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Protection of Groundwater Resources at Industrially Contaminated Sites PURE, WP7

In-situ technology for the simultaneous remediation of the saturated and unsaturated zones by co-solvent flooding (CSF) and thermally enhanced soil vapour extraction (TSVE)

<u>Goals</u>

The remediation efficiency of state-of-the-art in-situ remediation technologies (pump & treat) is often limited by the low solubility of organic contaminants and consequently long remediation times. In particular, this often causes problems when groundwater aquifers are contaminated with free phase product or residual free phase product.

Within the framework of the EU research project, PURE, an in-situ technology for the simultaneous remediation of the saturated and unsaturated zones was to be developed. It was intended to combine both remediation technologies: co-solvent flooding (CSF) and thermally enhanced soil vapour extraction (TSVE), and develop the technologies with respect to the industrially contaminated sites of the project partners. The technologies applicability was to be verified during hydraulic and remediation investigations in Large Tank experiments.

Research framework PURE

The research project PURE (Protection of Groundwater Resources at Industrially Contaminated Sites) is funded by the European Commission within the Fifth Framework Programme. The objective of the project was to provide innovative/cost effective solutions for the management of industrially contaminated sites in terms of the site characterization, site assessment and site remediation (Fig. 1). The project is carried out by a consortium of 13 members including 4 industrial site owners as problem-holders, 2 service providers as end-users and 8 R&D performers. At VEGAS a group worked on the subproject WP7 "Simultaneous remediation of the saturated and the unsaturated zone".



Figure 1: illustration of the framework of WP7

The overall objective of WP7 was the further development, the examination and the transfer of the two existing remediation concepts co-solvent flooding (CSF) for the saturated zone and thermally enhanced soil vapour extraction (TSVE) for the unsaturated and saturated zone into technologies for use under natural conditions as well as in combination with each other. The expected output was a design of a full-scale application of TSVE and/or CSF for the unsaturated and the saturated zone, including an evaluation of its economical feasibility. This design should be realized in a pilot scale application of TSVE and/or CSF at an industrially contaminated field site owned by one of the project partners.

Technology Co-Solvent Flooding (CSF):

Alcohol flooding is used to remediate aquifers from contaminated source zones. A well directed alcohol injection and extraction is necessary to flush the alcohol respectively the alcohol mixture through the contaminated zones in the aquifer.

In comparison with normal P&T methods the removal rate is higher and the remediaton time is shorter with alcohol flushing. The contaminant is removed by solubilisation and controlled mobilization. By choosing a suitable alcohol for the contamination, the solubility of the contaminant will be increased and the interfacial tension between the water and organic phase will be decreased.

An important criterion for alcohol flushing is the contaminant density. LNAPLs (Light Nonaqueous Phase Liquid) can be removed by a mixture consisting of a single alcohol and water because the mobilised contaminant is always hydraulically controllable as a result of density differences. Removing DNAPLs (Dense Nonaqueous Phase Liquid) from an aquifer is more difficult because of the high risk of a downward migration (mobilised DNAPL). A suitable alcohol cocktail with lipophilic fractions can lower the DNAPL density as far as the former

DNAPL is hydraulically controllable. A vertical upward flow is necessary for a well directed alcohol cocktail injection and to prevent uncontrolled DNAPL downward migration.

For ecological and economic reasons, the extraced alcohol-water-contaminant mixture is separated and the alcohol can be reused for further alcohol flushing (waste water treatment/alcohol recycling).

To remediate saturated and unsaturated zone CSF will be applied to prior remediate the saturated zone, then groundwater fluctuation zone and the unsaturated zone will be remediated by thermally enhanced soil vapour extraction (TSVE), see Fig.2.



Figure 2: Schematic of the simultaneous remediation of the saturated and unsaturated zones by the combination of CSF and TSVE

Technology steam-air-injection (TSVE, subTSVE)

The injection of a steam-air mixture below the water table (subTSVE) heats both zones quickly, increasing significantly the volatility of the contaminants. The increase in temperature increases the extraction rate of the contaminants compared to those of a standard (cold) Air-Sparging application and soil vapour extraction. The remediation time is significantly reduced. SubTSVE extends the range of application of steam-air remediation processes from the injection in the unsaturated zone (TSVE) to remediate parts of the groundwater and the capillary fringe.

The investigations were based on previous research work concerning TSVE, in German "TUBA" technology by the group of Färber A. (1997), Betz C. (1998) and Schmid R. (2001). Schmid had investigated the steam-air injection into the saturated zone during small scaled Flume experiments. Outstanding was to enhance the technical development of SubTSVE on a site related scale and investigate technologies performance during large scale experiments. The remediation efficiency and steam propagation was to be investigated to define technological requirements and costs of following field trials and field site remediation activities.



