Microbiological in situ remediation of an aquifer contaminated with waste oil from a refinery

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Abstract In an R&D project running from 1988 to 1993, a process was developed for the in situ remediation of the former Pintsch waste oil refinery site in Hanau, Germany. The study work was performed with regard to the entire scaling-up (batch tests → column tests → in situ box tests → field tests). As an optimum oxygen (or electron acceptor) supply is the most important factor in in situ remediation, the efficiency of the three electron acceptors was compared: oxygen ($O_2$); nitrate ($NO_3$); and hydrogen peroxide ($H_2O_2$). The developed process provides for the infiltration of two water cycles (primary and secondary cycle). Both cycles receive nutritive salts (N, P). The primary cycle purified in the groundwater treatment plant is additionally given $H_2O_2$, the deferrized secondary cycle additionally receives nitrate. In the in situ field tests, the hydrocarbons (HCs) and BTEX were efficiently microbially degraded using simple cycles supplied with different electron acceptors; the chlorinated hydrocarbons were preferentially washed out. At the end of the test, the hydrocarbon and BTEX concentrations were below the remediation target values stipulated for the groundwater, and the chlorinated hydrocarbon levels were drastically reduced.

INTRODUCTION

The microbiological remediation of complex contamination cases that moreover also have a large spatial extent continues to be a difficult task, and requires, in addition to microbiological techniques, generally a combination with chemical-physical process elements. When the research project on the development of microbial processes for the remediation of the "Pintsch-Öl" site in Hanau (Germany) commenced in 1988, this site was considered to be ideal for in situ remediation.

Pintsch-Öl comprises a land area of ca. 24 000 m$^2$, and is located on a peninsula between the river Main and the inland port of the city of Hanau. The former — now dismantled — industrial plant served for the refining of waste oil. An improper handling of feedstocks and final products and of wastes have led to a massive contamination of the soil and the groundwater with mineral oil hydrocarbons (HCs), benzene-toluene-ethyl benzene-xylenes (BTEX) and chlorinated hydrocarbons (CHCs), and a number of further contaminant classes in lower concentrations. The aquifer contains an inventory of 400-500 t HCs, 0.46 t BTEX, and 2.85 t CHCs. An oil phase of ca. 70 cm thickness was found floating on the groundwater table in the centre of the contaminated area.

As concerns the geological stratification, the topsoil consists of a heterogeneous layer of made ground of varying thickness (1-2 m), interspersed with building remnants
and debris. This is followed by a 0.5-1.8 m layer consisting of meadow loam flood deposits of the river Main, this mainly being sandy silt. Below the meadow loam follows, in depths of 3-9 m, Quaternary sands and gravels (Main terrace), interspersed with silt lenses of varying horizontal and vertical magnitudes. This layer has a relatively high hydraulic conductivity \( k_f = 10^{-3} \) to \( 10^{-4} \) m s\(^{-1}\). The groundwater table is located ca. 3.5 m below ground surface. At the basis of the sand layer, there is a 5-10 m thick sedimentary Tertiary layer (clays and silts), which functions as a barrier for water and contaminant.

Due to the encountered contaminant inventory and geology, the site can not be remediated with in situ technology alone. Instead, a four-phase remediation plan was drawn up. After the construction of an encircling bentonite sealing wall reaching down to the Tertiary, the Pintsch site could be considered as a hydraulically isolated basin. The installation of groundwater wells served purposes of hydraulic control and pumping-out of the oil phase (scavenger pump) (Phase I). The backfill and the meadow loam were purified microbially on site by means of the windrow technique (Phase II). The sand of the unsaturated zone and 0.5 m of the saturated zone were excavated and, because of the oil remnants partly still encountered in phase, decontaminated by means of soil washing (Phase III) (Ripper & Früchtenicht, 1989). After backfill of all the layers, the contamination remaining in the aquifer will be treated by means of in situ techniques (Phase IV).

The microbial degradation of the HCs mainly requires, beside nitrogen and phosphorus compounds, high quantities of oxygen donors (= electron acceptors; aerobic degradation). Beside these nutrients, the degradability of the contaminants is also regulated by physical-chemical parameters such as, among others, the pH-value and the redox potential, but also by the bio-availability (put in simplified terms: only substances dissolved in water can be degraded). The degradation of BTEX and CHCs is generally also possible under these aerobic conditions. Higher chlorinated CHCs can only be anaerobically decomposed, i.e. by using a process that excludes oxygen. However, these CHCs have a comparatively good water solubility, and can therefore be efficiently washed out.

