESORPTION/DECHLORINATION OF PCB'S

PCB's are chemically produced compounds which are very stable, hence their advantages for industrial products such as dielectrics and high temperature lubricants.

This characteristic also makes them difficult to destroy chemically so that, after the toxic characteristics of the compound became know, destruction by high temperature oxidation was, for some time, the only effective way to break the chlorine-to-biphenyl bond. PCB's vaporize at temperatures of 325°C to 425°C so they can be stripped away from the host solids at the appropriate temperature.

In the late 1970's, there were several discoveries that reagent mixtures of an alkali and glycols could detoxify chlorinated aromatic compounds, which include the PCB's. Most of these findings addressed liquid-state PCB's. Since these discoveries, there have been many efforts to develop industrial processes which could be used efficiently and economically to treat, using the alkali-glycol chemistry, the great quantities of PCB's and PCB-contaminated materials which have been collected and identified for destruction.

One of the difficulties encountered is the variability of the materials in which PCB's are dispersed, the worse being soils and sludges where PCB concentrations can vary upwards from zero, and the host solids can include almost the whole range of natural and man-made inorganic materials. For process detoxification, the difficulty these materials presents is largely the need for a process vessel which can condition and present the contaminated solids in a manner in which the alkaline reagents can address the PCB's so that the dechlorinating reaction can occur uniformly, economically and reliably in a continuous flow.

The AOSTRA-Taciuk Processor was designed to process soils and rock materials which can vary in consist and particle size up to 75mm. Although it functions best in processing coarse materials, it can also handle the fine silts and clays which are so commonly found as the host for drainage-collected contaminants like PCB's. The Processor internal zones, Preheat and Reaction, are designed to vigorously and simultaneously mix and heat the feed solids in the turbulent, tumbling action of the rotating vessel. This process condition was considered desirable for enabling reagents such as NaOH and PEG400 to address the PCB's in the aroclors and askarels coating the solids particles of the feed soil.

In the summer of 1989, UMATAC, in cooperation with the U.S. EPA Risk Reduction Engineering Laboratory (RREL) in Cincinnati, carried out an initial series of batch tests using various ratios of NaOH and PEG400 to chemically dechlorinate PCB's. These

studies continued in early 1990, based on the previous experience, including desorbing the PCB's from the soils. Communication was continued with the EPA RREL, which was also actively developing the dechlorinating technology. Extensive batch tests were conducted at laboratory and bench scale. UMATAC uses a small, rotating batch reactor which simulates the reactions of the Processor Preheat and Reaction zones. Numerous test runs were made with various alkalis, concentrations, etc. The test work concentrated on studying methods of mixing, reagent preparation, sensitivity of reactions to time and temperature, and ability to recycle (reuse) reagents not consumed by the reaction.

The basis of the UMATAC testing was to introduce alkaline metals into the water-free and oxygen-free environment of the Preheat Zone to react with the chlorine of the PCB molecules to produce salts, i.e., the alkali strips the chlorine from the PCB's leaving biphenyl and salt. The polyethylene glycol is used as a carrier for the alkaline metals and probably acts as a catalyst for the reaction between chlorine and the alkali. Sodium hydroxide (NaOH) was used as the source of the alkali. The results were positive and showed that the dechlorinating reaction, known as the phase transfer catalysis effect, occurs in the temperature range and residence time of the Processor Preheat Zone.

The fraction of PCB's reduced in the tests was consistently high, but was rarely 100%. Thus, there would be some carry-over of the PCB's from the Preheat to the Reaction Zone where the higher temperature would ensure vaporization and/or thermal cracking. This was considered desirable in that these PCB molecules would be recovered in the condensates from the vapor product streams, directed to and recycled with the PEG for treatment again in the Preheat Zone.

The results were similar with Na and K, and Na was selected for the confirming tests and further development because its use is more practical. The overall results are shown graphically in Figure 1 as a plot of PCB's remaining (wt%) versus contact time in the reactor.

These UMATAC R&D programs resulted in the conclusion that the ATP System is commercially capable to undertake remediation treatment of soils and sludges, using one of the two processes; a) desorption, or b) dechlorination. In effect, as explained above, the dechlorination process is used followed by desorption in the Reaction Zone, wherein the latter is used to ensure removal of the PCB's from the treated soil. This is important since the consumption of chemical can be minimized by utilizing the reactor

for final and absolute removal from the solids of any remaining PCB's and PEG400 reagents. However, overall dechlorination of the PCB's is accomplished by way of the recycling for retreatment of any carry-over PCB's with the PEG reagent charge.

On the basis of the experience, developmental and commercial, which UMATAC has with the technology, the factors and/or limitations to the applicability of the ATP for PCB decontamination of soils and sludges relate mostly to the physical characteristics of the feed material, the water content, and the size and variability of the particles. Higher water content reduces the throughput capacity of a given size of Processor because of the higher heat loading versus heat transfer capacity. Throughput is also reduced with higher fines content because heat transfer capability is less than with coarser solids. Conversely, throughput increases with coarse feeds. Feed stocks, with materials larger than can be processed, can be pre-separated or sized (screened or crushed) with ancillary equipment to a size which the Processor can handle. The conditions and requirements of each site or feed material must be carefully examined to determine the overall configuration and plant in which the basic ATP Processor and plant can perform most effectively.

The following tabulations of "ATP Proof-of-Process Emission Results" provide a summary of test results obtained during performance testing of the 10 ton/hour plant at the Wide Beach Superfund Site.

TABLE 1
SUMMARY OF THERMAL DESORPTION OF PCBs FROM SOILS

MATERIAL	PCB CONCENTRATION, ppm	
	TEST 1	TEST 2
Feed Soil	7,000	16,000
Product Soil	ND (0.1)	ND (0.1)
Oil Product	65,431	157,725

TABLE 2
SOIL CHARACTERIZATION DATA
WIDE BEACH SUPERFUND SITE

	ESTIMATED	ACTUAL
Total Volume to Remediate, cu.yds.	19,000	30,000
Soil Particle Size Distribution (weight percent):		
Clay	0	16.0
Silt	8	26.3
Sand	65	32.3
Gravel	27	25.4
Moisture Content (weight percent)	8 to 15	12 to 30
PCB Concentrations:		
Discrete Samples from the Site Characterization Studies - Test Samples, ppm (1 was 5,300)	0 to 1,000	
Plant Operations - 12 hour Feed Composites, ppm		0 to 46
Treated Soil Residual (detection level 70 ppb)		Not Detected

TABLE 3[2]
WIDE BEACH SUPERFUND SITE
ATP PROOF-OF-PROCESS EMISSIONS RESULTS

	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	TARGET
Test Date	90-09-07	90-09-07	90-10-04	90-10-05	90-10-05	
Soil Feed to Plant (TPH)	8.1	8.1	7.1	7.1	7.1	
PCBs in untreated soil[(b)] - ppm	0-46	0-46				25 (avg)
PCBs in treated soil[(b)] - ppb	<63	<63	--	--	--	2000
Stack Gas Flow (dscfm)	3600	3500	3160	2964	3013	3233
Stack Temperature - °C	63	64	58	59	50	57
PCBs in stack gas (gm./hr)	0.0048	0.0027	--	--	--	0.015
Polyethylene Glycol (gm/hr)	(a)	<0.019	--	--	--	0.019
CO (kg/hr)	1.6	2.25	--	--	--	5.59
CO_2 (volume %)	6.4	6.6	7.2	7.3	4.7	
O_2 (volume %)	11.4	11.2	10.8	10.7	13.9	
Particulate gm/m^3	0.76	0.69	0.023	0.09	0.07	0.11
SO_2 (volume %)	0.03	0.02	--	--	--	3.3
NO_2 (gm/hr)	613	618	--	--	--	1200
2,3,7,8 PCDD/PCDF(ng/dscm)						
EPA equivalents	<0.062	<0.076	--	--	--	--
New York State equivalents	<0.015	<0.019	--	--	--	0.2

PCDD/PCDF - polychlorinated dibenzodioxins and dibenzofurans summed according to EPA and New York State Toxic equivalent factors, referenced to 2,3,7,8 tetra-form cogeners.

- dscfm - dry standard cubic feet per minute
- gm/m^3 - grams per cubic meter
- TPH - tons per hour, average
- ng/dscm - nanograms per dry standard cubic meter, at 7% residual oxygen

(a) The first PEG sample exhibited a high detection limit, such that the permitted emissions limit for PEG could not be detected.

(b) Proof of performance for treatment of PCBs and associated organics was done in Tests 1 and 2. Tests 3, 4 and 5 were run to prove particulates removal with the repaired baghouses.

Much more complete data and results of various UMATAC's test programs, as well as batch testing of any candidate feedstocks, is available at UMATAC's facilities in Calgary.

ACKNOWLEDGEMENT

The author expresses his appreciation of the financial and technical support received from the Alberta Oil Sands Technology and Research Authority. Their representatives have visited many countries of the world and completed "memoranda of understanding" agreements with these countries. UMATAC has carried out test and evaluation programs resulting from these government-to-government agreements and these joint efforts are continuing with the purpose of developing new technology and applications for the ATP as well as other AOSTRA-funded technologies.

Appendix 7-C

Case Studies on Chemical Treatment of Contaminated Soils: APEG

AOSTRA-SoilTech Anaerobic Thermal Processor
Wide Beach, United States

United States
Environmental Protection
Agency

EPA/540/MR-92/008
March 1992

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Demonstration Bulletin

AOSTRA-SoilTech Anaerobic Thermal Processor: Wide Beach Development Site

SoilTech ATP Systems, Inc.

Technology Description: The anaerobic thermal processor (ATP) was developed by UMATAC Industrial Processes under the sponsorship of the Alberta Oil Sands Technology and Research Authority (AOSTRA) and is licensed by SoilTech ATP Systems, Inc., a U.S. corporation. The ATP technology involves a physical separation process that thermally desorbs organics such as polychlorinated biphenyls (PCBs) from soil and sludge. The ATP process was used in conjunction with optional dehalogenation reagents to chemically treat over 42,000 tons of PCB-contaminated soils at the Wide Beach Development site in Brant, New York. For this demonstration, the contaminated soils are sprayed with a diesel fuel and oil mixture containing alkaline polyethylene glycol (APEG) reagents before entering the preheat zone. The oil mixture acts as a carrier for the dehalogenation reagents.

In the preheat zone (400-650° F), water and volatile organic compounds (VOC) vaporize (Figure 1). At the same time, the reagents dehalogenate or chemically break down chlorinated compounds (including PCBs). The vaporized contaminants and water are removed via a vacuum to a preheat vapor cooling system consisting of a cyclone, condenser, and 3-phase preheat separator. The noncondensed light organic vapors are then fed by a blower directly into the combustion chamber of the processor. The oil fraction is recycled to a reagent blending tank, and recovered water is sent to the onsite treatment system.

From the preheat zone, the hot, granular solids pass through a sand seal to the retort zone (900-1,150° F). Here heavy oils vaporize, and thermal cracking of hydrocarbons forms coke and low molecular weight gases. The vapor stream from the retort zone is removed via a vacuum and passes first through a two-stage pair of cyclones to remove entrained particles. The vapor is then cooled by oil circulating in two packed columns, acting as a two-stage direct contact condenser for the higher boiling point compounds. The uncondensed vapors are then cooled in a water-cooled noncontact condenser and pass through a 3-phase

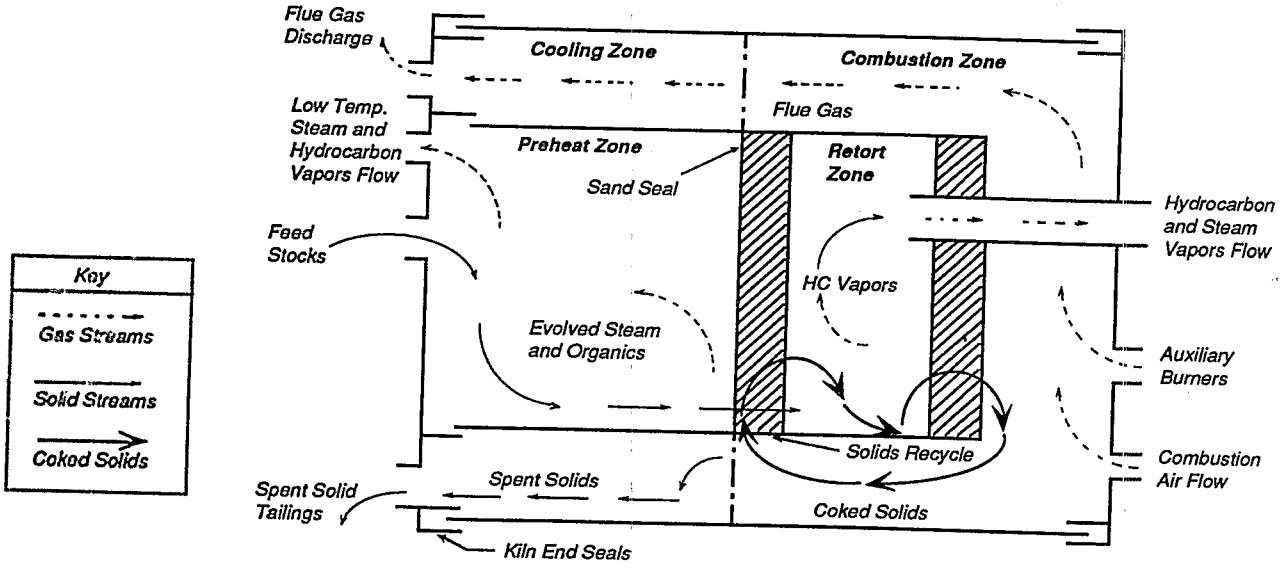


Figure 1. Simplified sectional diagram showing the four internal zones.

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separator. The final noncondensable gases are returned to the combustion chamber of the process. The oil phase is combined with the condensate from the packed columns. This oil condensate is then sent to the reagent blending unit to mix with the APEG reagents. The blend is pumped at a measured rate and is applied to the untreated soils in the feed chute of the processor. Condensed water is pumped directly to the onsite treatment system.

The coked soils pass through a second sand seal into the combustion zone (1,200-1,450° F). Here the coked soils are combusted and either recycled to the retort zone or sent to be cooled in the cooling zone. Flue gas from the combustion zone is treated in a system consisting of a cyclone and baghouse that remove particulates; a scrubber that removes acid gases; and a carbon adsorption bed that removes trace organics. The treated flue gas is then discharged to the atmosphere through a stack. Treated soils exiting the cooling zone (500-800° F) are quenched with water and are then transported by conveyor to an outside storage pile.

Waste Applicability: SoilTech reports the following specifications of the ATP system. The optimal moisture content of the waste to be treated is between 5 and 10 weight percent. Wastes with a moisture content up to 20 percent can be treated, but will impact the net throughput rates. Wastes with a moisture content greater than 20 percent may need to be dewatered to optimize process economics. The ATP system is also designed to treat wastes with a nominal hydrocarbon concentration of 10 percent. Heavy oil contaminants have been reduced from as high as 60 percent in the feed to near detection limits in the treated solids.

The rate of contaminant desorption and dechlorination from soils and sediment is influenced by the contaminant concentration. SoilTech reports that the contaminant concentration in the treated solids is generally independent of the contaminant concentration in the feed waste and will be near the detection limit for the contaminant. The processor treats wastes containing contaminants with low boiling points more effectively than wastes containing contaminants with high boiling points. However, high boiling point organics such as PCBs and polycyclic aromatic hydrocarbons can be removed to concentrations below detection limits of 1 part per million (ppm).

Demonstration Results: The ATP technology was demonstrated at the Wide Beach Development Superfund site in Brant, New York, in May 1991. Three test runs were conducted during the SITE demonstration, each 5½ hours. The solid and liquid locations that were sampled during each run were contaminated feed soil, treated soil, combined flue gas cyclone fines and baghouse dust, preheat vapor cyclone fines, scrubber liquor, condensed water before and after treatment, vapor scrubber oil, and preheat oil. The noncondensed preheat and retort off-gases were also sampled during each run.

Laboratory analyses included analyses of the solids and liquids for PCBs, dioxins/furans, VOCs, and semivolatile organics (SVOCs) to determine the PCB removal efficiency of the processor, the potential degradation products of the PCBs, and the potential formation of dioxins and furans. Total chlorides and total organic halogens (TOX) were also analyzed in an attempt to trace the fate of chlorine throughout the system. In addition, a variety of other parameters were analyzed to characterize the feed and treated soils.

Key findings from the Wide Beach site demonstration are summarized below:

- The SoilTech ATP unit removed PCBs in the contaminated soil to levels below the desired cleanup concentration of 2 ppm. PCB concentrations were reduced from an average concentration of 28.2 ppm in the contaminated feed soil to an average concentration of 0.043 ppm in the treated soil.
- The SoilTech ATP does not appear to create dioxins and/or furans.
- No volatile or semivolatile organic degradation products were detected in the treated soil. There were also no leachable VOCs or SVOCs detected in the treated soil.
- No operational problems affecting the ATP's ability to treat the contaminated soil were observed.

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Appendix 7-D

Case Studies on Chemical Treatment of Contaminated Soils: APEG

Site Demonstration of the SoilTech "Taciuk" Thermal Desorber, Waukegan Harbor, United States

SITE DEMONSTRATION OF THE SOILTECH "TACIUK" THERMAL DESORBER AT WAUKEGAN HARBOR

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INTRODUCTION

The Outboard Marine Corporation (OMC) operates a recreational marine products manufacturing plant on the western shore of Lake Michigan in Waukegan Harbor, Illinois. From 1961 until the early 1970s, OMC used a hydraulic fluid containing polychlorinated biphenyls (PCBs) in its operations. In the process of plant cleaning operations, large quantities of PCBs escaped into Waukegan Harbor and onto OMC property. Over one million pounds of PCBs were estimated to be contaminating the harbor sediments and property.

In 1984, the U.S. Environmental Protection Agency (USEPA) signed a record of decision (ROD) authorizing site cleanup; however, litigation between OMC and the USEPA suspended implementation of this Decision. In 1988, OMC and the USEPA signed a consent decree, which specified the final terms of the cleanup. Generally, OMC is required to excavate or dredge all PCB contaminated soils and sediments, treat some soils and sediments, and place all treated and untreated solids in containment cells.

Beginning in 1991, OMC initiated the cleanup of the PCB contaminated sediments and soils. Based on the 1988 Consent Decree the following actions were taken (Figure 1):

1) A new ship slip (#4) was constructed.

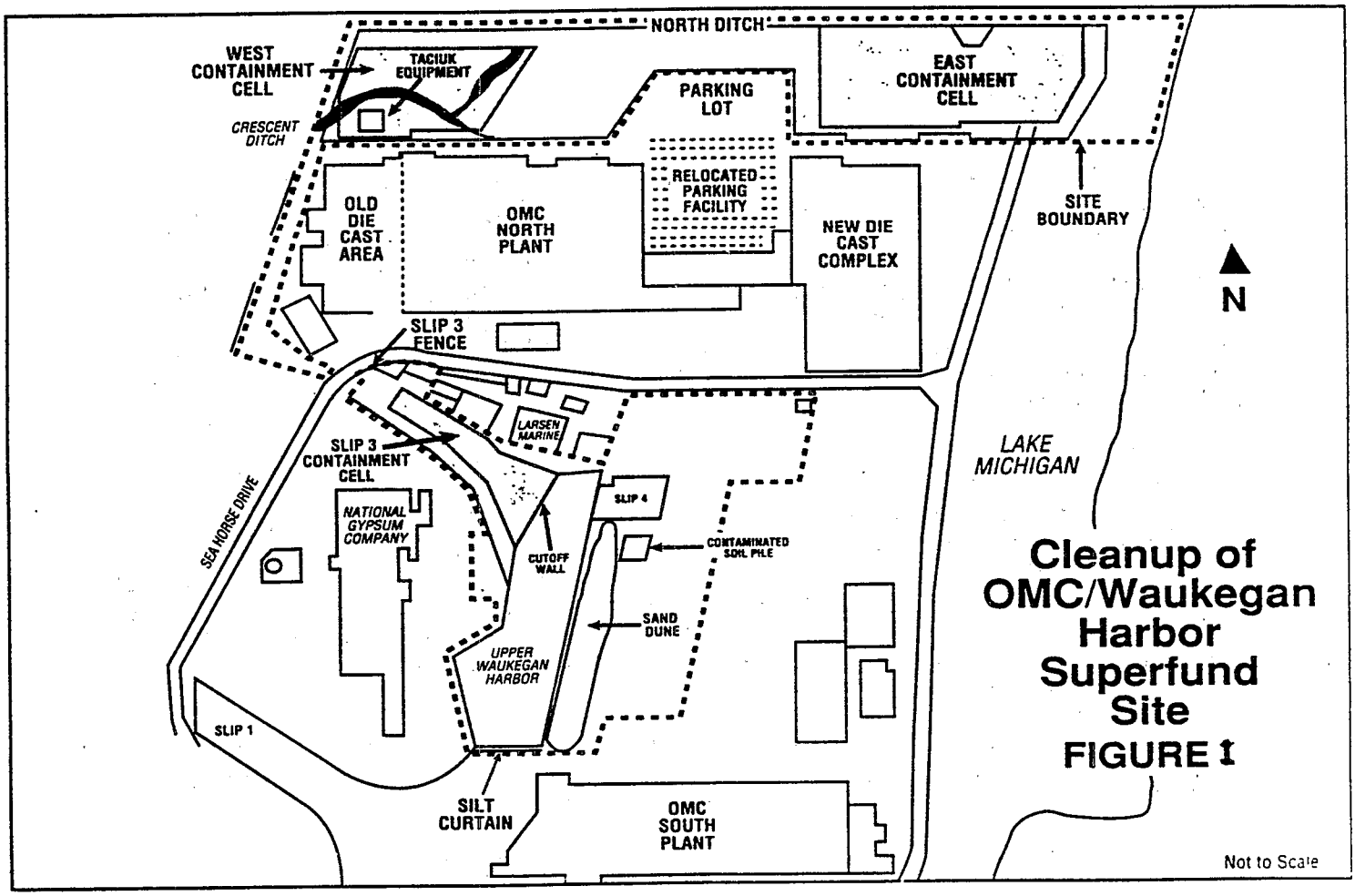
2) Ship slip #3 was isolated from the upper harbor by construction of a double-walled sheet-pile cutoff wall and slurry wall.

3) Two other (East and West) containment cells were constructed.

4) Ship slip #3 is now being dredged and the sediments dewatered.

Those solids with concentrations greater than 500 ppm PCBs are to be treated by the SoilTech "Taciuk" thermal desorption process. The treatment requirements are 85% removal or 500 ppm whichever results in the lower final PCB concentration. The treated solids and any solids with an initial concentration of less than 500 ppm will be placed in one of the three isolation cells (i.e., ship slip #3, and East and West containment cells).

The SoilTech "Taciuk" process is being set up in the West Containment cell. Contaminated sediments will be pumped to this cell and dewatered before treatment. Contaminated soils will be trucked to the cell.



SITE DEMONSTRATION PROGRAM

Before final approval is given by the USEPA and the State of Illinois a "proof-of-process" test of the Taciuk process is being required. This test is a full-scale demonstration of both the treatment effectiveness of the process, and the gas treatment and air pollution control systems. Treatment effectiveness is defined as the PCB residual level, percent removal of PCBs, and identification of any contaminants created by the thermal process and left in the soil or sediments. Contaminants removed from the soils and sediments are supposed to be recovered in the gas treatment and air pollution control systems. Effectiveness of the gas treatment and air pollution control systems is defined by the mass and emission rate of PCBs, organics and dioxins/furans emitted from the stack.

The test of the Taciuk process is tentatively scheduled for January/February 1992. A SITE Demonstration will be performed during this "proof-of-process" test to provide supplemental information to the USEPA Region V (Chicago) office and to develop the detailed information necessary for other regulatory offices to consider use of thermal desorption technologies. The SITE Demonstration includes sampling to meet the objectives of the "proof-of-process" test previously described, and additional evaluations required by the SITE program.

All SITE Demonstrations are designed to determine the technology treatment effectiveness, field (mechanical) reliability and operating cost. How these objectives are measured depend on the technology. Table 1 lists sampling required to meet these general SITE objectives for the five thermal desorption SITE Demonstrations to be performed in 1991 and 1992.

WIDE BEACH SITE DEMONSTRATION

In May 1991 a SITE Demonstration was performed using the SoilTech "Taciuk" process at the Wide Beach Superfund site in Brant, New York. Dirt roads of this community were contaminated with PCBs when used oil was applied to control dust problems. A combined process of thermal desorption (Taciuk) and dechlorination (APEG) was used to treat the contaminated soils. Preliminary results from this demonstration are:

1) Greater than 99 percent PCBs were removed from the soil and residual levels were less than 2 ppm,

2) No dioxins or furans appeared to be created, and

3) No volatile or semivolatile organic degradation products were detected in the treated soil.

TABLE 1

SITE PROGRAM

THERMAL DESORPTION SAMPLING STRATEGY

Treatment Effectiveness

1) Measure the contaminant removal efficiency and residual levels,

2) Measure the air emission rates,

3) Determination if dioxins, furans or other toxics are being created by the thermal process, and the fate of these compounds,

4) Determine if the physical properties of the soils and sediments are being changed (e.g. increased leaching),

5) Evaluate and compare the toxicological properties of contaminated and treated soils,

6) Evaluate the physical (stability) condition of the treated material and its possible future use, and

7) Determine the treatment efficiency of the condensed water.

Field Reliability

1) Document operating conditions of process and identify potential operating problems, and

2) Determine percent on-line during operating period.

Operating Costs

1) Document the capital and operating costs of the remediation.

Appendix 8-A

Microbial Treatment Technology Case Studies

Aerobic/Anaerobic *In Situ* Degradation of Soil and Ground Water, Skrydstrup, Denmark

Biodegradation - Chlorinated Aliphates

A SUMMARY OF

Research and Demonstrations at The Skrydstrup Site.