Figure 3: Schematic of the simultaneous remediation of the saturated and unsaturated zones by subTSVE

Procedure

Technology Co-Solvent Flooding

The further development of co-solvent flooding (CSF) was directly linked to two of the four industrially contaminated field sites owned by the project partners. A series of column experiments was carried out to optimize the process parameters of CSF for the aquifer material and contaminant cocktail from the selected sites.

Based on the results of the column experiments the influence of the upward directed flow velocity of the alcohol mixture on the stability of the alcohol plume was investigated in a 2D-flow domain. Aside from the stability study a remediation experiment was carried out in the flume to determine the efficiency of alcohol flushing by applying the aquifer material and the contaminant cocktail from the field site.

To determine the remediation efficiency of alcohol flooding under site realistic conditions two remediation experiments were conducted in one of the large VEGAS-containers with a length of 9 m, a width of 6 m and a height of 4,5 m.

The first experiment combined the sequential application of CSF and SubTSVE to remediate the saturated as well as the unsaturated zone and the capillary fringe. During the second CSF experiment the investigations focussed on hyraulic control and remediation performance of CSF in the saturated zone.

Based on the results obtained by this experiment a cost estimation of a field application and an evaluation of the economical feasibility was carried out.

Technology steam-air-injection

The development of the remediation technology for the simultaneous remediation of the saturated and unsaturated zones was based on two industrially contaminated sites (site 3 and 4). The sites were first characterised after a critical review of their data.

The relevant soil parameters (specific heat capacity and permeability) at the sites were determined in 1-D column experiments. The remediation efficiency of the thermally enhanced soil vapour extraction was determined in 2-D flume experiments for the injection of steam into the saturated zone (SubTSVE) using soil and contaminants from the sites.

From large-scale experiments, when one of the large tanks at VEGAS was filled with soil from one industrial site, the results of the laboratory experiments were transferred to the field scale. The technology of steam-air injection in the saturated zone was developed for the application according to site specific conditions.

Based on the data and experience gained during the technical scale experiment a full scale remediation for a site owned by one industrial partner was to be designed. The design included time, setup and operation of technology-specific treatment units and financial aspects. In cooperation with a service provider the costs for the application of SubTSVE were compared to those of the combined standard remediation techniques Air-Sparging and Soil Vapour Extraction operated at that site.

<u>Results</u>

The results of the site characterisation are summarized in Table 1.

Table 1: Characterisation of the industrially contaminated sites

site 3		site 4					
Contamination and spacial distribution		·					
BTEX:		BTEX, CHC:					
source zone: 7.000 m ² up to 10 m depths,		2.000 m ² up to 10 m depths (BTEX,) up to 27					
plume zone: 30.000 m ² up to 5 m depths		m depths (CHC)					
	Concentrations	of contaminants					
HC	BTEX	BTEX	CHC				
groundwater (mg/m ³)	1	1	1				
Ø 7800, max. 44600	Ø 6111, max. 53400	Ø 15700, max.92300	Ø 1160, max.26700				
soil vapour (mg/m³)	1	1					
not determined.	Ø 21, max. 120	Ø 250	Ø 160				
soil, saturated zone (mg/kg)							
Ø 433, max. 1350	Ø 3,28, max. 15	Ø 170,max. 700	n.b.				
soil, unsaturated zone	(mg/kg)						
Ø 391, max. 637	Ø 1850, max. 3020	highly contaminated sourece zone (0- 2 m bos) excavated					
	Geo	ology					
Rhine valley:		Rhine valley:					
loam: 0 - 4,5 m u. GOk	<	loam: 0 - 4,5 m bgs					
middle sand layer: 4,5	- 12,5 m bgs	coarse gravel layer: 4,5 - 6,9; fine sand: 6,9 -					
fine sand and fine grav	vel layer: 12,5 - 30 m	14,2 m bgs					
bgs		fine and middle sand layer (loamy): 14,2 -					
coarse gravel layer (sa	andy): $30 - > 37$ m bgs	18,5 m bgs					
aquiciude: sandy silt, c	ay: > 37 m u. bgs	fine gravel layer (sandy): 18,5 - > 21 m bgs					
		aquiclude: sandy silt clay: > 28 m u GOK					
	Hydr	ology					
system coupled to rive	r Phino	system offluent toward	le rivor Phino				
average water table. 8	mhas	average water table: 6.3 m bas					
effluent towards river Rhine for low water		high water table: 39.6 m. asl (4.8 m. bos)					
table (35 m asl 10 m bas)		low water table: 36.6 m. asl (7.8 m. bgs)					
parallel to river Rhine for medium water table		Itravel rate of groundwater: 0.3 m/d					
(37 m asl)							
diffluent from river Rhir	ne for high water table						
(39 m asl)							
travel rate of groundwa	ater:						
medium water table: 0,43 m/d							
low water table: 0,2 m/d							
high water table: 0,9 m	n/d						

The saturated and unsaturated zone of both sites are contaminated by BTEX and aromatic hydrocarbons (with higher boiling points). The relevant soil characteristics for the remediation technology were determined during laboratory investigations.

