

## **Environmental problem targeted**

### **General**

European soils contain many legacies from a less sustainable industrial past. Soils, sediments, and groundwater are sinks for many contaminating substances, and only through active clean-up operations can they improve in a reasonable length of time. Active clean-ups are very expensive, especially if the area that needs to be decontaminated is large and the contamination is persistent.

The European Environment Agency (EEA) estimates of the number of contaminated sites in the EU that can be cleaned up (that is, where the source of the contamination is no longer present) range from 300,000 to 1.5 million; the agency estimates the total cost of cleanup for these sites to be between € 59 and € 109 billion. However, there also are many sites where the source of the pollution still is present. This means that the actual clean-up cost for contaminated sites in Europe will be a multiple of this estimated.

The major pollutants present at a large number of industrial sites in Europe are heavy metals, hydrocarbons, BTEX (benzene, toluene, ethylbenzene and xylene), and chlorinated aliphatic hydrocarbons (CAHs). These contaminants all have different chemical and physical characteristics and different means of biodegradation. Traditional remediation techniques (dual phase extraction, pump and treat, and so forth) are often suitable for one or several types of contaminants on the condition that they have comparable chemical and physical characteristics and when no pure product is present. In addition, different contaminants are biodegraded by different soil redox conditions (anaerobic versus aerobic), which makes bioremediation very difficult when different types of contaminants are present.

At this time, excavation is the only remediation technique available that can remediate a cocktail of contaminations in high concentrations. However, excavation is often not possible at a site in operation, due to the high impact excavation has on a site's industrial activities. This means that several traditional remediation techniques must be used successively in order to remediate a mix of contaminants at a single site. This makes remediation very difficult, expensive, and time-consuming. Because of this, the threshold for starting remediation efforts is high, and remediation projects are often postponed.

In addition, it is difficult to remove all the contamination that is present using traditional remediation techniques (e.g. pump and treat, dual phase extractions), and often a considerable amount of contamination remains in the source area. This remaining contamination will cause ongoing contamination of the plume area and cause severe groundwater contamination that can migrate off-site and cause risks there. This also makes remediation of the plume area more difficult and time-consuming.

In situ chemical oxidation (ISCO) is a technique that is suitable for the simultaneous remediation of a cocktail of organic contaminants without leaving significant amounts of contamination in the soil. This technique releases an oxidant into the subsoil, oxidizing all contaminants to harmless products. However, given the large number of different contaminants, the high concentrations present at the subject site, and the

dimensions of the subject site, not all types of oxidants will succeed in oxidizing the organic contaminants present.

Perozone is a newly developed oxidant that is able to do this. Perozone is a mixture of hydrogen peroxide and ozone. These two chemicals interact to produce very reactive OH radicals. Ozone also reacts with the contaminant, forming hydroperoxides, which in turn also creates OH radicals. This double formation of OH radicals ensures a highly reactive oxidant with a very high oxidation capacity. Because of this, all types of organic contaminants can be oxidized using this technique. In addition, perozone is a gaseous oxidant with a high radius of influence. This means that fewer injection filters are necessary compared with other ISCO oxidants. Fewer injection filters mean a decrease in cost and less interference with the site's activities. Both are crucial for carrying out remediation activities at an industrial site in operation.

At explosion-sensitive (EX-rated) sites, however, the presence of strong oxidants causes major issues with regard to health and safety. Contact between the oxidants and inflammable or explosive products at the site should be avoided, and the oxidants must not be allowed to leach into piping or accumulate in the sewer system. It is therefore crucial to draw up an extensive health and safety plan to define the safety measures necessary during the remediation process.

The ISCO technique is often part of laboratory testing and pilot testing; however, it has never been applied to the full-scale remediation of a chemical site in operation (with all the associated constraints). During this LIFE project, we will demonstrate that ISCO with perozone can be used for the full-scale soil and groundwater remediation of a site contaminated with a cocktail of organic components, using a limited number of injection points. Furthermore, we will develop an extensive health and safety plan defining the necessary health and safety measures for this technique. The project will also demonstrate that an EX-rating is not a major constraint against using ISCO as a remediation technique.

