



Code of good practice:

In- situ chemical oxidation





Summary

In-situ soil remediation techniques are techniques that deal with soil contamination without a need to excavate. As no excavation is required, these techniques have less impact on the use of the land and can be applied in various locations. The soil composition and structure are also affected less.

In-situ chemical oxidation (ISCO) is based on a redox reaction in the soil between the injected oxidant and the contaminants present. The oxidant and any necessary auxiliary substances are injected into the soil, where they react with the contaminants present. As a result, the oxidant is reduced and the contaminants are oxidised and broken down to harmless products which are naturally present in the soil. This remediation technique is only suitable for the remediation of organic contamination.

The principle of chemical oxidation has been known for some time; it has been used to treat waste water for decades. Based on this experience, chemical oxidation was used as an in-situ remediation technique for the first time in the United States in 1984 to treat groundwater contaminated with formaldehyde. In Flanders, the first soil remediation projects proposing chemical oxidation were approved in 2001. ISCO can be used for remediation of both the saturated and the unsaturated zone, and for zones with high contaminant concentrations (source zone) and zones with lower contaminant concentrations (plume). Experience shows that ISCO is usually used in the saturated zone for the remediation of (source) zones with high contaminant concentrations.

An attractive advantage of ISCO is the limited duration of the remediation compared to many other soil remediation techniques. The time needed to break down the contaminants depends on the amount of contamination, the contaminated soil volume, the oxidant, the speed with which the oxidant can be injected and the composition of the soil. As with any other in-situ soil remediation technique, the specific characteristics of the site play a crucial and often limiting role. Therefore, it is very important to previously reflect the different site characteristics in the conceptual site model (CSM) of the site in as much detail as possible. Based on the data collected during the injection and the follow-up of the soil remediation, this conceptual site model must be updated constantly.

On the one hand, this code of good practice wants to provide an overview of the current theoretical knowledge on ISCO. On the other hand, this report is intended as a guide to decide whether ISCO is a relevant soil remediation technique. This document doesn't pretend to be complete. The knowledge and experience of the contractor remains equally important.

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Part 1: Theoretical aspects of ISCO

1 Introduction

1.1 CityChlor and the integrated approach

Space is scarce in Europe. Even in the subsurface it is getting busier. Large-scale soil and groundwater contamination with chlorinated solvents are often an obstruction for urban developments. The traditional way of dealing with polluted soil and groundwater does not work in all cases and is not economically and sustainable feasible. In urban environments multiple contaminations with chlorinated solvents are often mixed with each other and spread underneath buildings. This not only leads to technical problems for remediation, but also to liability and financial discussions and hence has an impact on society. An integrated approach and area-oriented approach is needed to tackle the problems. The CityChlor project has demonstrated that remediation and sustainable development can evolve on a parallel timescale.

An integrated approach combines all aspects that are relevant to tackle the problems that pollution with VOC in urban environment causes. Depending on area, site and context different aspects together or parallel to each other can be used. Not only technical solutions are included, but also socio-economical aspects as urban development, communication, financial and legal aspects, time, space, environment and actors (active & passive) have to be handled.

CityChlor did not remain at single case remediation, but looked at the area as a whole in a bigger context: the area-oriented approach. A technical approach that makes it possible to remediate, monitor and control multiple groundwater sources and plumes within a fixed area.

1.2 CityChlor and technical innovations

The managing of knowledge and technical innovations are one of the key to achieve a sustainable city development. A development project has to cope with loads of information coming from different disciplines in different (technical) languages and with different uncertainties. With chlorinated solvents, the knowledge about the pollution will always have a certain uncertainty that can have an impact on the course and the costs of the remediation. An efficient 'managing of knowledge' will try to decrease this degree of uncertainty.

CityChlor therefore also worked on the technical aspects of characterization and remediation. The conventional techniques that are applied for investigation and remediation have their limitations dealing with chlorinated solvents. Promising innovative techniques exist, but do not easily find their way to current application. This barrier is often caused by lack of knowledge on different levels. Experts and contractors do not always have the means to invest in experiments with new techniques, authorities are reluctant to accept techniques of which the results may be uncertain and clients aren't eager to pay for experimental techniques.

