USING ISCO WITH PEROZONE® FOR REMEDIATING A COCKTAIL OF ORGANIC CONTAMINANTS AT AN OPERATIONAL, EX-RATED INDUSTRIAL SITE

Introduction

The site of a chemical storage company in the Port of Antwerp, Belgium, has shallow groundwater contamination (upper 5 m) consisting of a cocktail of petroleum hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX) and chlorinated aliphatic hydrocarbons (CAH) in high concentrations. The contaminants are below the chemical facility's infrastructure, for example, aboveground storage tanks, pipes and loading areas. Laboratory and pilot tests showed that traditional remediation techniques, i.e., bioremediation and dual-phase extraction, were unsuitable. Currently, no tried-and-tested remediation techniques, except excavation, are available to remediate contamination by such a cocktail of organic contaminants in high concentrations. As the site is operational, excavation as a remediation technique is only partially feasible.

One suitable technique that would not leave significant contamination in the soil is in-situ chemical oxidation (ISCO) using Perozone.[1] This oxidant reacts with organic contaminants in an exothermic reaction that causes the soil's temperature to rise and releases oxygen, water and carbon dioxide. It is clear that this type of ISCO must be carefully controlled to avoid incidents, as there are serious safety risks. Moreover, the chemical facility for where this ISCO remediation technique was proposed is explosion sensitive (EX-rated) in operation. This project aimed to demonstrate the full-scale application of the innovative remediation technique taking into account the necessary safety measures. The safety methods and measures developed for this project are easily transferable to other contaminated sites.

Innovative ISCO treatment using Perozone

Perozone is an oxidant mixture of hydrogen peroxide and ozone created by coating nano- to micro-sized bubbles of air-encapsulated ozone with a liquid oxidant (hydrogen peroxide). The reaction of this coating is as follows:

$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2$

During this reaction, hydroxyl (OH·) free radicals form, which creates a high oxidation potential. This high oxidation potential means that different types of contaminants can be treated with Perozone. In addition, the reaction releases oxygen, which enhances the biological aerobic degradation.

The Perozone is injected into the soil using injection filters with two compartments, an inner and an outer tube, known as laminar sparge points. The outer tube contains liquid hydrogen peroxide. Ozone is injected into the inner tube under pressure, which causes it to be forced through the outer tube, thereby coating the ozone bubbles with the hydrogen peroxide, see Figure 1.

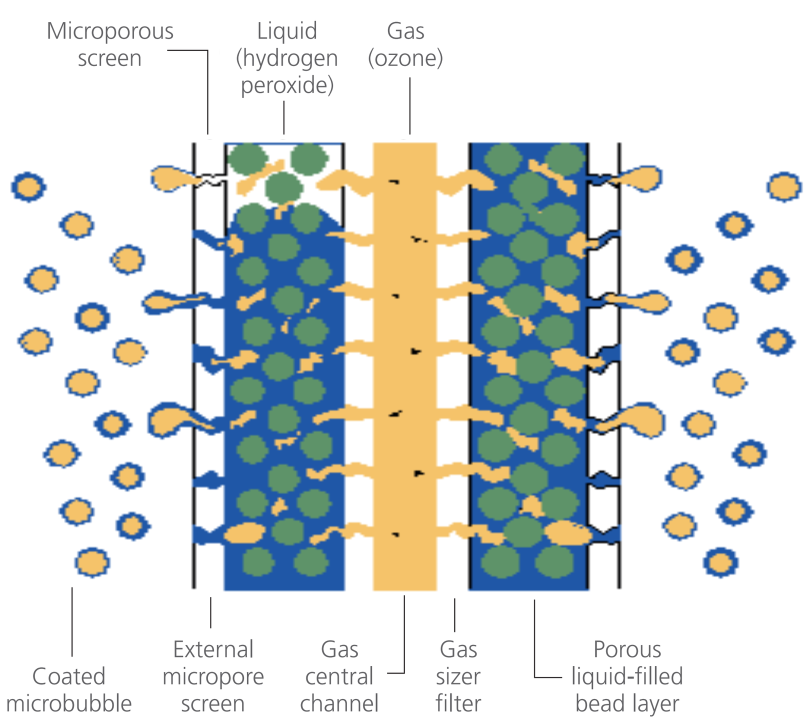


Figure 1: Coated microbubbles in laminar sparge points.

