Theme D: Remediation Concepts & Technologies

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ALCOHOL FLUSHING IN LABORATORY EXPERIMENTS: IN-SITU REMEDIATION OF DNAPL CONTAMINATED GROUNDWATER

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Abstract

Alcohol flushing within an upward directed flow field provides a safe technology for in situ remediation of DNAPLs. If the vertical velocity is larger than the required critical velocity partitioning of the DNAPL and the alcohols occurs forming a LNAPL and the reduction of the interfacial tension by the injected alcohols is no longer a risk. The vertical flow field was established by a groundwater circulation well (GCW), that is a very robust hydraulic system that enables a directed injection of alcohols. By several experiments these technology was investigated. Two-dimensional flume experiments at the Institute for Hydromechanics, Universität Karlsruhe, were conducted to develop the hydraulic conditions under which the alcohol injection could be controlled hydraulically with respect to the different kinematic viscosity and density of the selected alcohol mixture. Two similar remediations of an artificial PCE source has been demonstrated successfully, one by the use of partitioning tracer tests (PTT). Almost the complete PCE mass was recovered within a very short time by exchanging only about two pore volumes. Three-dimensional experiments at VEGAS facility, Universität Stuttgart, were conducted in order to transfer those results to field application. The directed and controlled alcohol injection into a heterogeneous aquifer was demonstrated successfully, too. The controlled extraction of the alcohols was much more difficult because of the heterogeneity, which is very important with regard to the recycling of the used alcohols.

Introduction

Groundwater contaminations by DNAPLs have a high risk potential because of their toxicity and persistence in the natural environment. Dissolved in groundwater they migrate without almost any resistance and could therefore arrive also at drinking water supply plants. Until now there exists no in-situ technology to remove DNAPLs safely and efficiently from the saturated zone since existing technologies require long remediation time or there remains the risk of uncontrolled downward migration of DNAPL phase due to their high density.

Alcohol flushing within upward directed flow fields (Fig. 1) such as the vertical circulation flow field generated by a groundwater circulation well (GCW) provides a technology that prevents the uncontrolled downward migration of DNAPLs and can be very efficient. The presence of alcohols affects the mobility of DNAPLs. The lower interfacial tensions between alcohols and DNAPLs compared to the interfacial tension between water and the respective DNAPLs increase the mobility of the DNAPLs, i.e. a possible downward migration due to gravity. On the other hand, DNAPLs are partitioning into hydrophobic alcohols and the resulting fluids becomes a LNAPL. That turns the possible downward directed into an upward directed migration (Hofstee et al. 2003). If the technology can be designed so that the time scale of such a downward migration is slower than the time scale of partitioning alcohol flushing provides a safe in-situ remediation technology. The efficiency of that technology is based also on the partitioning process which enables very short remediation times. A

DNAPLs can be remediated by flushing only a very low number of pore volumes with alcohols which is much less than the flushing of about 1000 pore volumes with water for the same result.