Dissemination of knowledge can break this deadlock. CityChlor therefore collected experiences from field application of innovative techniques and implemented itself a number of techniques in pilot projects. For the detailed outcomes, the reader is referred to the specific reports.

CityChlor - "new solutions for complex pollutions" http://www.citychlor.eu/
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1.3 Glossary

BATNEEC:	Best Available Technology Not Entailing Excessive Costs.
Carbonate system:	This system is partly responsible for the buffering capacity of the soil and is a combination of the following reactions: <div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> $\text{Ca(OH)}_2 \leftrightarrow \text{CaOH}^- \leftrightarrow \text{Ca}^{2+}$ $\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$ $\text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$ </div>
Catalyst:	A substance that affects the reaction speed of a chemical reaction without being used up in the chemical reaction itself. Usually an increase in reaction speed is meant.
Conceptual site model (CSM):	A model of thinking that includes a description and/or visualisation of the sources, pathways, potential risks and receptors of soil contaminants in relation to the soil system. The conceptual model can serve as a framework for taking research and remediation measures and identifying knowledge gaps.
DNAPL:	Distinguishable layer of organic (non-aqueous) liquids with a higher density than water on a less permeable layer below the groundwater table.
Free radicals:	Highly reactive intermediate products in the redox reaction. They have one electron or two odd electrons in their outer shell or are in an oxidation state which makes them highly reactive. Due to their high reactivity they are also very unstable.
Groundwater:	The water in the pores below the water table in an aquifer.
H and P phrases:	All packaging of hazardous substances must contain H and P phrases. Hazardous substances or mixtures containing hazardous substances have to be put in one or several categories. For each category there are a pictogram, a signal word, corresponding hazard statements (H phrases) and precautionary statements (P phrases). H and P phrases replace the former R and S phrases and are mandatory on labelling from 1 December 2010 onwards for pure substances and from 1 June 2015 onwards for mixtures.

MSDS:	The Material Safety Data Sheet is a form containing the composition and properties of the substance as well as recommendations for its safe use at work.
Soil:	The solid part of the earth, including the groundwater and the other components and organisms present in it.
Soil oxidant demand (SOD):	The amount of oxidant consumed by the oxidation of the soil material present, excluding the soil contaminants.
Solubility:	A measure that expresses the maximum amount of a product that can be dissolved in water without forming precipitation or a LNAPL or DNAPL.
Oxidant:	Chemical substance with a high redox potential. The oxidant is reduced and acts as an electron acceptor in the redox reaction. The oxidation state of the oxidant decreases in the redox reaction.
Permeability:	A material property that describes the degree to which a solid substance lets another substance through. The permeability of a material differs according to the substance to be let through.
Preferential flow:	Process whereby groundwater or soil air mainly flow through the soil via large pores or cracks.
Post-remediation value:	Contaminant content in the soil which is aimed for with the soil remediation works.
Reagent:	A chemical substance that reacts in a chemical reaction.
Redox reaction:	Chemical reaction whereby electrons are transferred from the electron donor to the electron acceptor.
Redox potential:	Unit used to express the degree to which electrons are available for redox reactions. The higher the redox potential, the easier electrons move towards the oxidator.
Reductant:	The reductant is oxidised and acts as an electron donor in the redox reaction. The oxidation state of the reductant increases in the redox reaction.
Stoichiometry:	The proportion in which chemical compounds react with each other and the relation between the reactants and products of a chemical reaction. Stoichiometry can be used to calculate amounts, such as the amount of product that can be produced with the given reagents. It is based on the law



of conservation of mass: the mass of the reactants is equal to the mass of the products.

Saturated zone:

Zone in the soil which is filled with groundwater.

Unsaturated zone (or vadose zone):

Zone in de soil above the groundwater table.