The need for an environmental protection and remediation policy for soil has only recently been recognized in most countries. With the goal of developing a strong policy on soil protection and remediation, it is very important to couple international expertise to local decision making. The EU can play a vital role in this by continuing to develop a European soil directive. Input from LIFE projects such as this proposal may help facilitate the decision-making process and the approval of the directive by member states.

This LIFE project focuses on a cost-efficient, energy-efficient (i.e. EU-target) and environmentally advantageous innovative remediation technology that may be the solution for in situ remediation systems at sites where a mix of contaminants is present in very high (pure product) concentrations. If the project is successful, the innovative technique in this proposal can be used at several other sites throughout the EU, which will facilitate the intent to begin cleaning up contaminated land in Western, Central and Eastern Europe.

### Environmental problem at the subject site

The site, owned by Vopak since 1999, had been in operation since the early 1970s; its main activities were (and still are) storage and transfer of liquid bulk. Early operations caused soil contamination with BTEX, chlorinated CAHs, and TPH. The contamination present today is the legacy of past chemical-handling methods. The Flemish authorities consider it “historical contamination”, which means the contamination originated prior to 1995.

Since 1990, several precautions have been taken to prevent new soil and groundwater contamination from arising:

- In the early 1990s, the loading and unloading bays were equipped with liquid tight flooring and secondary containment.
- The tank farms and drum storage areas have been equipped with liquid tight flooring.
- A very strict storage-tank inspection program has been implemented.

The contaminants and their estimated volumes are presented in the table below.

Product	Volume (m <sup>3</sup> )	Amount of product present (kg)
BTEX	3135	212
Chlorinated CAHs		
Chloro-ethanes	2687	1792
Chloro-ethenes	2687	103
Chloro-methanes	796	0
TPH	2616	3200

Since 2005, several laboratory tests and pilot tests have been carried out at the site to determine potential remediation techniques.

The first test was a detailed groundwater modeling to determine groundwater flow velocities and directions and to determine potential remediation goals for several different remediation techniques.

A second test was carried out in the laboratory to determine whether the contaminants present at the site were susceptible to anaerobic biodegradation by enhanced natural attenuation (i.e. anaerobic bioremediation). This laboratory test showed that the chlorinated CAH contamination could be completely biodegraded to harmless products by anaerobic bioremediation. However, the test also showed that benzene was not degraded, and that benzene concentrations remained constant. Following this test, a second laboratory test was conducted to determine whether benzene could be degraded under aerobic conditions (i.e. aerobic bioremediation). The test showed that under aerobic conditions, benzene was rapidly degraded to harmless products.

Following the laboratory tests, a pilot test was carried out at the site to investigate the potential of anaerobic bioremediation in the field. The test was carried out by injecting molasses into the aquifer. This pilot test confirmed the results of the laboratory test;

i.e. the contamination with chlorinated CAH was degraded to harmless products, while the benzene and TPH concentrations remained the same.

The laboratory tests and pilot test demonstrated that consecutive anaerobic and aerobic conditions are required in the aquifer in order to bioremediate all the contaminations present. This means that we would need to start by making the aquifer anaerobic (by injecting of molasses or other carbon sources) for the anaerobic degradation of the chlorinated CAHs. Afterward, we would need to oxidize the anaerobic aquifer to create aerobic conditions for the aerobic degradation of TPH and benzene. This would require enormous amounts of energy and would cause many problems, such as the clogging of filters and subsoil. Because of this, we do not consider enhanced natural attenuation as a remediation technique to be BATNEEC (Best Available Technology Not Entailing Excessive Costs).

A second on-site pilot test investigated dual phase extraction with a non-dig drain and vertical wells. Dual phase extraction has partly the same disadvantage as simple groundwater extraction; after a certain time, groundwater concentrations will almost cease to lower (the trailing effect). The pilot test showed that dual phase extraction was not a suitable remediation technique for the contamination at this site. However, the pilot test did show that the radius of influence for air or other gaseous components is large at the Vopak site.