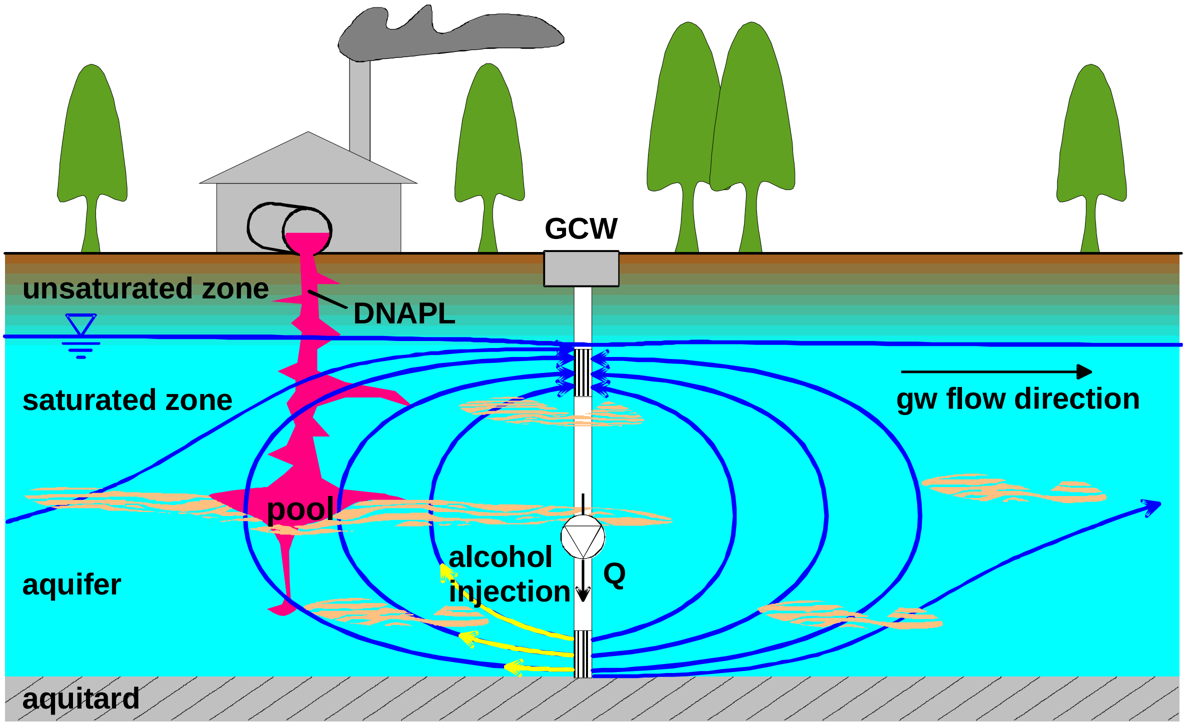

Figure 1: Principle of in-situ groundwater remediation by alcohol flushing within a upward directed circulation flow field generated by a groundwater circulation well (GCW).

The recently developed in-situ remediation technology is based on the GCW technology provided by IEG Ltd., Reutlingen. Such a flow field is quite robust and enables the directed hydraulically controlled alcohol injection in the region of the aquifer where the DNAPL source is located without inducing migration. Therefore, this technology is able to remove the formed alcohol DNAPL mixture from the aquifer under controlled conditions. In parallel investigations the most effective alcohols for the partitioning process have been determined (Hofstee et al. 2003, Greiner et al. 2003) and the conditions for hydraulic control of the system have been developed (Heinrich et al. 2003, Mohrlok & Heinrich 2004). The hydraulic system for such a directed and controlled injection has to account for the differences in density and viscosity of the selected alcohols and groundwater. As the hydraulic system provides the extraction of a concentrated remediation solution the alcohols could be recovered and the technology is also economically efficient.

Laboratory Experiments

Different kinds of laboratory experiments were conducted. One-dimensional columns experiments were conducted at the Institute for Hydraulic Engineering, Universität Stuttgart, in order to determine the most effective alcohol mixtures for the partitioning of different DNAPLS and also the minimum necessary flow velocity that prevents the downward migration (see Greiner et al. 2005). In two-dimensional flume experiments the hydraulic system for the directed and controlled alcohol injection was developed and proved by the remediation of a PCE contamination source. In three-dimensional container experiment at the groundwater remediation facility (VEGAS) at University Stuttgart the developed technology should be tested under field like conditions at large scale. The two- and three-dimensional experiments are discussed in this paper.

The two-dimensional experimental set-up at the Institute for Hydromechanics, Universität Karlsruhe, consists of a flume with length 3.17 m, height 1.26 m and width 0.25 m. It was filled homogeneously with a gravel sand mixture. 68 sampling ports for the determination of the groundwater flow and transport have been installed by measuring piezometric heads and taking water samples for chemical analyses. The front of the flume was built in glass in order to enable the visualisation of tracer transport and remediation processes. The injection and extraction unit, each with a height of 30 cm, of the GCW consist of separated chambers, where different boundary conditions can be applied (Fig. 2). The corresponding chambers define an inner, a central, and an outer circulation zone. The alcohols have been applied only to the central circulation zone. At each chamber the flow rates and the piezometric heads can be controlled providing a high flexibility for hydraulically regulated simultaneous circulation of water and alcohol in the aquifer. The size and location of the chambers were designed to direct the alcohol circulation to the proposed location of an artificial PCE source.