1.4 List of abbreviations

°C:	degrees Celsius (temperature)
E_0	standard potential of the half-reaction
BTEX:	benzene, toluene, ethylbenzene, xylenes
SOD:	soil oxidant demand
CSM:	conceptual site model
DCA:	dichloroethane
DCE:	dichloroethene
DNAPL:	dense non-aqueous phase liquid
ISCO:	in-situ chemical oxidation
kPa:	kilo Pascal
mbgl:	metres below ground level (depth)
mg/l:	milligrams per litre (concentration)
MTBE:	methyl-tertiary-butyl ether
pH:	acidity
PAK's:	polycyclic aromatic hydrocarbons
PCB's:	polychlorobiphenyls
g/l:	grams per litre (concentration)
PCE:	tetrachloroethene
TBA:	Tertiary butyl alcohol
TCE:	trichloroethene
TCA:	trichloroethane
TOC:	total organic carbon
V:	volt (voltage)
VC:	vinyl chloride
VOCL:	chlorinated volatile organic compounds

2 The chemistry of oxidants

2.1 Oxidants

The products most often used for ISCO are the following oxidants or are based on the following oxidants, whether or not in combination with auxiliary substances:

- hydrogen peroxide;
- sodium and potassium permanganate;
- sodium persulphate;
- ozone.

Currently solid peroxides such as sodium percarbonate and calcium peroxide are also being used, as well as combinations of the above mentioned oxidants (e.g. ozone in combination with hydrogen peroxide, permanganate in combination with hydrogen peroxide). Some solid peroxides (magnesium peroxides, calcium peroxide) are less reactive and are rather used to release oxygen in order to stimulate aerobic bioremediation. As this is a different remediation technique, we will not discuss these solid peroxides any further here. A potential new oxidant for chemical oxidation is ferrate (hexavalent iron). Ferrate combines the advantages of activated hydrogen peroxide (formation of radicals and thus high redox potential ($E_0 = 2.2$ V), environmentally friendly) with the advantages of permanganate (stable and long life). The only disadvantage is the cost for the production of ferrate, which is still very high.

A redox reaction means the transfer of electrons of a molecule (reductant) to another (oxidant). The higher the redox potential, the easier electrons move to the oxidant. The oxidant, characterised by a high redox potential, acts as an electron acceptor in the chemical reaction (redox redaction). This means that when the oxidant is injected an electron transfer will take place. Electrons are transferred from the contaminant to the oxidant. As a result, the oxidant is reduced and the contaminant is oxidised. This leads to an increase in the oxidation state¹ of the contaminant.

The chemical reaction can take place in two ways: via a direct reaction path, or indirectly via a radical reaction process. With a direct reaction path the oxidant attacks the chemical bonds of the contaminant. This results in an unstable situation in which the contaminant is broken down into harmless products (e.g. CO₂, H₂O, H⁺, Cl⁻). With a radical process the reaction takes place via free radicals. These have one electron or two odd electrons in their outer shell, which makes them highly reactive. Consequently, the retention time of the radicals in the soil is very short (a few seconds) and they will hardly migrate into the soil.

¹ The number of electrons in a not yet completely filled electron shell.

