

PAPER:

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DNAPL TREATED BY APPLICATION OF SURFACTANTS FOLLOWED BY ISCO

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Introduction

The presence of DNAPL is often limiting factor for the removal of chlorinated aliphatic hydrocarbons (CHCs) from the subsurface. Residual DNAPL usually results in the rebound effect causing repeated increase of contaminants concentrations. Surfactants (surface active agents) are chemical compounds with specific molecular structures typically composed of a strongly hydrophilic head and a hydrophobic tail. In a DNAPL-contaminated aquifer, this specific property of surfactants can increase DNAPL solubility and lower DNAPL-water interfacial tension to the point that physical mobilization takes place. Application of surfactants thus can enhance the remedial action. Surfactants flushing is a mature technology in the petroleum-engineering field. The technology has been shown to be effective also for DNAPL sites recently. A surfactant flushing system typically consists of a network of injection and extraction wells. A mixture of injected fluid and mobilized contaminant is captured through extraction wells that requires further treatment. This treatment could be technically demanding (e.g. due to the tendency of surfactants to form foam). Considering that coupling of surfactants application with another remedial technology seems to be suitable. In-situ chemical oxidation (ISCO) is promising technology for the combination with surfactants. In addition, the main weakness of ISCO application to treat DNAPL thus could be solved.

Test site

The mechanical engineering site situated in the western part of the Czech Republic has been selected for the pilot test performance. The hotspot area is located in the north-eastern portion of the main production hall where degreasing by trichloroethylene TCE and tetrachloroethylene PCE was performed in the past.

From the geological point of view, the site belongs to Upper Proterozoic Unit of Central Bohemia, called Tepelský crystalline complex formation. The complex is formed by two-mica schist. In the area of the pilot test, the upper most layer is formed by fill represented by sandy-clayey loams with fragments of stones thick approximately 0.3 to 1 m. Fill materials are underlain with mica-schist elluvium formed by sandy to sandy-clayey loams with fragments of bedrock stones up to 12 cm. The bedrock was encountered in a depth of 1.2 to 2.5 m.

The shallow aquifer is bound to the zone of weathered bedrock and overlying sandy to clayey loams. The aquifer permeability is relatively low represented by hydraulic conductivity of 10^{-6} to 10^{-7} m/s.

The groundwater contamination at the area of pilot test before its performance indicated presence of DNAPL (PCE 31.3 mg/l and TCE 23.1 mg/l).

Pilot test set-up

The test comprised two phases: 1) separate application of surfactant (i.e. without subsequent injection of oxidant); and 2) combined application of surfactant and oxidant. Concentrations of chlorinated aliphatic hydrocarbons, surfactant and other relevant parameters were monitored during the pilot test.

The separate application of surfactant was based on injection of solution of surfactant into two wells IN-1 and IN-2. Another two wells MV-1 and MV-2 were used of groundwater extraction. The extracted water was treated via stripping and trap of chlorinated hydrocarbons on activated carbon. The treated water was then injected again to wells IN-1 and IN-2.

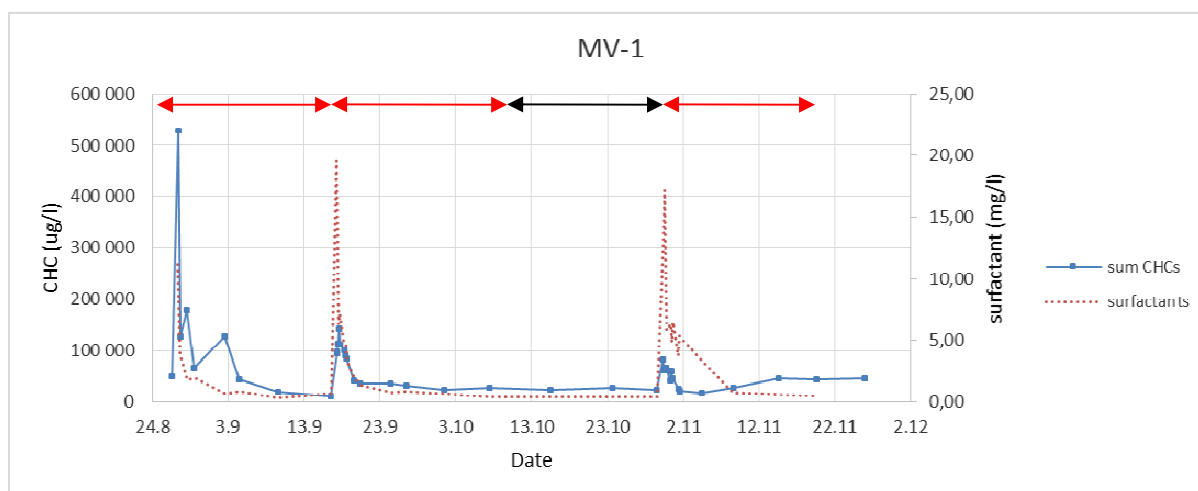
This phase of pilot test was performed in three in three sequences, each in duration of 30 days. The volume of surfactant was the same in all three sequences of 100 kg. The initial concentration of surfactant was 50 g/l, the latter two ones of 100 g/l. Surfactant was distributed equally 1:1 to both injection wells IN-1 and IN-2. The groundwater extraction was initiated approximately 16 hours after surfactant injection from wells MV-1 and MV-2. The extraction was conducted for period of 21 days.