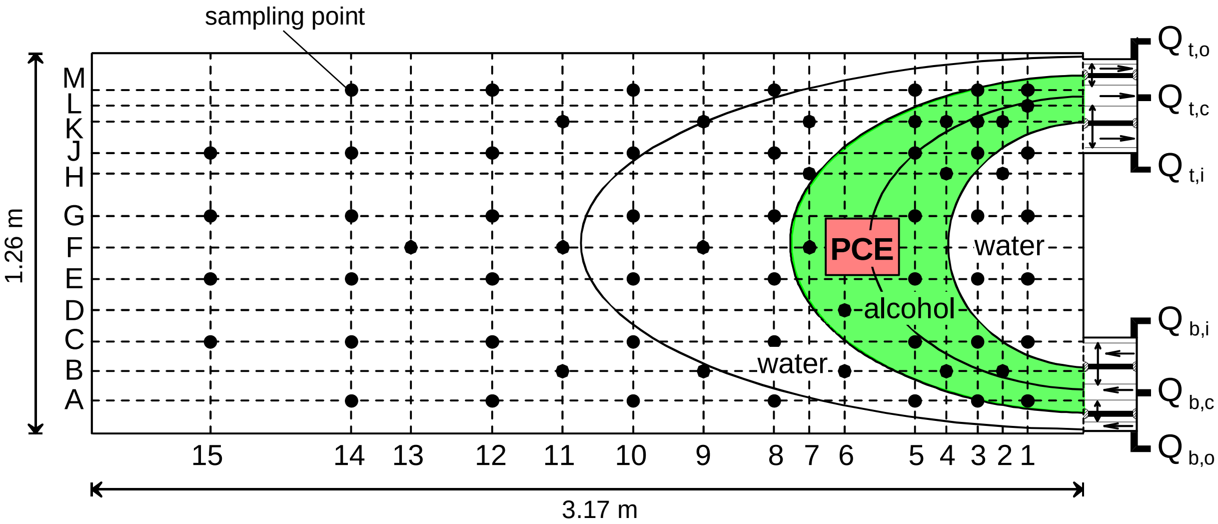

Figure 2: Two-dimensional experimental set-up: injection (bottom) and extraction (top) unit with three chambers each defining an inner, central and outer circulation.

The selected alcohol mixture consisted of 23 vol-% hexanol, 54 vol-% isopropanol and 23 vol-% water (Greiner et al. 2003). This mixture forms a stable fluid phase miscible with water. It has a density of about 0.865 kg/L and a kinematic viscosity of about 3.8 x 10^{-6} m^2/s (at 20° C). As the amount of water in the mixture increases, i.e. an decrease of the co-solvent isopropanol, hexanol will separate and two immiscible phases will be formed. Such an evolution has to be avoided, since the hydraulic system has to provide a stable combined circulation of alcohols and water. This can be guaranteed by vanishing transversal pressure gradients perpendicular to the streamlines of the circulation flow field and by the reduction of mixing processes at the alcohol water interfaces. Therefore, the boundary conditions were defined in such a way that the viscosity differences of the alcohols and water has been respected and that the density differences generating buoyancy effects have been diminished.

The reference situation was set as a system with pure water circulation, where no pressure gradients and velocity differences at the interfaces of the three circulation zones occur. In order to compensate the large alcohol viscosity that reduces the hydraulic conductivity of the aquifer material, the inflow rate of alcohols has to be reduced by 3.8, the ratio of the kinematic viscosities of alcohol and water. By that, transversal pressure gradients are avoided. On the other hand, this operation generates strong velocity differences at the interface and a certain degree of mixing remains. Fortunately, this mixing is less effective in the case of porous media. The buoyancy effects are much more critical since they cause a much stronger mixing at the interface. The application of additional transversal pressure gradients by a certain increase of the inflow rates at the inner, $Q_{b,i}$, and central circulation zone, $Q_{b,c}$, are able to compensate these effects mainly.