Denmark

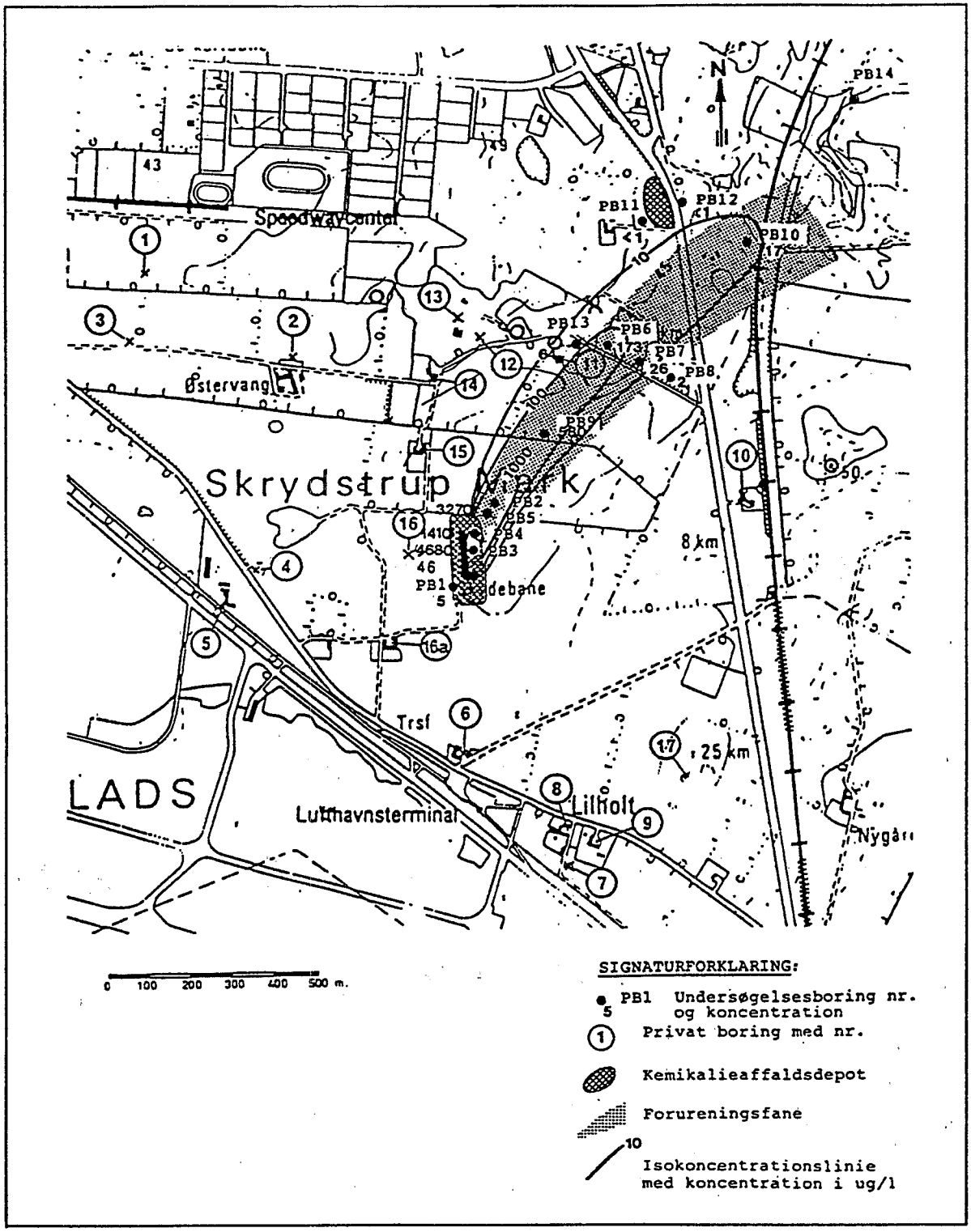


Fig. 1.1 The Skrydstrup Site and the location of the pollution plume.

Biodegradation of Chlorinated Aliphates.
A Summary of Research and Pilot Tests at The Skrydstrup Site.
The Municipality of Vejens, The County of Sønderjylland, Denmark.
(ed. Neel Strøbæk, M.Sc., Danish EPA).

1. The Skrydstrup site.

The Skrydstrup Site is a former landfill, where chemical waste from a refrigerator manufactory was dumped during the period from 1963 to 1974. A gravel pit was used a dumping site, and the waste was left without any form for protection against percolation. This has caused a considerable contamination of the groundwater by chlorinated solvents and organic phosphoruos compounds.

Investigations and clean up's have taken place, and today, the waste is removed and a full scale plant for a pump and treat remedy to clean up to groundwater have been in operation since '89.

The progress of the activities in connection with the Skrydstrup site was phased as follows from a wish to place the decision-making at the lowest possible level:

Phase 1	Orientation survey
Phase 2	Boring inspection
Phase 3	1. Draft project for excavation of the disposal site
	2. Investigation of spread of contaminant
	3. Testing methods for cleaning of groundwater
Phase 4	1. Excavation of the waste disposal site
	2. Draft project for cleaning of groundwater contamination
	3. Supplementary investigations of spread of contaminants
Phase 5	Establishment of groundwater cleaning plant.

The waste disposal site was excavated in 1986, and by that time, no treatment plant for the additional excavated soil was in operation in Denmark. The soil was, therefore, re-deposited in a new controlled depot on the site.

The treatment plant for contaminated groundwater consists of 3 treatment units: An airstripper (3 plates in series) for removal of volatile aliphates, quartz-filtration (pre- and after filtration in columns) to remove iron and manganese and active carbon filtration (3 columns in series) for removal of the organic phosphorous compounds. The cleaned groundwater is discharged to a stream app. 1,5 km from the site, even though, it can meet the Danish drinking water standards.

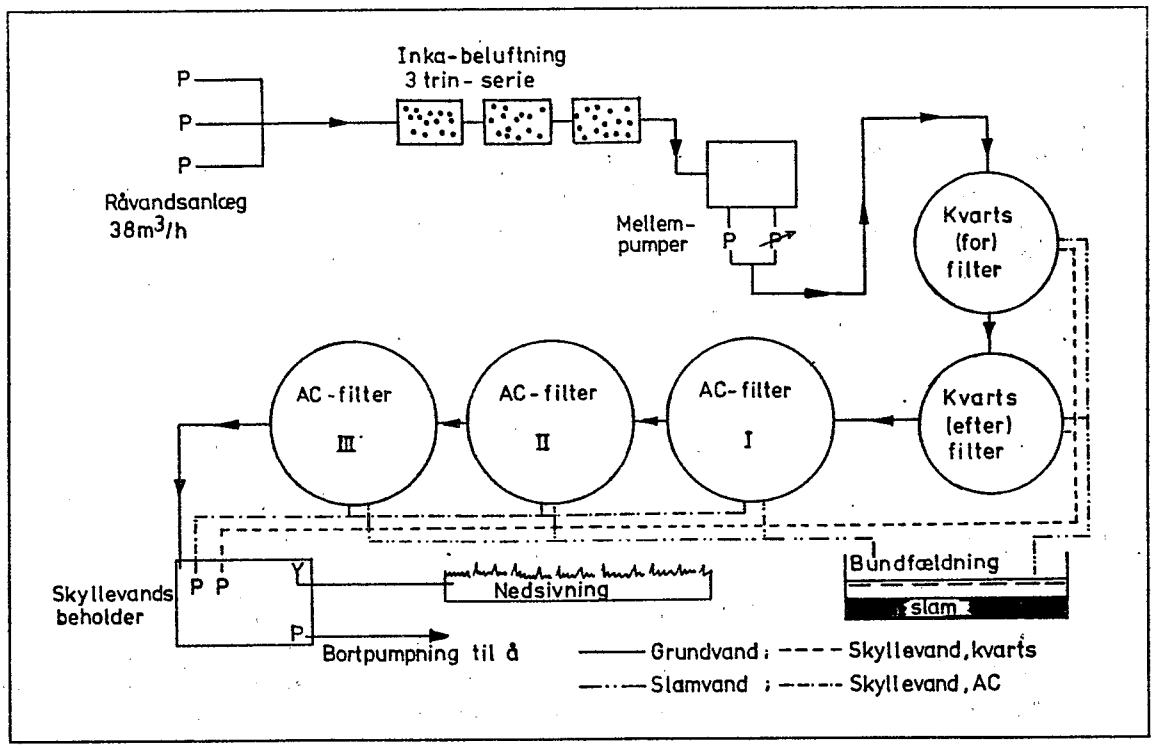


Fig. 1.2 Process diagram of full-scale groundwater treatment plant.

As the remedy at the site contains unsolved problems in forms of the diposited contaminated soil, and the airstripping, which only remove the contaminants from the water to the air, research and development projects have been carried out in order to look into biological methods as alternative remedies.

This paper summarizes the results from the projects concerning biodegradation of the contaminated soil in the on-site depot and from the on-site pilot plant for biodegradation of chlorinated aliphates in groundwater. As an introduction, a brief summay of the results of the laboratory experiments is presented in order to give a review of the framework for the work done. The Danish EPA has laid down the funding for the laboratory experiments as well as for the pilot demonstrations. The work is primary carried out at The Technical University of Denmark, Department of Environment Sciences, supported by the Department of Microbiology at the University of Copenhagen together with the Danish Environmental Survey and Kemp & Lauritzen A/S, Consulting Eng.

The following chapters are a translation of parts of the report: "Biologisk nedbrydning af klorerede opløsningsmidler. Projekter gennemført ved Skrydstrup Specialdepot. Rapport A1, 1991" (ed. Jens Aamand og Kim Broholm).

2. A summary of Laboratory Experiments.

Some laboratory batch and column experiments have been carried out to examine the possibilities of carrying out in-situ biodegradation of chlorinated aliphates in the unsaturated soil. The experiments showed, that it was possible to build up a methane-oxidizing biomass which was able to degrade tri-chloroethylene (TCE) and 1,1,1-tri-chloroethane (1,1,1-TCA) but not tetra-chloroethylene (PCE). The column experiments revealed that stripping due to the addition of methane and air was a significant removal process in columns without recirculation of the injected air. In practices it is difficult to avoid stripping, which means that the biological processes have to be optimized before the technique will be useful.

Laboratory batch experiments have been carried out to examine the degradation of chlorinated aliphates in groundwater.

Aerobic degradation experiments showed that the degradation of TCE and methane in the groundwater at Skrydstrup was slow compared to the degradation of TCE and methane in a mineral medium. In opposition to that, the degradation rate of TCE was increased 88 times when bacteria grew in absence of copper. It is unknown whether the natural concentration of copper in the groundwater at Skrydstrup results in copper limited growth or not.

The groundwater at Skrydstrup contains high concentrations of chlorinated aliphates. Therefore the toxicity of 1,1,1-TCA and TCE towards a mixed culture of methane-oxidizing bacteria was examined in batch experiments. The consumption of methane was inhibited even by small concentrations of 1,1,1-TCA and TCE. A total inhibition of the methane consumption was observed at a TCE concentration of 13 mg/l, whereas a total inhibition was not observed at a

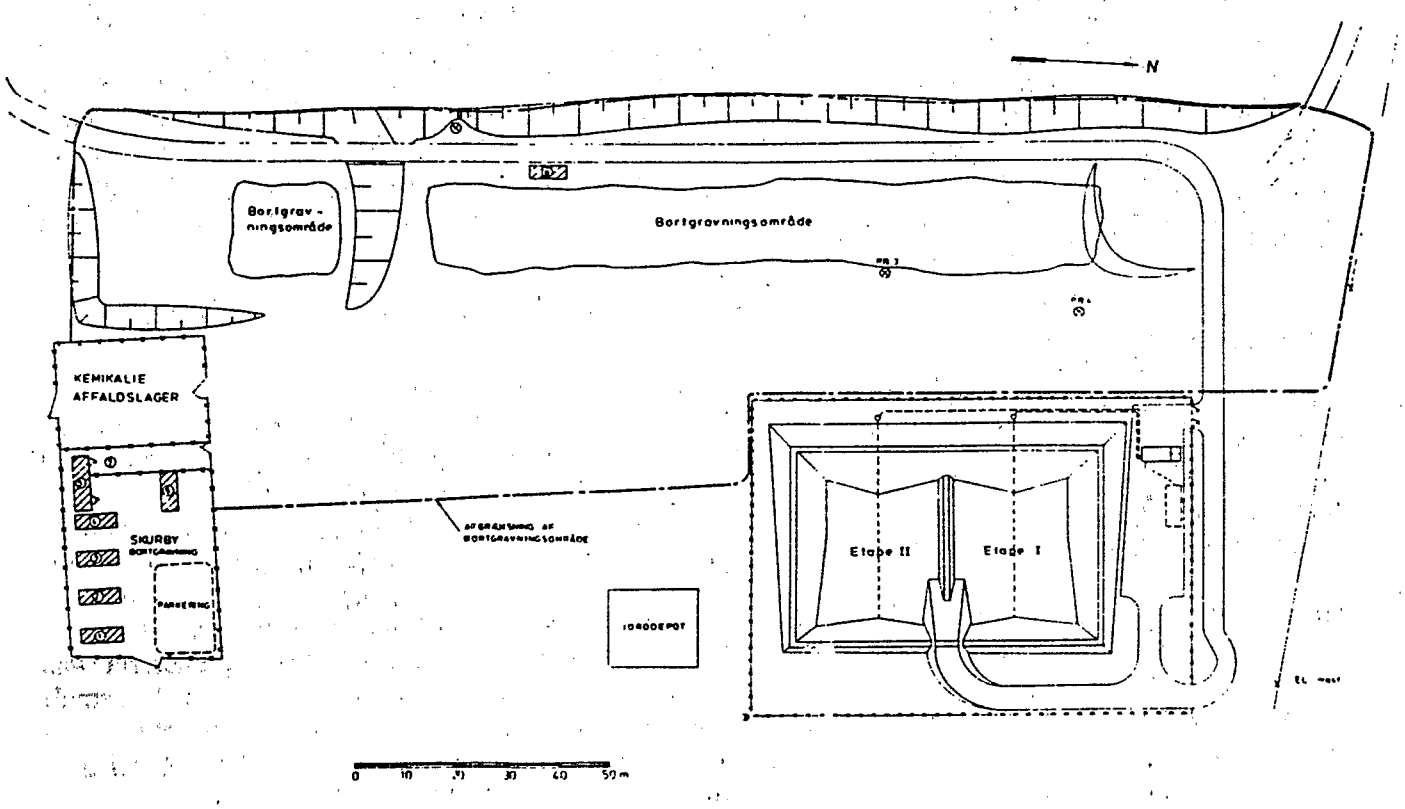


Fig. 2.1 The Skrydstrup Site with the controlled soil depot.

1,1,1-TCA concentration of 103 mg/l. Experiments also showed that the presence of methane inhibited the degradation of TCE. A mathematical model describing the growth of bacteria and the degradation of methane and chlorinated aliphates is proposed. The model was able to simulate the observed degradation curves for methane and TCE but not for methane and 1,1,1-TCA.

The use of methanol instead of methane as primary substrate for the methane-oxidizing bacteria was examined. The experiments show that methanol did not stimulate the degradation of TCE probably because methanol does not induce methane monooxygenase.

Anaerobic biodegradation of chlorinated aliphates have been investigated with groundwater from Skrydstrup, groundwater sediment from the site Mørkhøj Bygade, and methanogenic sludge from different wastewater treatment plants. No degradation of PCE was observed in the groundwater from Skrydstrup, probably because of the high redoxpotential in this reservoir. The reservoir contains high concentrations of oxygen, nitrate and sulphate. The anaerobic degradation of chlorinated aliphates depended on the presence of a primary substrate.

Laboratory experiments show that the primary substrates resulting in formation of hydrogen sustained the fastest degradation of PCE.

3. Biodegradation in The Soil Depot.

In connection with the remedies at The Skrydstrup Site, a separat soil depot was establish in 1986. In the depot excavated contaminated soil and slag from the original waste site were deposited. The depot was established with an anaerobic compartment (section 1), and an aerobic compartment (section 2). Tests for biological degradation was carried out.

3.1 The Soil Depot.

The anaerobic compartment contains app. 3.000 m3 of contaminated soil. The aerobic compartment contains app. 500 m3. The soil was placed on a HPDE liner, and the anaerobic compartment was covered with a LPDE liner to secure anaerobic conditions in the compartment.

In the two sections, waste water sludge was build in, to secure an anaerobic and aerobic activity, respectively. In each section, separate leachate collection systems and recirculation-facilities was established. The leachate from the two sections is separately collected. In the anaerobic section, the leachate has been recirculating since the beginning of 1987 by a rate of 100 % and without contact to the surrounding environment.

The leachate from the aerobic section is recirculating through a storage tank, with contact to the surrounding environment. Dependent of the local precipitation and evaporation from the section, the storage tank is emptied.

Methaner	Ethaner	Ethener
diklormethan	klorethan*	vinylklorid*
triklormethan	1,1-diklorethan*(1,1-DCA)	1,1-diklorethen*(1,1-DCE)
tetraklormethan	1,1,1-triklorethan (1,1,1-TCA)	cis-1,2-diklorethen*(cis1,2-DCE)
		trans-1,2-diklorethen*(trans-1,2-DCE)
		triklorethen (TCE)
		tetraklorethen (PCE)

Table 3.1 Scheme of analysis for chlorinated aliphates in the soil depot.
* means that the compound may be a degradation product of 1,1,1-TCA, TCE or PCE.

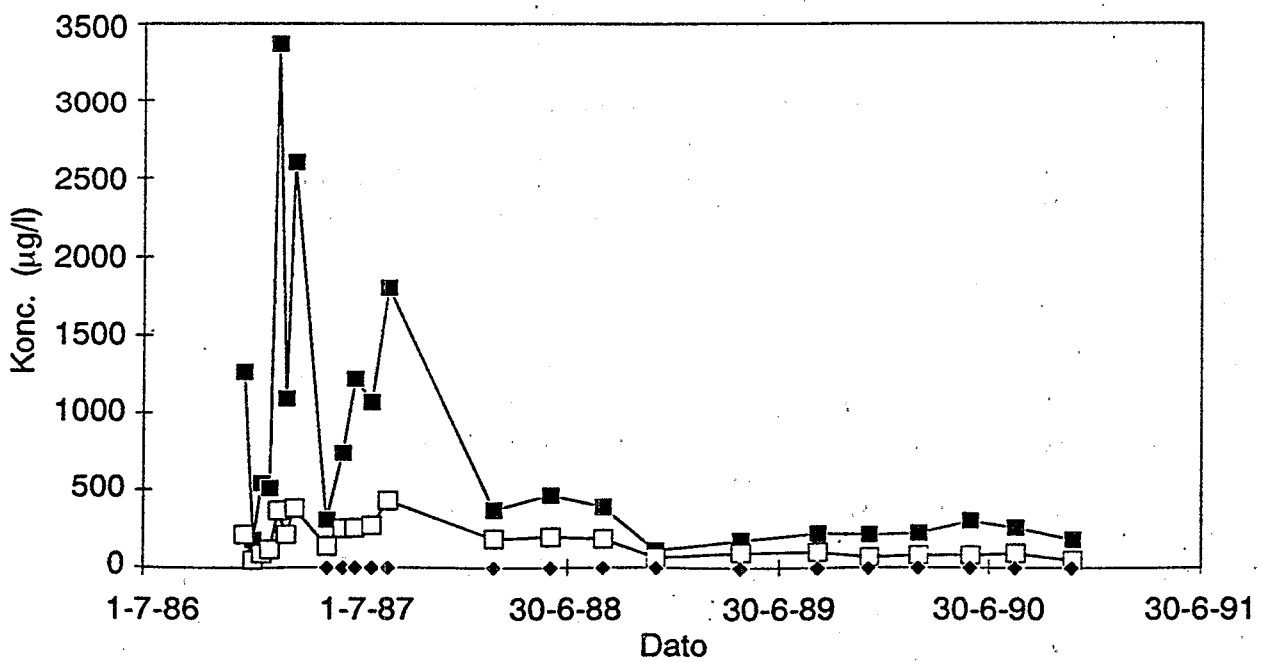


Fig. 3.2 A time dependend describtion of the occurrence of contaminants in section 1.
1,1,1-TCA(■), TCE(□) and PCE(♦).

From Dec.'86 the concentrations of chlorinated aliphates and their degradation products are monitored by sampling and analysis of the leachate. From 1987 exist several sampling reports, while in the later years 3-4 sampling schemes have been carried out each year. All leachate samples are analysed in a scheme including inorganic parameters, chloro-alkyl-phosphates and chlorinated aliphates, as shown in table 3.1.

The methods of analysis are head space GC with a electron capture detector (GC/ECD), and for vinyl chloride by GC with a mass spectrometer as a detector (GC/MS).

Besides the chemical analysis monitoring, a microbiological investigation in both sections was carried out in 1990. The aim of the investigation was to determine the microbial activity in the contaminated soil.

Soil samples from different depths in the two sections were taken to the laboratory, and the number of bacteria was determined by direct counting. The rate of growth was determined by incorporating titrated thymidine in bacterial DNA under anaerobic and aerobic laboratory conditions. Furthermore testing of the ability of the bacteria to transform PCE and TCE under laboratory anaerobic and aerobic conditions was carried out.

3.2 Anaerobic Compartment (Section 1)

At the time of establishing, it was estimated, that section 1 in total contained 109 kg of 1,1,1-TCA, 31 kg of TCE and 0,6 kg of PCE.

The first leachate was sampled Dec. 22, 1986, while the latest sets of samples dates to Nov. 20, 1990. In fig. 3.2. the connection between meassured concentrations in leachate samples and the dates of sampling is illustrated.

In the evaluation of the concentrations of the contaminants in the anaerobic section, the closed conditions in the section, and the recirculation of the leachate must be taken into account.

Assuming the leachate is recirculated 100 % anaerobic, the very small concentrations of contaminants in the beginning of the monitoring period, probably can be explained by the lack of equilibrium concerning the partition between the soil and the leachate. Later in the first year (1987) a substantial increase of especially 1,1,1-TCA and TCE is seen. The increase is followed by a decrease, which for 1,1,1-TCA constitutes app. 90 % of the highest value in 1987. For TCE the decrease is app. 80 % of the highest value in 1987. The concentrations of these two contaminants have in the later years been app. 50-250 microgram/l.

Looking at PCE, the concentrations have been low and at changing levels in the monotoring period.

In fig. 3.3 the connection between meassured concentrations of degradation products and the dates

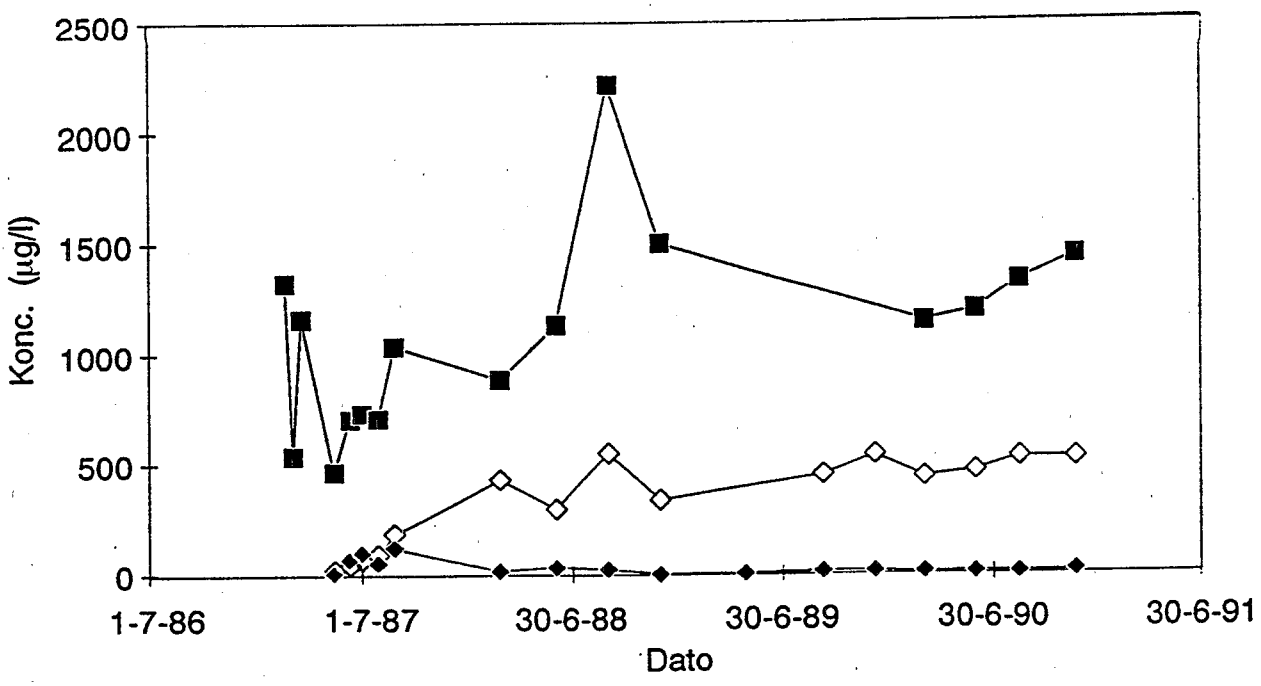


Fig. 3.3 A time dependend describtion of the occurrence of pressumed degradation products in section 1. 1,1-DCA(■), cis-1,2-DCE(◇) and 1,1-DCE(◆).

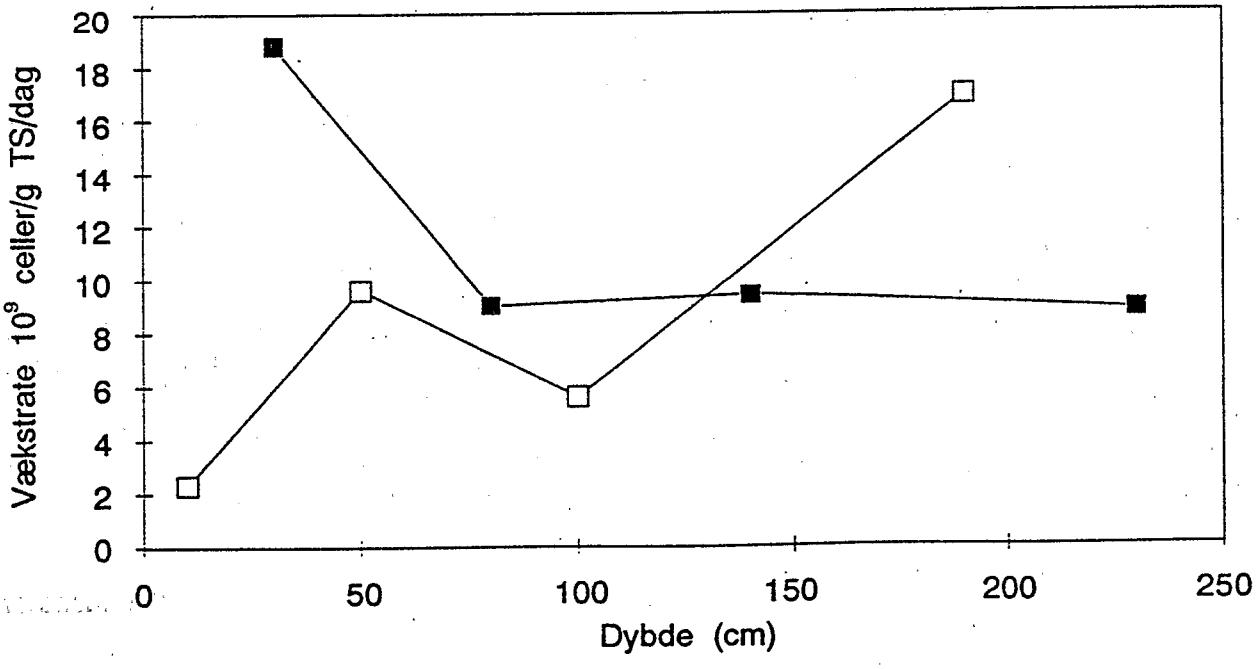


Fig. 3.4 Microbial activity determined by incorporating radioactive marked thymidine and re-calculated to cells produced per gram soil dry matter per day. Section 1(□) and Section 2(■).

of sampling is shown. At an early stage in the monitoring period, high concentrations of 1,1-DCA are seen. This level of 1,1-DCA is re-found in general in the monitoring period. Some months later in the same year (1987) as well 1,1-DCE as cis-1,2-DCE are detected. The concentration of the latter is increasing by time. Twice in 1988, vinyl chloride is found in concentrations approximately at the detection limit of 1 microgram/l.