As the hydrocarbons at the Pintsch site have a high proportion of long-chain (C > 20), non-water-soluble molecules (Wanior & Ripper, 1993), which can only be made accessible to biological degradation by drastic measures (e.g. intensive soil movements, and thus a high energy input, or by the massive application of surfactants and electron acceptors; cf. Held et al., 1993), the responsible authorities accepted that this immobile proportion remains as residual contamination in the soil, particularly as the groundwater here, at 4 m below terrain, has no exposure pathway. With further regard to (eco-)toxicological considerations, the following remediation target values were set for the groundwater: 500 \( \mu \)g l\(^{-1}\) HC, 50 \( \mu \)g l\(^{-1}\) BTEX (10 \( \mu \)g l\(^{-1}\) benzene) and 30 \( \mu \)g l\(^{-1}\) CHC (3 \( \mu \)g l\(^{-1}\) chloroethylene) (Held & Rippen, 1994).

On the basis of the site conditions (contaminant inventory, geology) and the microbiological requirements, the objective of the R&D project was to optimize the parameters, in particular to determine a suitable electron acceptor and to optimize the process engineering, and to determine the achievability of the remediation target values. This required performing the entire scaling-up from batch test over column test and in situ box tests through to field tests and finally full-scale remediation, whereby each individual scale provided answers to different issues. As much work on laboratory tests
has already been published elsewhere, we shall focus in the following particularly on the in situ box and field test scales.

Viable oxygen donors (electron acceptors) are: technical oxygen, hydrogen peroxide ($H_2O_2$), and nitrate ($NO_3^-$). These were examined in the laboratory and in the field tests (see below).

**Laboratory tests**

$H_2O_2$ is subject to an abiotic and biotic (enzymatic) splitting to $O_2 + H_2O$. $Fe^{2+}$, $Mn^{2+}$ and a series of unknown constituents function as abiotic catalysts. Batch tests with differently concentrated soil suspensions showed that $H_2O_2$ is subject to an immediate decomposition after infiltration into the soil of the aquifer.

We were able to show in column tests that the released oxygen is transported successively ever further along the direction of flow of the infiltration water, the further the decontamination (microbial HC degradation and chemical oxidation of the $H_2O_2$ break-up catalysts) progresses. It can therefore be assumed that the impact of the $H_2O_2$ is, at least in the early phase of decontamination, locally contained.

Column tests with nitrate-supplied columns (Column I: 475 mg l$^{-1}$ $NO_3^-$, Column II: 475 mg l$^{-1}$ $NO_3^- + 200-500$ mg $H_2O_2$) showed no significant differences in the denitrification rate (measured as $NO_3^-$ depletion, i.e. the difference between the $NO_3^-$ concentrations at the inlet and outlet) (Fig. 1). The maximum $NO_3^-$ depletion rates were calculated at 3.5 mg h$^{-1}$ (kg d.m.$^{-1}$) (d.m. = dry matter) (Column I) and 2.8 mg h$^{-1}$ (kg d.m.$^{-1}$) (Column II). It must be noted, however, that nitrate depletion already breaks down at a residual HC concentration of ca. 50%, while $O_2$ depletion (from $H_2O_2$) continues.

Nitrate infiltration does otherwise lead to a low degradation efficiency, but on the other hand also to a certain long-distance effect due to its low retardation in soil.
Thereby it is to be noted that high oxygen contents in the groundwater impede denitrification. Finally, the expensive H₂O₂ can at least partially be substituted by the less costly nitrate.

**In situ box tests**

With the *in situ* boxes (Fig. 2) (100 × 50 × 40 cm), we were able to closely simulate the *in situ* measures, and in particular to completely inventorize the degradation processes in the soil. Moreover, the tests permitted the monitoring of process engineering problems. These include: the detection of regions undersupplied with O₂ (through formation of black FeS); the formation and microbial reformation of O₂ bubbles in the soil (after massive H₂O₂ infiltration); the remobilization of the residual oil saturation and the formation of oil droplets due to hydromechanical stresses on the soil; and the influence of the location of infiltration (i.e. either above the groundwater table or at the bottom of the aquifer).

The monitoring of the O₂ and CO₂ concentrations in the soil vapour and of the O₂ concentrations in the groundwater (sampling points I-IV) showed that an efficient O₂ utilization and thus an HC degradation takes place, even when the normally applied H₂O₂ concentration of 1000 mg l⁻¹ was drastically raised in brief intervals to 5000 mg l⁻¹. Such high concentrations did, however, lead to O₂ bubble formation, this strongly reducing the hydraulic conductivity of the soil. After interrupting H₂O₂ infiltration, the bubbles receded microbially within 2 to 3 days. At 0.6-0.7% of the total HC inventory, the hydromechanical output of dissolved HCs within ca. 430 test days was low.