To establish the hydraulic boundary conditions for a controlled and directed alcohol injection several different kinds of experiments were conducted in the two-dimensional flume. Several dye tracer tests within a pure water circulation were visualised and breakthrough curves of uranine were quantitatively analysed. The results of experiments with a injected coloured alcohol phase were analysed in the same way. For the demonstration of the developed technology two remediation experiments with an emplaced PCE source were conducted. This source was built by creating a residual saturation of PCE of about 5%, i.e. 175 mL PCE, in an aquifer volume of about 12 L, with its bottom located at the centre of the vertical distance of infiltration and extraction unit. The horizontal distance between PCE source and GCW was about 70 cm. Approximately 80 L of the alcohol mixture were injected for about 1.5 h followed by a period of pure water flooding of about 2 h to remove the injected alcohols from the aquifer.

Within the second experiment prior and posterior to the remediation by alcohol injection partitiong tracer tests (PTT) were performed to demonstrate the removal of the PCE source. 2-Metyl-1-butanol, 2-Etyl-1-butanol and 1-Heptanol were selected as partitioning tracers with an increasing affinity to partition into PCE. They were injected as a 5 min pulse into the inflow $Q_{b,c}$ at the central circulation zone Between the remediation experiments and the respective PTT the circulation flow field was stopped for different time periods (see Fig. 5).

The three-dimensional experiments at the VEGAS facility, Universität Stuttgart, were conducted in a heterogeneous aquifer, 9 m long, 6 m wide and 4.5 m high, with a meandering block structure (Fig. 3). The hydraulic boundary conditions were applied to four sections at the injection and six at the extraction filter screen by adjusting the proposed flow rate and piezometric heads. Three sections at the injection unit were positioned vertically above each other covering the whole depth like in the two-dimensional set-up and supporting an azimuth angle of about 60°. The fourth section was defined by the remaining filter screen section. The extraction unit consisted of six sections arranged similar to the injection unit, except two more sections separating the central circulation zones vertically from the large remaining section. Only the central injection segment of the three-dimensional circulation was used for alcohol injection (Fig. 3), so that most of the alcohols should arrive at central section of the extraction unit. The section arranged around this section were used for management and should catch the dispersed alcohols due to the aquifer heterogeneity. Sampling points for measuring piezometric heads and taking samples were installed in a regular three-dimensional grid (horizontal planes levels 1-6, longitudinal cross sections A-G, transversal cross sections a-I) all over aquifer and at each injection and extraction section of the GCW.

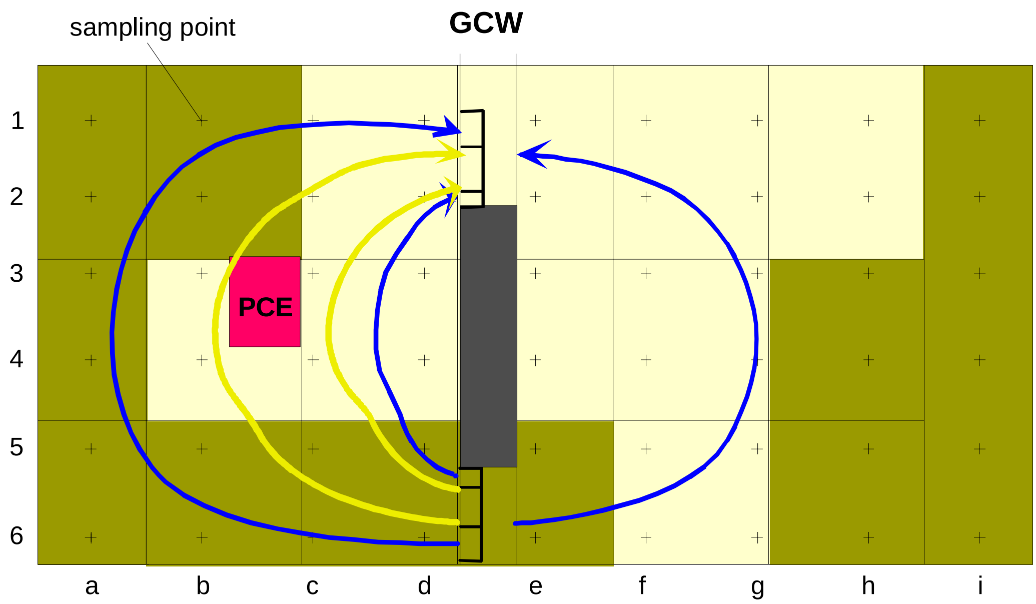

Figure 3: Central vertical cross section along sampling point plane D of the three-dimensional experimental set-up: aquifer with block structure (light colour highly conductive, dark colour low conductive), location of sampling points, proposed PCE source and computed streamlines.

