

## **Paper A 31**

### *Remediation of 1,2-dichloroethane (1,2-DCA) and vinyl chloride (VC) contaminated groundwater: lab and field pilot test.*

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#### **ABSTRACT**

This presentation describes lab and field pilot-test made to design remediation of a chlorinated compounds contaminated area located inside a petrochemical plant (Northern Italy). The site suffers from a contamination in groundwater and soil: it is contaminated by 1,2-dichloroethane (about 300.000 µg/L in groundwater) and vinyl chloride (about 500 µg/L in groundwater).

During lab tests different technologies were tested: two different chemical oxidants and bio-chemical anaerobic reduction. Lab tests have been set up in different phases, as to design the optimal configuration for future field test and full scale application.

One of the two oxidants tested was very effective in the degradation of main contaminants. The oxidant has been tested in two different configurations, with or without activation; surprisingly results proved that the oxidant was much more effective in 1,2-DCA and VC oxidation without alkaline activation (behaviour probably related to high natural iron -radical activator- concentration in groundwater).

Also bio-chemical anaerobic reduction resulted to be efficient for contamination treatment; reactions need a longer time to start, but main contaminants have been completely broken down by native bacteria in less than sixty days.

Enhanced natural attenuation by bio-chemical reduction has been chosen for field-pilot test, considering its minimal geochemical impact on soil and groundwater conditions. Field test area is approx. 50 sqm wide, and the total volume of saturated soil interested by treatment is approx. 700 cm<sup>3</sup>. 6300 kg of ammendant have been injected through nine injection points realized with direct-push technology.

Groundwater was monitored by four observation wells and the results show a widespread redox decrease in the area (-150 mV to -300 mV; the monitoring results show, after a first period of about 6 months with alternative results, a very high efficiency of the treatment on site contamination, as all the final concentration are now lower than the SSTL.

## 1. INTRODUCTION

This presentation describes lab and field pilot-tests realized for the groundwater remediation of a petrochemical plant area located in Northern Italy. This area is contaminated by high concentrations of chlorinated compounds in groundwater and soil. The main contaminants investigated are 1,2 dichloroethane (Cmax:11000 mg/L, Cm: 300 mg/L) and vinyl chloride (Cmax: 130 mg/L, Cm: 0.5 mg/L); these contaminants are distributed in an area of about 7000 sq.mt. and affect a thickness of 7 mt to 13 mt. The primary contamination source zone is located next to an old process water tank (cracking of 1,2-DCA to VC), which, because of progressive deterioration (probably due to the presence of HCl), caused a significant and enduring issue in aquifer of contaminant saturated water.

Because of the high status of contamination found at the source the remediation system has been spread in two separate stages. The first phase has been planned in order to get the peaks of higher concentrations (about 1 g/L) down, using a Pump & Treat technology, as to reach the average values found in the area, while the second and final phase is represented by an in-situ treatment, planned in order to reach the SSTL in the whole area.

This report describes the lab and field pilot tests that lead to the technology selection and final project for the second remediation phase.

In situ chemical oxidation (ISCO) and enhanced natural attenuation have been taken into account for the lab pilot tests; in particular, as ISCO reagents were selected activated sodium persulphate and RegenOx<sup>®</sup> (Regenesis), while permanganate was not used as recognized ineffective in the treatment of 1,2-DCA. For the enhanced natural attenuation the EHC<sup>®</sup> (Adventus) has been used, which is a formulation based on microscopic zero-valent iron and natural sources of organic carbon.

## 2. MATERIALS AND METHODS

The lab tests have focused on all three reagents selected and had the aim of assessing their efficiency, establish the optimal rates and determine their impact on the geochemical conditions of the site.

For the test samples of soil and groundwater were taken directly from the contaminated site through the use of direct push equipment (Geoprobe<sup>®</sup>). The samples collected were appropriately characterized and homogenized in the laboratory to carry out the lab tests. The test related to chemical oxidation was divided into two distinct phases: a first phase to be carried out on not contaminated water coming from the site, in order to calculate the Soil Oxidant Demand (SOD), (i.e. the amount of oxidant consumed from the soil matter and therefore not available for the degradation of contaminants dissolved in the aqueous phase). In the second phase the contaminated soil and groundwater were treated using the reagent amount calculated on the base of previously measured SOD and of the stoichiometric demand related to the maximum contaminants concentration.