In comparing the decrease of the concentrations of the original contaminants 1,1,1-TCA, TCE and PCE with the formation of the pressumed degradation products 1,1-DCA, 1,1-DCE, cis-1,2-DCE and vinyl chloride, there is a reason to believe, that microbial anaerobic transformation of chlorinated aliphates have taken place in the section.

The results of the microbial investigations in the anaerobic section show, that in that section, a relatively large and active bacteria population is present, especially in greater depths (190 cm beneath the top liner), ref. to fig. 3.4. Laboratory tests have shown, that the microorganisms are able to transform PCE under anaerobic conditions. The transformation velocity is dependent of the surrounding conditions, f.ex. the presence of primary substrates and essential nutrient.

There is concordance between the occurrence of degradation products and the presence of anaerobic active bacteria in the anaerobic section of the soil depot.

3.3 Aerobic Compartment (Section 2)

When the depot was established, it was estimated, that the aerobic section in total contained 0,2 kg of 1,1,1-TCA, 0,1 kg of TCE and less than 0,01 kg of PCE. Afterwards, there has been doubt of the correctness of this estimation, while later meassurements of concentrations in leachate from the section indicates, that the start concentrations probably have been higher. As mentioned beforehand, the section has no top liner, and is therefore flushed by precipitation, and evaporation from the top soil takes place.

In fig. 3.5 the connection between meassured concentrations in leachate samples and dates of sampling is illustrated.

As mentioned, the leachate is recirculating in the aerobic section via a storage tank in contact with the atmospheric air.

Taken into account the probable flushing and evaporation, it is difficult to evaluate the changes in concentrations of the contaminants in the section.

For 1,1,1-TCA it is seen, that the concentrations in the first year (1987) are of the same order of magnitude as for the anaerobic section, with a maximum of app. 3.000 microgram/l. In the later years the concentration has been app. 100 microgram/l, which is about half of the concentration in the anaerobic section.

Concentrations of TCE have in the monitoring period been lower than in the anaerobic section.

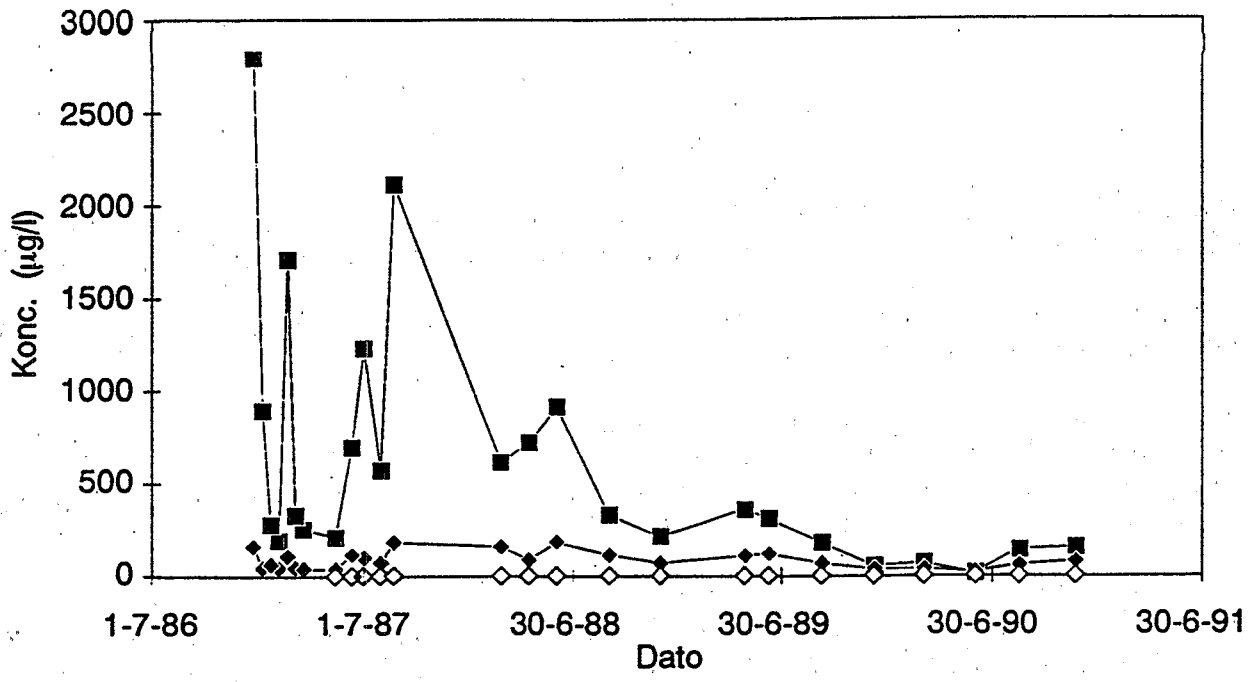


Fig. 3.5 A time dependend describtion of the occurrence of contaminants in section 2. 1,1,1-TCA(■), TCE(◆) and PCE(◇).

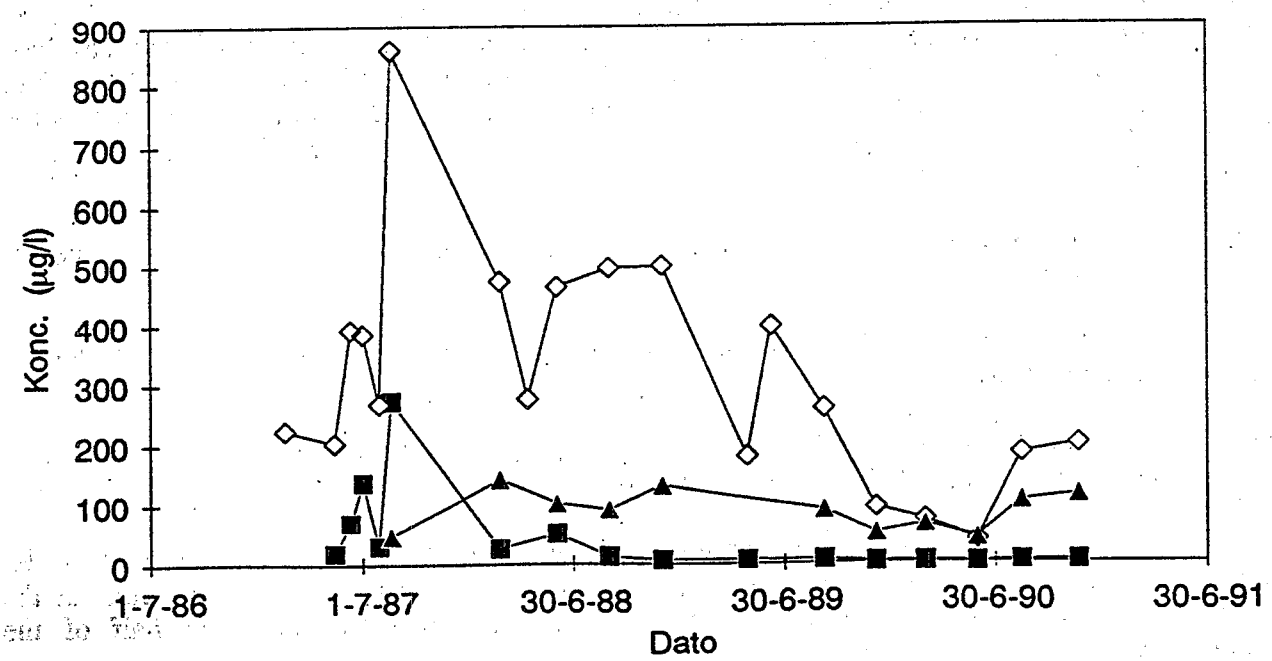


Fig. 3.6 A time dependend describtion of the occurrende of pressumed degradation products in section 2. 1,1,-DCA(◇), cis-1,2-DCE(▲) and 1,1-DCE(■)

A decrease in concentration of app. 50 % of the highest value is seen. The same tendency applies for PCE.

In fig. 3.6 the connection between meassured concentrations of degradations products and dates of sampling is shown.

In the aerobic section, 1,1-DCA is found from the beginning of 1987. The concentration amounts in the monitoring period only app. 15 % of what is found in the anaerobic section. Approximately at the same time, 1,1-DCE is found in concentrations in the same order of magnitude as in the anaerobic section. Cis-1,2-DCE is found, but in very low concentrations compared to the anaerobic section.

For the aerobic section, the decrease in concentrations of the contaminants can not be directly related to microbial transformation. As mentioned, the section is not covered, which will mean, that flushing and evaporation takes place. Anyhow, degradation products is found as for the anaerobic section.

The microbial investigation shows, that the rate of growth of the bacteria is comparable to the rate of growth of the bacteria in the anaerobic section. In contradiction to the anaerobic section, the highest rate occurs in the upper part of the section (ref. to fig. 3.4).

In comparing the occurrence of 1,1-DCA and 1,1-DCE to the bacterial activity, there seems to be possibilities of a partly degradation of contaminants in the aerobic section. Whether the degradation takes place under microbial aerobic or anaerobic conditions, or as a result of chemical degradation can not be stated from the microbiological investigations. Due to the thickness of the section, anaerobic microbial processes may take place in parts of the aerobic section.

Furthermore, it can not be excluded, that there has been small amounts of 1,1-DCA or 1,1-DCE at the time of establishing the depot, as low concentrations of these compounds often are found as inpurities in technical apllied 1,1,1-TCA.

3.4 Conclusions.

The degradation velocity in the anaerobic section of the soil depot of 1,1,1-TCA and TCE can be estimated to 0,5-1,5 years in terms of half life period. Due to flushing and evaporation, it will not be meaningful to estimate the half life period for the microbial processes in the aerobic section. In general, a substantial decrease in concentrations is seen in both sections in the monitoring period. In the anaerobic section, where the microbiological activity is highest, a substantial amount of degradation products is found, while, in the aerobic section, the contaminants and their degradation procucts are removed by flushing and evaporation as well.

In applying these processes as a remedy for contaminated soil, it can be stated, that the contaminants will degrade under anaerobic conditions, but other chlorinated compounds, which may be even more toxic, will be formed.

		Råvand, Skrydstrup specialdepot	Vand til pilotanlægget 2.fase
pH		6,5 - 7,5	7,0 - 8,0
Ledningsevne	mS/m	40 - 70	
Calcium	mgCa/l	50 - 110	
Magnesium	mgMg/l	2 - 6	
Natrium	mgNa/l	6 - 17	
Kalium	mgK/l	0,4 - 1,2	
Ammonium	mgNH_4/l	0,01 - 0,1	
Jern	mgFe/l	0,02 - 0,3	< 0,010
Mangan	mgMn/l	0,02 - 0,2	< 0,010
Kobber	µgCu/l	~1	
Bicaarbonat	mgHCO_3/l	100 - 300	
Klorid	mgCl/l	20 - 40	
Fluorid	mgF/l	~0,1	
Sulfat	mgSO_4/l	40 - 60	
Nitrat	mgNO_3/l	20 - 50	
Nitrit	mgNO_2/l	0,01 - 0,1	
Fosfor, total	mgP/l	0,02 - 0,1	
Opløst ilt	mgO_2/l	1-6	~ 10
1,1-DCA	ug/l	10 - 100	
1,1,1-TCA	ug/l	100 - 2000	20 - 100
1,1-DCE	ug/l	10 - 100	
TCE	ug/l	100 - 500	10 - 40
PCE	ug/l	0,1 - 2	

Table 4.1 Data on the overall groundwater quality at the Skrydstrup Site.
Column 1: Raw water, Column 2: Inflow to the Pilot Plant.

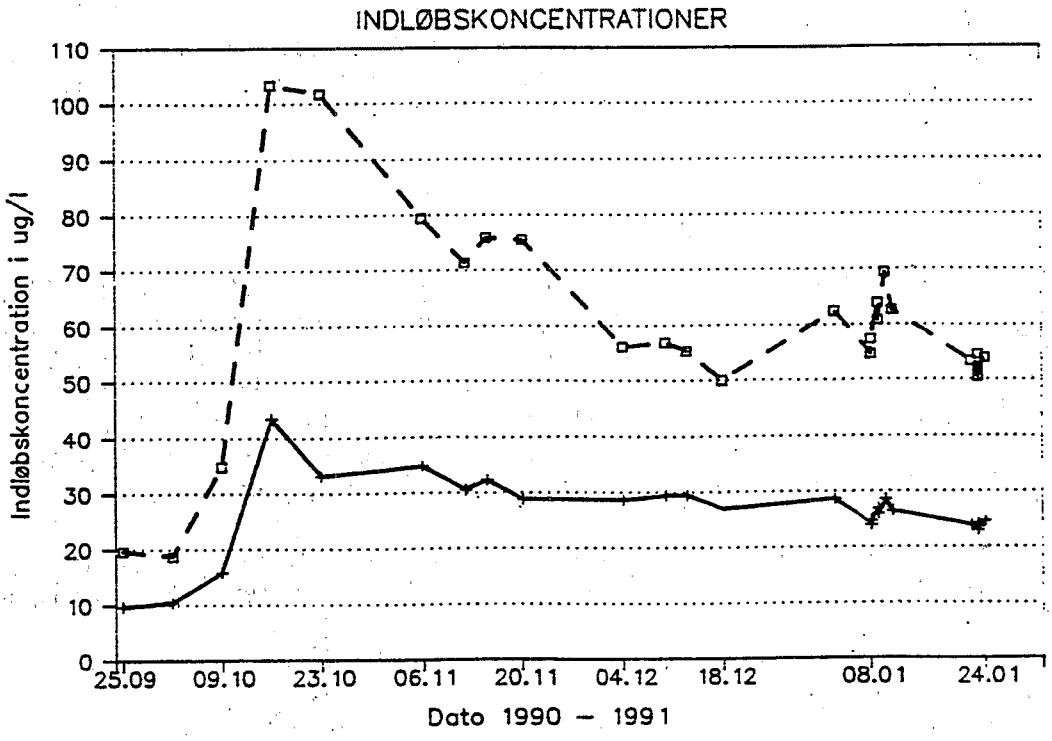


Fig. 4.1 Concentrations of 1,1,1-TCA(□) and TCE(+) in inflow to the Pilot Plant.

In the aerobic section, a large portion of the contaminants are presumeably removed physically from the soil medium to water and air. Furthermore, different processes have been difficult to control, f.ex. the partly anaerobic degradation of the contaminants.

In comparison with other remedy technologies, the biological anaerobic degradation is evaluated as functioning, however, the technique is slow, and problems with toxic degradation products can occur.

It will be of great interest to maintain the monitoring program in both of the sections, supplemented by further microbial investigations, which should be related to the occurance of organic and inorganic parameters and heavy metals.

4. On-site biodegradation - Groundwater

4.1 Introduction

In connection to the established full-scale treatment plant (air-stripping, quartz- and AC-filtration) a demonstration on biological on-site treatment was carried out.

The objectives were to investigate the aerobic biodegradation of TCE in a pilot-plant, secondary to optimize the process.

The demonstrations have been divided into 2 phases. In phase 1, tests were made with downstream filtration in a column with antracite carbon as filter material. In phase 2, tests were made with upstream filtration in a column with quartz as filter material. The following presentation includes the results from phase 2.

The perspectives of application of these processes are expected to be an alternative to the current used air stripping, where the contaminants are removed from water to air.

4.2 Grundwater Quality

Table 4.1 shows the overall water quality at The Skrydstrup Site. The figures are based on samples from 4 wells, which are used in the full-scale plant. It must be noted, that the concentrations of chlorinated aliphates in the raw water varies from well to well, dependent on their location in the pollution plume.

The inflowing water to the pilot plant was taken after the first of the three airering units of the full scale plant. In table 4.1 the water quality data are shown. The concentrations of 1,1,1-TCA and TCE in the inflowing water is shown in fig. 4.1.

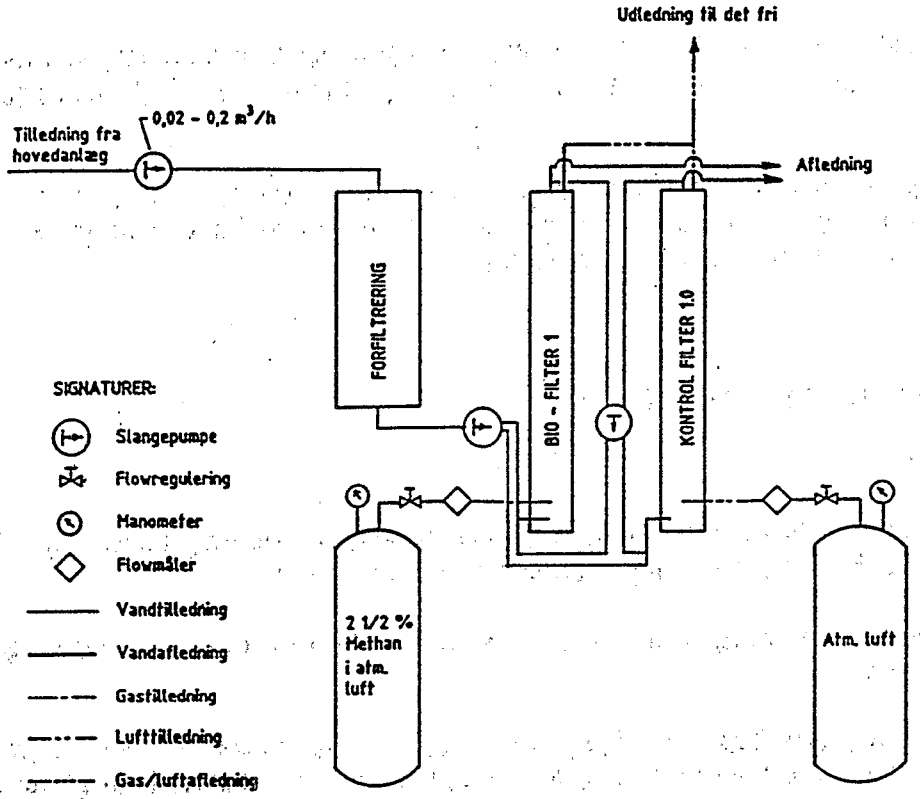


Fig. 4.2 Process diagram of Pilot Plant

4.3 On-site Pilot Plant

4.3.1. Configuration

Fig. 4.2 shows a process diagram of the pilot plant. The contaminated (oxidized) water was led to a pre-filter (column) with quartz as filter material for removal of iron and manganese. From the pre-filtration unit equivalent dicharge runs through the two test-filter columns, in the following named biofilter and controlfilter, respectively. The plant was primary made of glass and stainless steel. Packers and tubes of viton. Methane is added to the biofilter as primary substrate for methane-oxidizing bacteria. The methane (2,5 % (vol/vol)) was mixed with synthetic air (21 % (vol/vol) oxygen; 79 % (vol/vol) nitrogen). To the controlfilter an equivalent amount of synthetic air was added. In the tests, upstream filtration was used, where gas (methane/air and clean air, respectively) were added the test filters with the waterstream, ref. to fig. 4.2).

4.3.2 Filter and inoculation material.

Quartz with a grain size of 2-3 mm was used as filter material. The porosity was 0,4 and the surface of the material was less than 1 m2/g.

As inoculum filtersand (quartz) from a pre-filtration unit from a public waterwork was chosen. This waterwork treats groundwater from an aquifer which contains methane. Test made at The University of Copenhagen showed that this material contained a large population of methane-oxidizing bacteria. The degradation potential of TCE was tested on several other media (lake- and aquifer sediments) and the mentioned filter material was chosen due to a large potential and a relatively small methane consumption in the degradation process.

In the demonstration, the filters contained only quartz from the waterwork filtration unit. The material was thereby used as filter material as well as inoculum.

4.4 Operation

4.4.1 Running-in

The running-in of the process toke place the first month of operation. In that periode the methane-oxidizing bacteria was multiplied. During the period the methane consumption in the biofilter was meassured. The consumption was used as an expression of the biological activity in the filter.

4.4.2 The Demonstrations

To investigate the influence of the residence time on the biological activity and on the degradation of chlorinated aliphates, tests was made with different residence times (Th). In these

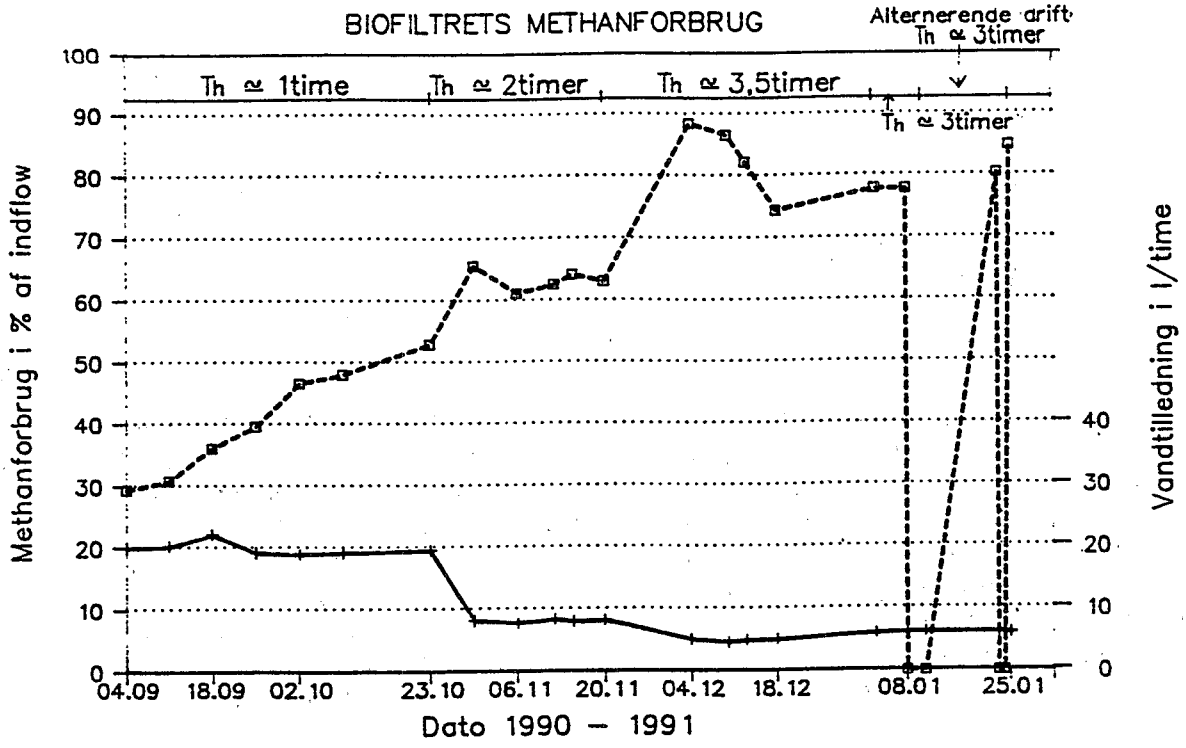


Fig. 4.3 Methane consumption in biofilter(□), fixed relatively to the added methane. Changes in inflow of water(+) and the thereby resulting hydraulic resistence time in the biofilter (Th=1, Th=2,Th=3 and Th=4). Gas to water rate is app. 1.

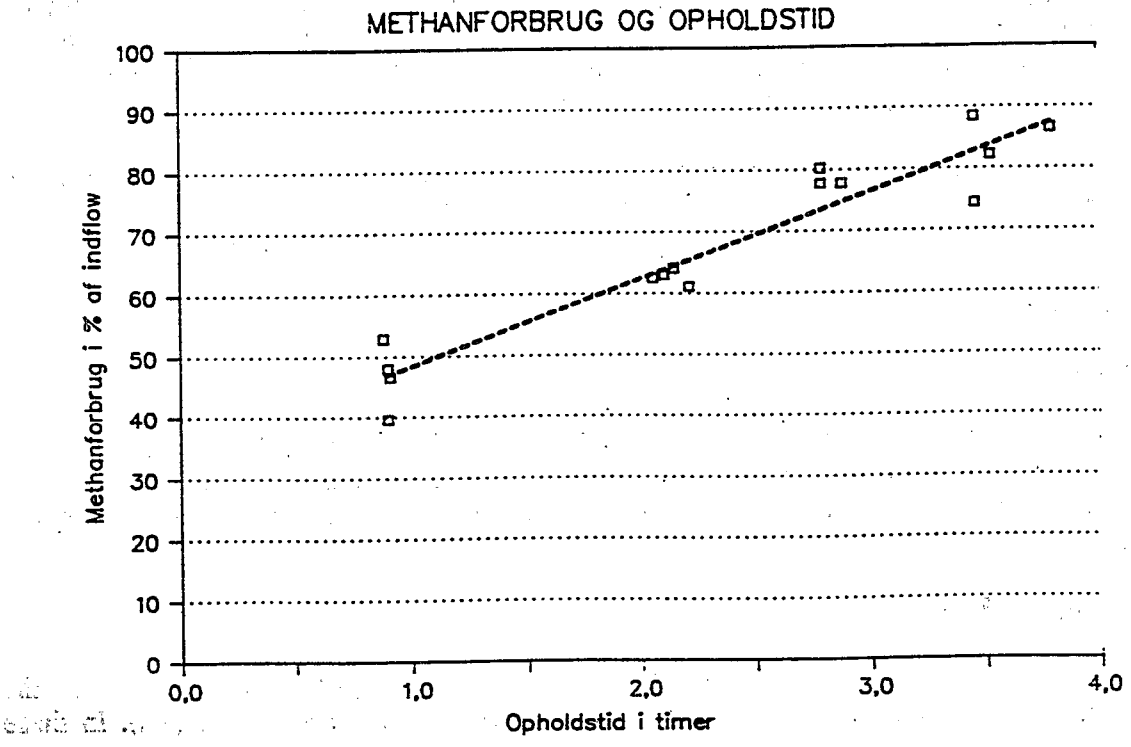


Fig. 4.4 Methane consumption in biofilter(□) as a function of the hydraulic residence time (Th). The methane consumption is fixed in relation to the added methane. Furthermore a regression line is shown.

tests, the gas to water rate was nearly constant at app. 1.