The applied boundary conditions were designed by the support of numerical simulations of a pure water circulation in the aquifer at VEGAS and the results obtained from the two-dimensional experiments. As it turned out from the simulation results the flow field was much more complex because of the block structure of the aquifer. All computed streamlines had a complex three-dimensional shape. An uranine tracer test and two alcohol injection experiments were conducted, where the breakthrough at several sampling points and at the outlet sections were determined. These two experiments were run with very different overall flow rates because of respecting the alcohol hydraulic properties. However, since similar flow rates were used to inject the uranine tracer and the alcohols the breakthrough occurred at similar a time scale. One part of the investigations at VEGAS was related to the possibility of removing the alcohols with high concentrations from aquifer by the constructed extraction unit in order to recover them efficiently by means of water treatment facilities.

Results and Discussions

The results of the two-dimensional experiments demonstrated the ability of a hydraulically controlled alcohol injection for the remediation of an artificial PCE source. By visualisation of the dye migration within a pure water circulation the shape of the circulation zones predefined by numerical modelling could be confirmed. The comparison of breakthrough curves at the sampling points E5 and G5 from a uranine tracer and an alcohol circulation experiment as well show that the necessary vertical velocity was established at the location of the proposed PCE source. The breakthrough curves from sampling points G5, F7 and H7 surrounding the PCE source demonstrate the stable combined circulation of alcohols and water (Fig. 4) in the first remediation experiment. The observed evolution of the piezometric heads within the aquifer as well as at the inflow and outflow chambers showed a feedback effect of the alcohol circulation on the hydraulic system. By means of these results the hydraulic boundary conditions necessary for a controlled alcohol injection were determined.

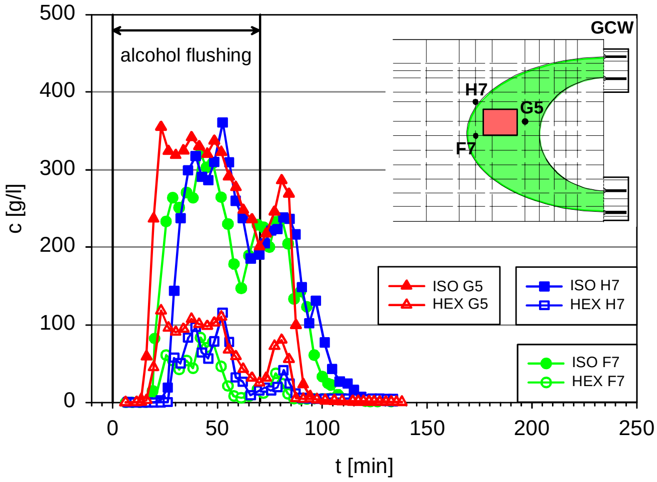

Figure 4: Breakthrough curves of the sampling points G5, F7, H7 surrounding the PCE source in two-dimensional experimental set-up.

The PCE removal in both remediation experiments was obtained by determining the breakthrough curves at the extraction unit. This turned as a strong challenge for sampling and analysing the concentrations as well, since in the second remediation experiment the main breakthrough of the PCE occurred within a very short time period of less than 20 min and the highest concentrations of more than 5 g/L were analysed in only three samples (Fig. 5) whereas the concentrations in the tailing were less than 1 mg/L. Therefore, the mass balance in this experiment exceeded 100% mass recovery by a few % for PCE and the alcohols as well. In the first remediation experiment the alcohol injection rate was a bit lower, so that the time scale of the processes were reduced slightly. The breakthrough of PCE lasted about 25 min and the maximum concentration was also about 5 g/L. In addition, the very fast remediation could be observed directly at glass front of the experimental set-up, since the PCE was coloured with Sudan IV. When the alcohol front reached the PCE source region the expected downward mobilisation took place for a short time. However, the mobilised PCE was immediately partitioning into the alcohols and transported upwards by the alcohol circulation. The results from the two PTTs are shown by the breakthrough curves at sampling point J5 downstream the PCE source (Fig. 5) and confirmed the almost complete remediation of PCE. Comparing the PCE removal of only a few % during the first PTT period it is obvious that the alcohol flushing technology can reduce the required remediation time by some order of magnitudes.