An inventorization of hydrocarbon degradation revealed precisely the value calculated (by means of stoichiometric factors) on the basis of the infiltrated H₂O₂ quantity in the case of infiltration into the saturated soil zone, and ca. 12% lower value in the case of infiltration into the unsaturated zone.

The *in situ* box thus proved itself as a valuable tool for the simulation of full-scale *in situ* remediation.

![Fig. 2 Process scheme of the in situ box tests.](image-url)

- contaminated Pintsch sand (< 4 mm) (unsaturated)
- contaminated Pintsch sand (< 4 mm) (saturated)
- filter gravel (4 - 8 mm)
- sampling points for soil eluate
Field tests

Using the previous examinations as basis, the process schematically shown in Fig. 3 was implemented in the field tests. The five *in situ* cells (5 × 10 m) were each encapsulated with bentonite sealing walls. The water enriched with mineral salts (8 mg l⁻¹ PO₄²⁻, 4 mg l⁻¹ NH₄⁺) was piped through five lines, loaded with NO₃⁻ (200 mg l⁻¹, Cell I), O₂ (40 mg l⁻¹, Cell II), and H₂O₂ (500 mg l⁻¹, Cell III), and infiltrated in the bottom of the cells (0.4 m³ h⁻¹). Cells IV and V served as control cells. The withdrawn groundwater was purified in the water treatment plant prior to its renewed infiltration. Soil vapour and groundwater were sampled at a number of measuring points. The monitoring programme covered physicochemical, microbiological and analytical parameters.

During an initial infiltration in the region of the groundwater table, distinct H₂O₂ losses caused by degradation and emanation in the unsaturated zone and a preferential flow of the infiltrated water along the cell bottom were found. In the subsequent refilling phase (524th to 651st day), the infiltration wells were extended down to the Tertiary, and infiltration implemented over the entire depth of the aquifer. The meadow loam and made ground were excavated, and additional surface irrigation (average: 0.1 m³ h⁻¹, intermittent operation) installed.

While in the first test phase CO₂ production and O₂ consumption proved the presence of microbial processes in the unsaturated soil zone, after the excavation of the upper soil layers an equilibrium was established between the soil vapour of the highly permeable sand and the atmosphere.

In the following, we present the most important results. The optimum C:N:P ratio for aerobic degradation is 100:10:1; but substantially larger quantities of phosphate had to be infiltrated, presumably because of its strong binding to the soil matrix. The NH₄⁺ and PO₄³⁻ concentrations were considered to be optimal when their concentration in the discharging well figured almost zero.

This boundary condition was also used for the NO₃⁻ and H₂O₂ infiltration, with the difference that these two substances were subject to maximum infiltration concentrations. If the nitrate concentration becomes too high, then for energetic reasons.

![Fig. 3 Process scheme of the *in situ* field tests.](image-url)
only a bacterial reduction to nitrite (NO$_2^-$) takes place, which then accumulates and has toxic effects on bacteria. The strongly oxidizing H$_2$O$_2$ is considered to be toxic at concentrations > 1000 mg l$^{-1}$. These considerations lead to the optimum infiltration concentrations of 200 mg l$^{-1}$ for NO$_3^-$, and 500 mg l$^{-1}$ for H$_2$O$_2$. The infiltration of dissolved O$_2$ was restricted to its limit of solubility (40 mg l$^{-1}$).

Contaminant elimination took three paths: microbial degradation, hydraulic washing out (0.7-1.0% of the total HC inventory), and remobilization and recovery of the residual oil saturation (0.2-1.1% of the total HC inventory). Microbial degradation is thus the elimination path of prime importance. At the same time, as had already been shown by the in situ box, a massive shifting of contaminants took place, that could scarcely be registered by groundwater or soil sampling, and distorted the inventorization of the degradation tests; this effect was particularly pronounced in the Cells IV and V, which had far higher contaminant levels at the beginning of the tests. Ultimately, the development over time of the HC (shown for Cell III and IV in Fig. 4), BTEX and CHC concentrations in the groundwater of the five in situ cells revealed no significant divergences with respect to the different electron acceptors that were infiltrated. The electron acceptors were therefore assessed on the basis of indirect parameters, which showed H$_2$O$_2$ to be the efficient electron acceptor.