Furthermore tests were made with alternating addition of methane, by means of excluding and including methane in the airstream to the biofilter. The waterflow through the filter was kept unchanged. The aim of these tests was to investigate the degradation of chlorinated aliphates by the methane-oxidizing bacteria without methane addition. Methane is a competitative inhibitor for the degradation of chlorinated aliphates. It was therefore expected, that the degradation of chlorinated aliphates would increase immediate after methane stop at the biofilter.

4.4.3 Methods of Analysis

The concentrations of methane in the air disharge from the biofilter were meassured on the site (IR-sensor URAS 10E from Hartmann & Braun). The concentrations of methane in the water disharge from the biofilter was analyzed by a GC with a flame ionization detector (GC/FID). Concentrations of chlorinated aliphates in samples from inflowing and outflowing water from the biofilter and controlfilter respectively, were extracted by pentane and analysed by GC with a electron capture detector (GC/ECD). Concentrations of chlorinated aliphates in the outflowing air from the biofilter and the controlfilter were collected on activated carbon in glastubes. The carbon was eluated by sulphur/carbon and analysed by GC with a flame ionization detector (GC/FID).

4.5 Methane Consumption

In fig. 4.3 the methane consumption in the biofilter is shown. The consumption is shown relatively to the ingoing quantity of methane to the biofilter. In the figure the quantity of inflowing water to the biofilter is shown as well as the order of magnitude of the hereby resulting hydraulic residence times (Th) in the biofilter. The hydraulic residence time is calculated as the residence time of water in the test columns without taken into account, that the gas "takes up space", and thereby reduces the real hydraulic residence time. From the figure it can be seen, that the methane consumption increases, as expected, when the hydraulic residence time increases.

In fig. 4.4 is the methane consumption in per cent drawn up as a function of the hydraulic residence time. It must be noted, that the first 3 meassurements of the curve of methane consumption in fig. 4.3 dates back to the period of running-in, ref. to sect. 4.4.1. These meassurements are not included in fig. 4.4. A linear regression a made on the per cent data of the methane consumption, and the regression line is included in fig. 4.4.

The gradient of the regression line differs significantly from 0 on all levels greater than 0,1 % in an inteval for the residence time on 1-4 hours. There is thereby stated a connection between the residence time and the methane consumption. In the latter part of the tests, the methane consumption decreases to 0 % at two times (Two periods where methane are excluded the inflowing air). In this case, as shown in fig. 4.3, a trial is made on alternating operation on methane, ref. sect. 4.4.2). By re-adding methane, a methane consumption on the same level as before the addtion was stopped, is seen. It is therefore evaluated, that there is no effects on the biological activity in the biofilter, when excluding methane in shorter periods of time.

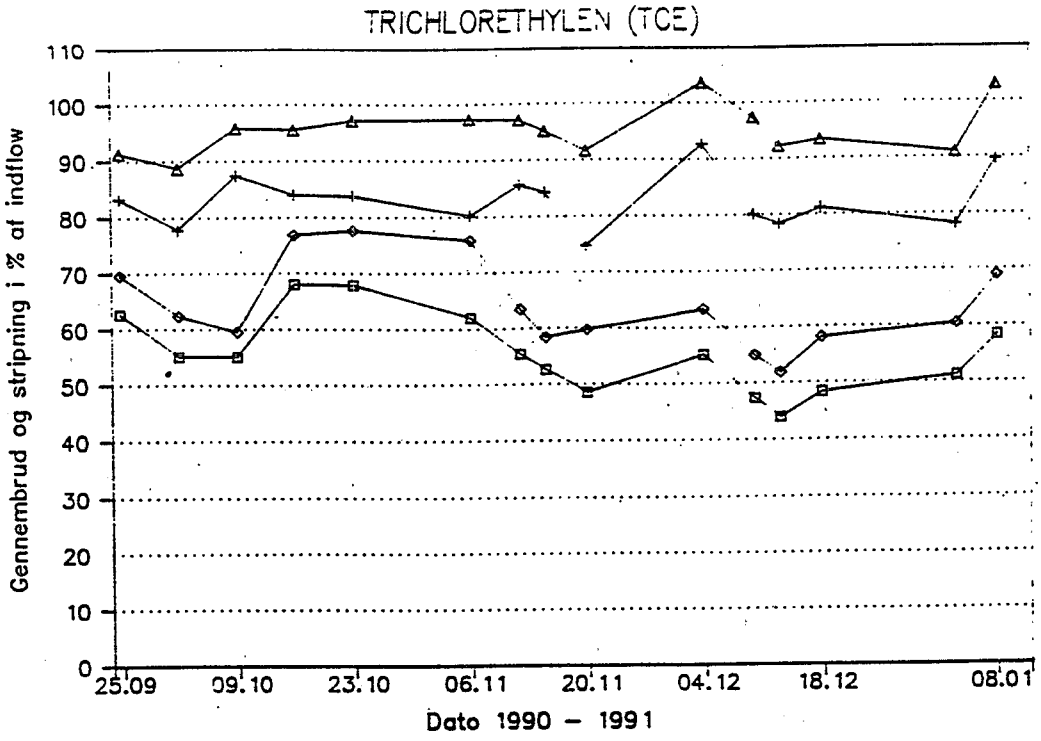


Fig. 4.5 Break-through(□) and Break-through+Stripping(◇) of TCE in the biofilter; Break-through(+) and Break-through+Stripping(△) of TCE in the controlfilter in test with the residence time(Th). The Break-through is calculated as the amount of TCE, removed from the filters by the outflowing water. Stripping is calculated as the amount of TCE, removed from the filters by the outgoing air. The residence time is changed according to fig. 4.3.

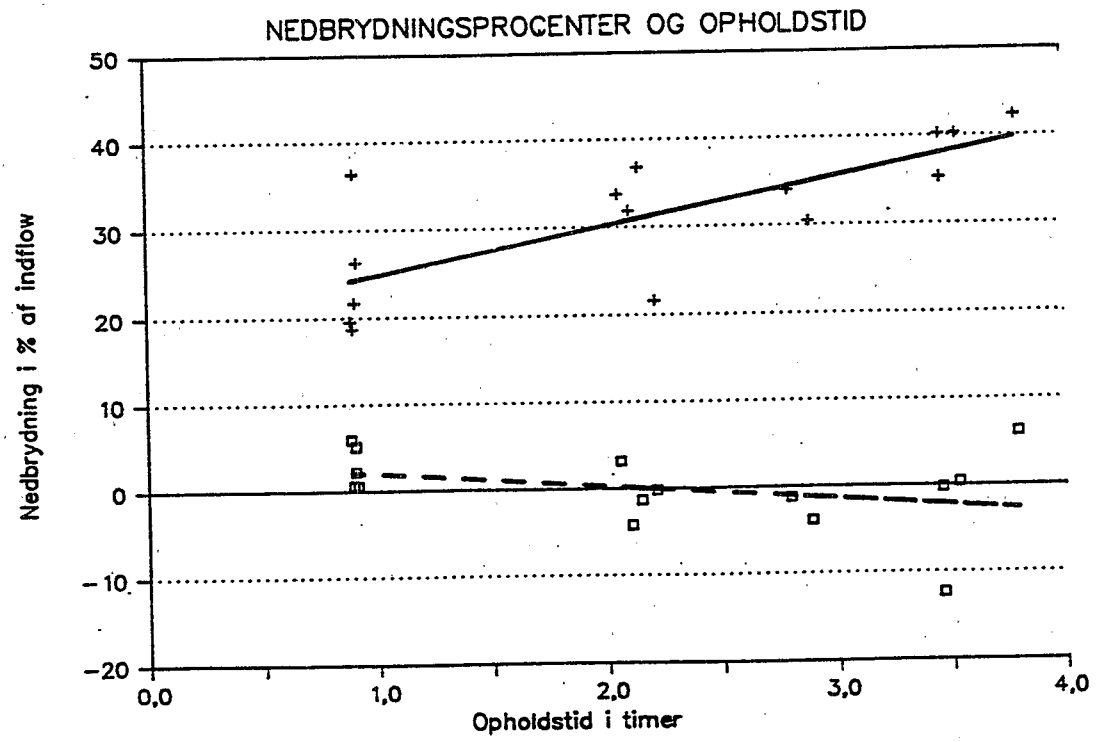


Fig. 4.6 Relatively degradation of 1,1,1-TCA(□) and TCE(+) in the biofilter as a function of the hydraulic residence time(Th). Furthermoore regression lines are shown.

4.6 Results from Tests with Residence Times.

In fig. 4.5, the break-through and stripping of TCE in the biofilter and controlfilter is shown for different residence times. Break-through is calculated as the amount of TCE leaving the biofilter and the controlfilter, respectively. Stripping is calculated as the amount of TCE in the outgoing air from the biofilter and control filter respectively. Break-through and Break-through plus Stripping is related to the ingoing amount of TCE to the filters. The curve of Break-through plus Stripping is at the level at 100 %, which shows, that a valid mass balance for the filter can be made. The difference in the values for Break-through plus Stripping for the biofilter and the control filter, respectively in evaluated as an expression of the degradation of TCE in the biofilter (degradation in per cent). For 1,1,1-TCA the per cent of degradation is calculated in the same manner.

In fig. 4.6 the calculated degradation per cents of 1,1,1-TCA and TCE are shown as a function of the hydraulic residence time. A linear regression is made on the degradation per cents and their dependence of the hydraulic residence time. In the figure the resulting regression lines are drawn up. The regression line for 1,1,1-TCA differs not significantly from 0 on levels less than 10 %. Furthermore is the line around 0 %. It is evaluated, that no significant degradation of 1,1,1-TCA has taken place in the biofilter in the test period. For TCE the regression line is significantly different from 0 on all levels greater than 1 % in an interval between 1 an 4 hours. There is thereby stated a relationship between the residence time and the degradation of TCE.

In fig. 4.7 the degradation per cents, re-calculated to absolute values (in microgram/hour) are shown as a function of the methane consumption, also re-calculated to absolute values (in mg/hour). A linear regression is made on the absolute values for the relationship between the absolute values of degradation and the absolute values of the methane consumption. In fig. 4.7 are the resulting regression lines shown. Furthermore, a linear regression is made on the relation between the degradation per cents and the methane consumption per cents. For these analyses of regression similar results are obtained, as for the hydraulic residence time. This is, however, not suprising, as a linear relationship between methane consumption and hydraulic residence time is stated, ref. to sect. 4.5.

By the regression analysis, the following linear relationship between the absolute values of the methane consumption and the degradation of TCE is found:

Degradation of TCE in microgram/hour = 0,7 x methane consumption in mg/hour.

The linearity is found in an interval of app. 50-200 mg/hour for the methane consumption.

Looking at the results of the tests, it is not possible to evaluate, if an increased degradation of TCE primary can be achieved by an increase in the residence time (time of contact) or by a larger methane consumption (larger biomass). It must be expected, that as well a longer residence time as well as a larger methane consumption will give an increased degradation of TCE.

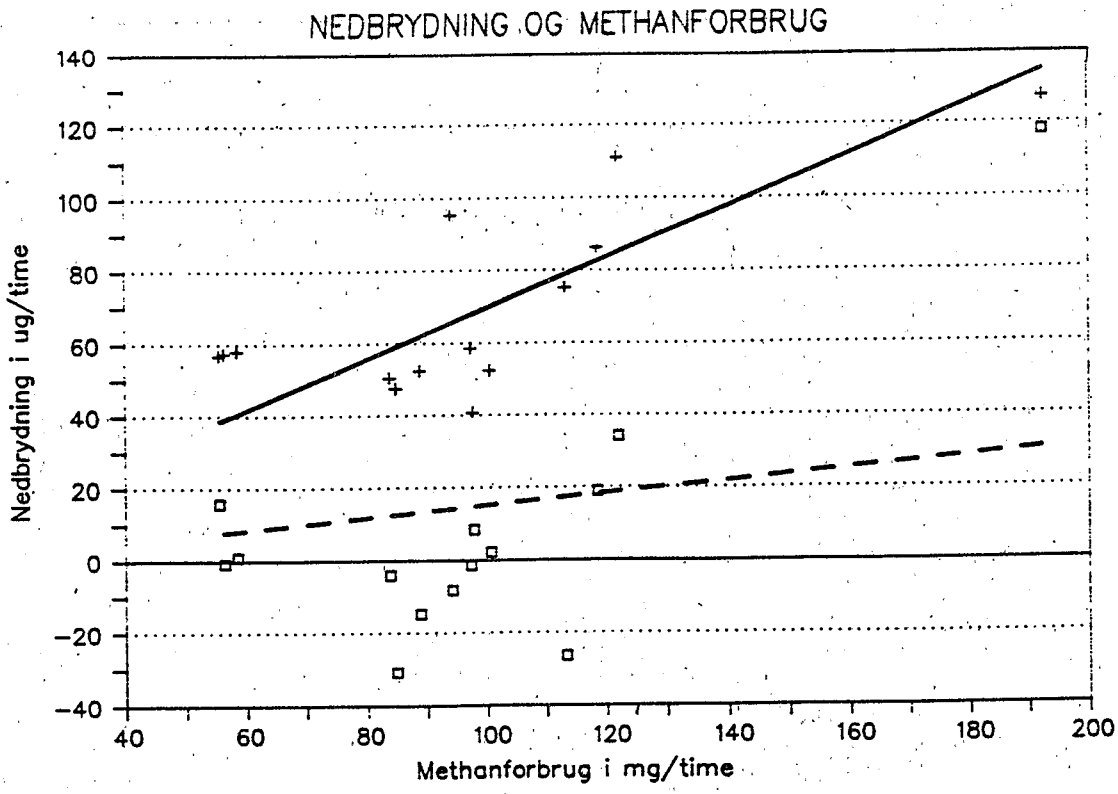


Fig. 4.7 Degradation of 1,1,1-TCA(□) and TCE(+) in the biofilter as a function of the methane consumption. The methane consumption is changing by changing the hydraulic residence time(Th). Furthermore regression lines are shown.

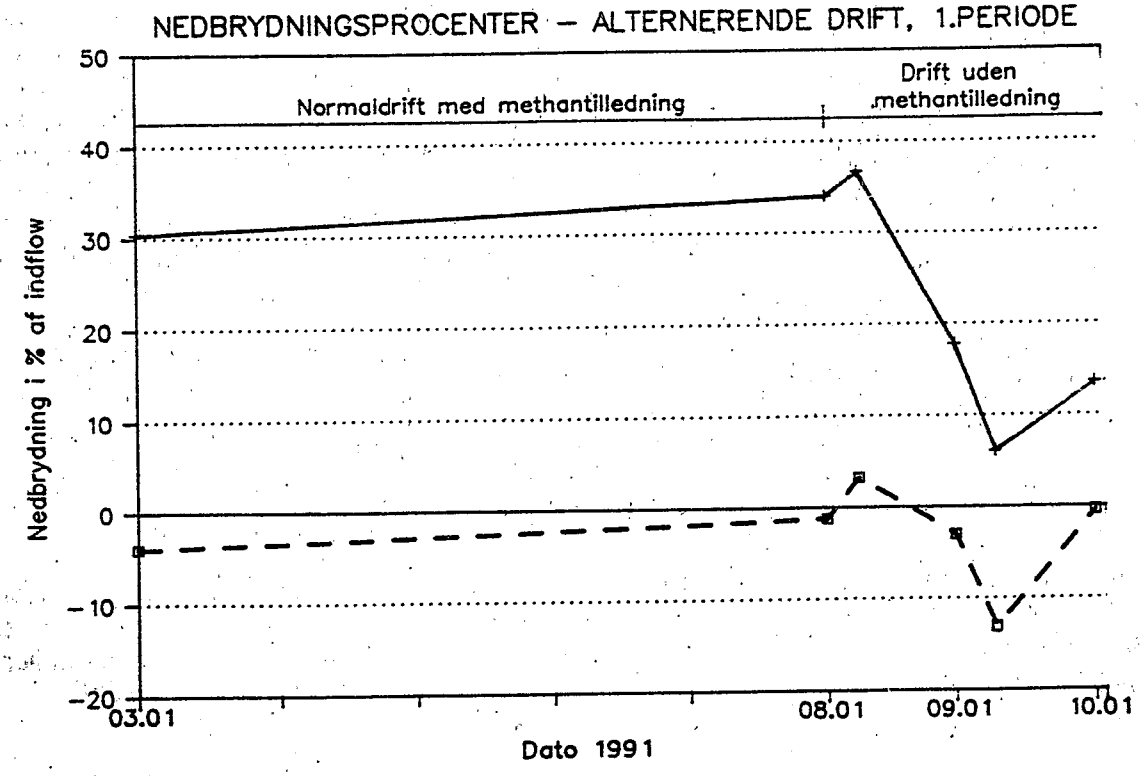


Fig. 4.8 Relatively degradation of 1,1,1-TCA(□) and TCE(+) i the biofilter in alternating operation. Methane addition is stopped on 1991-01-08.

The results from the tests of the residence time will to a certain extent be applicable when dimensioning a full-scale plant. It must, however, be noted, that for instance the results in fig. 4.6 can not be extrapolated the given interval of the residence time, if a higher per cent of degradation must be achieved. This is due to the assumption of linearity, which may not apply outside the interval. It is likewise relevant to note, that the tests are carried out in a given interval of concentrations of chlorinates aliphates in the inflowing water, ref. to fig. 4.1 and table 4.1. The tests have not reveiled, to which extent the degradation of TCE is dependent on the concentrations of TCE and other chlorinated aliphates in the inflowing water. Similar remarks must be noted on the overall groundwater quality.

4.7 Results from Test with Alternating Operation.

In fig. 4.8 the calculated degradation per cents for 1,1,1-TCA and TCE are shown from a test with alternating operation. The hydraulic residence time was kept constant at app. 3 hours. The first two calculation points on the curve represent the degradation of 1,1,1-TCA and TCE, respectively under testoperation with addition of methane immediate before a period without methane addition.

The figure shows, that alternating operation does not have any significant effect on the degradation of 1,1,1-TCA. Furthermore, it is seen, that the degradation of TCE all in all is unchanged right after the stop in methane addition, and that the degradation is decreasing after app. 24 hours without methane addition. The alternating operation has by that not showed a possitive effect on the degradation of TCE under the test conditions. Similar results are found in tests carried out in the US (Canter et al., 1990).

The decreasing degradation of TCE after app. 24 hours may be caused by the lack of an energy source for the methane-oxidizing bacteria, when the methane addition is stopped. An effect of alternating operation can therefore be determined by the addition of another energy source in the period without methane addition. As energy source, it could be revant to apply methanole og format (Semprini et al.,1991). The lack of effect of alternating operating can furthermore be determined by the low competitative inhibation, when methane addition in the operation. The effects in stopping the methane addition are thereby small. It must be noted, that the alternating operation have had an effect in relation to the methane consumption, while the degradation of TCE keeps on for a while after stopping the methane addition. Compared to operation with continuos methane addition, a similar degradation of TCE can be achieved, by a smaller methane consumption.

4.8 Conclusions

In the on-site tests, a methane consumption of between 40 and 90 % was meassured. A linear relationship between the hydraulic residence time and the methane consumption is found in an interval for the residence time of 1 - 4 hours.

Neither in the tests with the residence time, nor in the tests with alternating operation, any significant degradation of 1,1,1-TCA was seen. In contradiction to that, a substantial degradation of TCE between 20 to 40 % of the inflow was seen, which is equivalente to an absolute degradation of TCE between 40 and 130 microgram/hour. Furthermore linearity is found between:

- hydraulic residence time and degradation of TCE in an interval of 1 - 4 hours for the hydraulic residence time.
- methane consumption (in per cent) and degradation (in per cent) for TCE in an interval of 40 - 90 % for the methane consumption of the inflowing water.
- absolute values of methane consumption and degradation of TCE in an interval of the methane consumption of 50 - 200 mg/hour.

By alternating operation the same degradation of TCE was seen in periods with and without methane addition. The alternating operation has by that not showed a positive effect on the degradation of TCE under the test conditions.

4.9 Perspectives.

It is shown, that an increased biomass will give a relatively increase in the degradation of TCE. In the tests, the biomass may have been limited by the accessibility of nutrients (nitrogen, phosphor, iron etc.). An addition of nutrients will therefor be a possibility to optimize the utilization of the added methane, and by that be able to develop an increased biomass. The nature and structure and surface of the filter material have likewise importance for the size of the biomass.

The largest methane consumption in the systeme will probably take place at the the location in the filter, where methane is added. Under operation conditions, where the growth of the biomass is unlimited witout lack in accessibility of nutrients, a larger biomass can be obtained by applying methane at different locations in the filter. As an alternative, filters in series could be more succesful.

In laboratory test, it is shown, that a potential of increasing the degradation of TCE will be in alternating operation (Broholm et al.,1991). In the on-site tests this has not been proven, perhaps because the lack of an available energy source for the bacteria in the periods without methane addition. A possibility for increasing the degradation of TCE could therefor be in the alternating operation to apply f.ex. methanol or format in the periods without methane addition (Semprini et al.,1991). It must, however, be noted, that an addition of f.ex. methanol or format may give raise to other problems, for instance an unnessesary growth of heteretrofe bacteria.

In laboratory tests it is furthermore shown, that methane-oxidizing bacteria can degrade a relatively larger amount of TCE under conditions, where their growth have been limited by the availability of copper (Oldenhuis et al.,1989; Tsien et al.,1989). A possibility to increase the degradation of TCE can therfore be to etablish operation conditions, where copper is removed

from the contaminated water, before inflow in the filter with methane-oxidizing bacteria. It must here be noted, that in the contaminated water at the Skrydstrup site, the concentrations of copper have been so low, that this effect have been obtained.

In the tests it is shown, that it is possible to degrade TCE in an aerobic biological process. It is furthermore probable, that other chlorinated aliphates with a lower rate of chlorine can be degraded in a similar way - among others chloro ethylene (vinyl chloride) (Vogel et al.,1987) The degradation is running without an increase of toxic end products (Little et al.,1988).

Appendix 8-B

Microbial Treatment Technology Case Studies

In Situ Biorestoration of Soil, Asten, The Netherlands

No final text available.

Appendix 8-C

Microbial Treatment Technology Case Studies

In Situ Enhanced Aerobic Restoration of Soil and Ground Water, Eglin Air Force Base (AFB), United States

ENHANCED BIODEGRADATION OF JET FUELS EGLIN AFB, USA

A Case Study for the NATO/CCMS Pilot Study on Remedial Action Technologies for Contaminated Land and Groundwater - November 1988

Mr Douglas C. Downey
HQ AFESC/RDVW
Tyndall AFB, FL USA

COMBINED BIOLOGICAL AND PHYSICAL TREATMENT OF A JET FUEL-CONTAMINATED AQUIFER

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ABSTRACT

Early in 1987, the Air Force Engineering and Services Center (AFESC) initiated a full-scale enhanced biodegradation research project at a JP-4 jet fuel spill site on Eglin AFB near Ft Walton Beach, Florida. An underground pipeline leak discovered late in 1984 had released an estimated 20,000 gallons of JP-4 and contaminated soil and shallow ground water over a two-acre area. Following free product removal, a complete site characterization revealed that over 90 percent of the remaining fuel residuals were in the unsaturated zone. This project has place special emphasis on the treatment of residuals in the soil as they represent the source of long-term ground water contamination. A treatment system was designed to compare the operational benefits and limitations of three hydrogen peroxide/nutrient application methods: injection wells, infiltration galleries, and spray irrigation. A contaminated area receiving no treatment has been set aside as a control to compare natural degradation rates to enhanced rates in the treatment area. Pilot tests were conducted in the infiltration galleries to study the interaction of hydrogen peroxide and nutrient solutions with soil minerals. Studies concluded that hydrogen peroxide stability was impacted by biological enzymes, inorganic iron, and soil humic materials. Several methods of improving hydrogen peroxide stability have been attempted with limited success. Despite limitations in oxygen supply, a full-scale withdrawal

and reapplication system has been operating for over one year and a portion of the fuel residuals have been removed through a combination of biodegradation, hydraulic washing, and aboveground aeration. Observations on system operation and soil and ground water data from the initial 12 months of this field project are reported in this paper. Final soil and ground water sampling will take place in September, therefore only preliminary results were available before the publication deadline.

INTRODUCTION

Each year the U.S. Air Force stores and transfers millions of gallons of JP-4 jet fuel at over 200 Air Force installations. Fuel leaks and spills are by far the most frequent sources of soil and groundwater contamination on these installations. The Environics Division of the Air Force Engineering and Services Center (AFESC), located at Tyndall AFB, Florida, is responsible for developing and testing improved methods of soil and groundwater decontamination. Soil decontamination has been emphasized, because in most soils the majority of the JP-4 will remain in the unsaturated zone and slowly leach into the groundwater (Davis et al, 1972). These soil residuals represent the long-term source of ground water contamination and must be addressed in site remediation.

Enhanced in situ biodegradation is an innovative technology which has received much attention and research during the past two decades (Lee, et al, 1988). While several commercial firms have reported successful ground water remediations, published results have lacked sufficient data to determine the effectiveness of biodegradation in reducing fuel residuals in the vadose zone. For this and other reasons, AFESC has conducted independent field tests of this technology prior to recommending it for widespread Air Force application.

In 1984, AFESC initiated a pilot-scale test of enhanced biodegradation at a site on Kelly AFB, Texas. As this test progressed, problems with soil permeability were encountered reducing the delivery of hydrogen peroxide and nutrients through injection wells. This reduction in permeability was attributed to both natural silt and clay soils and the precipitation of calcium phosphates which formed as injected phosphates reacted with calcium in the soil (Wetzel, 1987). Permeability problems reduced the delivery of oxygen and consequently little biodegradation occurred. Based on these results, a second site with more favorable soil permeability was selected at Eglin AFB, Florida.

In 1986 AFESC awarded a competitive contract to EA Engineering, Science and Technology and their subcontractor FMC Aquifer Remediation Systems (now a part of IT Corporation) to conduct an enhanced biodegradation demonstration on the site. EA Engineering, Science and Technology was responsible for overall system design, operation and site monitoring while IT Corporation has provided microbiological support and operational expertise in nutrient and hydrogen peroxide application systems.

SITE PROFILE

In April of 1984 a leak was discovered in an underground jet fuel pipeline in the Eglin AFB petroleum storage area. A preliminary site characterization estimated 30,000-45,000 gallons of JP-4 jet fuel had contaminated approximately 4000 cubic yards of soil and shallow aquifer material (Weston, 1984). Follow up sampling in August 1985 decreased that estimate to 20,000 gallons. A series of shallow, gravel-filled trenches were installed perpendicular to fuel movement and skimmer pumps recovered over 7000 gallons of free product. By early 1986, free product had been removed to non-recoverable levels and skimmer pumps were turned off.

