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**DECHLORED:
DEVELOPMENT AND *IN SITU* IMPLEMENTATION OF A CHEMICAL PROCESS FOR THE
REDUCTIVE DECHLORINATION OF CHLORINATED SOLVENTS IN POLLUTED
GROUNDWATERS**

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ABSTRACT

Today, reductive dehalogenation (RDH), using strong reducers, is one of the most important emerging remediation techniques for halogenated hydrocarbons (HHC). The use of nano-sized materials, all alone or coupled with strong reducers, for RDH is emerging too as a good alternative and promising technological approach to clean up polluted environments by HHC. Although a number of publications are available in the literature (mainly for water, and less frequently for soils), they do not address mechanistic insights in RDH processes, but usually present certain gaps that prevent the optimized use of these new materials in full-scale pollution remediation applications.

This study is accomplished within the framework of DECHLORED, a project financed by ADEME, the French Agency for the Environment and Energy Resources (Eco-Industries 2011 program). This project aims to : i) develop and prove the efficiency of a novel *in situ* chemical reductive dechlorination process of chlorinated solvents in polluted aquifers by using strong reducers (Sodium Dithionite, DT) with or not the combined effect of Nano-sized zero-valent iron particles (NZVI), and ii) illuminate, by an improved monitoring, the field under RDC process. The purpose of the present communication is to present the work accomplished to set up an enhanced procedure for the reductive dechlorination (RDC) of CSs in polluted aquifers and practiced not only in batch and column experiments but also as *in situ* demonstration. The adopted method was the reductive dechlorination, which is a remediation-by-reduction strategy.

The perchloroethene (PCE) was chosen as the target compound in batch and column experiments as it is one of the most widely widespread chlorinated pollutants in groundwaters.

PCE treatment tests achieved initially in electrochemical cells and results show the effective reduction of PCE by NZVI, firstly by direct electron transfer and secondly from native hydrogen, whatever the investigated medium (milliQ water, K₂SO₄ or KCl). The association NZVI+DT was demonstrated to be more powerful; probably due to a concerted mechanism.

In addition to batch experiments carried out in hermetically closed cells, columns (height 50 cm; diameter 15 cm) are designed and constructed in Kynar® and fully equipped with sophisticated systems for non-destructive monitoring of time changing physical parameters and chemical compositions. This monitoring was complemented by physical and chemical probes (temperature, pH, redox, conductivity, oxygen, sulfide ion and chloride ion) and Gas Chromatography for PCE and its degradation products (DCE, ethene and ethane) and Ion Chromatography for Cl⁻ and SO₄²⁻ in water at the column output to correlate RDC, reactant migration and dispersion and electrical properties.

The entire system was placed in air-conditioned cupboard. Columns are implemented with two rings of Hasteloy® as electrodes for alternative sinusoidal current (AC) injection and six ports equipped with Ag-AgCl electrodes for potential measurement. Two methods are used: i) frequency-domain induced polarization (IP) measurements (which consist of imposing an AC current at a given frequency and measuring the resulting electrical potential difference between two other non-polarizing electrodes), and ii) galvanostatic electrochemical impedance spectroscopy (GEIS). Both of them, by measuring complex electrical conductivity in the mHz to kHz range, are sensitive to electrolytic conductivity, grain surface conductivity and metallic conductivity. Under time varying electric field, pore fluid/solid polarization effects could be measured from surface using IP impedance analyzer or time-domain resistivity meter. Indeed, IP can map real and complex

resistivities of the media at any time and particularly, before, during and after the RDC process application on the column.

Different matrixes (reference sand from Fontainebleau and Cuisian sand from the actual site of Néry-Saintines, 60, France) polluted or not by PCE, different solutions/suspensions of reactants (reducers or NIPs separately or reducers and NIPs together) at two different temperatures (12 and 25°C) are tried. Experiments in columns were carried out to test reactants behavior, in the absence and in the presence of PCE, and allow us to:

- estimate how reactants and PCE chemical degradation products transform electrical properties and assess reactant dispersion, distribution, transport and reactivity on PCE degradation, inside the columns (over all its length) and as a function of time and for different soils
- Improve understanding of reactant efficacy, their transformation and persistence, and also their potential negative effects and model these flow-through systems (1D or 2D column set up) by numerical modeling softwares (PHREEQC[®], Toughreact[®] and MARTHE[®] reactive transport simulations).

Sample analyses by ion chromatography confirm the superiority of the combination DT + NZVI than DT alone. Moreover, sample analyses by gas chromatography suggest the combination DT + NZVI lead to minimize the formation of chlorinated intermediate species; such a significant advantage for in situ groundwater treatments. Our results also recommend combining of geophysical measurements with electroanalytical measurements to monitor RDC processes and will allow us to give an advantageous method for monitoring and checking *in situ* remediation.

The real ambition of the previous work was to treat, at real scale, *in situ* and in saturated zone, the groundwater contaminated by CSs at Néry-Saintines site. To ensure the success of such method, it was necessary: i) to define, at laboratory scale, the operating conditions for an optimal result of the processes application; ii) to draw up the list of the equipment and the technical conditions of implementation on site, iii) to determine the performances of the processes and iv) to make a complete assessment of the processes application. This new process was economically evaluated before the *in situ* implementation.

A data basis of more than a decade aged chemical analyses of the Néry-Saintines site was assessed to illustrate the natural reductive bio-dechlorination and also to select the location for the implementation of the chemical process in site.

Representative samples from each depth were collected and analyzed from several boreholes that come through the contaminated zone. The interpolation of the data on CSs made it possible to obtain a 3D-representation of the pollution from -25 to 0 m, supplemented by a hydrological and geochemical modeling. Thus, the most optimized and safe operating conditions to be applied to the site were determined. A number of piezometers are dedicated to inject treating solutions and some other to monitor the process during and after the treatment application.

To chemically reduce the CSs contained in the selected contaminated zone, the operation consisted in injecting Na₂S₂O₄ solutions thanks to a network of wells. To avoid the exit of CSs and of the reagents out of the zone of treatment, it was imperative to imagine innovative sequences of injections. Indeed, several m³ of Na₂S₂O₄ solutions were injected in three phases and on selected levels (from -25 to 0 m), firstly creating a bowl-shaped hydraulic and reactive barrier. Thus, the confined soil was treated while starting the injections with the sections of bottom upwards.

The process is still under operation. At the end of the application, several representative samples from each depth will be collected and analyzed and the data on total CSs will be interpolated. The quantity of remaining CSs in soil after treatment will be evaluated and the CSs reduction percent will be determined. The whole process after the *in situ* implementation will be economically assessed and compared to other treatments in terms of efficiency, limits, and costs.

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