Technology Co-Colvent Flooding

Column experiments

A set of column experiments was carried out using the aquifer material (Fig. 4) and the contaminant cocktail of the respective field sites.



Figure 4: Grain-size distribution of the used porous media

The aquifer material in the column was residually saturated with the site specific contaminant cocktail. The sand pack was then flooded from the bottom to the top of the column with the alcohol mixture consisting of 60 % (v/v) isopropanol und 40 % water (v/v). After the injection of three pore volumes of the alcohol mixture 75 % of the initial contamination were recovered at the outflow of the column (Fig. 6).

Subsequent to an additional injection of three-and-a-half pore volumes of water to rinse out the isopropanol the sand pack was sampled and analyzed. The analysis resulted in a residual contaminant content of approx. 0.1% of the initial contamination, the residual isopropanol content was less than 1 %.



Figure 5: Experimental setup of column experiments



Figure 6: Cumulative fraction of NAPL recovered vs. injected pore volumes

At the beginning of the column experiment the outflow consisted of two phases: one aqueous and one non-aqueous phase. The density of the aqueous phase was around the density of water while the density of the non-aqueous phase matched the density of the contaminant cocktail (Fig. 7).



Figure 7: Density of the aqueous and non-aqueous phase vs. injected pore volumes

The occurrence of two phases indicates that at initially only small amounts of the isopropanol partitioned into the NAPL, the LNAPL was therefore mainly removed by mobilization. With increasing numbers of flooded pore volumes, more and more of the alcohol mixture partitioned into the NAPL, leading to a growing importance of solubilisation. After two injected pore volumes the effluent consisted of only one phase, it can therefore be assumed that by this time the contaminant cocktail was exclusively removed from the sand pack by solubilisation. The increasing density of the effluent towards the end of the flooding period is due to the increasing water content in the sand pack during the rinsing period.

Box experiments (2D)

During a field application of the remediation technology a hydraulically controlled flushing of the contaminated zone is of greatest importance. During vertically upward displacement of the pore water by the alcohol mixture instabilities can occur due to the low density of the alcohol mixture. Driven by buoyancy forces the alcohol mixture migrated upward while the water migrated

downward. The migration of both fluids created an instable flow regime. To prevent the occurrence of instabilities a minimum upward flow velocity of the alcohol mixture is needed. With increasing vertical upward flow velocity viscosity effects become more and more important. Since the viscosity of the alcohol-water mixture is approximately four times that of water, much higher pressure gradients are required within the alcohol plume. The high pressure gradients within the alcohol plume prevent a downward migration of the water while the smaller pressure gradients within the domain filled with water are unfavourable for an upward migration of the alcohol mixture. The high viscosity of the vertically upward displacing fluid thus stabilises the flow regime. At a certain upward flow velocity the high viscosity of the alcohol mixture compensates for its low density. From this Darcy velocity on no instabilities and thus no fingering will occur.

To investigate this issue a set of visualisation experiments was conducted in a 2D flow domain (0.60 m high, 1.40 m long and 0.08 m wide) packed as uniformly as possible using the uncontaminated aquifer material from the site (HOFSTEE et al. 1998).



fiberoptical fluorometers





Figure 8: Front and side view of the 2D-setup

The visualisation experiments showed a strong fingering of the alcohol mixture dyed with uranine at a mean Darcy flow velocity of 0.7 m×d-1 (Fig. 9, on the left) whereas no instabilities were observed during the experiment conducted with a mean Darcy flow velocity of 5 m×d-1 (Fig. 9, on the right).





Figure 9: Front view of the flow domain during the visualisation experiment using a Darcy velocity of 0.7 m×d-1 (picture on the left, flushing time: 480 min) and 5 m×d-1 (picture on the right, flushing time: 120 min)

As a next step a remediation experiment was carried out in the flume to determine the efficiency of the technique. A contaminant source zone between the injection and extraction well was created by injecting 220 g of the site specific contaminant cocktail (44 % m-/p- xylene (m/m), 35 % 1, 2, 4 trimethyl-benzene, 13 % o-xylene, 4 % 1, 3, 5 trimethylbenzene, 2 % ethylbenzene and 2 % toluene) into the sand pack by means of three long cannula connected to a syringe. A mean vertical upward Darcy velocity of 2 m/day was applied and the effluent was continuously sampled. Based on the measured contaminant concentrations, the weights and the densities of the extracted fluids a cumulative recovery of the contaminant cocktail at the outflow of the flume was calculated (Fig. 10).