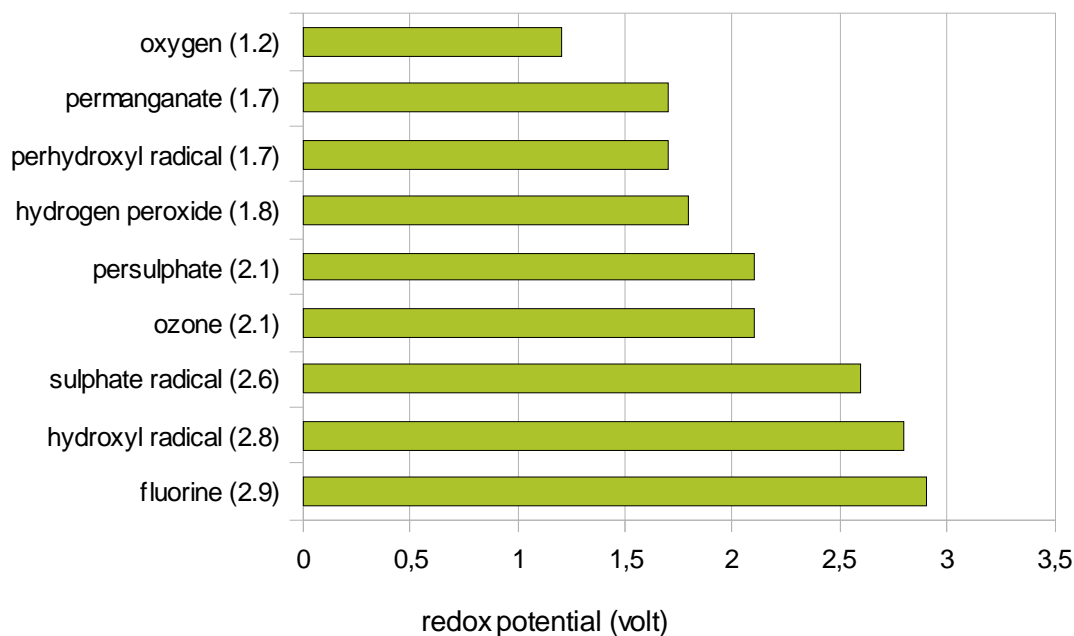


Figure 1: overview of some redox potentials

2.1.1 (activated) Hydrogen peroxide

General

The hydrogen peroxide molecule has one oxygen atom more than the much more stable water molecule. The bond between both oxygen atoms, the so-called peroxide bond, is highly unstable. Hydrogen peroxide is sold commercially as a colourless 30 to 50 % solution.

	Hydrogen peroxide H_2O_2
molecular weight (g/mol)	34
physical appearance	colourless solution
solubility (g/100 ml (20°C))	
density (g/cm ³)	1,45

Table 1: physical properties of hydrogen peroxide

It has a relatively low redox potential ($E_0 = 1.8 \text{ V}$) and a short half-life, which makes it less suitable than other oxidants for ISCO (in ambient temperature and pressure hydrogen peroxide is not powerful enough to achieve an effective mineralisation of hydrocarbons). Besides direct oxidation, hydrogen peroxide also has the potential to form radicals on condition that a catalyst is added. For instance, when iron is mixed with hydrogen peroxide, different types of free radicals are formed. A typical radical that is formed is the hydroxyl radical (OH^\bullet), this increases the redox potential to around 2.8 V . The hydroxyl radical acts as a very powerful, effective and non-selective oxidant. Due to the extreme reactivity the hydroxyl radical is also eliminated quickly through the reaction. Recent studies show that other radicals, such as the superoxide radical (O_2^-), also play an important role in the breaking down of (certain) contaminants.

However, there is a difference in the degree to which contaminants can be oxidised. The ease with which a compound oxidises depends in the first place on its 'tendency' to give up electrons. A chemical reaction between oxidant and reductant is only possible if through the transfer of electrons (the redox reaction) a system is created with a lower Gibbs free energy content², unless it is supplied with energy. However, other factors play a role in this, e.g. the activation energy. This is the (energy) 'threshold' which first needs to be overcome in order for the reaction to be possible, finally leading to a system with a lower Gibbs free energy content. A catalyst such as iron(II) lowers this activation energy in the peroxide and persulphate system. As a result, the reaction speed significantly increases.

There are various catalysts that speed up the formation of the free hydroxyl radical. With the application of hydrogen peroxide mainly iron is used as catalysts. Commonly applied as iron sulphate. Because iron sulphate has a low cost and both iron and sulphate are naturally present in the soil and hence do not negatively affect the soil quality. But also other iron salts could be used. When iron is added to a hydrogen peroxide solution as a catalyst, this is called Fenton's reagent. This reagent was invented by the British Henry John Horstman Fenton (1854 - 1929) around 1890.

The concentration of the hydrogen peroxide solution to be injected usually lies between 5 and 10 % (volume proportion). The specific proportions of H_2O_2 and iron cations is determined by laboratory tests. The right proportion depends on the pollutant loads present, the soil chemistry and the specific stoichiometry of the redox reaction. Based on all this it is determined how much oxidant and catalyst need to be added in order to bring the soil contamination below a certain value. In principle, other metal ions, such as copper or molybdenum, could also be used as catalysts. Taking into account the toxicity and the cost, among other things, iron is a logical choice for in-situ use. If there is already enough naturally iron (II) present (between 15 to 20 mg/l), there is no need to add additional iron.