Because of the mixing at the alcohol water interfaces hexanol was partly separated from the alcohol mixture and was found at the uppermost outlet chamber. Hence, the occurring two phase flow system could not be controlled anymore by the system hydraulics in the case that the amount of free phase hexanol was large, which occurred in those experiments, in which the hydraulic control was not well established. Usually, this was the result of not well established hydraulic boundary conditions. Therefore, it is very important in particular to control the buoyancy effects that are most important at the injection unit by an adaptation of the inflow rates.

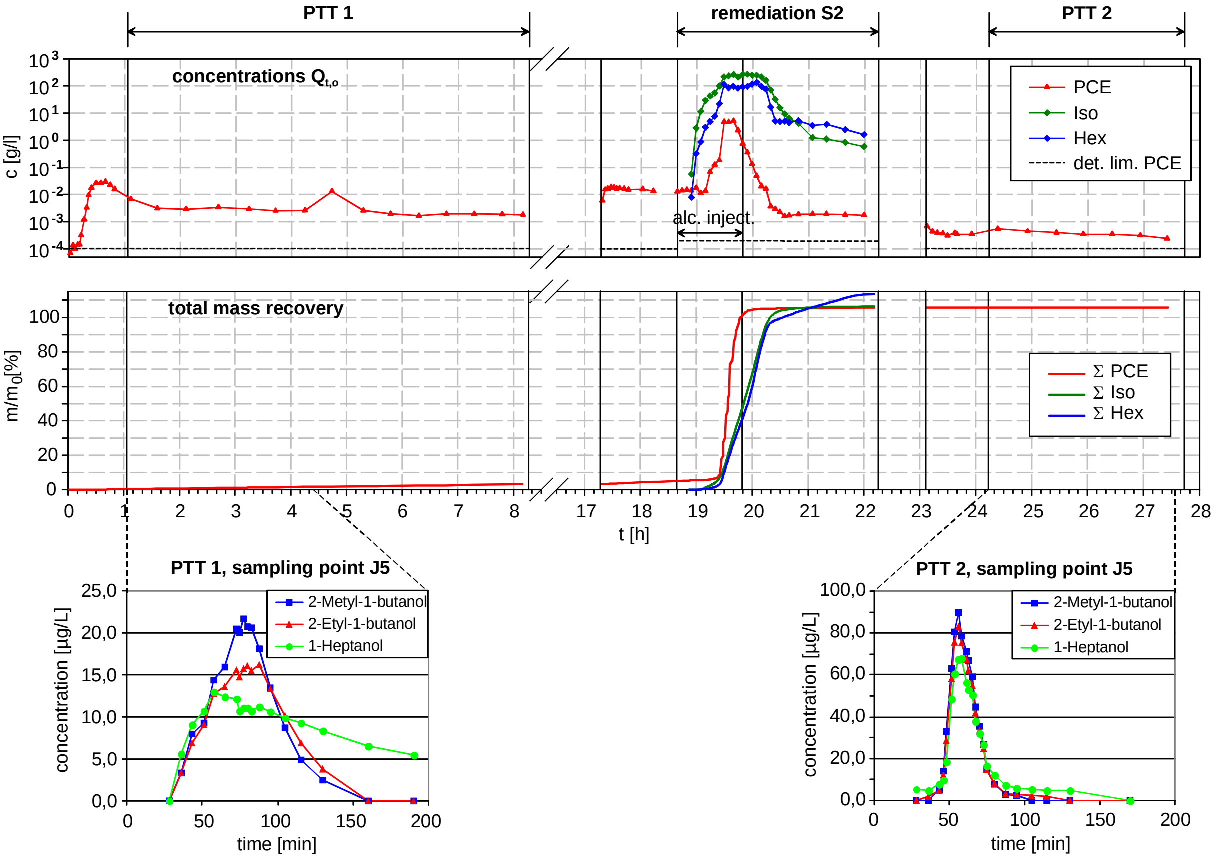

Figure 5: Breakthrough curves of the alcohols at the extraction unit and of the partitioning tracers at the sampling point J5 downstream of the PCE source in two-dimensional experimental set-up.