Figure 10: Recovery of the contaminant mixture and cumulative mass discharge of isopropanol at the outflow of the flume over injected pore volumes.

From the analysis of the outflow samples a mass of extracted contaminant cocktail was calculated of about 182.02 g. As initially 219.61 g of the contaminant cocktail were introduced into the filling this leads to a recovery of 82.88 %. The analyses of the soil samples taken after completion of the experiment showed a very heterogeneous distribution of the contaminant cocktail in the filling with concentrations between 0.5 mg and 542.8 mg per kilogram of dried soil. Averaging all measured soil concentrations results in a concentration of 73.11 mg contaminant cocktail per kilogram dried soil. Since the flume contained 116.86 kg of dried soil around 8.54 g of the contaminant cocktail were left in the whole filling after it had been flooded with the alcohol cocktail. This corresponds to a remediation efficiency of around 96.11 %. The discrepancy between the remediation efficiency and the recovered contaminant cocktail of more than 10 % can be attributed to the averaging procedure and to losses of the contaminant by volatilisation during sampling and sample preparation. By taking in account the measuring accuracy and the volatilisation losses a remediation efficiency of approx. 90 % is more realistic.

3D pilot study

Based on the experiences made on 1D- and 2D- scale the influence of the third dimension on the remediation efficiency and the required pore volumes of the alcohol mixture were investigated in a 3D-pilot study. The experiment was conducted in one of the large VEGAS containers which measures a length of 6 m, a width of 3 m and a height of 4 m. The container

was packed with natural soil material from a project partners owned "site 3".



start of container packing



packing of fine sand lens



installation of temperature

sensors

Installation of groundwater drainage pipes



installation of vertical wells



covering fine sand top layer

Figure 11: Filling and instrumentation of VEGAS large container

A contaminant source zone of approx. 2 m³ was created by injecting 15 kg of the site-specific TEX and trimethylbenzene mixture into the sandpack. Then the alcohol mixture consisting of 60 vol-% isopropanol was injected at the middle horizontal well and the two multi-level vertical wells were used for the extraction of the alcohol mixture loaded with contaminants (Fig. 12).



Figure 12: Operation of co-solvent flooding during remediation

The groundwater table was kept constant by means of 30 cm thick gravel pack drainage system located around the container boundaries Approximately 80 sampling ports were located in the saturated zone to determine contaminant and alcohol distribution and flow field.

The extracted alcohol-water-LNAPL mixture was purified and re-injected by H2. The groundwater capturing system was formed by the four vertical extraction wells (E1 to E4) installed around the centre of the container. The groundwater extracted at the wells E1 and E4 was purified and re-injected through the horizontal wells H1 and H3, located at the hydraulic boundaries of the flow regime. The fluids extracted at E2 and E3 were purified and re-injected into the aquifer by H2 due to their high isopropanol concentrations.

Following the alcohol and water flooding period, the remediation was continued by injecting a steam-air mixture into the saturated zone through the lowest screened level of the injection wells I1 and I2 (Fig. 13). The water table was located at a height of 2.3 m above container ground, approx. 1 m above the screened level of the steam injection. The groundwater capturing system was operated with a total extraction rate at the wells E1 to E4 of 700 l/h.The injection rate of steam-air was maintained between 30 - 45 kg/h steam-air. The soil vapour extraction rate was maintained at 80 m³/h for all wells E1 – E4.

Prior to the remediation experiment the contaminant mixture mass of approximately 25 kg was infiltrated by injection capillaries during lowering the water table. The contaminant was smeared along the groundwater fluctuation zone (Fig. 13).





Figure 13: Principle of operation of SubTSVE during combined remediation experiment

By the 78-hour alcohol flood (approx. three pore volumes) only approx. 30 % of the contaminant in place were removed (Fig. 14). According to the analysis of the extracted and injected fluids approx. 105 % of the injected alcohol mass (3040 kg) could be recovered during the alcohol injection period and the three days long water flooding period. One-third of the recovered isopropanol was extracted at the wells I1 and I2, approx. two-thirds at E2 and E3 and only less than 1 % at E1 and E4. Of the extracted isopropanol approx. 73 % were recycled downstream the activated carbon filters.

The observed low remediation efficiency can mainly be attributed to the drop of the isopropanol concentration in the injected alcohol mixture after ten hours of CSF application caused by the break down of a pump. Due to the drop of the isopropanol concentration the initially steeply increasing concentration of the contaminants in the extracted fluids strongly decreased. After approx. 13 h of CSF application the isopropanol concentration in the injected alcohol mixture increased but, as a result of the dilution by groundwater, the initial high isopropanol concentration of the alcohol mixture could not be regained.