The reaction of ozone with the contaminants forms hydroperoxides, which also create OH· radicals. This dual formation of OH· radicals ensures a very high oxidation capacity.

The interaction of the coated microbubble with the contaminant is shown in Figure 2.

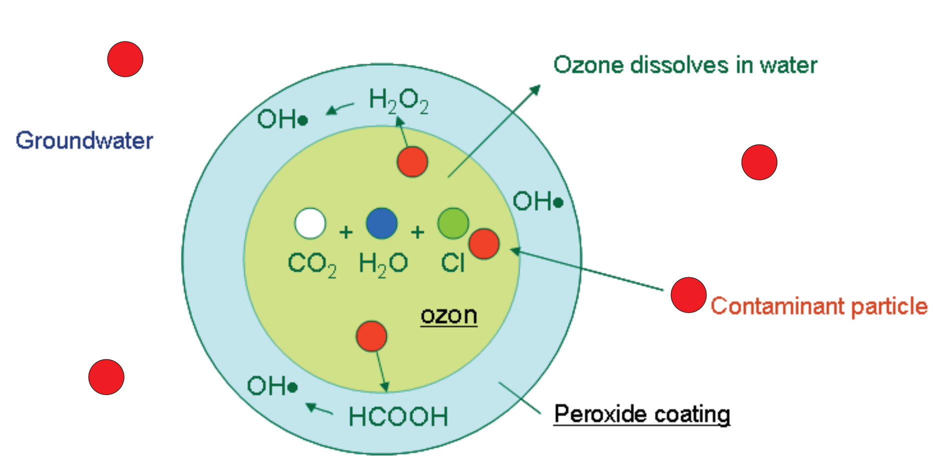
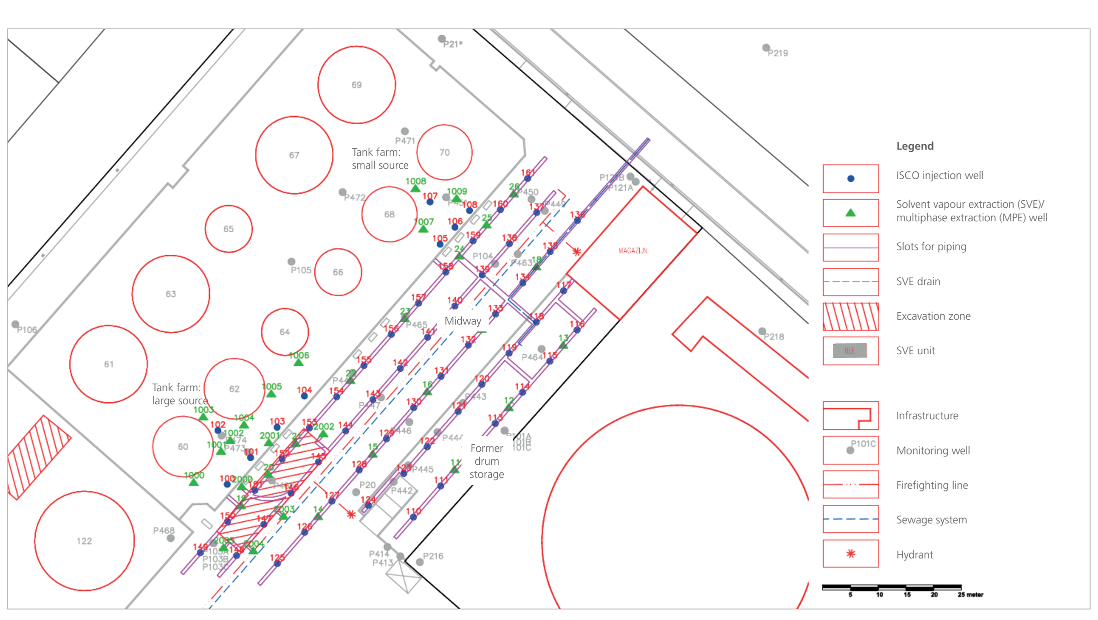


Figure 2: Reaction of a microbubble with contaminants.