² Thermodynamically speaking, a particle will be more reactive when, as a result of a chemical reaction, it can go to an energetically lower level. In other words: the Gibbs free energy (ΔG) of a reaction must be negative in order to obtain a reaction that is as spontaneous as possible. All particles strive for an energy state that is as low as possible.

The solubility of iron can be increased in different ways. Based on this, a division can be made into two different forms of execution:

1. The classical Fenton's reaction

In the classical or acid Fenton's reaction iron (II) is added as an iron sulphate solution (20 to 100 mg/l Fe (II)) and the soil needs to be acidified in order to keep the iron (II) in solution. The optimal pH to maximise these iron concentrations in the water lies between 3.5 and 5. In order to adjust the pH a strong acid, such as HCl or H₂SO₄, is often added to the soil. The effect of the addition of an acid is usually only temporary, in most soils the pH will quickly (within 1 to 3 days) rise back to the normal value.

2. The modified Fenton's-reaction

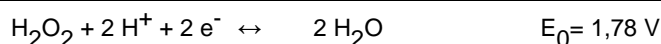
In the form of execution called the modified Fenton's reaction, the iron(II) is added together with an organic chelator. The chelator can also keep the metal ion in solution under conditions in which it would normally precipitate. In this case, acidification of the soil is no longer necessary. The oxidation reaction can take place at a pH of between 2 and 10. This reduces the risk of a mobilisation of heavy metals, which is present with the classical form of execution. Chelators that are often used in the United States are EDTA (ethylene diamine tetra-acetic acid), which is not easily biodegradable, or sodium triphosphate. In Europe, citrate, which causes only very slight damage to the environment (if any), is often used as a chelator. The modified Fenton's has a much longer life than the classical Fenton's, allowing a better distribution and a longer effect of the oxidant. As the reaction is less vigorous, the temperature of the ground water will increase less.

There are also commercial products that are based on H₂O₂ (see *paragraph activated sodium percarbonate*)

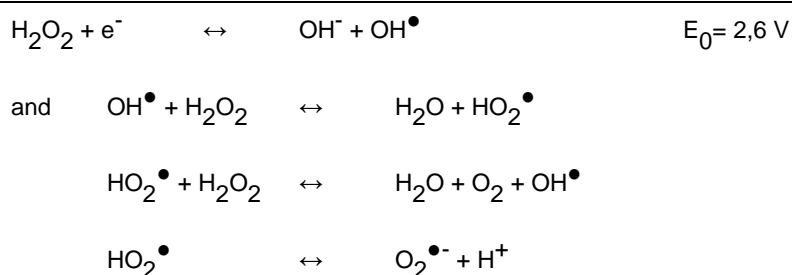
Reactions

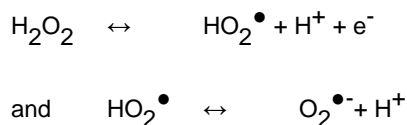
The chemical reactions are complex and take place both via direct electron transfer and via the formation of radicals, giving rise to different chain reactions. A few examples:

Direct oxidation half reaction:



Radical reaction (after activation):





The theoretical degradation products with a complete oxidation (H_2O , O_2 and CO_2) are harmless and are naturally present in the soil. In less than ideal circumstances the chemical oxidation also results in the generation of intermediate degradation products.

Characteristics

Free hydroxyl radicals (OH^\bullet) are highly reactive. Due to this high reactivity chemical oxidation takes place very quickly and very non-selectively. Due to this relatively high reactivity Fenton's reagent can be used for many different types of contamination.

The hydroxyl radical is characterised by a very short half-life, which results in an extremely small migration distance of the oxidant in the soil. This also has implications for the choice of the injection method, as a short retention time requires that when injecting the oxidant and the catalyst both come into contact with the soil contaminants fast and simultaneously. The volume of hydrogen peroxide that is injected must be sufficient to cover the entire area to be treated. If after injection of the oxidant there are still contaminants in the soil, these will be discharged into the groundwater. Due to the unstable nature of the oxidant there will be no 'after-effect'. As a result, the use of the oxidant is advised against in the case of soils with a relatively low permeability or in case of an uneven spread of the contaminants in the soil. Multiple injection rounds of the oxidant are usually required.