A second reason for the low remediation efficiency is the observed flow field which differed from the numerical simulations. The high recovery rate of isopropanol at the extraction wells E2 and E3, both being part of the groundwater containment, indicated that the alcohol was short circuiting from the injection well into the extraction wells of the groundwater containment resulting in an insufficient flooding of the source zone.

Subsequent to the rinse out of the isopropanol the SubTSVE technology was applied to clean up more than 75% of the total infiltrated mass during 2 days of steam-air injection. In total about 95% of the contaminant mass was recovered. About 3 % of the total contaminant mass was extracted from the groundwater table since the air injection rate was selected to low to avoid the condensation of the contaminants close to the extraction wells.

Total extracted LNAPL combined remediation experiment	CSF	SubTSVE		
LNAPL by phase extraction	<0.1%	3.1%		
LNAPL by condensed soil vapour		8.5%		
aqueous solved LNAPL	< 0.1%	0.4%		
sorbed on activated carbon	17.2%	66.3%		
soil after steam	< 0.1%			
recovered by co-solvent flooding	17.2%			
recovered by steam injection		78.3%		
total recovery	95.	5%		

 Table 2:
 Kind of recovery of contaminants during combined remediation experiment

In order to prove the contaminant removal potential of CSF for a proper designed hydraulic remediation avoiding technical problems a second CSF remediation experiment was conducted on the pilot scale of the large container.

The simulation of the isopropanol propagation within the large *VEGAS* container using the Modflow code and an injection rate of the alcohol mixture at the middle horizontal well of 160 l/h and an overall extraction rate at the two vertical wells of 200 l/h resulted in an isopropanol distribution after two days of alcohol injection shown in Fig. 15. As can be seen from the particle tracking plot, after 2 days the contaminant source zone was flushed thoroughly by the alcohol mixture which was very promising for the physical experiment.



Figure 15: Simulated isopropanol distribution after 2 days of alcohol flushing

During the CSF application a constant high isopropanol inlet concentration between 380 mg/l to 450 mg/l was mainained. After two days of alcohol flushing the measured isopropanol concentrations in the groundwater of the aquifer model indicated that the contaminant source zone was flushed by the alcohol mixture thoroughly. This was in accordance with the results of the numerical simulation.

Approx. 88 % of the initial contaminant mass were extracted after an injection period of the alcohol mixture of four days (Figure). After additional ten days of water injection the used isopropanol was completely recovered.



---- Contaminant concentration [mg/l] ---- Cumulative contaminant mass removal [%]

Figure 16: Contaminant concentration in the extracted fluids and cumulative contaminant mass removal over time of injected alcohol mixture.

Based on the results of the second CSF application on pilot scale it can thus be concluded that this remediation technique is both efficient and safe.

The CSF technology is especially beneficial for the remediation of sites contaminated by DNAPLs since an uncontrolled downward migration of the contaminants which might occur by reducing the interfacial tension between the aqueous and organic phase can be prevented by choosing the right co-solvent and upward flow velocity.

The remediation of a DNAPL spill was investigated during a feasibility study concerning the contaminant source zone remediation of a carbondisulphid spill in the saturated zone on a former production site owned by one of the industrial project partners and located in England

The results and gained experience of the PURE project were transferred to define the required mass of alcohol and its recycling technology. During additional investigations in 2D experiments the expected mass removal of CS2 were determined and the costs for CSF were estimated in comparison to standard hydraulic remediation activities based on the flume and large tanks experiments.

Standard hydraulic remediation was estimated to be less expensive than CSF. Additionally there was found another advantage of the hydraulic remediation. Investment costs are comparatively low compared to CSF. The higher consumable and maintenance costs for a longer lasting hydraulic remediation strengthens the economical aspect since less cash flow is required at the very beginning of the project.



Figure 16: cost comparison of Co-Solvent-Flooding versus hydraulic remediation of a $\mbox{CS}_2\mbox{-spill}$ in England

Technology Steam-Air Injection

The basic soil properties for a steam-air were determined and summarized in table 3.