Samples of soil and water were placed in glass bottles of 2 L with appropriate sealing cap to prevent the volatilization of contaminants.



As to the test of enhanced natural attenuation, because of the longer reaction times, a test consisting of a single phase was designed, again performed on a sample of saturated matrix taken from the site. The optimal dose of the reagent was assessed by the same manufacturer of the reagent on the basis of the site geochemical characteristics and of the contamination to be treated. Again, the sample was placed in glass bottles of 2 L with special cork tight; collection and analysis system have been arranged in order to characterize the eventual gas produced by the reactions of biological degradation.

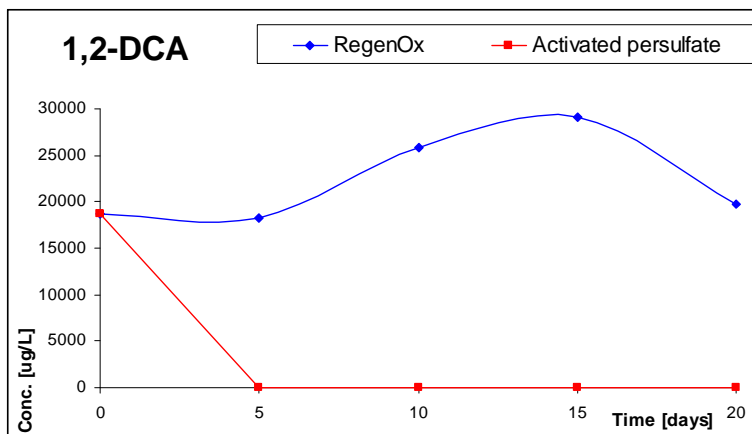
The analytical protocol was the same for both types of treatment (ISCO or enhanced natural attenuation), but were differentiated by the analysis timing as to the different expected reaction times (very rapid for chemical oxidation, longer for the reductive biodegradation). Samples of soil and water have been subjected to a complete characterization (analysis of metals, inorganic compounds, VOCs) before and after the test, while intermediate analysis have been realized just for the water, monitoring only the VOCs.

As for the field test a specific area of about 50 sq.mt. was selected, considering that it should be representative of the mean state of contamination of the site; within the area to be treated the injection of reagents has been performed by direct-push technology and four monitoring wells were realized in order to monitor the water quality.

As the technical specifications for injection are closely related to the type of compound to be injected, they were decided only after the lab tests, which led to the selection of the reagent to be used (EHC).

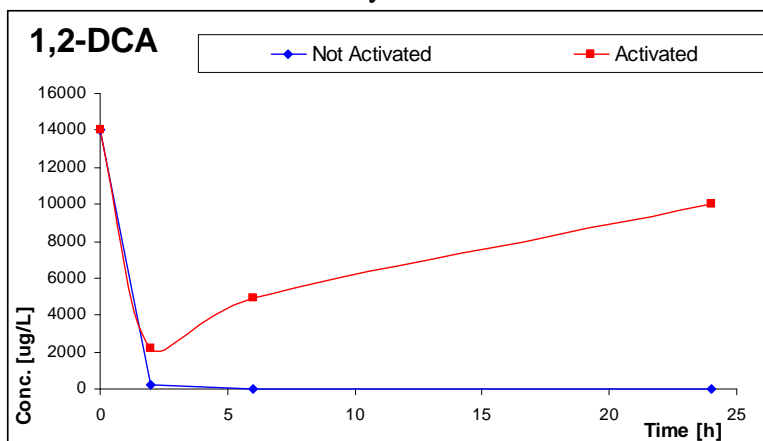
### 3. RESULTS AND DISCUSSION

Although intended to estimate site specific SOD, the first phase of lab test for chemical oxidants showed a low efficiency for RegenOx<sup>®</sup> in the treatment of target contaminants. This testing phase involved the treatment of site clean water and contaminated soil; thanks to the mixing of the two matrices a significant amount of contaminants was dissolved in water (due to their solubility); following this transfer phase has been observed that, in the presence of sodium persulphate (with activator), the concentration values of all the contaminants in water and soil have fallen down very quickly to reach values close to the SSTL concentrations, while the sample treated with RegenOx<sup>®</sup> showed no evidence of concentration decreasing for the compounds of interest. Here are the trends in concentrations of 1,2-DCA for the first phase of the test.