The reaction between iron and hydrogen peroxide is very fast. Hydrogen peroxide and iron therefore need to be injected through different filters, or alternately through the same filter. In soils, naturally rich in iron, the reaction can be stabilized (delayed) by injecting phosphate. The phosphate will bind with the dissolved iron, and make it is less available for the reaction with hydrogen peroxide.

Peroxide cannot be applied to soils that are rich in carbonate, because carbonate accepts free radicals. Hence, the technique is suitable especially for acid soils.

Side effects

The reaction with hydrogen peroxide or free hydroxide radicals is highly exothermic. Sometimes a fast and considerable increase in temperature is found as a result of the fast reaction of hydrogen peroxide and the slow spread of the heat in the soil. Additionally, oxygen is formed through the reaction with soil water. The combination of both factors with the presence of volatile organic components can in some cases lead to dangerous situations (steam formation, fire or explosion hazard). Sufficient attention must be paid to this in the design phase. The reaction speed of hydrogen peroxide is generally controlled by adding the reagent to the soil in low concentrations (solutions under 11 %).

The chemical oxidation and the potential addition of an acid to the soil to increase iron concentrations in the water can (temporarily) increase the mobility of heavy metals as a result of the following processes:

- The oxidation of metals can increase their mobility (and sometimes toxicity).
- The breaking down of the bond between the metal and the organic material in the soil.
- The increasing of the solubility of metals as a result of the lower pH.

The presence of auxiliary substances, such as chelates, can also affect the mobility of the metals.

Furthermore, during the chemical oxidation a lot of oxygen is formed, which can have the following effects:

- Aerobic biodegradation of organic contaminants is additionally stimulated.
- Evaporation of volatile components (strip effect), with the corresponding risks.
- The moving of groundwater and the dissolved contaminants.
- Permeability decreases and the groundwater flow is affected. (A case study in the United States showed that on one of the 11 studied sites where Fenton's reagent was injected a decrease in permeability was found as a result of gas formation.)

(activated) sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$)

As shown from the chemical formula, sodium percarbonate carries hydrogen peroxide in the same way as another molecule hydration water.³ As a result, sodium percarbonate is more stable than hydrogen peroxide. Activated sodium percarbonate makes use of a basic oxidant compound and consequently creates alkaline conditions (high pH). Therefore, no acid conditions (low pH) are required, unlike for other catalysed hydrogen peroxide (Fenton's reagent). Fenton's reagent is usually applied with a low pH to keep the iron in solution. With a low pH the production of perhydroxyl and superoxide radicals is inhibited.

The formation of radicals with a high pH is very different than with a low pH. In acid-catalysed reactions the hydroxyl radical plays an important role, whereas in base-catalysed reactions other radicals, such as the perhydroxyl radical ($\text{HO}_2\bullet$) will play a dominant role.

2.1.2 Potassium and sodiumpermanganate

General

Permanganate is extracted from mines. The extracted permanganate salts contain auxiliary components and impurities (heavy metals, mainly chromium and arsenic). Generally, these auxiliary components and impurities do not affect the environment-technical quality of the oxidant. Even so, it is advised to check the oxidant first or use commercial solutions with lower metal concentrations made for ISCO.

The use of permanganate as a chemical oxidant for the remediation of soil contamination with chlorinated solvents (e.g. PCE, TCE) and other organic components (e.g. naphthalene, phenanthrene, pyrene and phenols) has been extensively studied.

³ Water molecules built into the crystal lattice of a salt.

The most frequently used types of permanganate are potassium permanganate (dark purple solid salt) and sodium permanganate (dark purple liquid). Potassium permanganate is supplied as a solid salt, while sodium permanganate is supplied as a liquid. For soil remediation a standard 40% solution with low concentrations of heavy metals as impurities is available. Potassium permanganate is cheaper, but it is only available as a solid, which means it needs to be dissolved for injection, with the corresponding disadvantages (safety aspects and dust formation). In addition, the maximum solubility of potassium permanganate is lower (solubility around 6%) than that of sodium permanganate.