Prior to system design a complete site characterization was accomplished to better define hydraulic, contaminant, and microbiological conditions. The site is located in an area of unconsolidated and relatively homogeneous coastal sands that extend from the surface down to 40 feet. Below the sand, a 400-foot confining clay layer protects the deeper Floridian Aquifer. The contaminated shallow aquifer is only three to five feet below the surface across the site and has an average hydraulic conductivity of 7 X 10-2 cm/sec. The highly permeable soils and the shallow depth to contamination make this an excellent site for testing enhanced biodegradation.

One of the primary objectives of this test was to insure that a sufficient number of ground water and soil samples were taken to assess the performance of this technology. An initial soil vapor survey was performed to delineate the extent of free product influence and to assist in monitoring well locations and application system design. A Photovac 10S50 portable gas chromatograph was used to analyze soil gas samples taken at a constant depth of two feet on a radial grid across the site.

Monitoring wells and soil sampling locations were selected on the basis of the soil vapor survey. Initially 22 monitoring wells were constructed and soil samples taken at one-foot depth increments at 12 locations. During the course of the research, the number of ground water monitoring wells has increased to 40 and soil sampling locations to 16. In order to compare natural degradation rates to degradation rates under enhanced nutrient and oxygen conditions, monitoring locations were established in a control contaminated area which received no nutrients or hydrogen peroxide. The "control area" was a unique feature of this test which is normally unacceptable for commercial site restorations.

Total Organic Carbon (TOC) was selected as the general indicator of fuel contamination in ground water. Background TOC levels of 15 mg/L were recorded upgradient of the site. Total Petroleum Hyrocarbons (EPA Method 418.1) was used as the general indicator of fuel contamination in the soil. Background levels of less than 20 mg/kg were common in uncontaminated soils.

A complete GC/MS analysis was performed on selected ground water and soil samples. The purpose of the GC/MS analysis was two-fold. The Florida Department of Environmental Regulation required that twelve representative compounds, including benzene, toluene, and xylenes be

monitored in the ground water. The list was expanded to 43 compounds to monitor the specific degradation rates of a broad range of aliphatic and aromatic fuel components. A complete discussion of GC/MS results is beyond the scope of this paper. This data will be included in an AFESC Technical Report to be published in early 1989. Figure One illustrates the areas of free product influence prior to biodegradation operations, and the location of initial monitoring wells in relation to the basic operation system discussed in the next section.

Microbial enumerations were also performed on soil and ground water samples at most monitoring locations. Microbial monitoring provided a measure of microbial response to nutrient and oxygen enhancements over time. Soil samples at each monitoring point were collected at two depth intervals, one from the capillary fringe zone above the water table and another sample one foot below the water table. The microbial populations at these two depths would be most likely influenced by ground waters enhanced with nutrients and oxygen. A summary of initial site conditions within the contaminated area is included in Table One.

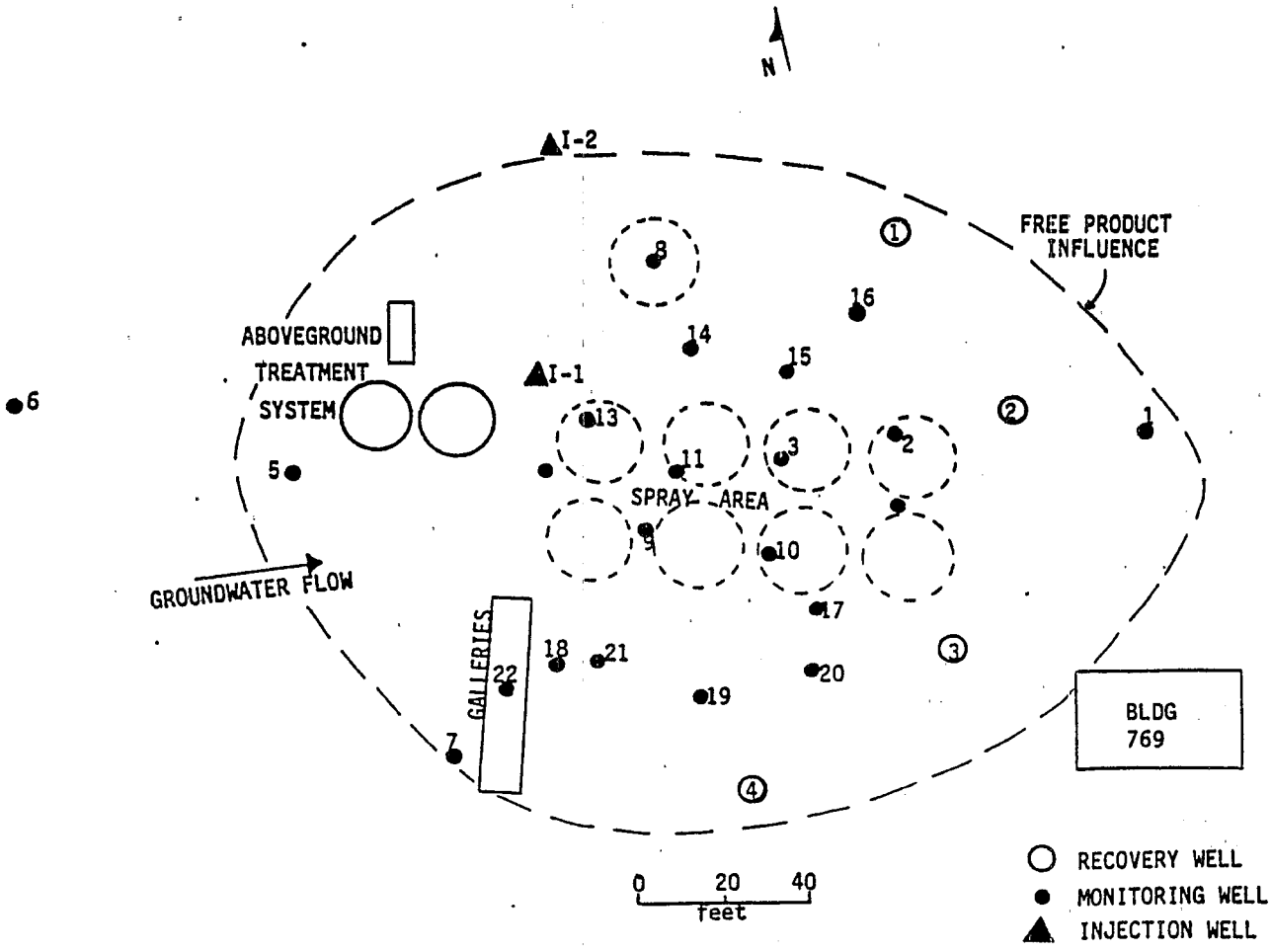

Figure 1. Eglin AFB Site Profile

TABLE ONE

Initial Site Conditions in Contaminated Area[1]

Parameter	Soil (mg/kg)	Ground Water (mg/L)
TOC	-	126 (18)
TPH[2]	2000 (20)	-
BTX	110	6
$C_8 - C_{17}$[3]	640	3
PO_4	-	<.2
NH_4	-	8
Fe(total)	850	12 (<.5)
pH	-	5.4 units (6)
Dissolve O_2	-	<1 (3)
Temp		20° C
Total Bacteria(10^5 CFU)	2	15
HC Degraders(10^5 CFU)	.9	1.6

1 Average of contaminated monitoring locations
( ) = Uncontaminated background level
2 Total benzene, toluene and xylenes
3 Total alkanes detected on GC/MS

Laboratory microbial enumerations were completed using a modification of spread plate-count method for heterotrophic bacteria (APHA, 1985). Ground water samples were prepared for enumeration by performing serial decimal dilutions of the sample in a sterile mineral salts broth. Subsurface soil samples were prepared using a modification of the method reported by Balkwill and Ghiorse, 1985. The method involves homogenization in a Waring blendor of five grams of soil in 50 mls of a solution consisting of 1% sodium pyrophosphate, 0.1% polyvinylpyrrolidone-360 (PVP-360). This homogenization step is designed to facilitate release of bacteria attached to particles. The homogenate is then diluted and plated in the same manner as for water samples.

The concentration of total heterotrophic bacteria is defined as the number of colony forming units per milliliter of ground water or per gram (dry weight) of soil, that can form macroscopically visible colonies on 0.23% nutrient agar after one week incubation at ambient temperature and oxygen. Hydrocarbon-degrading bacteria are defined as those capable of forming colonies on carbon-free mineral salts agar when incubated under a hydrocarbon-vapor atmosphere at ambient temperature for one week (Jamison, et al., 1976).

Laboratory Biodegradation Studies

One of the important tasks undertaken in the laboratory phase of this project was to conduct a bench-scale degradation study, using contaminated soils and ground water from the site, to determine the effects of nutrient and oxygen supplementation on the rate of contaminant biodegradation, and to estimate the extent of contaminant removal that is achievable biologically under laboratory conditions. These studies have historically been based on batch reactors, or "microcosms," which consist of soil/ground water slurries in sealed glass vessels. The microcosms are then treated with the appropriate nutrient and hydrogen peroxide amendments, and one set of microcosms is sterilized and/or inhibited with a biological poison to account for physical/chemical mechanisms for contaminant removal from the system. Aqueous samples can then be periodically withdrawn for microbial, nutrient and/or contaminant analyses, or the entire reactor can be sacrificed for analysis. While studies such as these provide a limited model of the natural aquifer environment, the resultant information is useful in determining the relative effectiveness of different nutrient types and concentrations on biodegradation rates, and for demonstrating the heterotrophic potential for contaminant destruction.

For reasons of simplicity and cost, most microcosm degradation studies monitor aqueous phase contaminant biodegradation. For the Eglin project, however, we attempted to quantify the degradation of the total amount of organic material within the reactors. Microcosms were prepared be combining 20 gms of contaminated soil and 20 mls of site ground water in a 40 ml VOA vial. Vials were tightly sealed and various nutrient concentrations injected through a septum to determine their effect. Excess oxygen was maintained through hydrogen peroxide additions. The microcosms were separately analyzed; the aqueous fraction was extracted with pentane and analyzed by capillary GC-FID. The soil underwent Soxhlet extraction according to Standard Methods 503D, followed by analysis of the extracts using capillary GC-FID.

A GC/FID analysis of the aqueous phase showed that biodegradation was enhanced by 25 ppm concentrations of Restore 375^{R} and that the total extractable organics were degraded from 35 ppm to <.2 ppm in nine days. This data confirmed that indigenous microbes would degrade soluable fuel components with minimal nutrient additions if adequate oxygen was available. Restore 375^{R} is a patented, prepared nutrient mixture consisting of 50% ammonium chloride and a blend of disodium phosphate, sodium tripolyphosphate and monosodium phosphate.

Analysis of the solid phase (soils) exhibited considerable noise and due to extraction problems actually showed an increase in organics. These analytical procedures cannot be reliably used to measure biodegradation of low solubility compounds adsorbed or occluded in soils. (We are currently repeating the microcosm study using a modified purge and trap procedure to measure organics removal from both the aqueous and soil phase. The results of this improved procedure will be published in the final AFESC Technical Report.)

SYSTEM DESIGN

Pump Tests

The ability of the shallow aquifer to produce sufficient water for recirculation of nutrients and oxygen was a critical design factor that was first determined through a series of pump tests on all recovery and injection wells. Four recovery wells were installed on the down-gradient perimeter of the contaminated area using the cable tool drilling method. The six-inch wells were constructed with 5 feet of .02 slotted PVC screen located 5 - 10 feet below the static water table to prevent free product drawdown and movement into the wells (Figure 2). Injection well design is discussed later in this section.

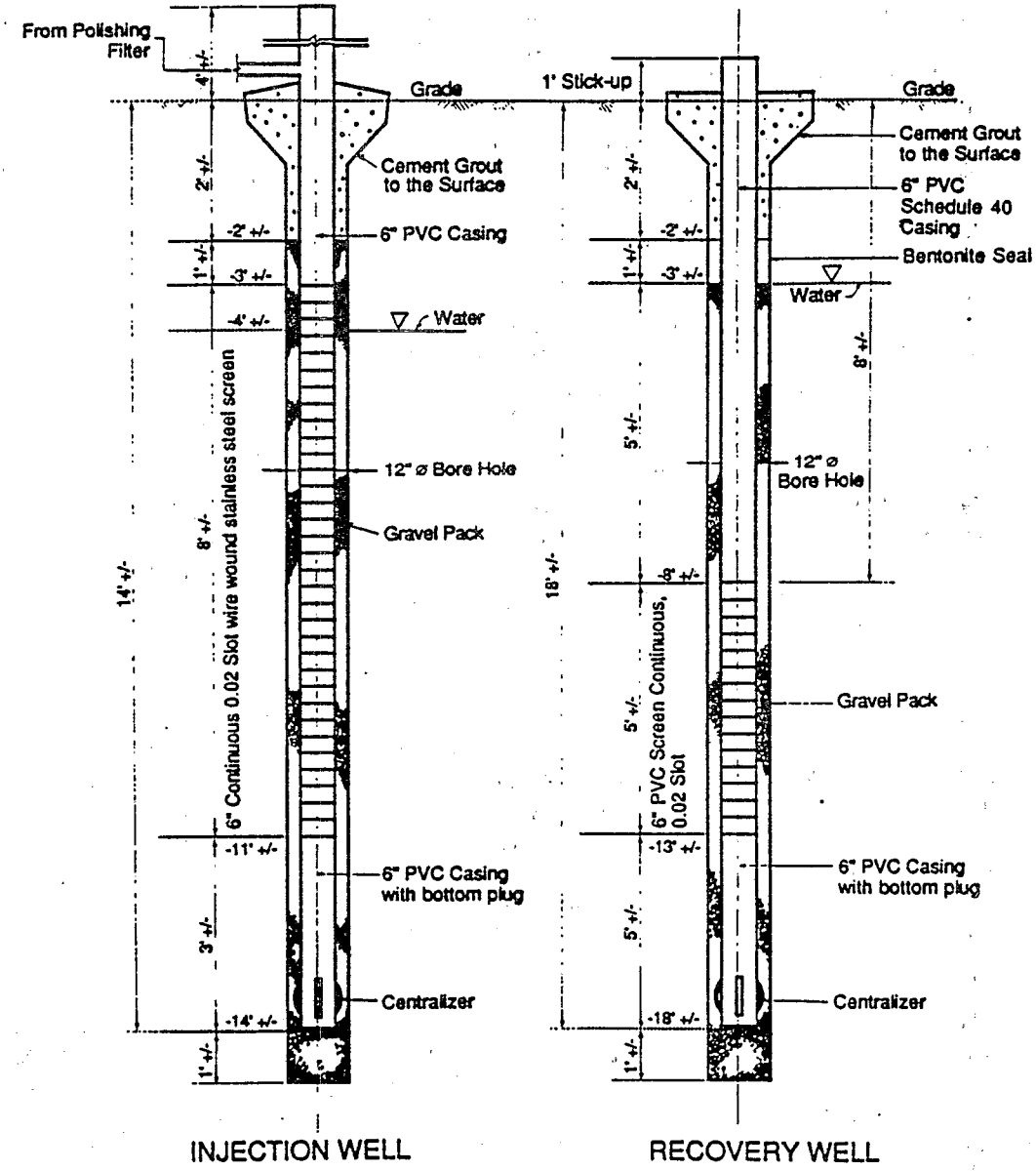

Figure 2. Recovery and Injection Well Design

After initial installation, the wells were air-developed. All wells were tested at maximum pump yield for three hours; this was sufficient to determine the hydraulic parameters of the highly permeable aquifer. Water levels were measured during testing using an electronic water level indicator or a MMC oil-water interface probe. Well yields were measured with a flow meter. Montoring wells located at varying distances from the pumped well were used as observation wells. In general, the treatment area can be divided into two zones based on the observed and calculated data:

1. a northern zone of higher elevation (wells IN1, IN2, R1, and R2) with transmissivity of approximately 20,000 gpd/ft (250 m^2/d) and permeability of 270 ft/day (9.5 10^{-2} cm/sec)

2. a southeastern zone of lower elevation with transmissivities of 10,000 gpd/ft (125 m^2/d) and permeability of 130 ft/day (4.7 x 10^{-2} cm/sec)

The lower transmissivity of well R4 may be related to an area of finer-grained sediments deposited by an old stream channel.

Discussion of O_2 Supply Requirements

Natural aerobic degradation at this site has been limited by depleted oxygen in the groundwater and capillary zone. Background oxygen levels of .5 - 1.0 ppm were measured in monitoring wells in the contaminated area. The primary objective of system design was the delivery of adequate oxygen for mineraliztion of fuel hydrocarbons. The oxygen required was calculated based on an estimate of the mass of hydrocarbons present and the stoichiometric requirement for complete mineralization. The basic mineraliztion equations for typical hydrocarbons follow :

$$C_6H_6 + 7\tfrac{1}{2}O_2 \longrightarrow 6CO_2 + 3H_2O \text{ for benzene}$$

or

$$C_8H_{18} + 12\tfrac{1}{2}O_2 \longrightarrow 8CO_2 + 9H_2O \text{ for octane}$$

Complete mineralization requires approximately 3.1 pounds of oxygen per pound of benzene or 3.5 pounds of oxygen per pound of octane for complete mineralization. Based on our site characterization, it was estimated that the 16,000 lbs of hydrocarbon remaining in the treatment area's soil and groundwater would require approximately 40,000 lbs of oxygen for mineralization. Assuming 100% oxygen utilization efficiency, the necessary oxygen and corresponding peroxide concentrations can be calculated for a variety of pumping rates:

Peroxide Concentration (mg/L)	Effective Oxygen Concentration (mg/L)	Required Water Volume (gallons)	(gpm/16 mo.)
0	8	650,000,000	1100
100	50	100,000,000	170
300	150	30,000,000	55
500	250	20,000,000	33

Based on pump tests and O_2 requirements, an initial peroxide concentration of 500 mg/l and a pumping range of 30-40 gpm were selected to deliver the required O_2 over the 16 month fixed contract length.

Iron Removal System

Iron concentrations in ground water were reported to be below 1.0 mg/l (Weston, 1984). Our sampling found iron levels in contaminated ground water in the range of 8 to 26 mg/l. The recovery well discharge water was found to contain an average of 12 mg/l of total iron. Due to highly reducing conditions common in anaerobic, contaminated groundwaters, this iron emerges from the wells in the ferrous (Fe^{+2}) form. Oxidation to the less soluble ferric (Fe^{+3}) form during aboveground treatment leads to precipitation, and clogging of the injection systems. The concentration of iron at injection points can also reduce the stability of the peroxide (Britton, 1985).

In order to reduce iron concentrations in the injection systems a sedimentation basin was added following the aerator. To further reduce iron concentrations going into the injection wells a pressure filter was installed. The combined sedimentation and filtration removed approximately 90 percent of the total iron entering the injection wells.

Three Application Methods

Three basic technologies are available for oxygen and nutrient injection; injection wells, infiltration galleries and surface application; each with its own advantages and disadvantages. The injection well most directly delivers the nutrients to ground water, however, nutrients are poorly delivered to the unsaturated zone. The injection well has a relatively small surface area and is therefore prone to clogging. Infiltration galleries and surface application deliver the nutrients in a more uniform pattern which allows more effective delivery to the unsaturated zone. At many sites the drawback to infiltration galleries and surface application techniques is the potential difficulty in delivering nutrients to the saturated zone. If an impermeable or less permeable strata exists above the groundwater it may prevent or limit percolation. In the case of the infiltration gallery, this can be overcome by placing the system beneath the less permeable strata. In general, the injection well is the most expensive application method, with the infiltration gallery being intermediate in cost and surface application being least expensive. In difficult situations such as paved or developed

sites, or sites with a relatively deep, less permeable strata, the infiltration gallery can be substantially more expensive than an injection well.

As the ground water is quite shallow at the Eglin site and no significant stratification exists in the unsaturated zone or the shallow saturated zone, surface application is the technique of choice. The site, however, is certainly amenable to all three technologies and due to the research nature of this project all three were demonstrated. It was not intended that three separate treatments be tested for remediation efficiency, rather the relative effectiveness of each technology was evaluated and each injection system modified as necessary to improve nutrient and oxygen delivery. The application systems were designed to receive approximately 10 gpm each or approximately 6,000,000-7,000,000 gallons over the course of the study.

Injection well construction is shown in Figure 2. The wells were screened from approximately one foot above ground water surface to a depth of nine feet below groundwater surface to allow uniform nutrient distribution. The design diameter of six inches was considerably oversized for the hydraulic needs of this site to provide a safety margin against plugging. The stainless steel screens allowed vigorous development, redevelopment and acid cleaning.

Shallow, gravel-filled trenches were used as infiltration galleries as illustrated in Figure 3. The large surface area of these galleries provided a broad distribution of nutrients and peroxide perpendicular to flow lines. Surface application was the simplest form of nutrient and peroxide distribution. The surface spray system provided an even application of nutrient and oxygen over an 1800 sq ft area using a sprinkler system. Figure 4 provides a schematic of the aboveground treatment and application system.

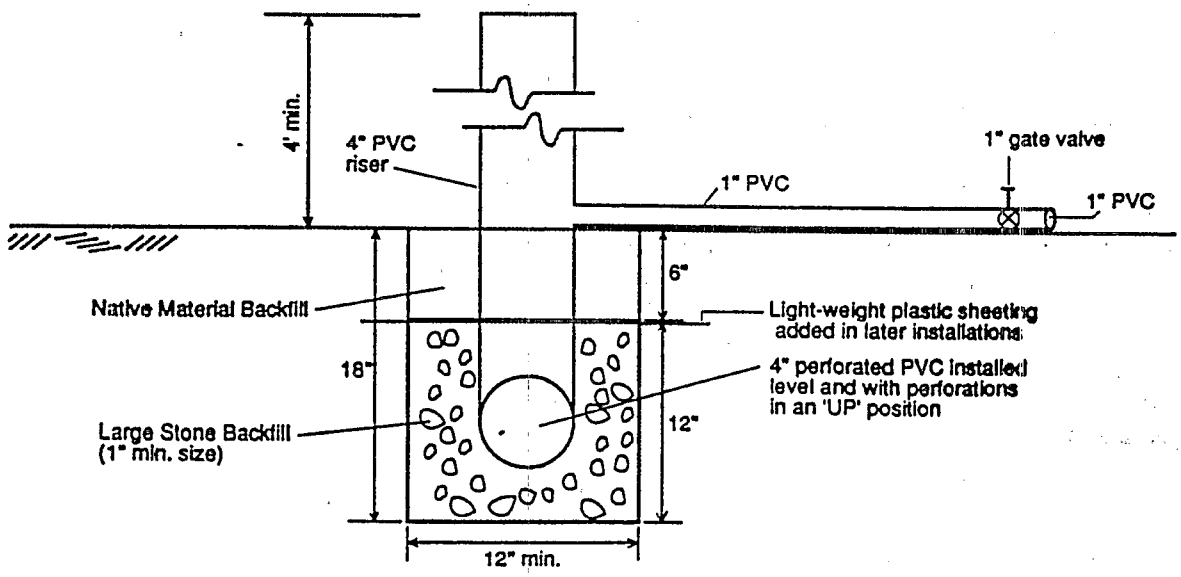

Figure 3. Infiltration Gallery Design

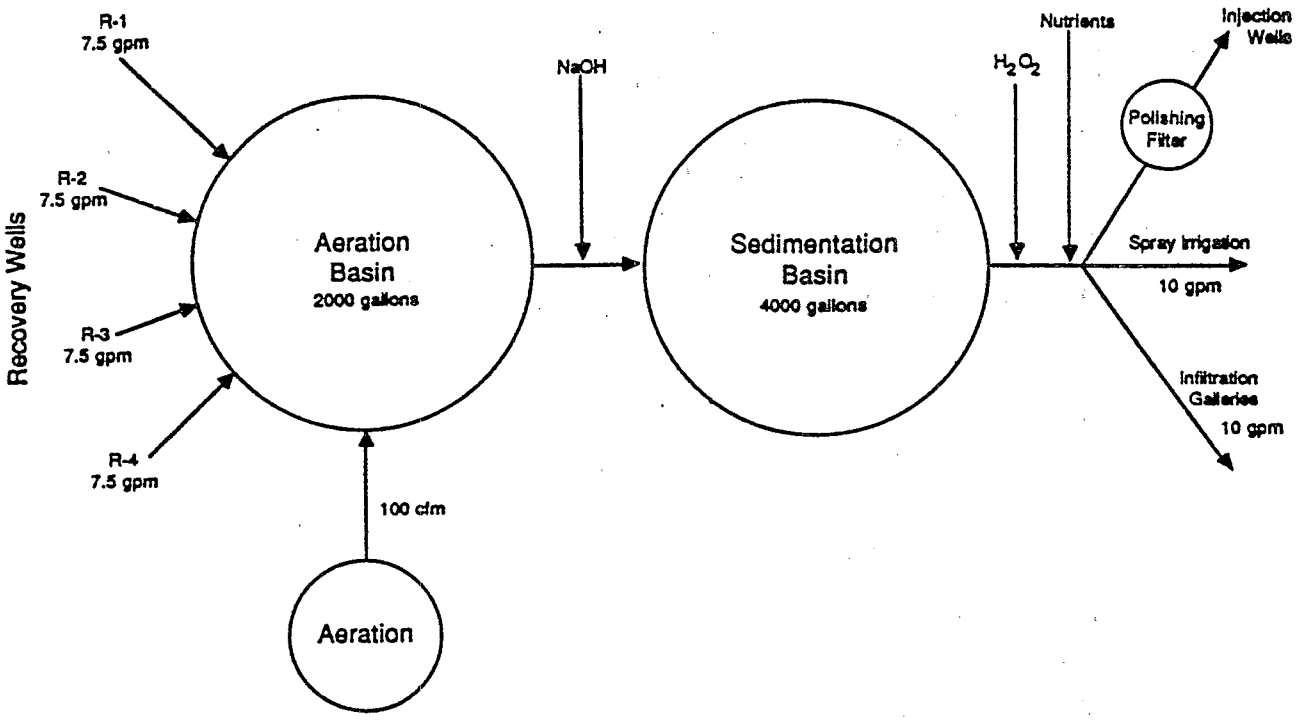

Figure 4. System Flow Diagram

Nutrient Addition

Nutrient addition was designed to be in excess of micriobal requirements. Laboroatory microcosm tests indicated that nutrient levels as low as 25 ppm would support microbial degradation. The decision to use excess nutrient addition was based on three factors. First the phosphate present in the nutrient solution could act to stabilize the peroxide (Britton, 1985). Second, laboratory column tests showed that orthphosphate precipitation in site soils was inhibited in the presence of sodium tripolyphosphate at Restore 375^R injection concentrations of at least 1000 ppm. Finally, an excess addition would insure that oxygen alone was limiting biodegradation. One concern of excess nutrient addition is the potential for precipitate formation such as calcium phosphates resulting in reduced aquifer permeability. The potential for aquifer plugging at the Eglin site was lessened due to the initial high permeability.