The CHCs — which can only relatively poorly be microbially degraded under the given conditions — were efficiently washed out (Fig. 5). Proceeding from a start concentration of ca. 67 000 $\mu$g l$^{-1}$, the CHC reduction during the first part of the test was practically linear against an exponential axis, and can be described by the following equation:

$$C_t = C_{0(1)} e^{-k_t t}$$

(1)

$k_t$ is influenced by the flow conditions in the aquifer (determined by the soil parameters), the water throughput, the contaminant concentration adsorbed to the soil (Tursman & Cork, 1992), and the diffusion from soil pores (Grathwohl, 1992). From roughly the 300th day onwards, the contaminant tailing evidently sets in, which can also be approximately described by a first order exponential equation:

![Figure 4: Development over time of hydrocarbon concentration in groundwater of two in situ cells (measuring point: central multilevel piezometer).](image)
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Fig. 5 Development over time of CHC concentrations in groundwater of the in situ cells (values averaged over all five cells).

\[ C_t = C_{0(2)} e^{-k_{2}t} \]  

(2)

Beside the parameters determining \( k_1 \), \( k_2 \) also depends upon further factors, in particular the adsorption/desorption, the self-encapsulation, and others (Schattney, 1992; Seifert & Schecker, 1993).

After switching off the infiltration during the refitting phase (524th to 651st day), higher CHC levels developed again in the groundwater due to the transition from a dynamic to a stationary equilibrium at a higher level. The washing out of these CHCs approximately followed equation (1). Due to the low starting level, however, the tailing set in sooner in this phase. As both effects overlap, we can add equations (1) and (2) to give:

\[ \ln C_t = \ln C_0 - t (k_1 + k_2) \]

with \( C_0 = C_{0(1)} + C_{0(2)} \)  

(3)

With this empirically derived equation, we can calculate a time requirement of ca. 6 years to reach the remediation target value of 30 \( \mu g \) L\(^{-1}\) CHC.

Soil sampling showed good elimination rates for HCs, very high rates for chlorinated HCs, and almost complete elimination for BTEX. However, the results were statistically relatively uncertain due to the highly heterogeneous soil-bound contaminant distribution.

At the end of the in situ field tests, after the contaminant concentration had already been in the tailing phase for several hundred days, it was examined whether switching off the infiltration followed by brief infiltration intervals would lead to a rise in concentrations comparable to that in the first refitting phase. As Fig. 6 shows, the contaminant concentrations remained almost uninfluenced by these measures, and the HC and BTEX levels remained consistently below the remediation target values (with the exception of the HC concentration in Cell III). The CHC levels were, as expected, above the remediation target value. The observed relatively high variations in the measured values are due to the circumstance that the concentrations of the individual substances are in the region of the detection limit. Only the hydrocarbon concentration
Fig. 6 Development over time of CHC, BTEX and hydrocarbon concentrations in groundwater during intermittent infiltration of the in situ cells.
in Cell III ($H_2O_2$-loaded) showed a distinctly rising tendency. This can be explained by solubilization effects due to the relatively high microbial activity in Cell III, and the thereby formed biosurfactants.

The balance shown in Table 1 summarizes the results. The stated theoretical hydrocarbon mineralization is based on a purely stoichiometric oxidation of the hydrocarbons on the basis of the quantity of infiltrated electron acceptors (Held et al., 1993).

In the three in situ cells supplied with electron acceptors, which all had relatively similar contamination inventories when the tests commenced, Cell III ($H_2O_2$) displayed the best total elimination, and the lowest ratio between experimental and theoretical elimination. The higher this ratio is, the more probable is the output of partially oxidized metabolites that are not detected by means of the utilized measuring method (infrared spectroscopy), and the more probable is the presence of massive contaminant shifting, as it is only this that can explain the apparently high elimination rates in the control cells IV and V.

Outlook

The results of the R&D project were sufficient to be able to plan the full-scale in situ process. After installing the infiltration and pumping facilities, in situ remediation will commence in early 1995. The process comprises two cycles. Both receive nutritive salts.

The primary cycle ($100 \text{ m}^3 \text{ h}^{-1}$) purified in the groundwater treatment plant will receive $H_2O_2$, and be infiltrated by means of infiltration wells in a plot accounting for a quarter of the surface area of the Pintsch site. The deferrized secondary cycle ($100 \text{ m}^3 \text{ h}^{-1}$) will receive nitrate, and be infiltrated in a second plot. The infiltration plots will rotate at specific intervals yet to be optimized. Groundwater withdrawal will be by means of a gravel packing installed at the elevation of the groundwater table. A duration of remedial action of about 5 years is expected.

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