

Use of Oxidant Chemicals and Slow Release Oxygen Compounds for the Remediation of a Site Contaminated by Organic Compounds

Virgilio Pagliarani*, Michele Paolucci, Stefano Di Nauta

Petroltecnica S.p.A. Via Rovereta, 32 Cerasolo Ausa Coriano (RN) - Italy
virgilio.pagliarani@petroltecnica.it

Chemical oxidation is a remediation technology that allows to break down the main organic contaminants through oxidation carried out by chemicals that are harmless to the environment. This work describes the application of in-situ chemical oxidation (ISCO) technology in a case of typical hydrocarbon contamination in an active petrol station where setting up bulky remediation systems was not feasible. The injection of the oxidant compound into subsurface soil has decreased contamination within the soil matrix and the subsequent transfer of the reaction by product to groundwater makes its treatment easier. The significant observed improvement of groundwater quality parameters, such as redox potential and the dissolved oxygen, confirms the effectiveness of the applied treatment.

1. Introduction

The remediation technology called "*chemical oxidation*" is based on the injection of a oxidizing agent within the impacted environmental matrix and by the reaction between the oxidant compound and the organic pollutant that allow the degradation into carbon dioxide and water.

Chemical oxidation processes have been widely used for the treatment of waste water ex-situ before being applied on site. Tanks to their proven effectiveness on a wide variety of compounds, chemical oxidation has been successfully tested together with injection technique for in situ remediation of soil and groundwater.

Chemical oxidation can be induced through the use of solid alkaline compounds, such as sodium percarbonate; it can react with hydrocarbon and chlorinated pollutants. *In situ* application is performed by injection of the alkaline compound in the subsoil with equipment for drilling or direct-push techniques.

Sodium percarbonate causes only slightly adverse effects on the environment, a moderate exothermic reaction. The exothermic reaction persist just for a weak and gradual increase of temperature over the course of the first 5 - 10 days; temperature of the groundwater turn into normal condition after 10 - 20 days. Pressures increase are normally.

All the chemical reactions produced by oxidizing agents may last up to 30 days after the injection date, moreover the reactions also produce a purposeful oxygen concentration in the groundwater that can be used by the aerobic biodegradation process for a long period.

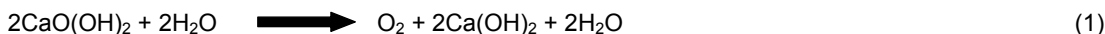
Enhanced Aerobic Bioremediation is an approach that provides a proven cost-effective method to accelerate the natural processes and decrease the time required for environmental remediation and consist in enriching the soil of oxygen. Consequently, the ideal habitat is created for the proliferation of

indigenous microorganisms capable of aerobically biodegradation of organic contaminants (hydrocarbons and MtBE).

In the study case, after the oxidant compounds, an injection of compounds of proven effectiveness in slow oxygen release is scheduled.

These products allow a controlled release of peroxide substances, hydroxyl-based, that allow the oxygenation of the subsoil. In the presence of oxygen, micro organisms are stimulate to perform the aerobic degradation of hydrocarbons and other compounds aerobically degradable.

The main compound, used in this in the study case, was calcium peroxide, which, after hydration with water, releases oxygen and calcium hydroxide and water as products of reaction, according to the following Reaction 1:



The calcium peroxide is a fine powder which was mixed in this case with water and displaced in the subsoil by direct injection of slurry.

2. Application of remediation technology

Chemical oxydation technology was used for the environmental remediation in an active petrol station where any type of traditional remediation technique was not possible to perform for logistical needs.

The site characterization was carried out in the site; a slight contamination, adsorbed to soil in the saturated subsurface (depth: 4.5 m - 5.0 m from the current ground level), was detected in correspondence of two of the six drillings equipped with monitoring wells installed on site; the drillings indicated the presence of a groundwater surface in a variable depth between 1.8 m to 2.5 m from ground level.

In order to define the extension of the contamination plume in the groundwater, an initial characterization was carried out; chemical-physical parameters were also analyzed.

Even the chemical analysis performed on the water samples highlighted the presence of a contamination.

Chemical analysis of the water showed the presence of a weak of contamination in correspondence of PM1 monitoring well and presence of MtBE in correspondence of PM1, PM2 and PM3 once.