Restore 375^R was added on a batch basis of 150 lbs/week and metered into the recirculation flow to make a delivery concentration of 1000 ppm. Nutrient solutions were added three times a week and each pulse was approximately four hours. Typically, nutrients were added on Monday, Wednesday, and Friday.

This application rate exceeded the minimum requirement for microbial degradation of fuels. Assuming 16,000 lbs of fuel hydrocarbons and a Carbon: Nitrogen: Phosphate ratio of 100:6:3, and that 33% of the hydrocarbon was converted to biomass (less than 33% would probably be converted), nitrogen requirements would be 720 lbs and phosphorus requirements 360 lbs. Despite reduced oxygen delivery rates due to peroxide stability problems, the design nutrient injection schedules were maintained and to date 750 lbs of nitrogen and 440 lbs of available phosphorus have been delivered to the site. Subsequent ground water sampling across the site indicate that increased levels of PO_4 and NH_4 were well-distributed in the saturated zone.

In-Situ Peroxide Stability

Tests of in-situ peroxide stability and oxygen transport were carried out in the infiltration galleries. Due to the shallow ground water at this site, mounding occurred in the vicinity of the galleries which resulted in saturation to the ground surface. Shortly after peroxide injection was initiated, gas bubbles were observed rising through the saturated sandy soil immediately above the galleries. This observation coupled with a failure to observe peroxide in any down gradient wells (including EA 18 installed 1 ft down gradient of the injection galleries) lead to the suspicion that peroxide decomposition was very rapid and resulted in off wasteful gassing of oxygen. Initial laboratory batch studies using a 3:1 ground water to soils ratio had indicated that a 500 ppm hydrogen peroxide addition would have a half-life of approximately six hours in the Eglin aquifer.

A monitoring well (EA-22) was installed directly in one of the injection galleries. While the system was operating under continuous peroxide addition, peroxide concentrations observed in EA-22 were very close to, or slightly below the 500 ppm measured in the feed lines to the galleries. To evaluate in-situ peroxide stability, tests were conducted in which the flow to the galleries was shut off and the disappearance of peroxide in EA 22 was measured over time. Peroxide half-lives, based on first-order decay rates, were observed in the 30 to 90 minute range, far less than the six hours predicted in the laboratory.

In order to determine the effect of phosphate pretreatment a new series of galleries were constructed. These galleries received nutrient solution, including phosphates, prior to initiating peroxide injection. Similar peroxide stability tests were conducted in these "pretreated" galleries, however, no significant increase in peroxide stability was noted. Due to the significant off gassing and waste of oxygen at the 500 ppm peroxide addition rate, a decision was made to reduce the operating concentration to 300 ppm.

Throughout the project several experiments have been conducted to determine the cause of hydrogen peroxide decomposition. Both biological and inorganic reactions have been identified as contributing to this instability. These findings are briefly discussed in the conclusions.

SYSTEM PERFORMANCE

Withdrawal and Application Systems

During the initial weeks of operation, the four recovery wells produced over 40 gpm of continuous flow. Over the past 15 months of operation, well production has decreased to 32 gpm. Regular treatments with acid and vigorous scrubbing have been required to clean both recovery and injection well screens.

The total volume of water passing through each of the primary application systems to date is:

Infiltration Galleries	6,500,000 gallons
Spray Irrigation	7,800,000 gallons
Injection Wells	1,000,000 gallons
Total	15,300,000 gallons

The infiltration galleries and injection wells have shown a tendency to clog and flow-through has been reduced. In the case of the infiltration galleries this problem was remedied by increasing their number. Initially, 4 galleries with 40 linear feet of injection area were installed and were capable of taking the full 10 gpm. After surface flooding was noted three additional galleries with an additional 30 feet of linear injection area were added. Finally four additional galleries were installed in an old free product recovery trench which was approximately 40 feet long, 10 feet wide, and was filled with approximately 4 feet of gravel (approximately 2 to 6 feet below land surface). The galleries have received a continuous 10 gpm flow for over one year.

Flow through the injection wells was significantly reduced over time. Efforts were made to acid wash and redevelop the wells by adding 1 to 2 gallons of 31% industrial HCl and applying 100 ± gallons of water. The wells were then allowed to sit for a 16 ± hour contact time. The wells were then purged until the pH returned to 6.0 or greater. At times the wells were also air surged and/or vigorously brushed. Despite the cleaning and redevelopment the wells continued to clog and within a few months were only able to accept only 1 ± gpm. For this reason the total volume introduced through the injection wells was signficantly less than design volumes.

The spray irrigation area performed well and consistently received 10± gpm over an area of 1,800 ft^2 without notable reduction in efficiency. Occasional roto-tilling of the soil improved permeability and reduced overland flow. Additionally, peroxide concentrations in water puddles on the ground were not significantly less than those in the feed to the spray irrigation area indicating little peroxide loss in the spray process. However, samples of infiltrate taken in the spray area vadose zone revealed that peroxide rapidly decomposed in the first six inches of the soil. In one test, dissolve oxygen in the infiltrate varied from 23 mg/l at the surface to 2 mg/l at 2.5 feet below land surface indicating oxygen utilization in the contaminated soils.

CONCLUSIONS

An Oxygen Shortfall

Due to rapid peroxide destabilization and oxygen loss at point of injection it was not possible to deliver sufficient oxygen for complete hydrocarbon mineralization. The causes of hydrogen peroxide instability at the Eglin site have been identified through a series of laboratory and field experiments (Spain et al, in press) They concluded that catalase enzymes released by aerobic bacteria near the points of injection are the major cause of rapid peroxide decomposition and oxygen off gassing. To a lesser extent, humic materials and inorganics such as iron also increase the rate of peroxide decomposition at the Eglin site.

Estimated Biodegradation

The extent of bioremediation, or hydrocarbon biodegradation may be estimated from the actual oxygen delivery rates. Peroxide was injected into approximately 16,000,000 gallons of water. Based on peroxide stability and oxygen measurements at the points of injection, it is estimated that an average 25 mg/l of oxygen was actually delivered in this water. Very low oxygen concentrations down gradient of the injection points indicated utilization. We estimate that sufficient oxygen was delivered to mineralize approximately 1,200 pounds of hydrocarbon. It is possible that some of this oxygen was incorporated into microbial biomass, and therefore, greater than 1,200 pounds of hydrocarbons may have been removed.

Estimated Volatilization

A significant quantity of fuel residuals were removed in the above ground aeration basin. Based on TOC analysis of groundwater entering and leaving the aeration basin, a loss of volatile organics (measured as 15-20 mg/l TOC) occurred throughout the past 12 months. This means that the aeration basin has removed at least 2000 pounds of hydrocarbons from the 16,000,000 gallons of water pumped through the site. Contributing to this process is an unknown quantity of fuel residuals which have been washed from the soils into the groundwater due to natural leaching and soils washing in the spray application system. A better understanding of the hydrocarbon mass balance is anticipated after all the site data has been collected and analyzed.

Four More Years

In order to deliver sufficient oxygen with the observed peroxide half-life and subsequent oxygen delivery rates, and assuming continued volatilization of 2000 pounds/yr, four more years would be required to deliver the minimum stoichiometric oxygen requirements. Oxygen utilization efficiency by microbes was difficult to estimate from field measurements. However, it is likely that less than 100% could be used. Volatilization rates would also decline over time as ground water quality contiued to improve. Therefore, more than four years would be required to remove and/or degrade remaining fuel residuals from the soil. Switching the entire site to the spray system would be a practical way of speeding up the clean up. The estimated non-research cost associated with this effort is $600,000.

Soil Contamination Data

To date fuel residuals in soils above the water table in areas influenced by injection wells and infiltration galleries have shown no solid evidence of enhanced biodegradation. There is no evidence that enhanced nutrient and oxygen levels in the ground water have influenced biodegradation in the soils above the water table. Soil samples from the spray application area have shown mixed results. Figure 6 illustrates the difficulty in assessing biodegradation in the unsaturated zone. Samples taken near EA-2 indicated a definite decrease in TPH has occurred. Unfortunately, samples taken at EA-3, which is also in the spray application area, show no consistency and even show an apparent increase in TPH. The TPH values at the EA-5 control area have also been subject to seasonal variations which have made data interpretation very difficult. There has been no increase in free product in these areas that would indicate a new fuel leak. However, we have observed small lenses of free product on the site which have randomly moved through our monitoring areas.

Microbial Data

Microbial enumerations of soil and groundwater have suffered from similar variability. Once again the most significant microbial activity appears to be taking place in the spray application area. Although not an impressive exponential growth, both total and hydrocarbon degrading bacteria have multiplied their numbers 10 to 15 times in the soils and groundwater within the spray area. Bacteria counts in the EA-5 control area have shown a ten-fold decrease in numbers over the past nine months. There has been a general increase in the proportion of hydrocarbon degrading to total bacteria suggesting an adaptation of microbial populations to growth on fuel substrate.

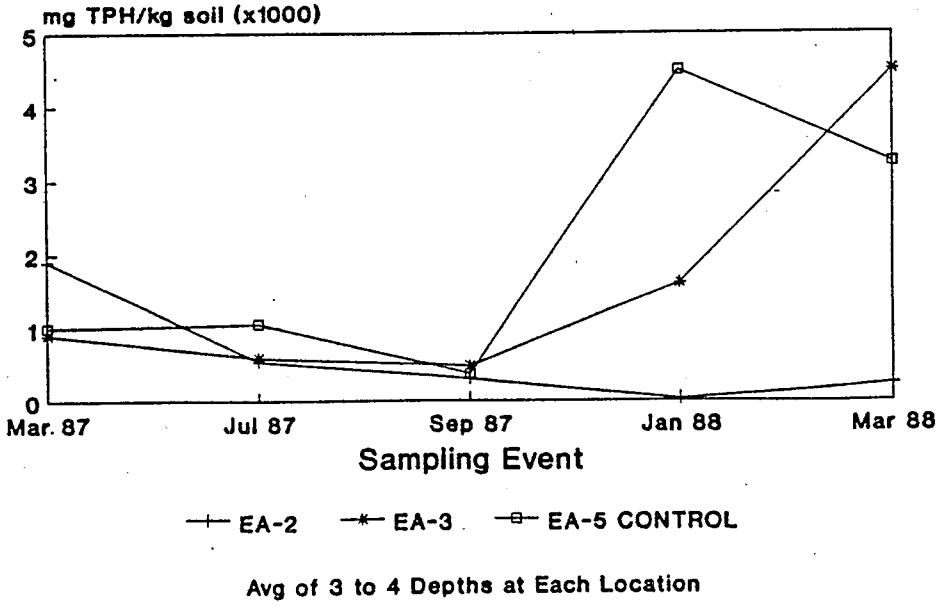

Figure 6. TPH Data From Spray Area

Volatiles Removal in Aeration System

The aeration basins which were originally installed to oxidize iron were upgraded to also remove the volatile organics. A series of tests to evaluate volatile organic removal efficiency were conducted at air to water ratios varying from 8-36:1. Based on these tests the ai to water ratio was increased to approximately 25 to 1 in order to achieve 95%+ removal of volatile organics. This inexpensive method of VOC removal must be factored into the overall mass balance on fuel removal and separated from biodegradation.

Ground Water Contamination Data

Data from two monitoring wells in the active treatment zone and two wells in contaminated control areas is provided in Figure 5. BTX was selected as an indicator of soluable fuel contamination for this comparison. EA-2 is located in the spray application area. EA-8 is in a control area receiving a spray of ground water without nutrients or peroxide. EA-EA-19 is located 12 feet downgradient of the infiltration galleries while EA-5 is located in a contaminated control area not influenced by nutrients or peroxide. Both EA-2 and EA-19 have shown decreased levels of BTX. Some removal of BTX has also occurred at EA-8, possibly due to the continuous application of partially restored/aerated ground water at the surface. Ground water at EA-8 has also been influenced by nutrient additions through the injection wells which may account for some BTX removal in the saturated zone. BTX levels in the EA-5 control area decreased in July 87 for an unknown reason but have remained stable over the past nine months.

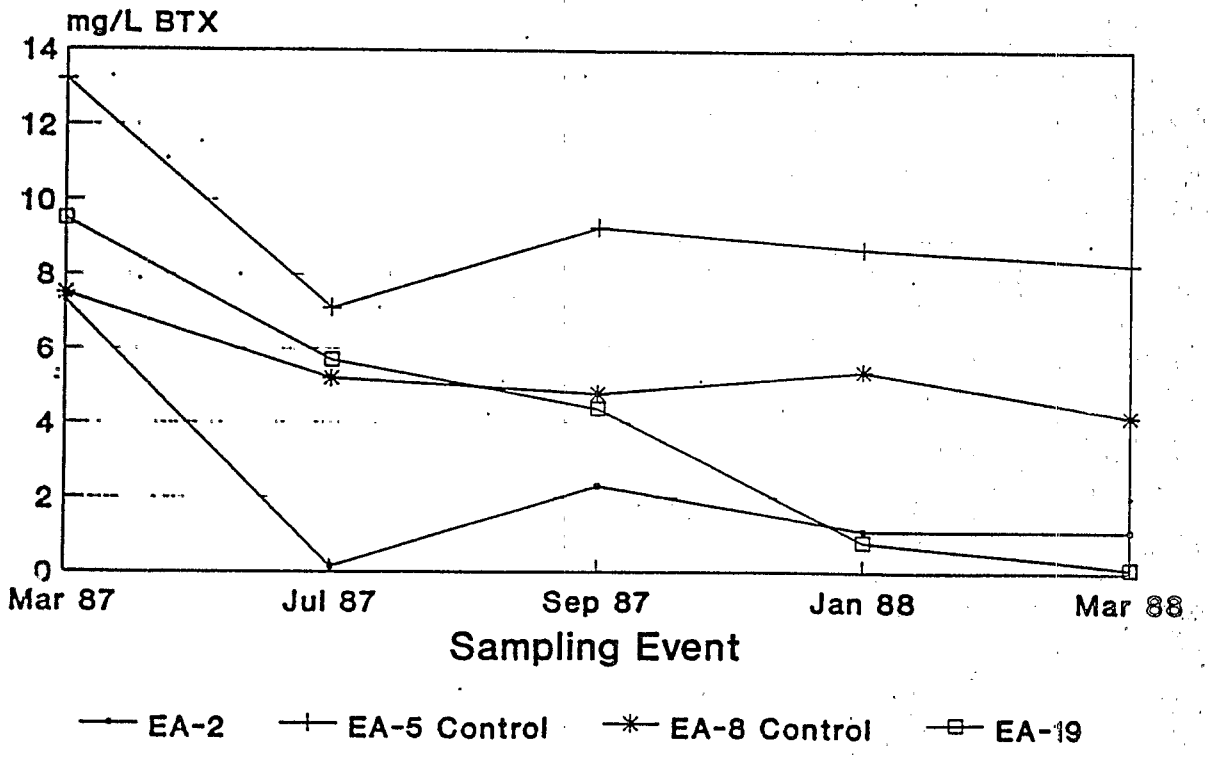

Figure 5. Removal of BTX From Ground Water

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The extent of bioremediation, or hydrocarbon biodegradation may be estimated from the actual oxygen delivery rates. Peroxide was injected into approximately 16,000,000 gallons of water. Based on peroxide stability and oxygen measurements at the points of injection, it is estimated that an average 25 mg/l of oxygen was actually delivered in this water. Very low oxygen concentrations down gradient of the injection points indicated utilization. We estimate that sufficient oxygen was delivered to mineralize approximately 1,200 pounds of hydrocarbon. It is possible that some of this oxygen was incorporated into microbial biomass, and therefore, greater than 1,200 pounds of hydrocarbons may have been removed.

Estimated Volatilization

A significant quantity of fuel residuals were removed in the above ground aeration basin. Based on TOC analysis of groundwater entering and leaving the aeration basin, a loss of volatile organics (measured as 15-20 mg/l TOC) occurred throughout the past 12 months. This means that the aeration basin has removed at least 2000 pounds of hydrocarbons from the 16,000,000 gallons of water pumped through the site. Contributing to this process is an unknown quantity of fuel residuals which have been washed from the soils into the groundwater due to natural leaching and soils washing in the spray application system. A better understanding of the hydrocarbon mass balance is anticipated after all the site data has been collected and analyzed.

Four More Years

In order to deliver sufficient oxygen with the observed peroxide half-life and subsequent oxygen delivery rates, and assuming continued volatilization of 2000 pounds/yr, four more years would be required to deliver the minimum stoichiometric oxygen requirements. Oxygen utilization efficiency by microbes was difficult to estimate from field measurements. However, it is likely that less than 100% could be used. Volatilization rates would also decline over time as ground water quality contiued to improve. Therefore, more than four years would be required to remove and/or degrade remaining fuel residuals from the soil. Switching the entire site to the spray system would be a practical way of speeding up the clean up. The estimated non-research cost associated with this effort is $600,000.

Based on current operating costs it is estimated that future operating costs of $210,000 per year for the additional years would be incurred. Therefore, a total cost of approximately $1,400,000 in non-research costs would be the minimum required for full site clean up. It should be noted that this is based on the assumption of 100% oxygen utilization, actual cost could be substantially higher. For those wishing to project these costs to other sites it should be pointed out that this site was in an open field and had minimum construction and maintenance costs.

RECOMMENDATIONS

1. In situ peroxide stability must be greatly improved to provide adequate oxygen downgradient of injection points. At the present cost of $3 - $4.20 per gallon for 35% hydrogen peroxide, the available oxygen is costing $1.50 - $2.40 per pound. In comparison, the cost of industrial grade liquid oxygen is only $.10 per pound. Therefore, if the effective oxygen concentration achieved with peroxide addition is not substantially greater than the 40 mg/l of oxygen saturation possible with liquid oxygen, then the use of peroxide is not cost effective.

2. Greater emphasis must be given to both vertical and horizontal distribution of contaminants. Oxygen delivery systems must influence the vadose zone where a majority of the fuel residuals remain. In this project the spray system was the only method which appeared to do this. Other technologies such as soil venting have a far geater potential for introducing oxygen into unsaturated soils.

3. Laboratory methods for predicting in situ biodegradation, peroxide stablity and geochemical side reactions must all be improved. Current procedures must be refined to account for site specific soil and ground water chemistries. On site pilot tests are recommended to determine in situ peroxide stability, oxygen utilizaion rates and potential plugging problems.

4. Finally, there is a need for more sharing of meaningful site data by those experience in the application of this technology. Data on peroxide stability and transport, oxygen utilization and the removal of fuel residuals from soils are all missing from the open literature.

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Appendix 8-D

Microbial Treatment Technology Case Studies

Biological Pre-treatment of Ground Water,
Bunschoten, The Netherlands

Biological treatment of groundwater polluted with HCH, chlorobenzene and benzene on a former pesticide production site in Bunschoten, The Netherlands.

Urlings L.G.C.M., F. Spuij and J.P. van der Hoek
TAUW Infra Consult B.V., P.O. Box 479 Deventer, The Netherlands

1. Introduction

From 1945 untill 1949 the factory Dagra (Bunschoten, The Netherlands) has produced the insecticide Lindane. Lindane (gamma-Hexachlorocyclohexane) was made by mixing benzene and chlorine gas under U.V. radiation; not only gamma-HCH was produced but also all other HCH-isomers.
As a result of these activities the factory grounds and the surrounding area were heavily polluted with HCH. Even the groundwater was contaminated with mainly HCH, monochlorobenzene and benzene. An outline of the production shed and the surrounding is given in figure 1.

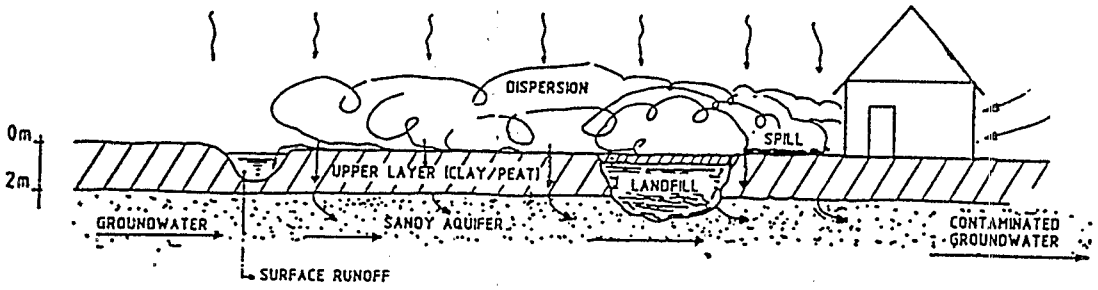

Figure 1. Pesticide pollution around the production shed

In 1985 the remedial action of the contaminated soil took place. More than 11.000 m^3 polluted soil was excavated and transported to a Temporary Storage Place waiting for treatment. Approximately 60 m^3 soil could be regarded as pure HCH (> 90%). The groundwater remediation which was continued after the excavation will be finished in the second part of 1988. The groundwater treatment originally consists of a physicochemical proces which is made up of two sand filters and three activated carbon filters. During the remedial action of the soil the maximum withdrawal was 60 m^3/h. In 1986 the groundwater was 40 m^3/h and has been reduced to 25 m^3/has a result of the cleanup action in the middle of 1987. In October 1988 the flow was 12 m^3/h.

In recent research it appeared that a lot of xenobiotics can be degradated by micro-organisms. Although there is hardly any experience with biological groundwater treatment TAUW Infra Consult B.V. started some small scale experiments with a trickling filter and a rotating biological contactor in 1986.

The results were promising: 50% removal of HCH and 99% removal of benzene and monochlorobenzene. The required activated carbon would be reduced in this situation to less than 10% when applying a full scale biological treatment.
In november 1987 two rotating biological contactors were installed for groundwater pretreatment (see figure 2). The research was partly financed by the Ministry of Housing, Physical Planning and Environment.

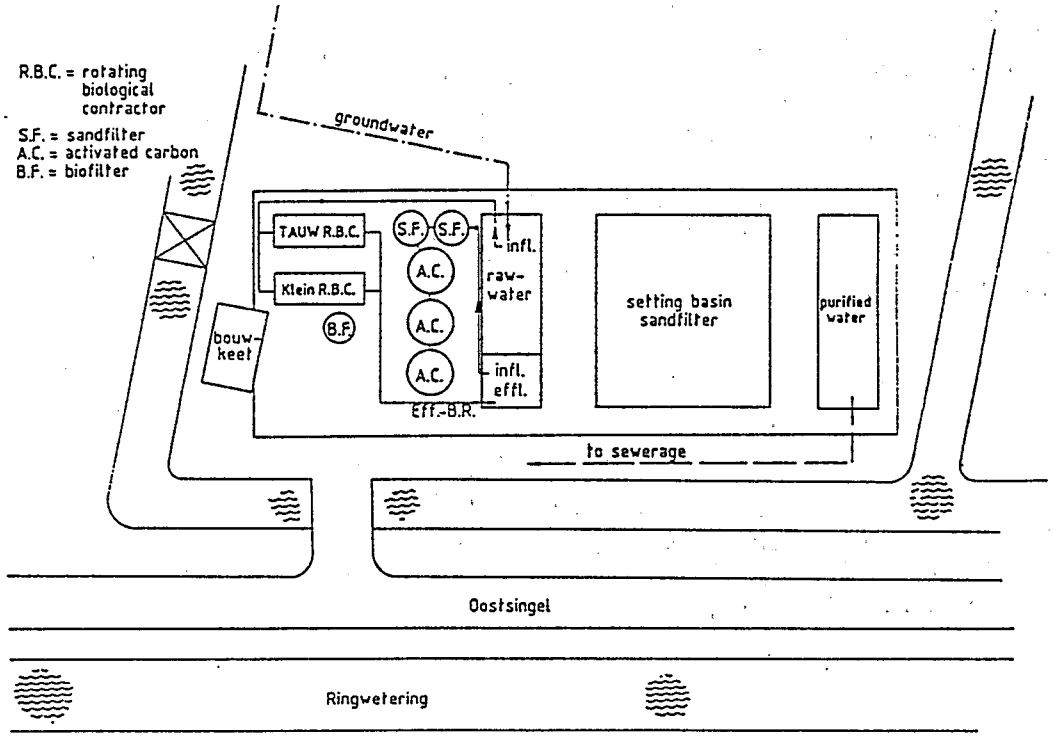

Figure 2. Groundwater treatment installation in Bunschoten, the Netherlands

Although the groundwater treatment installation has been scaled up, there is still an experimental character in the operation of the plant.

2. Apparatus and operation

The rotating biological contactor (RBC) installation consists of two RBCs. Firstly a TAUW RBC with an effective surface aera of 1000 m^2 placed in a trough of 9 m^3 and divided into 4 stages (figure 2), and secondly a KLEIN RBC with an effective surface area of 700 m^2 placed in a trough of 4.4 m^3, also divided into 4 stages. Both RBCs rotate with 1.5 rpm. There are no settling tanks and the effluent of the RBCs is treated in the sandfilter/activated carbon installation. The RBCs operate seperately (parallel) but they can be connected in series if wanted (figure 2).
To prevent contamination of the surrounding air by volatilization of contaminants from the groundwater both RBCs are roofed, and the air extracted from the RBCs is purified by a compost filter. The air extraction flow is approximately 150 m^3/h.

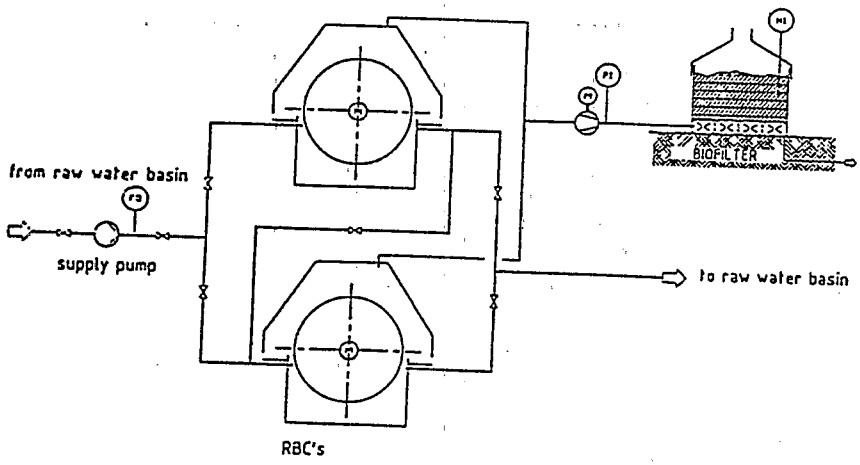

Figure 3. Flow diagram of the RBCs and compost filters.