The hydraulic system of the three-dimensional experiments was designed by means of numerical simulations, since there was no possibility of visualising the different circulation zones. The conducted dye tracer test injecting uranine in the central section, where also the alcohols were injected, was essential to proof the simulation results by obtaining breakthrough curve at several sampling points within and surrounding the alcohol circulation zone. The observed differences between the dye migration determined by breakthrough curves and the simulated streamlines were caused by a too large inflow rate at the tracer injection section (Fig. 6). Therefore, the dye was injected too far into the aquifer. This resulted additionally in a later dye breakthrough at the extraction unit as expected, in particular at the uppermost section. Furthermore, the large spreading of the dye was observed by sampling the whole aquifer after the experiment.

Two experiments with alcohol injection followed this tracer test. The injection rate was adapted to the different fluid parameters, as investigated in the two-dimensional experiments, and the results of the dye tracer test, that investigated the properties and behaviour of the flow field in the three-dimensional set-up. For a controlled injection of the alcohols it is essential that the construction of the sections provides a tight separation. Otherwise a buoyancy driven by-pass flow occurs at the section interfaces and mixing processes will destroy the alcohol solution. In the first alcohol injection experiment in VEGAS the sealing between the sections was not tight enough so that a preferential alcohol migration close to the GCW was observed, mainly by a high concentration breakthrough in the extraction section related to the inner circulation zone. The improvement of that sealing for the second alcohol injection experiment resulted in the directed and better controlled distribution of alcohols towards a proposed PCE source (Fig. 6). However, it seems that alcohols are by-passing the sampling points at the levels 3 and 4 in the planes b and c. Also a separation of a free hexanol phase was determined, that makes the hydraulic control of the system difficult. The tightness of the sealing between the injection sections needs to be improved further.

