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SILPHES – Investigation of chemical treatments for the remediation of recalcitrant chlorinated solvents: at the roots the development of an innovative in situ eco-friendly process

Romain Rodrigues, Stéphanie Betelu, Frédéric Garnier, Stéfan Colombano, Antoine Joubert, David Cazaux, Guillaume Masselot, Théodore Tzedakis, Ioannis Ignatiadis

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SILPHES – Investigation of chemical treatments for the remediation of recalcitrant chlorinated solvents: at the roots the development of an innovative *in situ* eco-friendly process

Theme 1. Dealing with contamination of soil, groundwater and sediment
Developments in technologies, policies, concepts, regulation, management
1c. Remediation technologies and approaches

Authors: Romain RODRIGUES¹, Stéphanie BETELU¹, Frédéric GARNIER¹, Stéfan COLOMBANO¹, Antoine JOUBERT², David CAZAUX³, Guillaume MASSELOT⁴, Théodore TZEDAKIS⁵, Ioannis IGNATIADIS¹

¹BRGM (French Geological Survey), 3, avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex 2, France.

²SERPOL, 2, chemin du génie, BP 80, 69633 Vénissieux Cedex, France.

³SOLVAY, 1, avenue de la République, 39501 Tavaux Cedex, France.

⁴ADEME (French Environment and Energy Management Agency), 20, avenue du Grésillé, BP 90406, 49004 Angers Cedex 1, France.

⁵Laboratoire de Génie Chimique, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex 9, France.

Contact:

Romain RODRIGUES, PhD student – 0033 (0)2-38-64-35-10 – r.rodriques@brgm.fr

Ioannis IGNATIADIS, PhD – 0033 (0)2-38-64-35-59 – i.ignatiadis@brgm.fr

Key words: *in situ* chemical remediation, oxidation, reduction, eco-friendly process development, recalcitrant chlorinated solvent, hexachlorobutadiene, hexachloroethane, hexachlorobenzene.

Abstract

This study is accomplished within the framework of SILPHES financed by ADEME, the French Environment and Energy Management Agency (AMI 2013 program). SILPHES is a "technology demonstrator" project which aims at developing innovative solutions for *in situ* remediation of a mixture of recalcitrant chlorinated solvent, mainly composed of hexachlorobutadiene, hexachloroethane, PCE, TCE and hexachlorobenzene. SILPHES is organized around two fundamental and complementary tasks:

- The remediation of chlorinated solvents point source pollution. This part is devoted to the optimization of the treatment of the point source, which includes physical, chemical and thermal treatments, associated with diagnostic and monitoring;
- The remediation of chlorinated solvents plume. This part is devoted to the improvement of environmental diagnosis and the design and monitoring of natural attenuation, bioremediation or chemical treatment.

This paper only covers a part of the first point stated above, i.e. the remediation of the residual phase of chlorinated solvents remaining after pumping.

Since the 1990s, *in situ* chemical remediation is frequently considered because of good treatment efficiency without carrying out an excavation or without additional processing step. Among the *in situ* remediation techniques, those for the treatment of chlorinated solvents are highly widespread, essentially for the treatment of PCE and TCE [1-4] by using strong oxidizing or reducing agents. The particularity of this study is the diversity of the chlorinated solvents mixture encountered *in situ*: both aliphatic and aromatic compounds. As a result, molecules have different chemical affinities with reactants, so both oxidation and reduction have been studied.

The chemical degradation of the mixture was investigated in vials to define the relative efficiency of various reagents. Three oxidizing agents (potassium permanganate, Fenton's reagent and sodium persulphate) and four reducing agents (a suspension of nanoscale zero-valent iron, with or without surfactant, sodium dithionite and sodium sulfide) have been used.

All experiments were performed in 100 mL vials filled with 50 mL of deionized water and 1 mL of the mixture of the chlorinated compounds. Different concentrations of reactants were added to the batch system after removing dissolved oxygen. Six replicates of each experimental condition were performed, and all sealed vials were stirred at 100 rpm in a thermostatic chamber at 12°C, the average groundwater temperature. Samples were analyzed at specified times in order to monitor the evolution of the amounts of chlorinated compounds. Ion chromatography was used to determine the production of chloride ions. A percentage of dechlorination was calculated from the measured concentrations of chloride ions by considering a complete dechlorination of all chlorinated compounds contained in the mixture. Gas chromatography–*injecting aqueous and headspace samples*– was used to determine the amounts of initial compounds and intermediate products of their degradation.

Experimental results have shown that, in these operating conditions, reductants are more efficient than oxidants. The highest percentage is about 12.5 % after 80 days of dechlorination, and is obtained with a ratio of sodium sulfide equal to 5 times the theoretical stoichiometry. This low value can be explained by worse operating conditions,

with amount of chlorinated solvents well beyond saturation. The maximum percentage obtained for both nanoscale zero-valent iron and dithionite is about 9%, but at different stoichiometry: at stoichiometry ratio for dithionite and at 0.39 the stoichiometry ratio for iron. Increasing the amount of iron should enhance the degradation of chlorinated solvents. Regarding oxidants, only KMnO_4 have shown relevant results, but lower than those obtained with reductants.

Results obtained by gas chromatography have illustrated the evolution of concentrations of chlorinated solvents. Hexachloroethane and PCE seems to be preferentially dechlorinated in the mixture: the most important variations in concentrations were observed with them or intermediate products of their degradation. Complex patterns of degradation have been observed, so individual chemicals mechanism could not be explicitly illustrated, except for the reduction of hexachloroethane and PCE. The products of this pathway were mainly PCE (β -elimination) and pentachloroethane (hydrogenolysis), but no quantitation could be obtained.

Further studies are currently in progress. The next phase consists in studying the degradation of the mixture with amounts of reagents widely in excess to define the limits of treatment efficiency. Others chemicals will also be tested, in particular potassium ferrate (oxidant) and palladium-doped microscale zero-valent iron (reductant). Once the best reagent compositions are known, several studies will be done with three chlorinated solvents – hexachlorobutadiene, hexachloroethane and hexachlorobenzene – taken individually to establish the reaction kinetics and mechanism at different experimental conditions (pH, temperature, concentration...).

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