Moreover, the groundwater analyzed was characterized by a high chemical oxygen demand (C.O.D.) and reduced dissolved oxygen values; these conditions match the application of the chemical oxydation technology for the environmental remediation.

Table 1, 2 and 3 summarizes the results obtained from chemical analysis performed on water and soil samples.

Table 1: Analytical result of pollutants in water samples (PM1-PM6 ID of the wells)

Sample ID	TPH	Benzene	Toluene	Etyl-benzene	Xylene	MtBE
	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$
PM1	579	1272	11	228	47	7490
PM2	<10	<0.1	<0.5	<0.5	<0.5	571
PM3	<10	<0.1	<0.5	<0.5	<0.5	243
PM4	<10	<0.1	<0.5	<0.5	<0.5	<0.5
PM5	<10	<0.1	<0.5	<0.5	<0.5	<0.5
PM6	<10	<0.1	<0.5	<0.5	<0.5	<0.5
Legislation Concentration limits	350	1	15	50	10	-

Table 2: Analytical result of water samples - chemical-physical and microbiological parameters

Sample ID	Total Nitrogen mg/l	Total Phosphorus mg/l	C.O.D. mg O ₂ /L	B.O.D.5 at 20°C mg O ₂ /L	Total microbial counts at 22°C UFC/mL	Total microbial counts at 36°C UFC/mL	pH	Redox potential mV	Dissolved oxygen mg/L
PM1	8.7	0.16	121.7	40.7	6.0x10 ²	9.5x10 ²	6.99	159	0.95
PM2	8.4	0.10	93.6	31.5	4.2x10 ³	6.4x10 ³	6.86	211	1.29
PM3	<5.0	0.04	18.9	6.5	5.0x10 ¹	2.0x10 ¹	7.13	213	3.39
PM4	<5.0	<0.01	<2.5	<1.0	5.6x10 ²	2.0x10 ²	7.09	230	2.32
PM5	<5.0	0.19	140.4	47.1	2.1x10 ⁵	2.1x10 ⁵	6.98	216	0.62
PM6	<5.0	0.05	65.5	22.1	4.2x10 ³	2.5x10 ³	6.81	122	0.64

Table 3: Analytical result of the pollutants in the soil samples (PM1 – PM6 ID of the drillings)

Sample ID	TPH C < 12 mg/kg s.s.	TPH C > 12 mg/kg s.s.	Benzene mg/kg s.s.	Toluene mg/kg s.s.	Etyl- benzene mg/kg s.s.	Xylene mg/kg s.s.	MTBE mg/kg s.s.
PM1 3.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	0.2
PM1 4.5 m	16	<20	0.2	0.1	<0.1	0.7	1.3
PM1 6.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM2 1.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM2 1.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM2 3.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM2 4.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM2 5.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM3 3.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM3 4.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM3 5.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM4 1.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM4 3.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM4 4.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM4 5.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM5 0.7 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM5 1.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM5 2.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM5 3.0 m	52	<20	0.8	0.2	<0.1	0.4	1.1
PM5 4.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM5 5.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM6 1.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM6 3.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM6 4.5 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
PM6 5.0 m	<5	<20	<0.1	<0.1	<0.1	<0.1	<0.1
Legislation concentration limits	10	50	0.1	0.5	0.5	0.5	-

2.1 Application of chemical oxydation technology

The remediation design was based on stoichiometric calculations that led to identify the best configuration for the application of technology to the specific site and determine the amount of oxidant substance necessary for the remediation of the site.

Sodium percarbonate was applied by a series of injections made directly into the aquifer (direct-push injection). The injection points were made using a Geoprobe™ drilling machine like connected to a system called pressure - activated injection probe, located at the end of the drill rods; it allows to make localized injections of the mixed product. The positioning of these points of injections was performed following a logical path of rational grid, depending also on the underground structures in the area.

The remediation procedure was carried out in different steps with a time interval called T1 ÷ T8 shown in Figure 1. The injections of the oxidant compound were performed with a consecutive series of No 3 interventions at the following times: at T1, between T4 and T5 and between T6 and T7.

In all the injection campaigns the applications of the oxidizing agent were performed either in a top-down way, releasing the oxidant compound from top to bottom during drilling, and down-top way, releasing the oxidant substance from the bottom to the top during the extraction of injection rode. The injections of the oxidant compound involved an aquifer thickness of 3.5 m, between 1.5 and 5.0 meters from the ground level, this procedure has allowed a greater mixing of the oxidizing agent and its uniform distribution within the aquifer.