3. Groundwater characteristics

Table 1 gives an indication of the concentrations of contaminants in January 1988.

Table 1. Groundwater concentration in January 1988

	ug/l	
Benzene	350	
Monochlorobenzene	350	
HCH*	200	
alpha-HCH		± 60
beta-HCH		± 5
gamma-HCH		± 80
delta-HCH		± 40
epsilon-HCH		± 15

Other xenobiotics are not substancially present in the groundwater (GC/MS-analysis).

Some important macroparameters are shown in table 2.

Table 2. Macroparameters groundwater

compound	dimension	august 1986	february 1988
COD	mg/l	56	47
BOD	mg/l	4	5
Kjeldalh nitrogen	mg N/l	3,5	
Ammonia	mg N/l	4,5	3
Nitrite	mg N/l	0,02	< 0,01
Nitrate	mg N/l	0,1	0,35
Total phosphorus	mg P/l	0,28	0,57
Temperature	°C	10	9
pH	--	7	6,8

4. Results and discussion

4.1 Start up

After one week of operation (3rd December 1987) a thin biofilm was observed. In addition sediment from the raw water basin was supplied to both biocontactors during one day of batch operation to enhance bacterial atachment. First results, 9th December , showed almost complete (> 98%) removal of benzene and chlorobenzene at a low flow rate of 3 m^3/h (hydraulic residence time 3 h). After a short freezing (2 weeks) period and shut down of the RBCs complete removal of benzene and chlorobenzene was measured after 3 days of the re-start (3 m^3/h). The first HCH biodegradation was found on day 28.

4.2 Overall removal efficiencies

The applied flow rates through the RBCs are shown in figure 4.

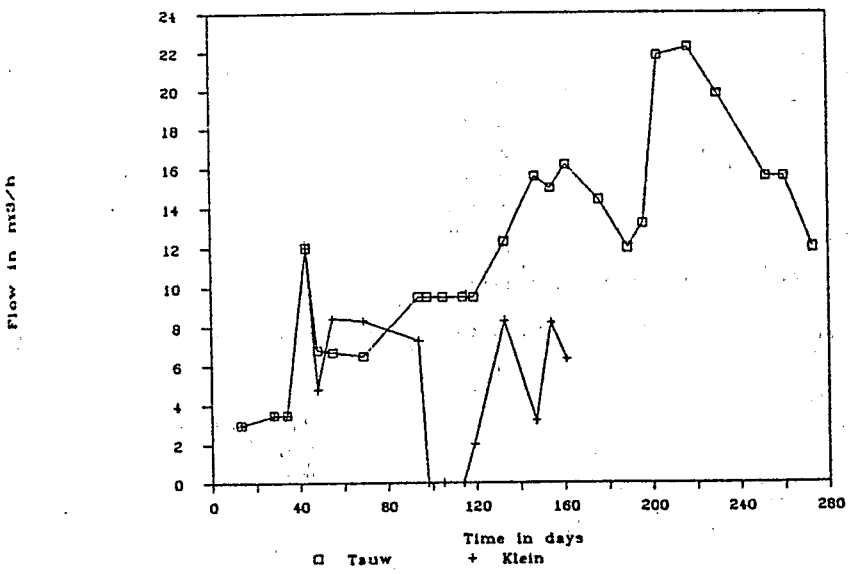

Figure 4. Flow rates through the RBCs

- HCH-removal

In figure 5 the removal efficiencies of alpha and gamma-HCH in the TAUW RBC is plotted against time, while in figure 6 HCH removal related to HCH loading is shown.

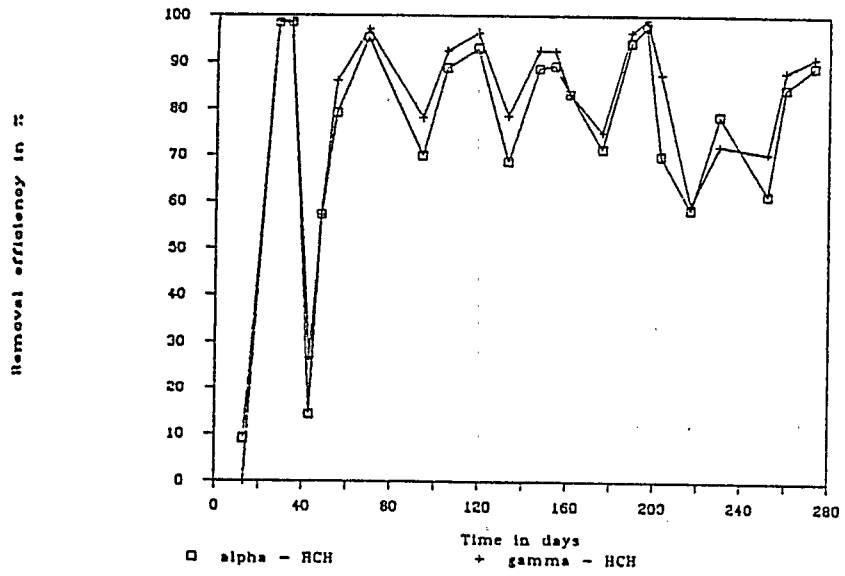

Figure 5. Removal efficiencies of alpha and gamma HCH (TAUW RBC)

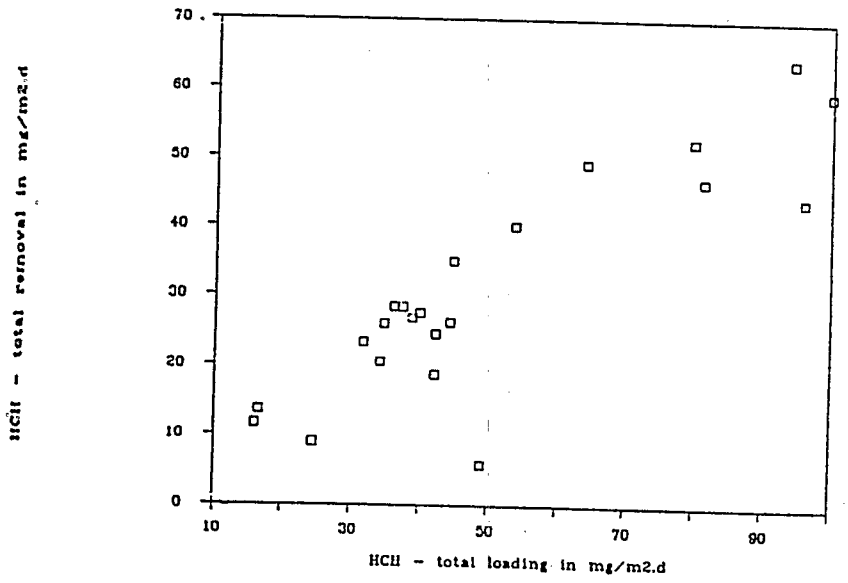

Figure 6. HCH removal versus HCH loading (TAUW RBC)

Figure 6 shows a linear increase of HCH removal with HCH loading. However at loadings of 50 - 60 mg/m^2d the line deflects and remains constant. This trend is confirmed by the compartiment sampling (see figure 12).

- Benzene removal
The performance of the TAUW RBC is given in figure 7.

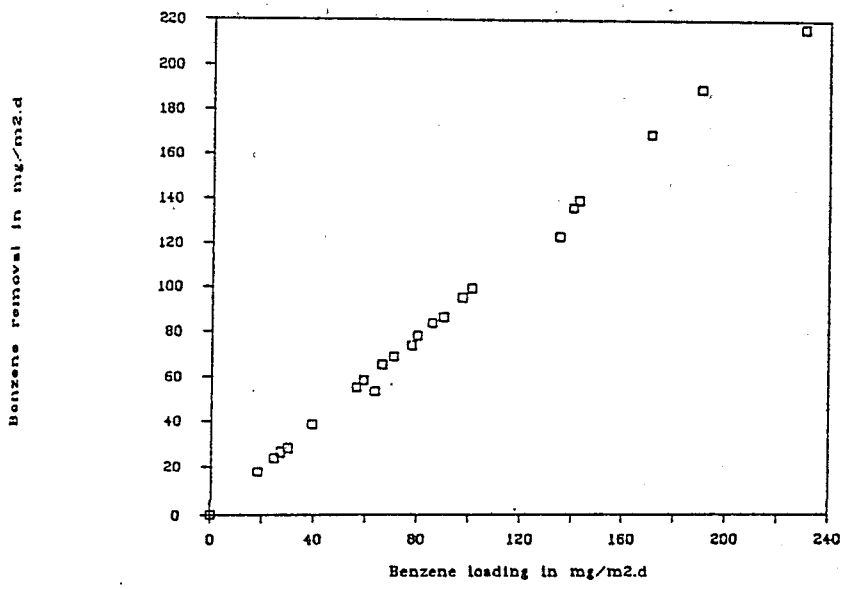

Figure 7. Benzene removal versus benzene loading

Figure 7 indicates that benzene removal is complete and no deflection is observed.

- Chlorobenzene removal
The removal related to loading of the TAUW RBC is shown in figure 8.

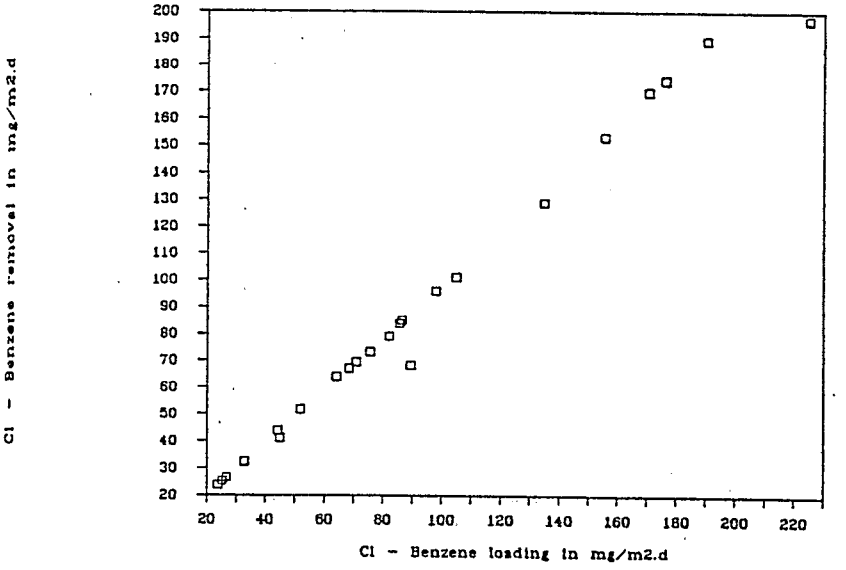

Figure 8. Chlorobenzene removal versus chlorobenzene loading

Figure 8 is conform to figure 7. Hence no maximum for the chlorobenzene removal can be given.

4.3 Mass balance for the TAUW RBC
An unknown factor in the determination of the removal efficency of the RBC is the volatization of components like benzene and chlorobenzene. Therefore 3 mass balance measurements were carried out.

- Experiment 1. flow 6.7 m^3/h, sampling during 2 h.

		Extracted air	
		benzene	65 mg (1%)
		chlorobenzene	101 mg (2%)
Influent			Effluent
benzene	5,900 mg		benzene 80 mg
chlorobenzene	6,300 mg	BIODEGRADATION	chlorobenzene 201 mg

For experiment 2 and 3 the following volatilization percentages are found.

- Experiment 2:	benzene	2% volatilization
	chlorobenzene	1% volatilization
- Experiment 3:	benzene	6% volatilization
	chlorobenzene	9% volatilization

The airflow in experiment 3 was extremely high (840 m^3/h) which explains the high volatilization. The HCH volatilization was less than 1%.

4.4 Compartment measurement

To obtain detailed information on removal rates, in individual compartments of the RBCs samples were taken in each compartment of the RBCs in serie. Both RBCs have 4 compartments equal in volume.

- HCH

The total-HCH concentration is given for the several compartments in figure 9. In the first two compartments the removal rate is comparable.

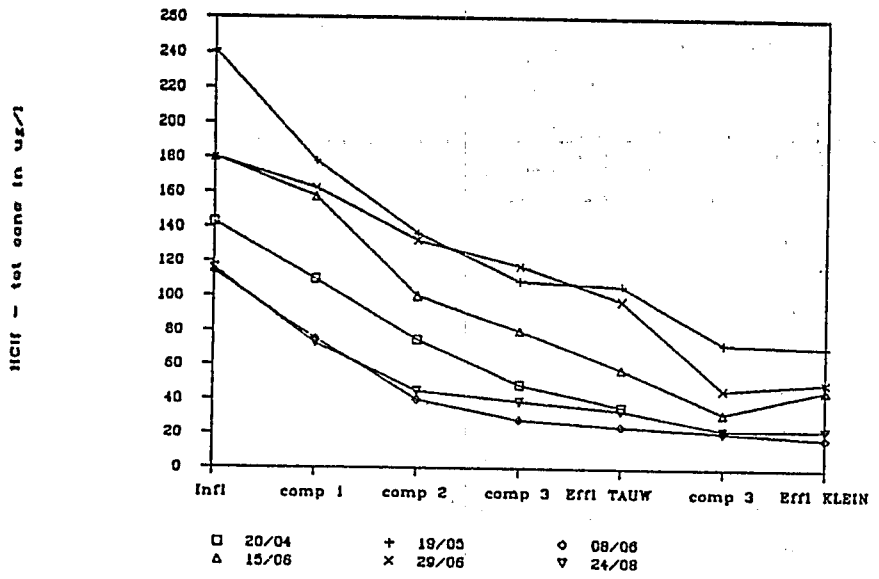

Figure 9. HCH compartment sampling at different flow rates

In figure 10 and 11 the 5 isomers of HCH are shown at a low and a high flowrate respectively.

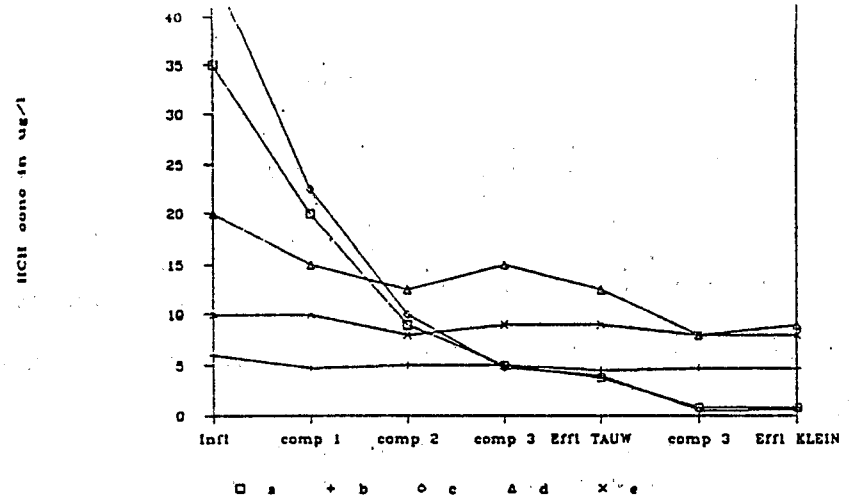

Figure 10. HCH-isomer compartment sampling on the 24th August (flow rate = 12 m^3/h)

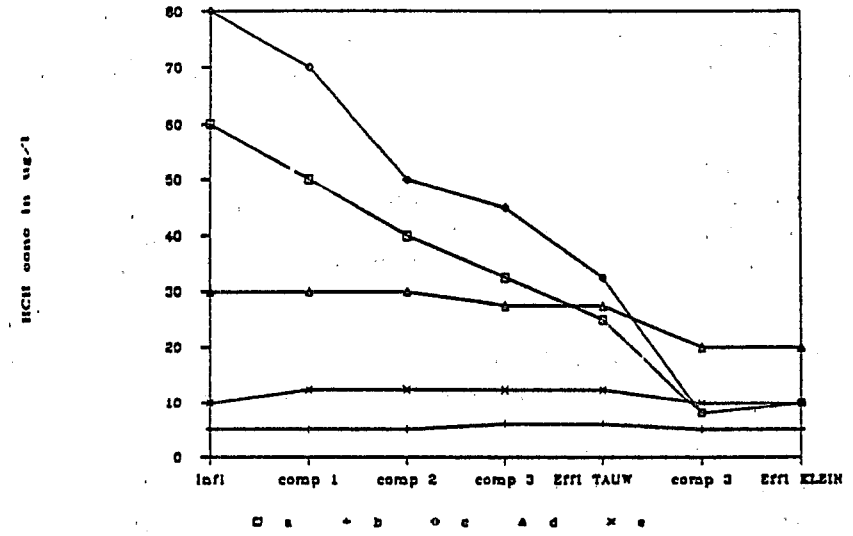

Figure 11. HCH-isomer compartment sampling on the 29th June (flow rate = 22 m^3/h)

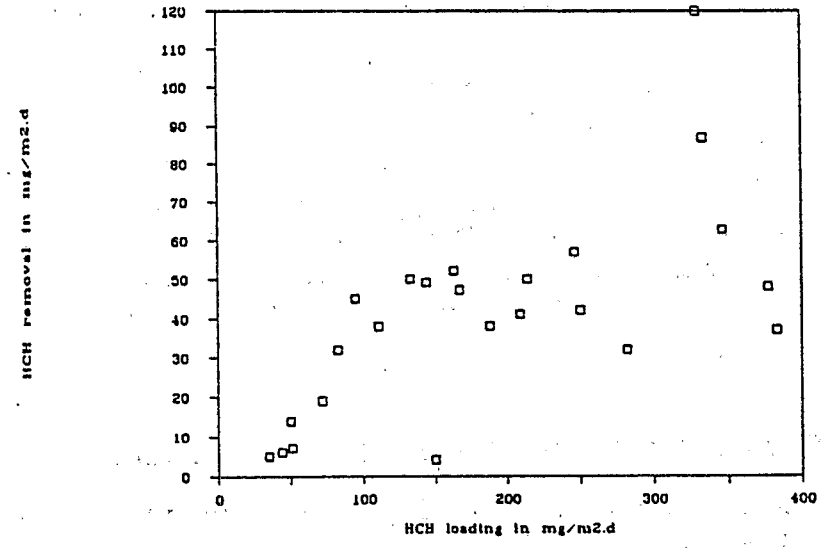

Figure 12. HCH loading versus HCH removal; compartment sampling

In figure 10 alpha and gamma HCH breakdown are almost complete after passage of two compartments while in figure 11 the total disc surface area is needed to complete the alpha and gamma HCH breakdown. Delta HCH biodegradation is also observed. The concentrations of the epsilon and beta HCH remain constant.
The results of the compartment measurements (figure 9) is presented in figure 12 in a loading/removal graph which shows a maximum removal rate of almost 50 mg HCH/m^2d.

- Benzene and chlorobenzene

In figure 13 and 14 the breakdown curves of benzene and chlorobenzene are given for the RBCs in series. The results for benzene and chlorobenzene are comparable and the highest removal rates appeared in compartment one of the TAUW RBC.

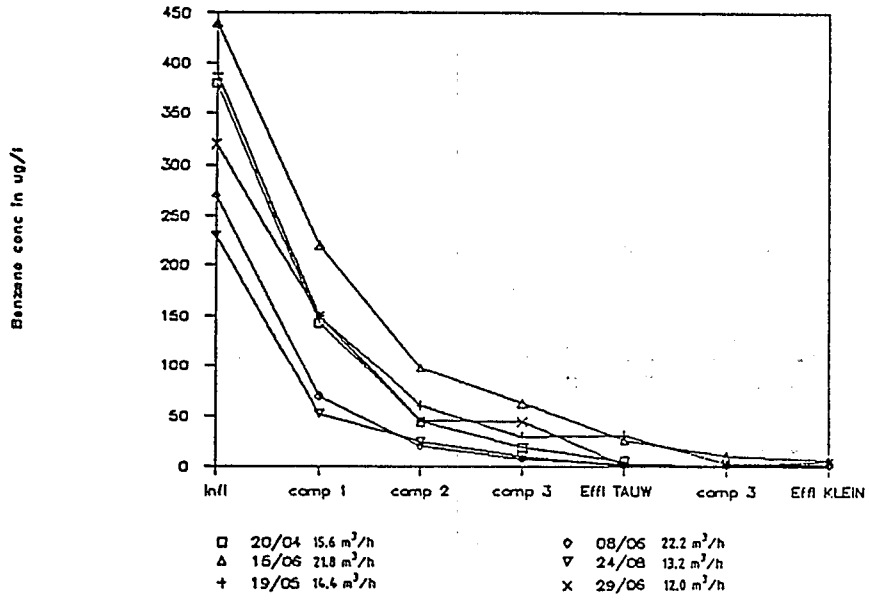

Figure 13. Benzene concentration in the compartments for different flow rates

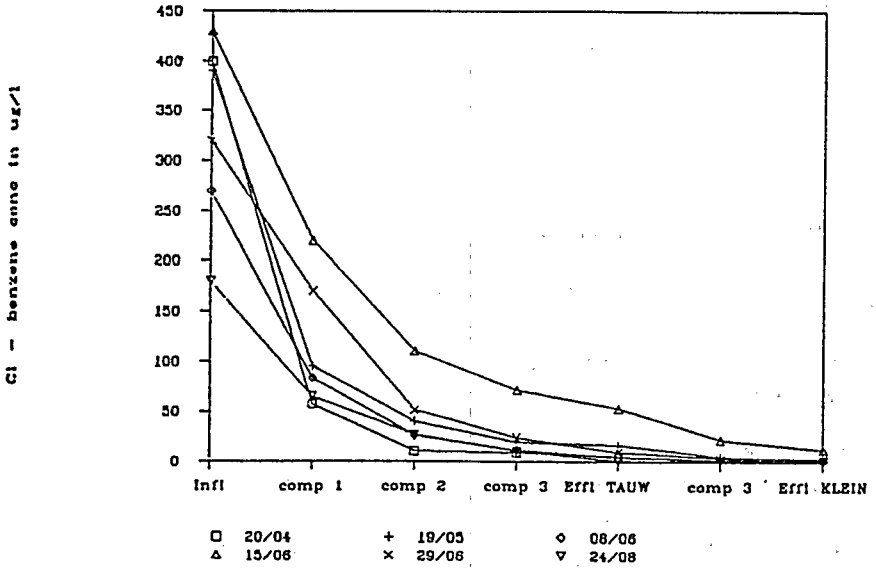

Figure 14. Chlorobenzene concentration in the compartments for different flow rates

Figures 15 and 16 give removal rates (mg/m^2d) versus loadingrate (mg/m^2d) for benzene and chlorobenzene. And indicate that when loadingrates exceed 200 mg/m^2d the removal can be estimated as a half order process. In figures 7 and 8 a zero order removal process was outlined, which means no limitation.

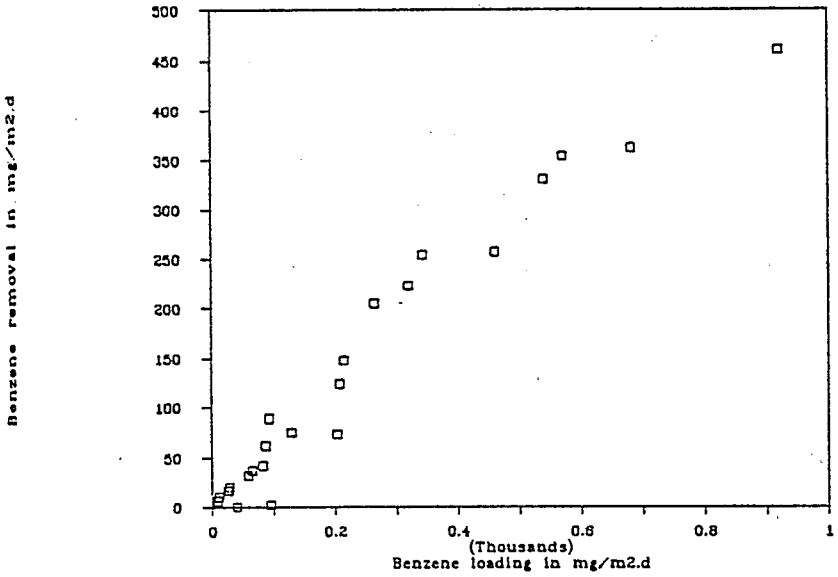

Figure 15. Benzene loading versus benzene removal as measured in compartment sampling

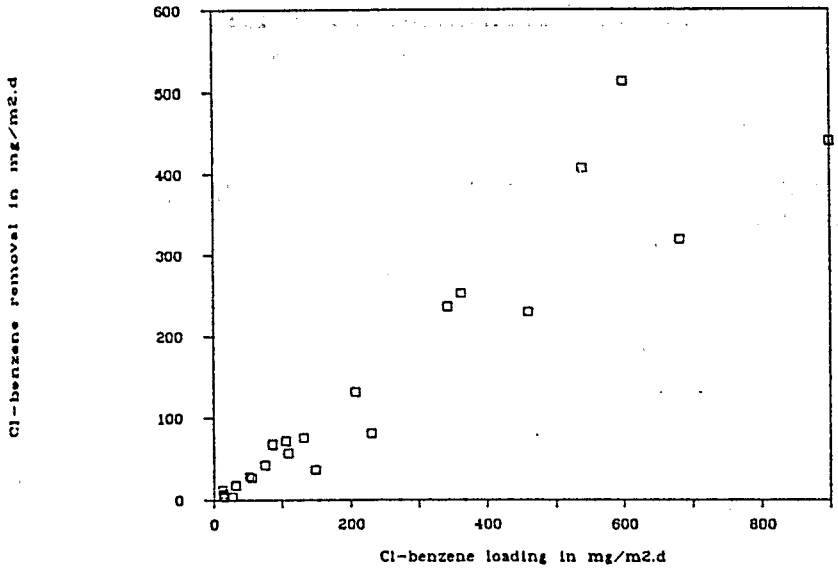

Figure 16. Chlorobenzene loading versus removal as measured in compartment sampling

4.5 Biofilm characteristics

The growth of biomass was measured in the 1st and 4th compartment of the TAUW RBC by using exchangeable disc packets. The biomass density was determined by removing the biofilm from 0.1 m^2 disc area. The biomass-wash out was calculated from the suspended solids concentration in the effluent.

Table 3 Biomass characteristics.

	dry matter	ash content (% of dm)
1st compartment TAUW	200 g/m^2	67
4th compartment TAUW	20 g/m^2	62
wash-out TAUW RBC	10 g/m^3	50
KLEIN RBC	10 g/m^3	50
growth		
- 1st compartment TAUW RBC	7 $g/m^2.wk$	
- 4th compartment TAUW RBC	2 $g/m^2.wk$	

Using an average HCH concentration in the sludge of 15 mg/kg it can be calculated that 1.6 g HCH adsorbed on the whole TAUW RBC. The HCH load of the RBC was approximately 100 g/d. Hence accumulation of HCH in the biomass does not occur. In the effluent only 0.2 ug HCH/l is adsorbed on the suspended solids.