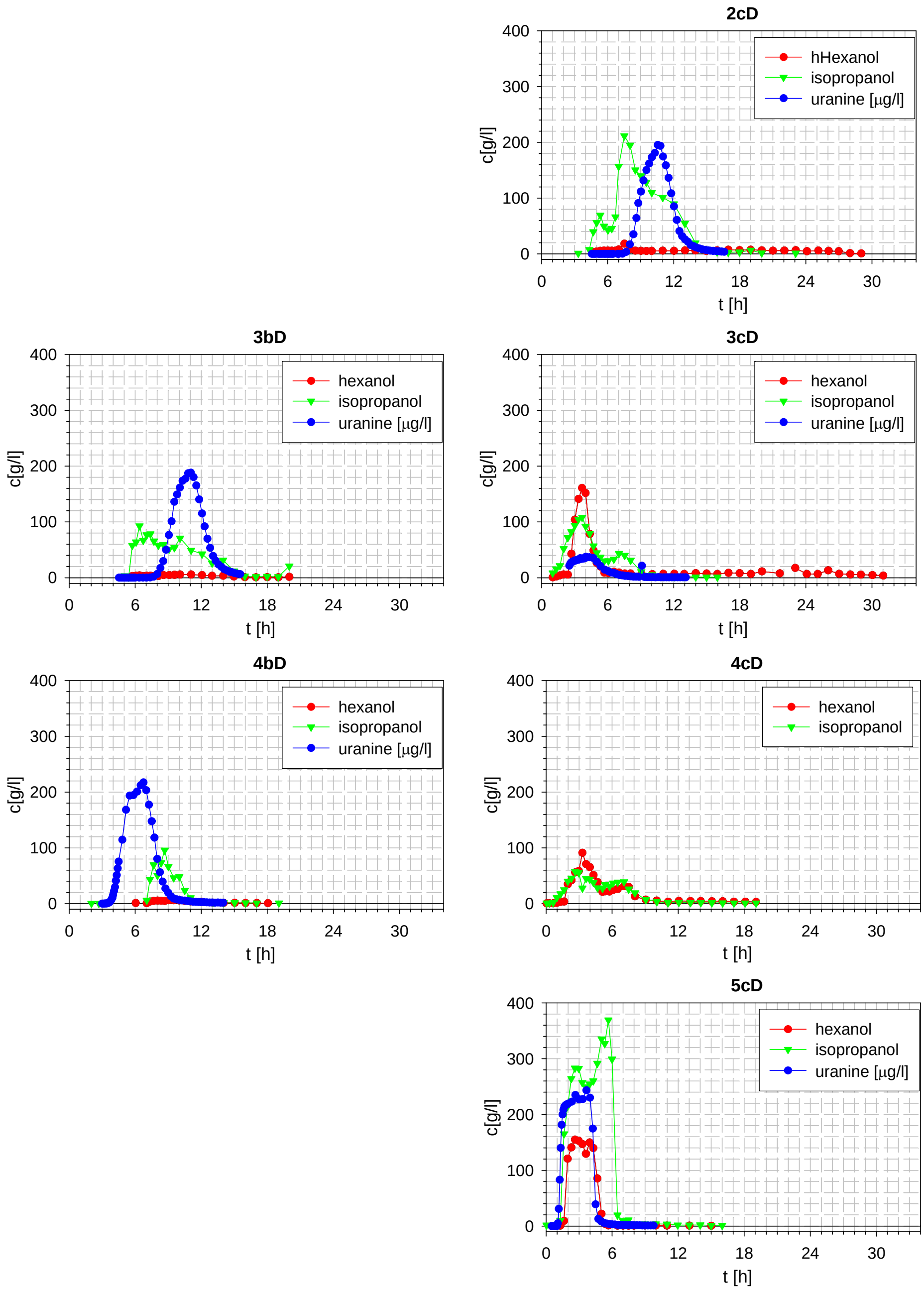

Figure 6: Breakthrough curves of the several sampling points in the central vertical cross section D, related to the centre of the injection section, of the three-dimensional experimental set-up and computed streamlines from the numerical simulation.

The alcohols were mainly removed from the aquifer at the central sections of the extraction unit with concentrations of about 10 times less the original concentration of the mixture. Since they were spread much larger over the aquifer volume also at the other sections significant alcohol concentrations were measured. The observed dilution of the alcohols even in the central extraction section was quite large. Only a small part of this dilution was related to the wide spreading of the alcohols. Mainly, the dilution was generated by the much larger flow rate at the extraction section for the alcohol circulation zone than the alcohol injection rate. An additional dilution effect was caused by the circulation flow field, since the estimated travel time along the outer part of the alcohol circulation zone and the injection period were similar. Only for much larger injection periods the dilution should vanish. The alcohols were not recovered from the experiments due to the low efficiency for the diluted concentrations.

Conclusions

The conducted laboratory experiments demonstrated successfully the controlled alcohol injection by use of the GCW technology. This technology provides a robust and hydraulically controllable flow field with large vertical flow velocities. Also very well directed injection can defined by that technology. The results of the experiments showed the large importance to adapt the hydraulic system to the different fluid parameters of alcohols and water in order to avoid effective mixing processes at the interfaces. Such mixing processes will separate the hydrophobic alcohol from the mixture, that is essential for the DNAPL partitioning. Since the buoyancy effects are mostly responsible for an effective mixing they have to respected properly by the applied hydraulic boundary conditions.

The large potential of alcohol flushing compared to simple hydraulic groundwater remediation technologies was demonstrated in the two-dimensional remediation experiments. Alcohol flushing by vertically upward directed flow fields enables very rapid and almost complete remediation of DNAPLs with additional safety against uncontrolled mobilisation of the DNAPL. Very important is the hydraulic control of the circulation zones, that is related mainly to the avoidance of by-pass flow caused by buoyancy effects at the injection sections. This needs to be demonstrated in a further large scale laboratory experiment or a pilot study in the field. The very short remediation time can compensate the required technical effort of alcohol flushing in the field.

Alcohol flushing using GCW technology will also be an economically efficient remediation technology if the applied expensive alcohols could be recovered from the remediation solution. As the three-dimensional experiments showed there are some inherent dilution effects in the designed system so that a technically efficient recovery gets difficult.

Acknowledgements

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