

Behaviour of Tensio-active Compounds Used in the Clean-up of Contaminated Manufactured Gas Plant Sites

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The contamination at manufactured gas plant sites is characterized by a diversity of organic compounds distributed, in many cases, in the heterogeneous fill soil. These contaminants that have migrated into the subsurface from sources such as product spills and leaking disposal facilities exist in three phases: 1) free product; 2) adsorbed to soil particles; and 3) dissolved in the groundwater. The amount of any phase varies, depending upon the characteristics of the contaminants and the subsurface, and its distribution used to be described in terms of the soil-water partition or sorption coefficients. In most cases, the mass in the solute phase is relatively small compared with the mass in either the adsorbed or free phases. This particular situation increases the difficulty in the removal of organic compounds from the subsurface using either chemical or biological methods. Consequently, the success of the clean-up of those sites depends on various parameters including the structure of hydrocarbon compounds as well as hydrogeological formation and localization of the contaminated area. Molecular weight, solubility, polarity of compounds and sorption capability, matrix heterogeneity, microorganism availability of subsurface are only a few of the most important parameters influencing successful clean-up.

Therefore, the removal of nonpolar hydrocarbons, such as PAH and aliphatic hydrocarbons, can be done by changing the solubility of hydrocarbons using exchange water with other solvents or by two other ways: changing the charge of clay surface using a modification agent and/or decreasing the water content. To accomplish those conditions, it is necessary to introduce the organic compound with dipole character into the soil medium. These compounds are able to associate the hydrocarbon molecule, but on the other hand, they have affinity to water.

The introduction of the tensio-active compounds (also called surface-active and surfactants) into the subsurface can improve various removal techniques. The surfactant compounds form the micelles with organic contaminants and change the properties of the contaminant-soil system. The adsorption of organic cations is not limited and is higher than the exchange capacity of clayey soil. The desorption process is available and the mobility of compounds increases.

The surfactants can be divided into four groups: 1) cationic (amine salts, quaternary ammonium salts, etc); 2) anionic (containing phenolates, carboxylates, sulfonates, etc); 3) nonionic (long-chain alcohols, ketones, etc); and 4) amphoteric, having both positive and negative groups under specific conditions (amino acid and imidazoline derivatives, etc).

The various behaviours of these compounds were tested during lab research work. The pH values varied between 5.9 to 7.0 for all tested surfactants. The interaction between clay particles and hydrocarbon molecules in the presence of a modification agent may be characterized qualitatively by electrophoretic mobility. The zeta potential, related to the double layer characteristic is the principal factor of this mobility. The tests provided with the zeta-potentiometer demonstrated the highest electrophoretic mobility of cationic surfactants ($2.5 \text{ } \mu\text{m s}^{-1} \text{ V}^{-1} \text{ cm}$). The tests were performed with anionic, cationic and nonionic surfactants in non-contaminated clayey soil; the same soil contaminated by diesel fuel; and in sandy clayey soil naturally contaminated by PAHs and in diesel fuel itself (Table 1). The best performance was presented by the cationic surfactant hexadecyltrimethylammonium bromide. Other cationic surfactants such as tetrabutylammonium bromide and triethylamine hydrochloride have their hydrocarbon part shorter and they did not provide interesting results during the tests. The anionic surfactant

Table 1. Zeta-potential measurements (mV)

Type of medium	Water	Cationic 101 normal conc.	Cationic 101 1:5 conc.	Anionic 201	Nonionic 301
Non-contam model soil		17.7 42.2	21.6	-29.6	
Contamin. model soil	11.2 -16.9	19.9	16.4	-22.8	-6.6
Silty natural soil	7.05 -4.3	14.5	20.8	-17.1	-7.9
Diesel fuel	-16.5	41.6	39.2	-54.2	

Hostapur SAS (C₁₆-C₁₇-n-paraffin ca 39%) and the nonionic Sapogenat T-300 (Tributylphenolpolyglycoether) were also used in all tests.

The presence of surfactants changes the direction of the movement of particles in a soil-contaminant medium. In the case of a cationic surfactant only, all particles are moving in same direction and the zeta potential value (42.2 mV) is the highest one. The mixture of clay particles with hydrocarbons have lower value of zeta-potential than micelles in hydrocarbon-surfactant emulsion. This test demonstrated the necessity of electrophoretic measurements in the medium which better represents the tested subsoil. The partitioning coefficient may play a very important role in the mobility and removal of particular contaminants from MGP sites. Consequently, improved measurements by the use of an electroacoustical method are suggested. This method can be used as a denser medium which will be able to keep higher similarity to the partitioning ratios (soil-water, octanol-water and organic-carbon) in natural soils. By the introduction of a chosen surfactant to this medium, the measurement of mobility can demonstrate the actual situation more adequately.

This information about soil-contaminant-surfactant behaviour is very useful in the context of various techniques of site remediation: flushing, biodegradation or electrokinetic. It is necessary to select the right surfactant for a particular soil polluted with specific substances.

The best control of all technical parameters can be achieved by a process which involves the excavation of contaminated soil and its treatment in specially prepared units. In many cases, however, the excavation of soil and treatment outside of the site is impossible for various reasons: extended and/or deep contamination, intensive use of the area for industrial purposes, etc. In these situations, *in-situ* treatment may be cost-effective.

An innovative electrokinetic method coupled with controlled chemical processes can be applied at MGP contaminated sites. The electrokinetic method, improved by using surfactants, can be a cost-effective technology. This method is based on the electroosmotic and electrophoretic processes which take place under the application of electrical current

(DC) to contaminated soil. In this case, the electrodes work as surfactant injected wells or contaminant discharged wells.

The results of lab research on this electrokinetic technique demonstrated the success of the application of cationic surfactant to the removal of diesel fuel and phenol from contaminated silty clayey soil. The soil was placed in polyethylene cells where two perforated cathodes and two anodes were installed. The cationic surfactant was injected through the anodes. Because of the strong oxidation process in the anode area, various materials for those electrodes were tested. The teflon perforated tube with carbon fibre demonstrated the best resistance to electrochemical processes. Every day liquid was collected in the cathodes which worked as discharge wells. Electrical gradient was kept constant during two weeks of tests. After 11 days of electrokinetic treatment in a 10 cm long cell, the initiation of diesel fuel removal was demonstrated. Considering the polar proprieties of phenols, it seems that an electrokinetic method could be the most suitable for them. In this case, electrokinetic washing can be applied without surfactants.

The sequential removal of various organic compounds via the application of different surfactants and use of an electrical field is the next step in the current research. All types of surfactants were subjected to electrochemical processes in electrolytic cells. Results of those tests demonstrated various behaviours of surfactants in the presence of diesel fuel. Changes of surfactant properties was very slow. After adding the diesel fuel emulsion to water, the precipitation process was observed. The highest precipitation was analyzed in the cell filled with the amphoteric surfactant (C₁₂-C₁₄-Alkyldimethylbetaine); the lowest in the cell with the cationic surfactant. Infra-red analysis demonstrated reaction of surfactants with paraffin compounds of diesel fuel. A slow decrease in the pH values near anode and an increase near cathode were also observed. Those results showed the importance of the extended research in this domain because the potential for new applications is extremely wide.

Recent lab results demonstrated the high effectiveness of those methods to the removal of mixed hydrocarbons from contaminated heterogenous soils. This method can be applied with success to MGP contaminated sites.