

Oxidation of PAHs and Their Byproducts (Polar PACs) in the Saturated Zone of DNAPL-Contaminated Subsoils

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Background/Objectives: The remediation of former industrial sites is, for many reasons (health and environmental impact, land use, etc.) of great concern. Soils encountered at closed steelwork sites, including coking plants, exhibit multiple chemical contaminations, and are often impacted by PAHs inherited from coal tar storage and dissemination. The present work specifically focuses on improving the effectiveness of in situ chemical oxidation (ISCO) to reduce dense non-aqueous phase liquids (DNAPL) remaining after pumping in the saturated zone of the impacted sub-soils. The study is part of BIOXYVAL project, which gathers many representative actors (private companies, academic laboratories, etc.), dedicated to the remediation of contaminated sites by coordinating various innovative processing techniques on a former coking plant in the north east of France.

Approach/Activities: The efficiency of four different chemical oxidation processes was first compared by some batch experiments. PAH degradation and formation/elimination of selected by-products were monitored, especially polar polycyclic aromatic compounds (PACs, including oxygen/nitrogen/sulfur-containing PACs) which have greater mobility in groundwater compared to PAHs and can be more toxic. Conventional oxidants, including sodium permanganate, Fenton-like (activated with magnetite), and heat-activated persulfate, were compared to an innovative and very promising oxidant made of potassium ferrate (Fe^{VI}). Potassium ferrate reaction products, consisting of iron hydroxides (iron III) have also coagulant properties and are expected to be less harmful to the environment than sulfate and sodium ions and Mn colloids resulting from the other techniques.

First tests were performed on a reference matrix (Fontainebleau sand) spiked with DNAPL sampled at the studied site, at what is expected to be on-site residual concentration after pumping. The sand-DNAPL mixtures were sampled after three reaction times (3 hours, 1 day and 1 week). PAHs and polar-PACs were quantified by GC-MS after freeze-drying and solvent-extraction of the samples. Same tests were then carried out on the site's contaminated sub-soil, previously cleaned from its pollutants and spiked at the same concentrations as sand. These preliminary experiments will be completed with some optimizations before the application of the two most efficient oxidants in laboratory column tests and, finally, on the field.

Results/Lessons learned: The batch-scaled oxidations on spiked sand gave various results: Fenton-like oxidation was not very effective (total mass loss of extractable organic matter (EOM) of 34.6%), but the treatment was not applied under optimal conditions. The two ferrates were also tested under unfavorable conditions, but managed to reach 44.4% and 65.9% total degradation after one week. The best oxidants were KMnO_4 and heat-activated persulfate which reduced the EOM up to 77.1% and 84.4%, respectively. Similar or even better degradation rates were obtained on the 16-US EPA PAH. However, some O-PAC were generated as degradation byproducts in different proportions depending on the oxidant.