After each injection, chemical analysis and the monitoring of various parameters, in order to verify the results achieved, were carried out.

2.2 Application of oxygen slow-release compounds

At the end of the first phase of the remediation, in order to eliminate the residues of contamination due to desorption of the contamination implemented by oxidant chemicals, was carried out on site a campaign of injections of oxygen slow release compounds was carried out at time T9.

The applications were carried out in top-down way between the depth of 2.5 m and 5.0 m.

At the end of the application chemical analysis of control and monitoring were conducted bi-monthly, represented by the time T10-T15.

2.3 Data analysis

The results of chemical analysis, performed at regular intervals after the injection of the oxidant compound, shown a general decrease of the levels of contamination with cycles of rebound effect particularly in PM1, the most impacted monitoring well. Also in PM3 a peak not in line with the time course was evident (Figure 1).

The increase of concentrations in groundwater may be due to the action of desorption carried out by the oxidizing agent (sodium percarbonate); as regards of the observed peak in PM3 this is surely correlated with the position of the well very close to the tanks farm.

Figure 1 shows the trends of the contaminants detected in correspondence of the monitoring wells PM1, PM2 and PM3.

The analysis of the groundwater parameters showed a relation between the injection of the oxidant compound and the increase in groundwater of redox potential and dissolved oxygen. Oxygen concentrations remained stable for a long period after the injection of oxygen slow release products. Figure 2 shows the results achieved.

3. Conclusions

The application of chemical oxidation technology on site has allowed to achieve the following results:

- Desorption of adsorbed contamination to soil, verified by the cyclical rebound effects after each application testing;
- Creation of ideal conditions for the removal of dissolved contaminants in groundwater through the use of oxygen slow release compounds, as demonstrated by the analyses of various parameters of the aquifer;
- Avoid the installation of bulky remediation systems in a site where logistical conditions would not allow it;

- Avoid the production of waste material as GAC (Granular Activated Carbon) and water discharge from water treatment plant;
- Avoid any excavation and disposal in landfills of soil;
- Preserve the downstream receptors by the migration of the contamination without the aid of additional supporting technologies.