	Sodium permanganate NaMnO_4	Potassium permanganate KMnO_4
molecular weight (g/mol)	142	158
Physical appearance	purple liquid	solid
solubility (g/l (20°C))	900	64
density (g/cm ³)	1,97	2,7

Table 2: physical properties of permanganate

For chemical oxidation with potassium permanganate usually solutions are used with a volume proportion of 0.5 to 2 % or sometimes to 4 % (40 g/l). With higher concentrations there is often precipitation of potassium permanganate in the mixing tank, pipes or injection well. When using potassium permanganate one must also take into account that solubility decreases at lower temperatures. There is a chance that higher concentrations of potassium permanganate coming into contact with relatively colder groundwater will cause precipitation in the area around the injection point, thus decreasing permeability. Sodium permanganate dissolves much better and up to 25 % solutions can be injected.

Permanganate is a selective oxidant (especially highly reactive with double bonds). Double bonds also abound in the natural organic material, which means that, besides the contaminants present, a considerable amount of organic material is oxidised as well, thus decreasing the efficiency of the permanganate injection. A soil oxidant demand (SOD) greater than 2 gram permanganate per kilogram of wet soil is often taken as the upper limit for cost efficient soil remediation.

Even though permanganate is a moderately strong oxidant ($E^0 = 1.68 \text{ V}$) in comparison with Fenton's reagent, the oxidant is used more in ISCO. Compared to hydrogen peroxide, permanganate will react more slowly (more stable), which is why it remains reactive and can continue to migrate over a longer period of time (up to a few months). The stability of permanganate is proportional to the injected volume and inversely proportional to the oxidant demand of the soil and the contaminants present.

The density of permanganate is equal to that of chlorinated solvents and it will spread both horizontally and vertically as a result of its long retention time in the soil. Consequently, it is able to oxidise more contaminants in the surroundings of the place of injection and downstream. Hence, permanganate is more suited for sites where the soil is characterised by a lower permeability. Due to its long retention time, the permanganate will also move by diffusion to less permeable lithological layers.

Reactions

The chemical reaction takes place via direct electron transfer and not via the formation of radicals.

$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e}^-$	\leftrightarrow	$\text{MnO}_2 \downarrow + 4 \text{OH}^-$	$3,5 < \text{pH} < 12$
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^-$	\leftrightarrow	$\text{Mn}^{2+} + 4 \text{H}_2\text{O}$	$\text{pH} < 3,5$
$\text{MnO}_4^- + \text{e}^-$	\leftrightarrow	MnO_4^{2-}	$\text{pH} > 12$

The redox reaction produces manganese oxide precipitation (MnO_2), CO_2 and degraded organic components. Examples of stoichiometric degradation reactions:

		oxidant demand (1)	generated MnO_2 (2)
tetrachloroethene	$3 \text{C}_2\text{Cl}_4 + 4 \text{MnO}_4^- + 4 \text{H}_2\text{O} \leftrightarrow 4 \text{MnO}_2 + 6 \text{CO}_2 + 12 \text{Cl}^- + 8 \text{H}^+$	0,96	0,7
trichloroethene	$\text{C}_2\text{HCl}_3 + 2 \text{MnO}_4^- \leftrightarrow 2 \text{MnO}_2 + 2 \text{CO}_2 + 3 \text{Cl}^- + \text{H}^+$	1,81	1,32
dichloroethene	$3 \text{C}_2\text{H}_2\text{Cl}_2 + 8 \text{MnO}_4^- \leftrightarrow 8 \text{MnO}_2 + 6 \text{CO}_2 + 6 \text{Cl}^- + 2 \text{OH}^- + 4 \text{H}_2\text{O}$	3,28	2,39
vinyl chloride	$3 \text{C}_2\text{H}_3\text{Cl} + 10 \text{MnO}_4^- \leftrightarrow 10 \text{MnO}_2 + 6 \text{CO}_2 + 3 \text{Cl}^- + 7 \text{OH}^- + \text{H}_2\text{O}$	6,35	4,64
phenol	$3 \text{C}_6\text{H}_5\text{OH} + 28 \text{MnO}_4^- + 5 \text{H}_2\text{O} \leftrightarrow 28 \text{MnO}_2 + 18 \text{CO}_2 + 28 \text{OH}^-$	11,8	8,62

Table 3: oxidative degradation with permanganate

(1) theoretical oxidant demand in grams of MnO_4^- per gram of contaminated material (without taking into account the organic material present in the soil)

(2) theoretical amount of manganese oxide produced in grams per gram of degraded pollutant

The amount of permanganate that is necessary to degrade chlorinated ethenes is inversely proportional to the degree of chlorination. As the higher chlorinated ethenes are more oxidised, less oxidant is needed to mineralise them.