The installations for the remediation work.

[1]Perozone is a trademark and patented technology of Kerfoot Technologies Inc.

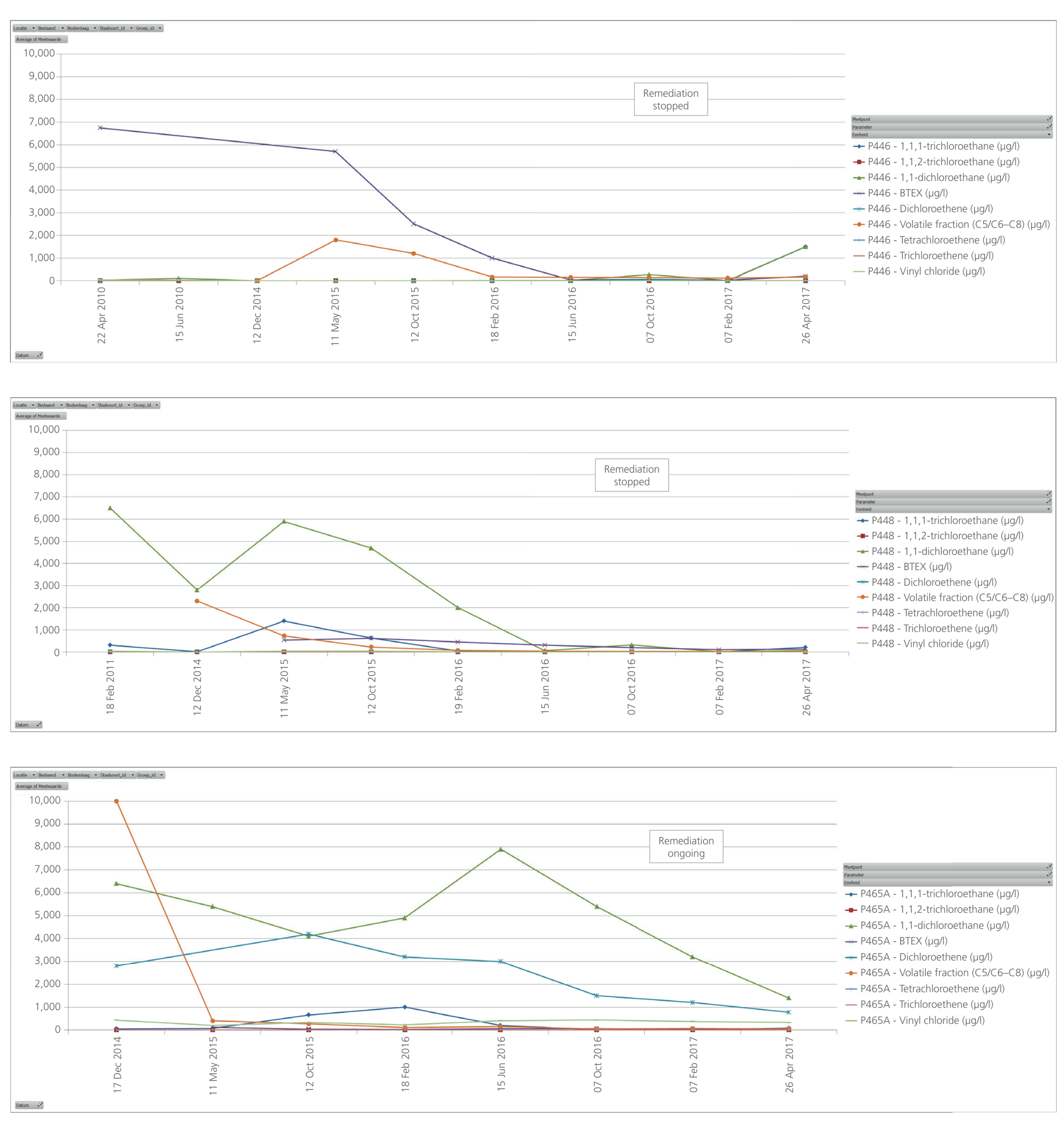
Environmental advances

The aim of the ISCO treatment was to bring the concentrations of contaminants below the cleanup goals in the different areas (former drum storage area, midway and the source zones at the tank farm), as shown in Table 1.