Table 3: Characteristic soil parameters for both industrial sites

	site 3						
	DPS6 1-2 mbgs	DPS6 1-3 mbgs	DPS19 3-4 mbgs	DPS20 4-7 mbgs	DPS6 7-8 mbgs	samples 4-5 mbgs	samples 4-5 mbgs
Bulk density (kɑ/m³)	n.m.	n.m.	n.m.	n.m.	n.m.	1,68	1,73
Heat capacity (kJ/(kgxK))	n.m.	n.m.	n.m.	n.m.	n.m.	1	.11
Porositγ (-)	n.m.	n.m.	n.m.	n.m.	n.m.	0,32	0,30
Hydraulic conductivity (m/s)		2,0E-04	n.m.		1,8E-04	1,6E-04	1,9E-04
d ₁₀ (mm)	0,350	0,236	0,292	0,380	0,369	0,195	0,217
d50 (mm)	0,745	0,586	0,646	0,775	0,696	0,392	0,434
d ₈₀ (mm)	2,914	2,717	1,285	2,976	2,041	0,672	0,774
	site 4						
	site 4						
	Gas station 2-4 mbgs	Gas station 4-5 mbgs	Gas station 5-6 mbgs	Gas station 6-7 mbgs	Gas station 7-8 mbgs	Gas station 9-10	erial nents
Bulk densitγ (kg/m³)	a Gas station 2-4 mbgs	Gas Notation 14-5 mbgs	Gas 1- station 06-6 mbgs	Gas station 7 mbgs	⇒ Gas ∋ station 7-8 mbgs	⊐ Gas ∋ station 9-10	naterial eriments
Bulk densitγ (kg/m³) Heat capacitγ (kJ/(kgxK))	as Gas Bation 2-4 mbgs 2-4 mbgs	Gas N station 0 4-5 mbgs	Gas Gas 08' L station 6' 6 mbgs	Gas 1 station 86-7 mbgs	ia ia Gas ia is station 7-8 mbgs	ra ra Gas ra station 9-10	= material xperiments
Bulk density (kg/m®) Heat capacity (kJ/(kgxK)) Porosity (-)	7 ation Battion 2-4 mbgs	Gas Cas 007 2 4-5 mbgs	Gas Gas 160 180 5-6 mbgs	Gas B ¹ L station B ⁶ -7 mbgs	ra ra Gas ra ra Gas ra station 7-8 mbgs	ra ra Gas ra ra Gas ra station 9-10	ed = material n experiments
Bulk density (kg/m³) Heat capacity (kJ/(kgxK)) Porosity (-) Hydraulic conductivity (m/s)	site 4 Bastation n.m. n.m. n.m. 2,1E-04	Gas Gas 00 ¹ 2 2 ¹ 0 4-5 mbgs	Gas Gas 160 7-6 mbgs 170 170 10 10 10 10 10 10 10 10 10 10 10 10 10	Gas Gas 1, station 1,9 6-7 mbgs	Cas 7-8 mbgs 7-8 mbgs 7-8 mbgs	0-10 n.m. n.m. 0-10 2-10 2-10	arked = material id in experiments
Bulk density (kg/m³) Heat capacity (kJ/(kgxK)) Porosity (-) Hydraulic conductivity (m/s) d ₁₀ (mm)	site 4 station n.m. n.m. n.m. 2,1E-04 0,313	Cas Cas 2,00 4-5 mbgs 2,0 2,0 3,1E-05 0,361	20,221 0,21 0,21 0,21 0,21 0,21	20,30 0,30 0,30 1,95-04 0,287	2,4E-04 0,295 0,295	0-10 station n.m. n.m. n.m. n.m. 2,1E-04 0,210	marked = material used in experiments
Bulk density (kg/m³) Heat capacity (kJ/(kgxK)) Porosity (-) Hydraulic conductivity (m/s) d10 (mm) d50 (mm)	site 4 Statiou n.m. n.m. 2,1E-04 0,313 0,848	2,00 9,25 0,25 0,25 0,25 8,1E-05 0,361 0,361 0,917	s6 9-9 0,94 0,94 0,94 0,94 0,31 1,0E-04 0,221 0,521	Cas Cas 1,84 0,30 1,9E-04 0,287 0,988	segun n.m. n.m. n.m. 2,4E-04 0,295 0,792	0,538	rey marked = material be used in experiments

Flume experiments

The investigations from the flume experiments (2-D) showed the applicability of injecting saturated steam into the saturated zone to remediate the groundwater fluctuation zone (saturated zone plus capillary fringe) of the soil used from the sites.



- size 140 x 60 x 8 cm
- steam rate ~ 0.8 1.6 kg/h
- mass of soil ~ 100 kg
- groundwater level at 30 cm
- flow regime: constant head
- 98 temperature sensors installed
- mass of contaminant ~ 250 g BTEX and HC mixture

Figure 17: Set-up and experimental conditions of the flume experiments

The propagation of the steam front foran injection in the saturated zone can be summarized as.



Mechanism of Steam Front Propagation

Figure 18: Mechanism of the steam front propagation during the flume experiments

The temperature plots of the measured soil temperatures during the experiments illustrate the mechanism of steam front propagation.