Between the second and third sequences the extraction was prolonged for another 21 days in order to compare the efficiencies of steps with and without surfactant injection.

Approximately one year after the initial phase of pilot test his second phase has been performed comprised combined application of surfactant and chemical oxidant. Surfactant in concentration of 50 g/l has been injected to the groundwater via 4 injection wells MV-1, MV-2, IN-1 and IN-2 in total volume of 2 cubic meters. Subsequently, after 16 hours, 10 cubic meters of activated sodium persulfate in concentration of 100 g/l was injected to the same four wells. The groundwater monitoring followed the application. Once certain increase of CHCs has been detected the injection of persulfate was repeated after 70 days from the start of test.

Results

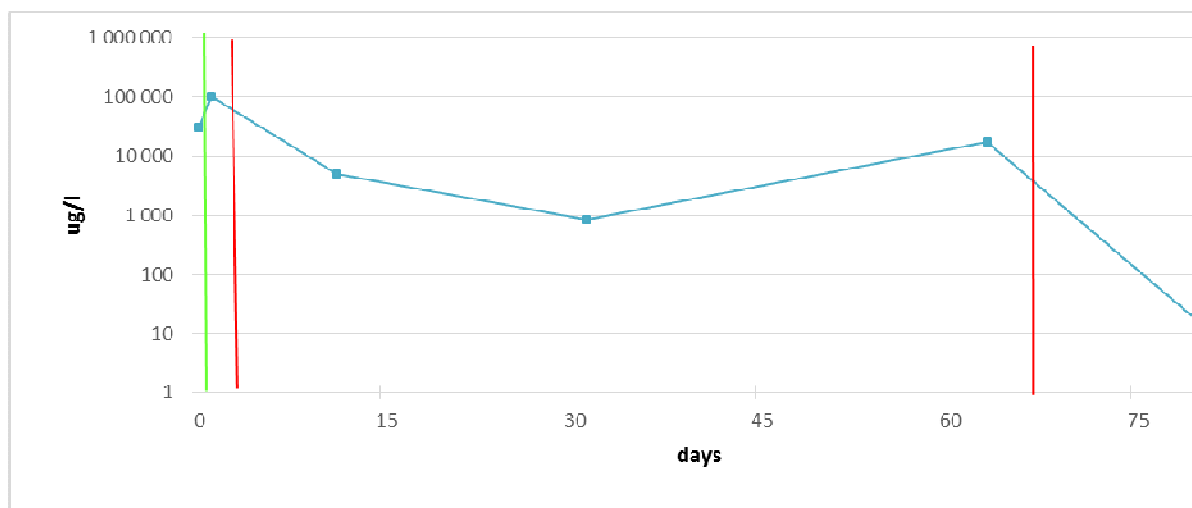
The application of surfactant resulted in the multiply increase of concentrations of chlorinated hydrocarbons (up to 13 times) confirming the efficiency of surfactant to mobilize the residual DNAPL; see following graph for well MV-1.



Graph 1: Development of CHCs and surfactant concentrations during surfactant injection, the arrows show individual sequences of surfactant injection (red ones injection of surfactant and subsequent groundwater extraction, black one only extraction without preceding application of surfactant)

The application of surfactant was also evaluated from the remedial efficiency point of view. The pump&treat method applied at the site prior the pilot test removed 2.2 kg of chlorinated hydrocarbons during 4 months. In comparison, 10.6 kg of CHCs, i.e. approximately 5 times more, was removed by the pilot test in duration of 85 days (incomplete 3 months).

In case of combined application the similar effect of surfactant has been observed, i.e. immediate increase of CHCs concentrations up to factor 6. Application of oxidant resulted in reduction of chlorinated hydrocarbons mobilized by surfactants. The low level of CHCs remained for 65 days where certain increase of concentrations was observed and another injection of oxidant was performed (without previous preceding application of surfactant). More intensive drop of CHCs concentrations was observed after the second injection (see following graph). The similar development has been observed in all four injection wells.



Graph 2: Development of CHCs during combined application of surfactant and oxidant (the vertical lines show injection of surfactant (green) and oxidant (red))

Conclusion

The results of pilot test indicate the applicability of combined use of surfactants and in-situ chemical oxidation at the DNAPL-contaminated sites. Surfactant has very positive influence of dissolution and desorption of DNAPL that become available for the subsequent chemical oxidation.

Surfactant does not remain in high concentrations for long time, it is being degraded and chemically oxidized. The results of the pilot test and previous laboratory experiments do not conclude that oxidation of surfactant is preferential to oxidation of chlorinated hydrocarbons.

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