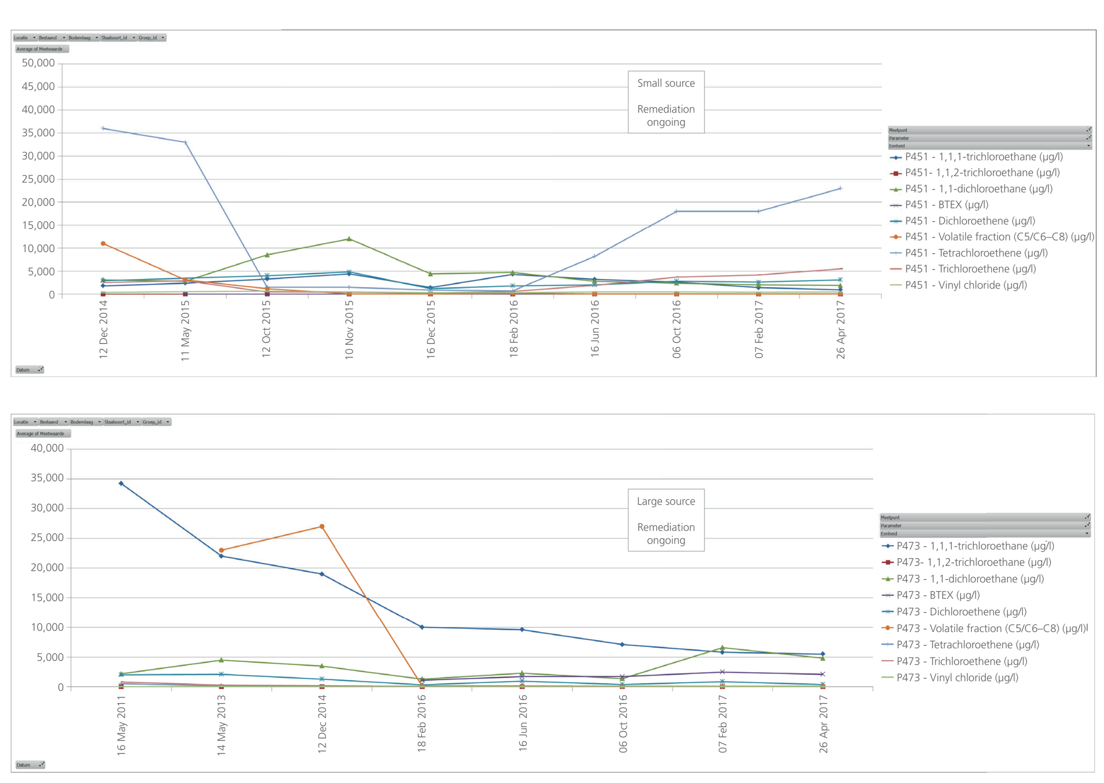
Contaminant	Maximum concentration (µg/l)	Target concentration (µg/l)
BTEX		
Benzene	140	100
Toluene	17,000	7,000
Ethylbenzene	10,500	3,000
Xylene	8,700	5,000
CAH		
Chloroethenes		
Tetrachloroethene	6,900	400
Trichloroethene	1,300	700
1,2-dichloroethene	48,000	500
Vinyl chloride	2,068	50
Chloromethanes		
Trichloromethane	12	
Dichloromethane	3,200	200
Chloroethanes		
1,1-dichloroethane	266,000	3,300
1,2-dichloroethane	2,100	300
1,1,1-trichloroethane	348,000	5,000

Table 1: Contaminant concentrations and cleanup targets.

Former drum storage area: ISCO treatment between August and October 2013.



Midway: optimised ISCO treatment from July 2014.



Tank farm: remediation from January 2015.

Safety-related aspects

To keep the safety-related aspects under control, an intensive monitoring programme (weekly or fortnightly, as appropriate) was developed for oxygen and ozone concentrations, and lower explosive limits (LEL) and photoionisation detector (PID) measurements at critical points in the soil vapour, ambient air and granular activated carbon (GAC) treatment areas. This monitoring programme is being conducted by the commissioner, the contractor and by an accredited remediation expert. This monitoring programme is indispensable for maintaining safety and its data are compared with the action values shown in Table 2.