Figure 19: Comparison of the heat front propagation between the injection of steam into the saturated zone (SubTSVE, left side) and into the capillary fringe (TSVE, right side)

The mass removal of contaminants for the application of SubTSVE is slightly higher compared to that of TSVE.



Figure 20: Comparison of the remediation efficiency between SubTSVE and TSVE

The main part of the contaminant mass was extracted as free product LNAPL phase from the groundwater table. In order to reduce the condensation of evaporated contaminants in the cold soil and the groundwater, causing floating free phase, the technology was improved by the addition of air (TUBA), following the proposed method of Färber, A., Betz, C. & Schmidt, R. (1997 - 2001). TUBA was designated and approved during field site applications for the unsaturated zone.

The technology of the injection of a steam-air mixture into the saturated zone (SubTSVE) was implemented during the technical scale experiments (container experiments). One of the large tanks at VEGAS (5.8 m long, 2.9 m wide and 4.0 m high) was filled with soil from site 3. A fine sand lens was packed in the lower part of the container (Fig. 21). The groundwater table was kept at a constant level by means of a coarse sand pack of 30 cm thickness surrounding the soil from site 3. 120 temperature sensors were installed in the saturated and unsaturated zone to measure the temperature distribution during the experiments. Four extraction wells (5", completely screened) were used for the extraction of soil vapour and groundwater. Additionally floating organic phase could be extracted by means of water-cooled lances. The injection level of the steam-air mixture could be selected (3 different levels, Fig. 21) for two 4" multilevel injection wells.



Schematic of SubTSVE Remediation concept

Figure 21: Schematic of steam-air injection into the groundwater (SubTSVE)

The range of heat propagation was investigated in a heat experiment. The steam propagation shape was comparable to that observed in the flume experiments. After 12 hours of steam-air injection the radial extension of the heat front was approx. 0.5 m on top of the groundwater (2.9 m height) and approx. 0.7 m in the saturated zone (Fig. 22). After 17 hours the heat front arrived at the extraction wells. The radius of the heat front was approx. 0.7 m at that moment. The increase of the steam injection rate resulted in a homogeneous propagation of the heat front in the saturated and unsaturated zones. After 200 hours of steam-air injection, the radius of the heat propagation was more than 1 m on top of the groundwater table. The injection level was approx. 1.7 m below the groundwater table. The propagation in the saturated zone was characterized by a steep vertical heat front and a wide horizontal extension.



Figure 22: Steam propagation during the large scale heat experiment (SubTSVE))

During the subsequent remediation experiment the groundwater elevation zone (2.5 - 3.5 m height) was contaminated by infiltrating 20 kg of a TEX-trimethylbenzene mixture in a composition matching that of site 3. The groundwater table was adjusted to a level of 3 m.

After 24 hours the soil vapour extraction was started and a steam-air mixture (30 kg/h steam and 15 kg/h air) was injected at the lower level of the injection wells. The extracted hot soil vapour was treated by condensation and phase separation of the condensate. Ambient air was added to the cooled-down soil vapour to prevent the formation of an explosive atmosphere (0.1 x lower explosion limit). The concentration of the contaminants in the soil vapour was continuously measured by a GC-PID. The off gas was treated by sorption on activated carbon downflow of the piston blower. No organic free product phase could be detected or extracted from the groundwater table during the experiment.

The heat front propagated according to the heat experiment. The mass removal of the low and medium boiling TEX components was approx. 98%. Approx. 93% of the high trimethylebenzene was extracted during the remediation. The contaminant mass was mainly extracted by the soil vapour (98%) containing approx. 10% to be removed as condensed LNAPL throughout the condensation of the soil vapour. None of the soil samples taken from the initially contaminated source zone by driving probe sampling showed concentrations of contaminants above the detection limit of 1 mg TEX p. kg dry soil.

The mass extraction curve for the soil vapour started with standard Air-sparging technology for the time until the steam breaks through at the extraction wells (Fig. 23, 14 hours), then the concentrations and the mass extraction significantly increase. With an increase in the steam injection rate, to enhance the heating of the soil, there is a limited increase in the concentrations in the soil vapour, whereas the concentrations in general are continuously decreasing. At the end of the remediation (50 hours) the soil vapour concentrations of TEX components were below 1 ppm of the soil vapour (air) and that of trimethylbenzene below 5 ppm. This meets German regulatory target limits for soil remediation.







Based on the experience gained during the large scale experiments, the remediation of the project partners industrial sites was designed, and the costs of a thermal remediation were estimated. Depending on the size of the sites and the location of the contaminants, there are 19 (37) steam injection wells and 34 (50) extraction wells designed for site 4 (site 3). The injected power is approx. 250 kW (1250 kW), the total soil vapour extraction rate is approx. 1100 m³/h SATP (1900 m³/h SATP). The remediation time is estimated to be 10 months (15 months).