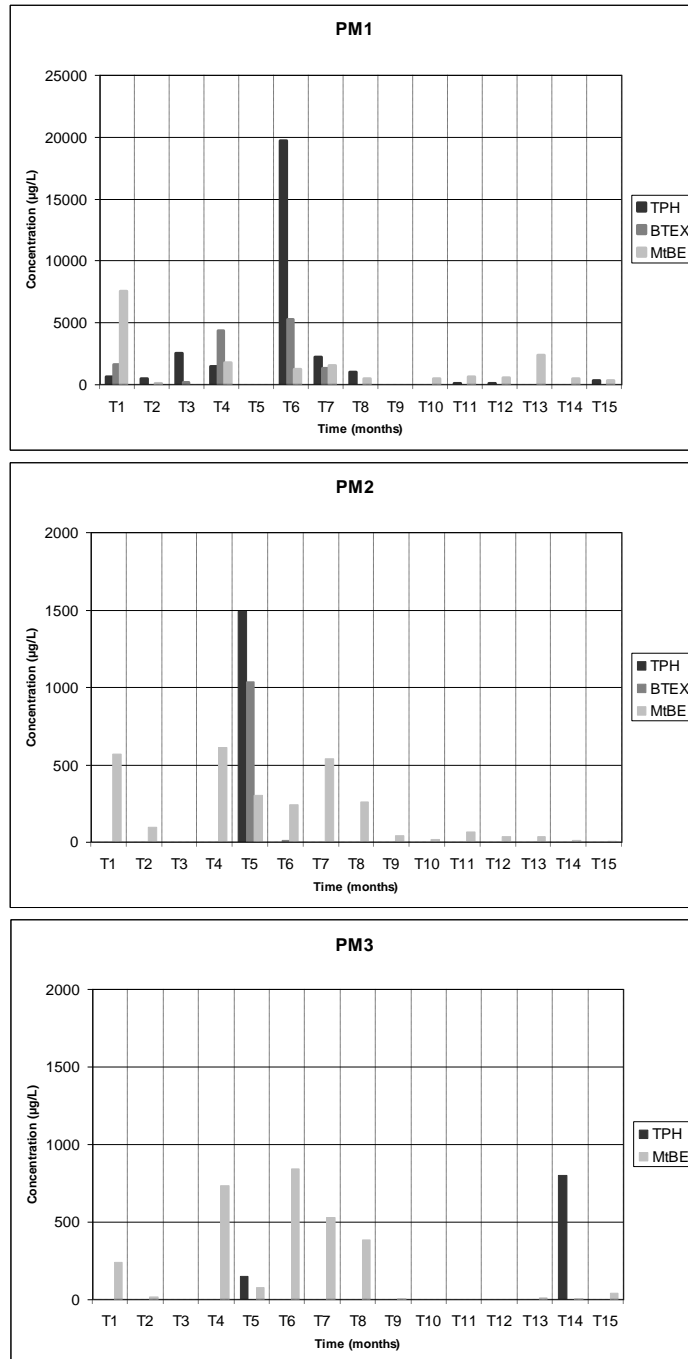


Figure 1: Contamination trends in three polluted wells (PM1, PM2, PM3)

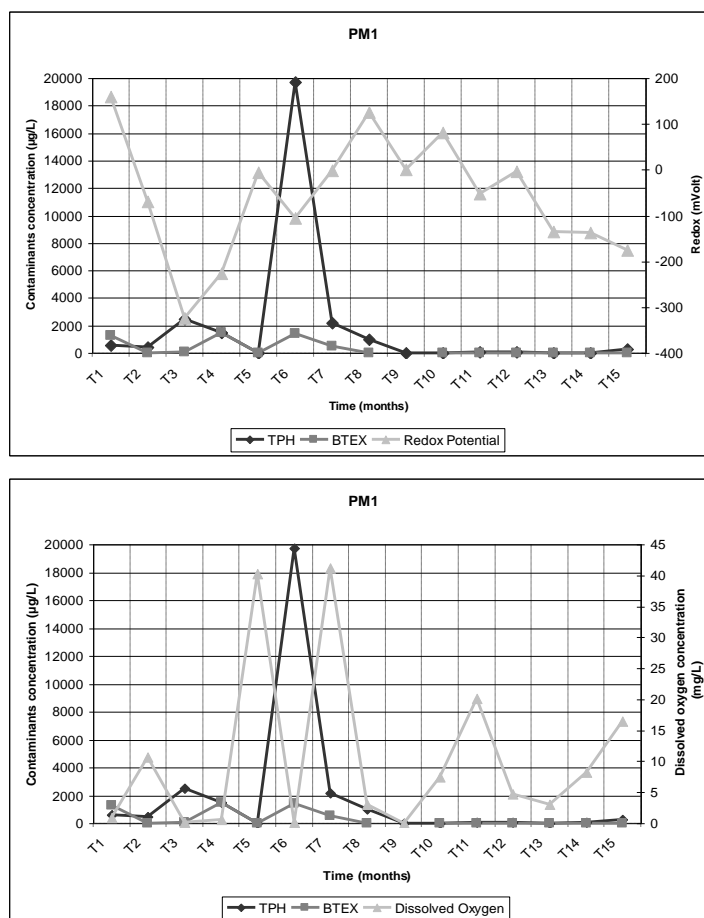


Figure 2: Groundwater parameters trends in PM1 well

References

- ITRC (Interstate Technology & Regulatory Council). 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd ed. ISCO-2. Washington, D.C.: Interstate Technology & Regulatory Council, In Situ Chemical Oxidation Team. <www.itrcweb.org> accessed 26.04.2012.
- Regenes Bioremediation Products, 2010, Principles of Chemical oxidation Technology for the Remediation of Groundwater and Soil. Regenes inc., San Clemente, California, USA.
- Robert L. Siegrist, Michael A. Urynowicz, Olivia R. West, 2001, Principles and Practices of in Situ Chemical Oxidation Using Permanganate. Battelle Press 2001, Columbus, Ohio, USA.
- Robert L. Siegrist, Michelle Crimi, Richard A. Brown, 2011, In Situ Chemical Oxidation for Groundwater Remediation, doi: 10.1007/978-1-4419-7826-4_1, # Springer Science+Business Media, LLC 2011.
- Scott G. Huling, Bruce E. Pivetz, 2006, In-situ Chemical Oxidation. EPA/600/R-06/072, 1-60. 8-1-2006 USEPA.