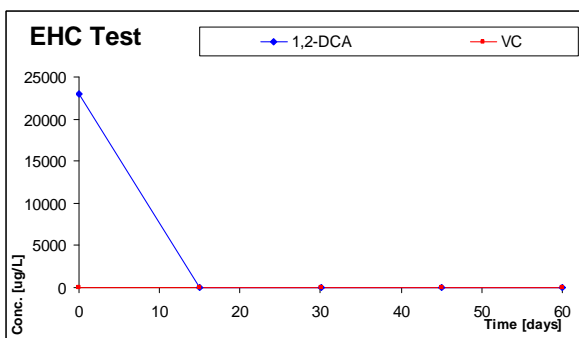
At the end of the test the titration of residual persulphate has been carried out in order to calculate the amount of oxidant consumed to oxidize contaminants and all oxidable matter adsorbed on the treated soil. Based on these results the test for RegenOx<sup>®</sup> has been suspended and the next phase of the lab test has been realized only for sodium persulphate. Knowing the amount of persulphate necessary because of SOD and stoichiometric oxidation of contaminants, the second lab test phase has been prepared using the site contaminated water and soil. During the test has been observed that, as the oxidation reactions are non-selective ones, the use of alkaline activation (NaOH) led to a solubilisation of some metals and in particular to the oxidation of Cr (III), naturally contained in the soil, to Cr (VI), a contaminant very soluble in water, not present in the site groundwater. Additional tests were carried out using different doses of reagent and activator as to identify the optimal amount and ratio reagent/activator as to ensure the oxidation of contaminants minimizing the solubilisation of metals and especially the oxidation of Cr (III) to Cr (VI).

The results of this test showed that using just the reagent, without the activator, determines the best efficiency of the treatment with the least release of metals in water.



As previously related, lab pilot tests using EHC were carried out in a single phase in which a sample was treated for a period of 60 days. Intermediate samplings showed that main contaminants concentrations, in particular 1,2-DCA, were greatly decreased after only 15 days and they achieved values near to D.L. at the end of the test.

Also the last gas analysis collected during the test showed a great fermentative microbial activity and a consequent gas generation at first not present in the reaction environment.



Analyte	U.M.	Blank	EHC <sup>®</sup>
methane	mol/mol %	0.000	0.013
carbon dioxide	mol/mol %	0.682	5.370
ethylene	mol/mol %	0.000	3.423
ethane	mol/mol %	0.000	0.011
oxygen	mol/mol %	20.491	18.525
nitrogen	mol/mol %	78.827	72.657
Totals (ideal)	mol/mol %	100	100

Lab tests showed a comparable efficiency between ISCO and enhanced natural attenuation. Therefore, considering 1- low geochemical impact on soil and groundwater conditions, 2- major selection of bio-chemical reduction and 3- longer time of reagents persistence in groundwater, enhanced natural attenuation by bio-chemical reduction has been chosen for field-pilot test, that is trough EHC reagent injection.

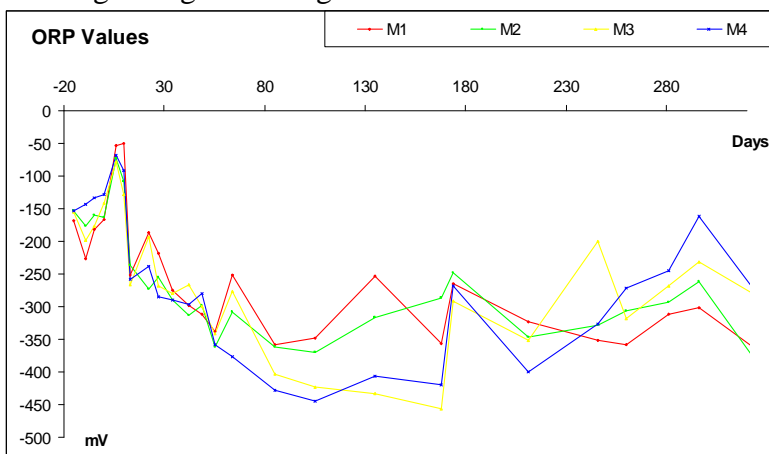
As previously related, field test area is approx. 50 sq.mt. wide, and the total volume of saturated soil interested by treatment is approx. 700 cu.mt.. 6300 kg of reagent have been injected through 9 injection distributed with a 3 mt x 3 mt grid.