4.6 Costs

The cost evaluation for the Bunschoten site is based upon the contractors fee for physicochemical treatment (activated carbon) and estimated cost for biological treatment. For the latter the results of the above discribed experiments are used. The total amount of removed contaminants are:

- HCH 100 kg
- Benzene 250 kg
- Chlorobenzene 200 kg

For a combined biological/physicochemical treatment three different biological removal efficiencies, as well as for an one-stage physicochemical treatment the costs are compared in table 4.

Table 4. Treatmentcosts (in Dfl) versus techniques

Removal efficiency		Costs			
HCH	Benzene/Chlorobenzene	RBC	Activated carbon	Physicochem. install.	Total
70%	> 95%	110.000	15.000	80.000	205.000
60%	95%	90.000	20.000	100.000	210.000
20%	60%	35.000	100.000	125.000	260.000
0	0		200.000	150.000	350.000

Biological pretreatment results in a cost reduction for the groundwater remedial action of 30 - 40% for the Bunschoten site.

5. Conclusions and recommendations

5.1 Conclusions

Biodegradation:

- the removal of HCH, benzene and chlorobenzene in the RBC can be attributed for more than 90% to biodegradation. Volatilization and adsorption onto the sludge are of minor importance to the total removal;
- loadings up to 200 mg/m^2d for both benzene and chlorobenzene and a hydraulic residence time of app. 30 min. lead to average effluent concentrations of less than 10 ug/l;
- only alpha HCH and gamma HCH show a good biodegradation rate (each 25 mg/m^2d). Delta HCH shows little breakdown, while epsilon HCH and beta HCH concentrations in the RBC remain constant;
- the mineralisation of contaminants is complete, viz. there are no metabolites found (GC/MS analysis). The applied biotechnology is environmentally attractive;
- The performance of the compost filter for air treatment shows poor results.

Costs

- for the Bunschoten groundwater remedial action the cost reduction by RBC pretreatment is at least 30%;
- cost minimizing of hazardous waste treatment (less volume of contaminated activated carbon).

Application

- RBCs need little maintenance;
- in wintertime (-10°C) RBCs are applicable when the groundwater flow rate is not to low;
- the adaptation time for benzene and chlorobenzene biodegradation was only two weeks and for HCH four weeks in the RBC-system.

5.2 Recommendations

More biological techniques like RBCs should be applied in the groundwater remedial action, especially for aromatic contaminants.

From literature it is known that a lot of organic micropollutants can be biodegradated. Probably a combined aerobic-anaerobic (dechlorination) system can tackle a wide variety of organic contaminants in an environmental friendly way.

Acknowledgement

Thanks to the critical and inspiring contribution of the advising board. The board consited of dr. ir. A. Klapwijk (chairman, Agricultural University Wageningen), dr. ir. M. v. Loosdrecht (Agricultural University Wageningen/Technical University Delft), ing. P.J.C. Kuiper (Institute for Inland Water Management and Waste Water Treatment), ing. A.W.J. van Mensvoort, ing. J.C. Hoogendoorn (Province of Utrecht), ir. A. v.d. Vlugt (Ministery of Housing, Physical Planning and Environment).

Appendix 8-E

Microbial Treatment Technology Case Studies

Rotary Composting Reactor of Oily Soils, Soest, The Netherlands

PRODUCTION SCALE TRIALS ON THE DECONTAMINATION OF OIL-POLLUTED SOIL IN A ROTATING BIOREACTOR AT FIELD CAPACITY

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SUMMARY

A biological treatment method has been developed for the decontamination of oil-polluted soil at field capacity. Soil is treated in a rotating bioreactor in which soil temperature, oxygen, moisture, and nutrient levels can be adjusted. Following laboratory scale studies to determine the optimum environmental conditions for oil biodegradation, production scale trials were carried out with oil-polluted soil (1,000 to 6,000 mg/kg dry soil) at field capacity. In five batch experiments and two semicontinuous experiments with 50 tonnes of soil, end concentrations after 1 to 3 weeks' treatment varied from <50 to 350 mg/kg dry soil. Microbial activity and oil breakdown was highest in the first 3 to 4 days. This technique warrants further investigation as it is environmentally friendly, energy saving, and the end product is a living, fertile soil.

FRAMEWORK

As part of the development of biotechnological methods for cleaning soil, Witteveen+Bos Consulting Engineers, Deventer, has carried out production scale trials on the decontamination of oil-polluted soil in a rotating bioreactor at field capacity. The aim was to develop a method for

quick cleaning of polluted soil under controlled conditions at field capacity.

The Microbiology Department of the Wageningen Agricultural University and Broerius Soil Sanitation Ltd., Voorthuizen, also took part in the study, which was partially financed by the Netherlands Ministeries of Housing, Physical Planning and Environment (VROM) and of Economic Affairs (EZ).

FEASIBILITY STUDY

A feasibility study was carried out at the Microbiology Department of the Wageningen Agricultural University from July through November of 1988. Optimum environmental conditions for biological decomposition were determined in incubation experiments with soil in which oil degradation was monitored by respiration measurements and oil analyses.

Mesophilic decomposition of oil was shown to be most efficient at a temperature of 30 to 35°C, a moisture content of approximately 10 percent by weight, and in the presence of 150 mg N nitrogenous fertilizer per kg of dry soil (oil concentration of 5,000 mg/kg d.s.). Under these conditions, on a laboratory scale, oil is completely decomposed (to <100 mg/kg d.s.) within two weeks.

THE ROTATING BIOREACTOR

The reactor used in the production scale trials was a modified DANO-composting installation for household garbage operated by the Municipality of Soest and Baarn (Figure 1). Broerius Soil Sanitation Ltd. renovated and adapted the installation for soil treatment. The reactor is 25 m long and 3.5 m in diameter. As the reactor rotates, the soil is mixed and homogenized so that biomass and oil substrate come into close contact. Temperature

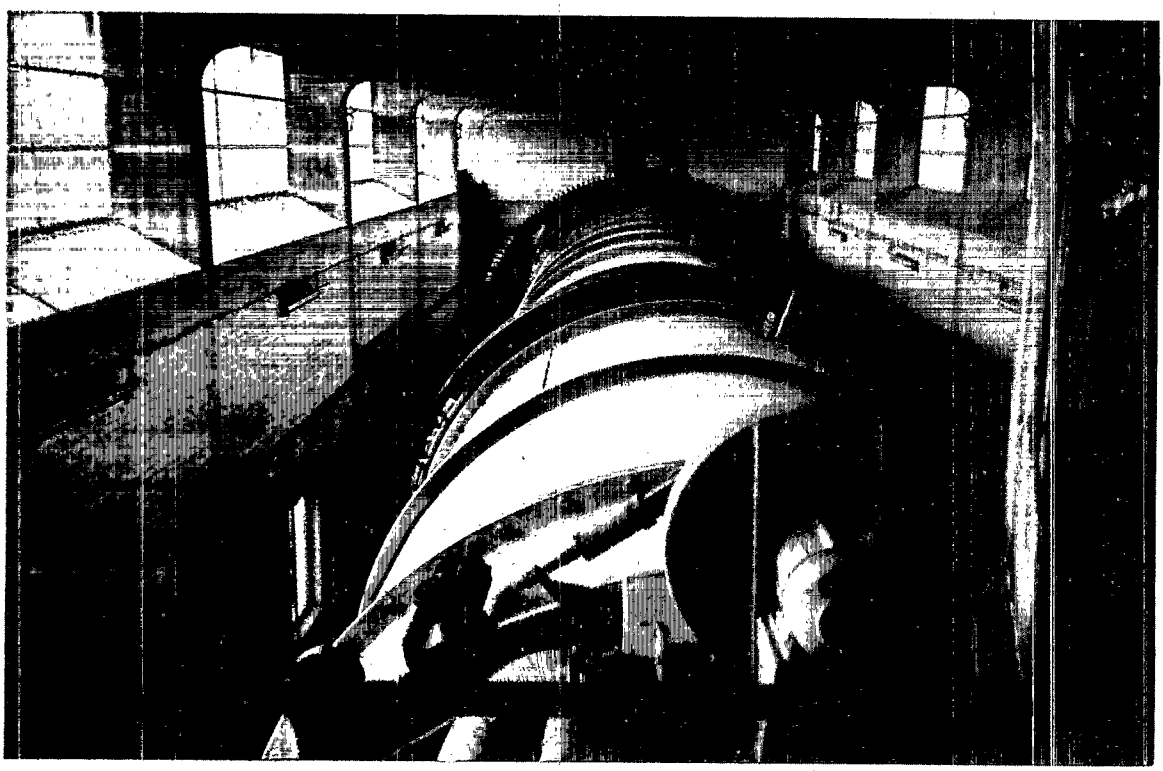

Figure 1. The bioreactor

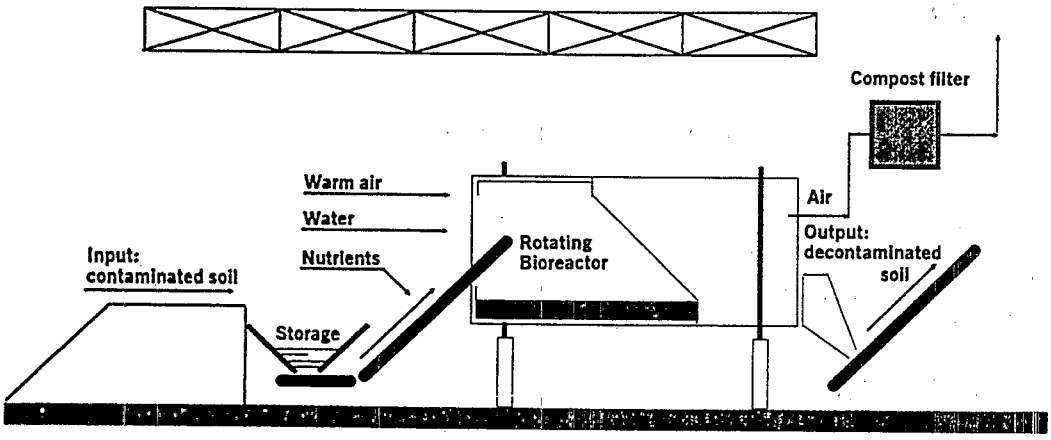

Figure 2. Biological treatment process in the rotating bioreactor

and oxygen levels are maintained with the aid of a warm air blower, and soil moisture content is adjusted with a sprinkler installed in the bioreactor. Nutrients are added to the soil on the conveyor before entering the reactor. The soil treatment process is shown schematically in Figure 2. Witteveen+Bos has obtained the patent for this treatment process.

PRODUCTION SCALE TRIALS

Batch Experiments

Five loads (batches) of oil-polluted soil, each weighing 50 tonnes (wet weight), were treated in the reactor as follows: one batch of petrol-polluted soil, three batches of diesel-polluted soil, and one batch of soil polluted with both diesel and lubrication oil. The oil concentrations in the soils varied from 1,000 to 6,000 mg/kg dry soil. Four of the five batches consisted of fine to loamy fine sand, and one batch consisted of fairly coarse sand.

Each soil was incubated in the reactor under optimal environmental conditions as determined in the laboratory feasibility study. This was only partly successful because the soil temperature in the reactor did not rise above 20 to 22°C. In addition, the structure of the relatively loamy soil batches partly deteriorated. Some soil particles tended to stick to one another around small particles of rock, thus forming soil balls sometimes several centimetres in diameter.

Soil and air samples taken from the reactor were analyzed at regular intervals to monitor and manage the microbial degradation process. To take the soil samples, three sampling flaps were made, at a quarter, half, and

three-quarters of the length of the reactor (sampling points 1, 2 and 3, respectively). In addition to the chemical analyses such as moisture content, humus content, pH, oil concentration, volatile aromatics, and PAH, counts were done of oil-degrading microflora, for which the most probable number (MPN) method was used. The air samples were analyzed for oil and volatile aromatics to establish a mass balance (degradation versus volatilization).

For comparison with the measurements in the reactor, respiration measurements were also done on soil samples from each batch in the Microbiology Laboratory at Wageningen Agricultural University. The results of the measurements on oil biodegradation in the five batches are summarized in Table 1, and presented in Figures 3, 4 and 5.

In the rotating bioreactor at a soil temperature of about 20°C, the end concentration of the oil biodegradation was reached on average within a period of approximately 2.5 weeks. Biodegradation was most rapid in the first week. The end concentration of oil varied from <50 to 250 mg/kg dry soil.

The maximum level of oil-degrading microflora in the reactor was reached within one to three days. The numbers of microorganisms grew from MPN/10^6 to MPN/10^8 per gram of soil.

The laboratory respiration measurements indicated that at a temperature of 30°C biological degradation was largely completed in a period of 1 to 1.5 weeks. In the humus-poor, fairly coarse sandy soil in batch 1, it took longer, 2 to 3 weeks. This indicates that, if a soil temperature of 30°C can be achieved in the bioreactor, then an average degradation period of 1

Table 1. Results of the batch experiments

Batch no	Soil type	Oil type	Oil-concentration (mg/kg ds) start	Oil-concentration (mg/kg ds) end	Degradation time (weeks)	Point in time max. level microflora (days)	Results of respiration measurements (% of total respiration)	Volatilization (weight %)
1.	poor coarse sand	diesel oil	6,000	<100	2.5-3.0	3	80% after 2 weeks	
2.	fine sand	petrol	920	<50	0.5			>30
3.	loamy fine sand	diesel oil/ lubrication oil	730	<100 (GC) 180 (IR)	2.5-3.0	3	90% after 1 week	30
4	fine sand	diesel oil	1,000	140 (GC/IR)	2.5	2-3	85% within 1½ week	0.5
5.	loamy fine sand	diesel oil	1,000 1,500	250 (GC/IR)	1.5	1-2	90% within 1 week	0

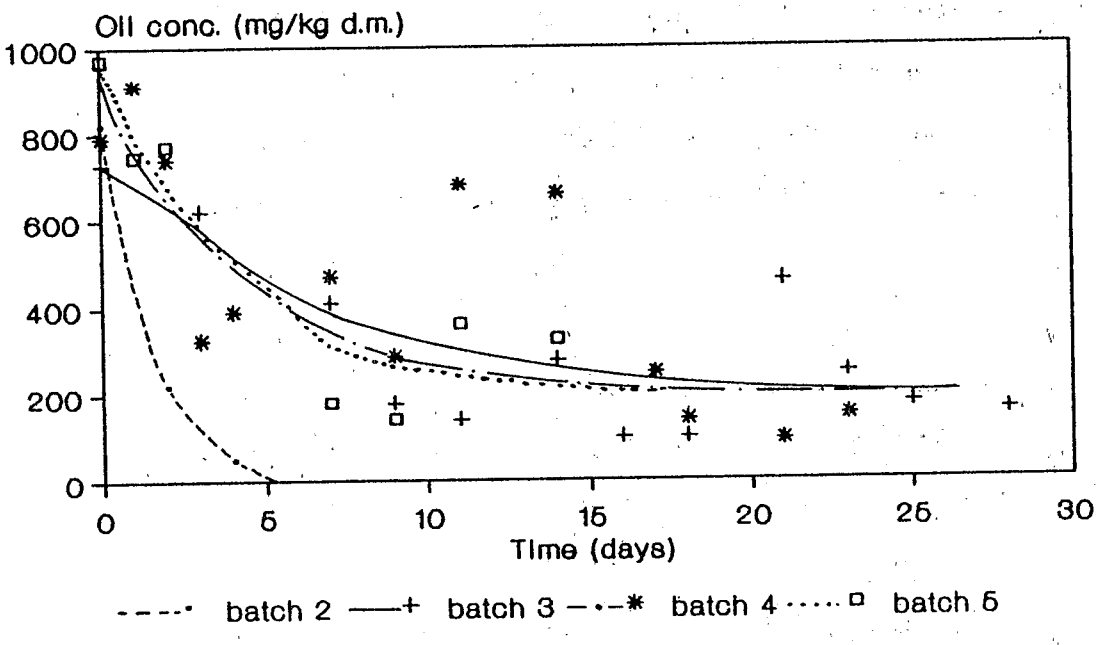

Figure 3. Decrease in oil concentration in the batch experiments 2, 3, 4 and 5

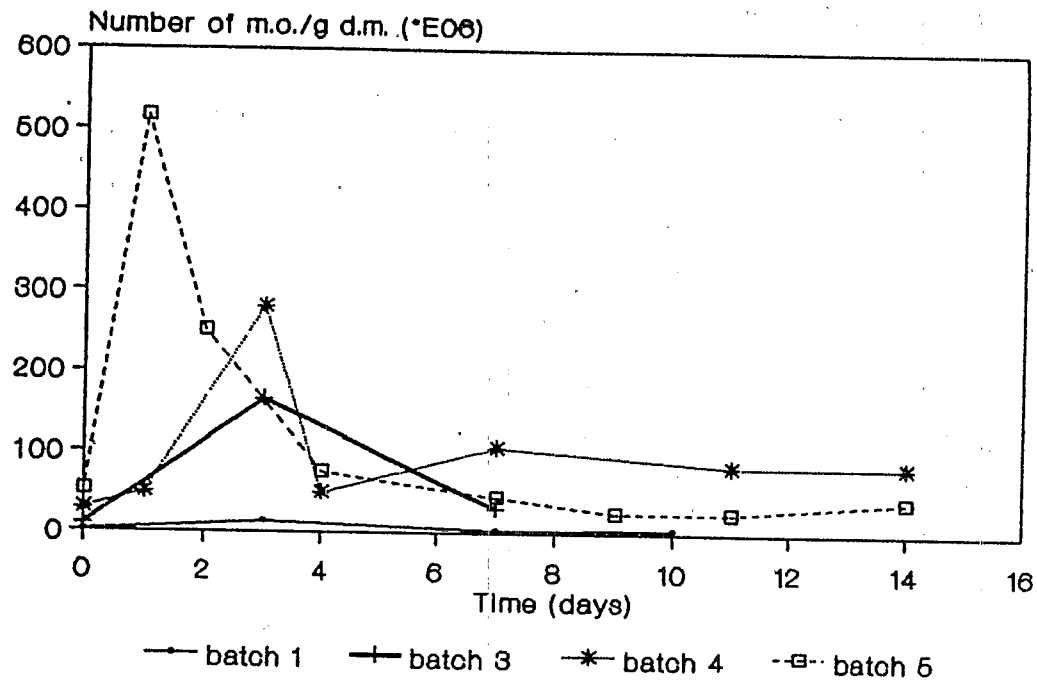

Figure 4. Development of oil-degrading microflora in batch experiments 1, 3, 4 and 5

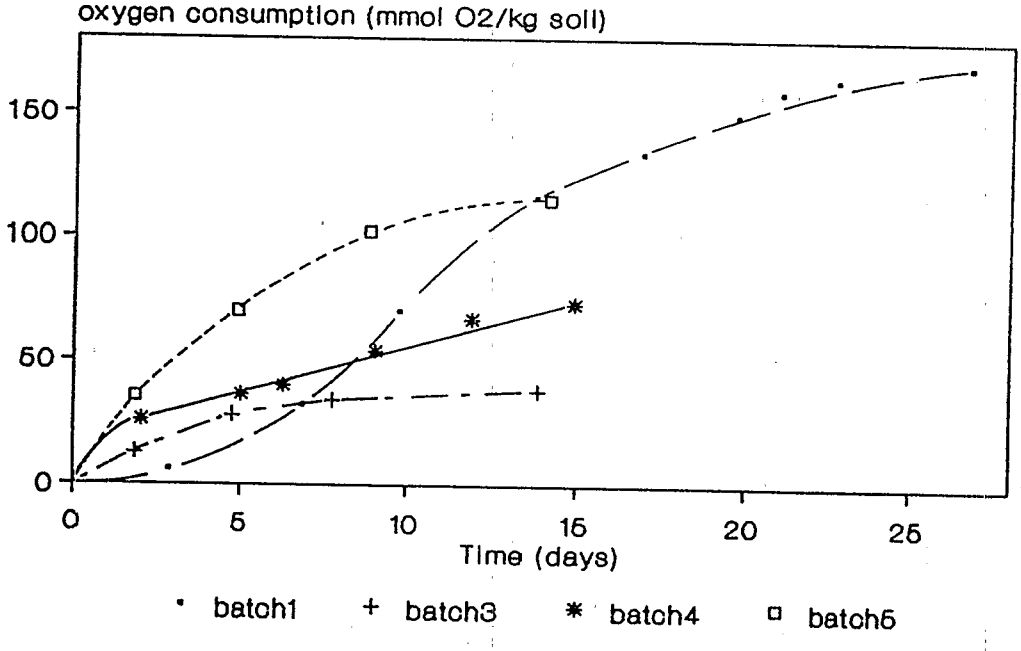

Figure 5. Oxygen consumption assessed by laboratory respiration measurements on soil samples from batch experiments 1, 3, 4 and 5.

to 1.5 weeks is feasible.

Based on these results, treatment in the reactor is not guaranteed to achieve an end concentration of oil below the Dutch Standard for unpolluted soil (A-level) of 50 mg/kg d.s. However, treatment of petrol- and diesel-polluted soils in the reactor removed the most critical pollutants. The remaining oil components are mainly alkanes, which are highly branched and/or of long chain length. Compared to the original oil product, these components are less volatile and less soluble, do not cause odor nuisance, and are probably less toxic.
Thus treatment in the bioreactor is environmentally beneficial.

Petrol-polluted soils should not be treated in the rotating bioreactor without provisions to reduce emission of volatile aromatics into the air. There are no significant emissions of aromatics from diesel-polluted soils. However, sometimes at the beginning of the incubation, hydrocarbon emissions of up to a few hundred mg per m^3 may occur.

Semicontinuous Experiments

In the semicontinuous experiments, 3.5 tonnes of decontaminated soil were removed daily from the end of the reactor and the same amount of contaminated soil placed in the front section. The total quantity of soil in the reactor remained at 50 tonnes and the average retention time was 14 days.

Two semicontinuous experiments were carried out, one for one week (experiment 1) and the other for two weeks (experiment 2). Each day soil samples were taken at all sampling points, analyzed for oil concentration, and MPN

counts of the oil degrading microflora made. The results are summarized in table 2.

Table 2. Results of semicontinuous experiments

Parameter	Sampling point				
	input	sp 1	sp 2	sp 3	output
* Mean oil concentration (IR) (mg/kg ds)					
- expt. 1	980	215	370	350	350
- expt. 2	995	220	205	190	230
* Mean of MPN-counts ($.10^6$/g. soil)					
- expt. 1	25	183	33	16	16
- expt. 2	26	131	46	4	

The soil entering the reactor had an average oil concentration of about 1,000 mg/kg dry soil. At the defined sampling points 1, 2, and 3 and in the soil leaving the reactor, the oil concentration was the same, namely 200 to 350 mg/kg dry soil. Thus it may be concluded that biodegradation to 200 to 350 mg/kg dry soil occurred quickly (within 3 to 4 days). The highest microbial activity occurred in the front section of the reactor (up to sp 1). At sp 1 counts of oil degrading microflora were MPN 10^8 to 10^9 per gram of soil. At sp 2 and sp 3, the number of oil degrading microorganisms had declined to the level in the soil entering the reactor (MPN 10^7 per gram of soil).

The results for the semicontinuous experiments are in line with those of the batch experiments. The highest microbial activity and the greatest breakdown occurred in the first 3 to 4 days. The end concentration was slightly above the Dutch A-level for unpolluted soil. On the basis of the

available data, preference cannot be given to either semicontinuous or batch incubation.

PROGRESS AND PERSPECTIVE

The production scale trials indicate that, at a soil temperature of approximately 22°C, oil can be decomposed within one week to an end concentration varying from <50 to 350 mg/kg dry soil. In this process, the highest microbial activity occurs in the first 3 to 4 days.

For the present Dutch situation, a soil-cleaning technique is only fully applicable if the end concentration of a contaminant is below the A-levels defined in the Interim Act on Soil Sanitation. For mineral oil in a standard soil (containing 10% organic matter) this A-level is 50 mg/kg d.s.

On the basis of the results of these experiments, soil treatment in the bioreactor cannot be guaranteed to achieve the required A-level for mineral oil. But the same is also true for land farming by which oil concentration is reduced to between 500 and 1,000 mg/kg d.s. after two years.
We must therefore conclude that, on the basis of current Dutch policy, there are no practical applications for the biotechnological cleaning of oil-polluted soil. Further research is recommended. In comparison to other techniques, biotechnological treatment is environmentally friendly and energy-saving, and the end product is a living, fertile soil. Further research should be directed not only to microbiological but also to environmental hygiene aspects.

Microbiological Aspects

Further laboratory and pilot scale studies would determine the optimal process parameters to increase biological availability and rate of oil breakdown, and to reduce the end concentration. Attention should be given to the effects of introducing selected microorganisms and chemical pretreatment. With a degradation time of up to one week, the bioreactor treatment is competitively priced with such other techniques as thermal decontamination.

Environmental Hygiene Aspects

The Dutch A-level for mineral oil was established on the basis of physical and chemical properties and the toxicity of oil products. However, during the biological breakdown process the oil changes in composition. This means that environmental hygiene characteristics, such as ecotoxicity and leaching, may have changed to such an extent that it would be appropriate to reconsider the risks to public health and the environment.

Compared with the oil-polluted soil, the components of biologically treated soil are less volatile, less soluble, and probably less toxic. Thus the question arises, to what extent is the A-level for mineral oil applicable to biologically treated soil?

There is draft legislation in the Netherlands (the "Concept Bouwstoffenbesluit" of 1989) which allows for the use of decontaminated soil with an end concentration above the A-level. The "Concept Bouwstoffenbesluit" states that decontaminated soil from which no environmental hygiene problem is expected may be used without restriction. To evaluate more precisely the

environmental hygiene quality of oil-polluted soil that is biologically decontaminated (and of soil in general), it is important that appropriate ecotoxicological tests (bioassays) and leaching tests be developed.

REMARKS

Recently in the Netherlands draft legislation on the use and re-use of building materials and soil is presented. This latest "Concept Bouwstoffenbesluit" (of July 9, 1991) allows for the use of decontaminated soil with oil concentrations up to a maximum of 250 mg/kg dry soil.
The production scale trials in the reactor indicate that end concentrations below 250 mg/kg ds will be reached. Therefore, based on the latest Dutch draft legislation, treatment of oil-polluted soil in the bioreactor can be regarded as a fully applicable soil-cleaning technique.

Ger van den Munckhof
Deventer, November 12, 1991.

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