Action values	LEL (%)	PID (ppm)	Oxygen (%)	Ozone (ppm)
Extracted soil vapour	10	–	22.5	0.3
Influent vapour GAC	10	–	22.5	0.3
Effluent vapour GAC	1	5	22.5	0
Headspace of monitoring wells	–	–	25	–
Ambient air ISCO zone	10	–	20.9	–
Soil vapour below tank bottom	–	–	20.9	–

Table 2: Safety-related action values.

Additionally, soil subsidence potentially related to the ISCO treatment is monitored quarterly for the aboveground structures.

Uncontrolled emissions

The site is a storage terminal for chemicals. No oxidising agents are allowed near the aboveground storage tanks. Contact between ozone and the chemicals could result in flammable and explosive reactions. To prevent such contact, a soil vapour extraction (SVE) system has been installed to capture ozone and hydrocarbons in the vadose soil zone. Vertical wells have been installed in the tank farm and there are drains in the former drum storage area and the midway.

At the beginning of the project, measurements showed elevated ozone concentrations in the atmosphere near the surface and at breathing height, and elevated concentrations of 1,1,1-trichloroethane and volatile total petroleum hydrocarbons in the fissures in the concrete of the midway. Consequently, the ISCO treatment was temporarily shut down. To resolve this, the concrete floor of the midway was renewed and injection tests for optimising the ozone injection scheme were undertaken. With the optimised injection scheme, no ozone and hydrocarbon emissions have been measured in the atmosphere to date, see Table 3.

Parameter	Ozone injections characteristics	
	Former drum storage	Midway and tank farm
Injection time laminar sparge point/ total injection cycle time (min)	10/150	2/18
Injection discharge rate (Nm³/h/valve)	12	4–6
Ozone load (g/h)	200	46–100
Peroxide (7% solution) dose at laminar sparge point (ml/min)	80	40

Table 3: Ozone injection characteristics.

Corrosion

Ozone and oxygen can corrode underground structures such as the steel bottoms of storage tanks, so inclined soil vapour monitoring wells were installed at the tank bottoms. Intensive monitoring did not show any increased concentration of oxygen or ozone. Inspection of two tanks from the large source area when they were removed from the tank farm during the LIFE+ project showed no corrosion caused by the ISCO treatment.

Soil subsidence

One concern relating to the injection of Perozone in soil is soil settlement. Consequent differential settlement could cause storage tanks to burst. A land surveyor measures and monitors possible settlement of the infrastructure quarterly and has not found any ISCO treatment related settlement in the last five years.

Fire and explosion

Adsorption of hydrocarbons by GAC filters and oxidation of hydrocarbons are exothermic reactions. A large contact area such as GAC could induce spontaneous ignition more easily. The flashpoint of many substances in this contact area is lowered by the increased oxygen concentration in the soil vapour. Consequently, the cocktail of oxygen and hydrocarbons becomes more flammable and explosive in the places where it accumulates. Intensive monitoring of the GAC filters is undertaken to monitor the flammable conditions. No exceedance of the action values has been seen under the optimised injection regime.

Failure

When applying Perozone in an active industrial environment, it is very likely that third-party, and thus untrained, personnel may be working near the ISCO machinery and infrastructure. Therefore, working procedures and protocols were established for the

- startup and shutdown of the ISCO treatment and SVE extraction equipment
- supplier delivery and storage of hydrogen peroxide
- extinction of carbon filters
- emergency stops
- cleaning and refilling of the GAC carbon filters.

The general action plan is elaborated and available on the project website as a summary of the LIFE+ project: www.vopak-expero3.be.

Conclusions

ISCO remediation of contaminants using Perozone at a chemical storage facility with EX-rated areas is feasible and can be conducted safely if the following conditions are respected:

- an optimised injection process for Perozone to minimise the sparging of ozone and volatile organic compounds to soil vapour
- an SVE system enabling the removal of accidental excesses of ozone in the vadose soil zone
- an intensive monitoring programme for evaluating the relevant safety parameters weekly or fortnightly, as appropriate.

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