During projects runtime site 4 was remediated by air(bio)-sparging and pump & treat technology. The biological degradation of the contaminants was aprrox. 50 % of the mass removed during year 2002. 5% were removed by phase extraction and groundwater capturing and approx. 45 % of the contaminants were extracted by the soil vapour. Assuming a constant high extraction rate (data of 2002) the remediation will last for almost another five years. The costs of this standard remediation technology were compared to the application of SubTSVE (Fig. 24). The costs for the standard technology were approx. 180 € / m³ soil, whereas the application of SubTSVE should cost approx. 120 € / m³ soil.

The technical design, the selection of process apparatus and machines as well as the costs assumptions were verified for the British market by one of the project partners, a consultants and remediation company.

Cost Savings of SubTSVE



Figure 24: Comparison of remediation costs between standard technology and SubTSVE for site 4

Summary and Outlook

Within the framework of the EU research project, PURE, a technology for the simultaneous remediation of the saturated and unsaturated zones was developed and successfully tested on a large scale. The remediation of two industrially contaminated sites owned by project partners was designed and the costs were estimated. Comparing the costs of standard remediation technology and the application of subTSVE it was found SubTSVE to be more cost effective.

Up to now, the design for the prediction of the heat front propagation is based on simplifying assumptions. It is intended to develop a method for steam front propagation forecast based on numerical simulations during future projects.

The investigations concerning co-solvent flooding (CSF) clearly indicate the necessity of a intensified field investigation to be able to select the most appropriate composition of the solvents and its ratio for a successful application. The hydraulic design of this multi-phase hydraulic remediation technology requires a careful review of the local hydrogeological situation as well as a numerical simulation based design.

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Literature

Färber, A. (1997): Wärmetransport in der ungesättigten Bodenzone: Entwicklung einer thermischen In-situ-Sanierungstechnologie. Mitteilungsheft Nr. 096, (Promotionsschrift) Institut für Wasserbau, Universität Stuttgart, 1997. ISBN: 3-921694-96-5.

Betz, C. (1998): Wasserdampfdestillation von Schadstoffen im porösen Medium: Entwicklung einer thermischen In-situ-Sanierungstechnologie. Mitteilungsheft Nr. 097, (Promotionsschrift) Institut für Wasserbau, Universität Stuttgart, 1998. ISBN: 3-921694-97-3

Schmid, R. (2001): Wasserdampf- und Heißluftinjektion zur thermischen Sanierung kontaminierter Standorte. Mitteilungsheft Nr. 106, (Promotionsschrift) Institut für Wasserbau, Universität Stuttgart, 2001. ISBN: 3-933761-09-3, 2001.

Trötschler, O.; Hofstee, C.; & Koschitzky, H.-P. (2001): Kombination von Dampfinjektion und Alkoholspülung zur Entfernung von organischen Kontaminationen in der gesättigten und ungesättigten Bodenzone. - Vorträge zum VEGAS Statuskolloquium am 12. Oktober 2001, Stuttgart.

Trötschler, O.; Färber, A.; Weber, K.; Haslwimmer, T. & Koschitzky, H.-P. (2003): "Development and technical implementation of the thermally enhanced soil vapour extraction using steam injection for the saturated and unsaturated zone." pp. 1868 – 1877 in: Proceedings of Consoil 2003, May 16 –18, 2003, Gent, Belgium.

Gudjberg, J., Trötschler O., Färber, A., Sonnenborg, T.O. and Jensen, K.H. (2003): Unphysical behavior during numerical simulation of steam injection into water saturated soil. Journal of Contaminant Hydrology 75 (2004) 297 – 318

Trötschler, O., Färber, A , Koschitzky, H.-P.,. (2003): Wasserdampf-Luftinjektion im Grundwasser zur Extraktion von organischen Schadstoffen, Symposium Ressource Fläche und VEGAS-Statuskolloquium 2003, pp. 163 – 172, Eds. Schrenk, Batereau, Barczewski, Weber, Koschitzky, Heft 124, Institut für Wasserbau, Universität Stuttgart

Kueper, BH and Frind, EO (1988): An overview of immiscible fingering in porous media. Journal of Contaminant Hydrology, Vol. 2, No. 2, pp. 95-110.

Weber, K., Trötschler, O., Koschitzky, H.-P. (2003): Investigation of Remediation Options for a CS2-Contaminated Aquifer Applying Alcohol Flushing. Technical Report 03/09(VEG03), Institut für Wasserbau, Universität Stuttgart.

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