The reagent in fine powder has been injected as a slurry with 30%v concentration, starting from the bottom to the surface.

Before injection, 3 monitoring campaigns have been done in order to evaluate the average contamination in the area and to analyze main chemical-physical parameters.

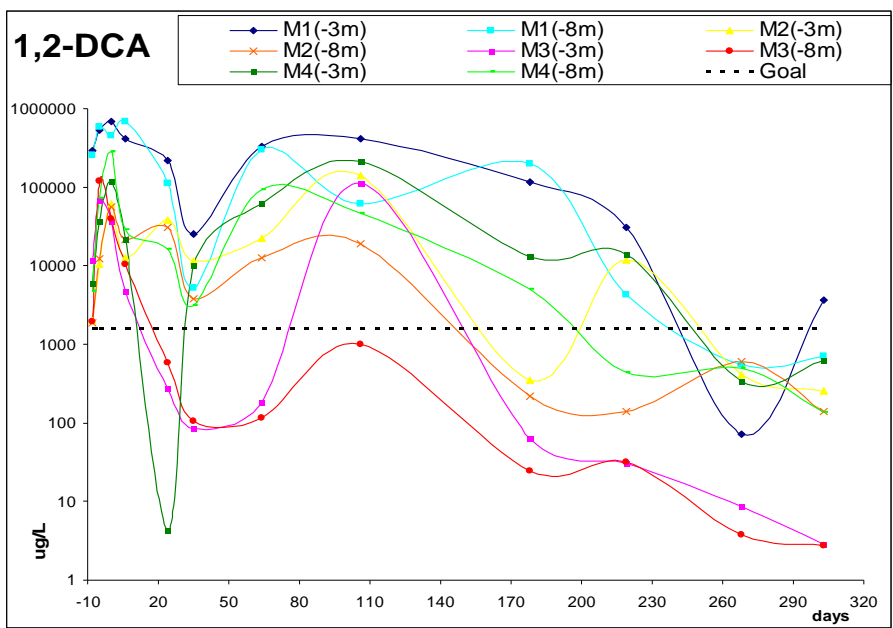
The monitoring of these parameters, in particular the ORP, is important to evaluate the growth of anaerobic microorganisms due to ammandant injection present in EHC.

In fact, a great decrease of ORP value (from -150 mV to -300mV) was detected showing an high reducing environment.



Also the monitoring of chemical parameters showed positive results: after about 300 days from reagents injection nearly all groundwater samples collected in the area have reached contaminants concentrations lower than remediation goal equal to approx. 1,5 mg/L.

Furthermore, VFAs (volatile fatty acids) values higher than 100 mg/L were detected, as by-product of organic-carbon fermentation. Organic carbon is utilized by microorganisms as electron donor for contaminants reduction.



It is possible to observe that contaminants concentrations have a different flow among the monitoring wells, mainly in the first test phase. This is due to the non-homogeneous distribution of injected reagent for the presence of soil strata's with different grain size that could cause privileged pathways for reagent diffusion.

This non-homogeneous distribution is compensated by the power of the reagent to create an homogeneous reducing environment consequently to the fermentation reaction due to the ammandant presence.

#### 4. CONCLUSIONS

Following the results obtained by lab and field pilot tests, design of full-scale remediation with EHC injection is at the present time on-going; a further limited monitoring of the field test is still on-going in order to verify the effective reagent life. Remediation project is foreseen to be ready in Summer 2009, and full scale remediation is foreseen to start in about one year later, with an estimated duration of approx. 2 years. From preliminary dimensioning, it is foreseen to inject (after first treatment step with Pump & Treat technology) a quantity of reagent ranging from 600 to 700 ton, for the treatment of an area of approx. 7000 sq.mt.