Side effects

Manganese oxide precipitation

In normal soil conditions, the redox reaction between organic matter (soil contaminants or naturally present organic material) and permanganate results in the formation of manganese oxide (MnO_2) when ISCO is carried out. Manganese oxide is a natural mineral. During ISCO large amounts of permanganate are injected into the soil. As a reaction product, manganese oxide precipitation is formed, especially around zones with high contaminant concentrations (DNAPL) and injection points. Manganese oxide is insoluble in the soil and forms a dark brown to black mineral crust.

Permanganate is therefore best not used with DNAPLs. This is because permanganate will react with the contact surface of the DNAPL, creating a mineral crust which will shield the remaining pure product from the permanganate. Over time, the manganese oxide crust will shield the contamination less and concentrations in the groundwater will rise again.

The formation of manganese oxide can also have a negative influence on the permeability of the soil. Lowering the injected permanganate concentrations and increasing the injection rate can provide a solution to considerably reduce the formation of precipitation around the injection points. Furthermore, laboratory tests have shown that the use of auxiliary substances (stabilisers), such as hexametaphosphate, can be a solution to limit manganese oxide precipitation.

However, the manganese oxide will slightly increase the sorption capacity of the soil for heavy metals.

Coloring of the groundwater

The addition of permanganate causes a purple discolouration of the groundwater. As the permanganate is eliminated through the reaction, the purple colour will disappear as well.

2.1.3 Sodium persulphate / activated sulphate

General

Persulphate has a lot of industrial applications, but it has only been used as an oxidant in ISCO recently. Persulphate has turned out to be a suitable oxidant for the oxidation of different types of contaminants. However, due to the more limited experience, knowledge is not equally extensive yet for all processes linked to persulphate. The most frequently used form of persulphate for ISCO is sodium persulphate. This is usually supplied in powder form. The oxidant is injected into the soil in up to approx. 5 % solutions.

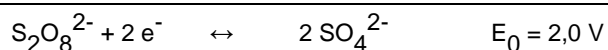
	Sodium persulphate $\text{Na}_2\text{S}_2\text{O}_8$
molecular weight (g/mol)	238
physical appearance	white powder
solubility (g/l (20°C))	556
density (g/cm ³)	2,4

Table 4: physical properties of sodium persulphate

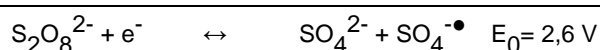
Reactions

The chemical reactions are complex and take place both via direct electron transfer and via the formation of radicals (e.g. sulphate radical, hydroxyl radical).

Direct oxidation half reaction



Radical reaction (after activation)



The final degradation products of the reaction (H_2O , CO_2 and sulphate) are harmless and are naturally present in the soil.

Characteristics

Persulphate is a fairly stable oxidant with a relatively high redox potential. It is more reactive than permanganate with some contaminants and more stable than peroxide and ozone. Compared to permanganate, persulphate has a high molecular weight, which is why more oxidant is needed for the oxidation of contaminants.

In general, persulphate reacts relatively slowly. The activation of the persulphate will increase the speed of the reaction and reduce its selectivity. Through the use of an activator or catalyst various radicals are formed. The most important ones are the sulphate radical ($\text{SO}_4^{\cdot-}$) and the hydroxyl radical. The persulphate can be activated in different ways:

- with iron (most frequently used) or other metals, metal chelates. The activation of persulphate with Fe^{2+} , whether or not in combination with chelates, is similar to the activation of hydrogen peroxide (Fenton's reagent). This activation is the least reactive.

- heat (temperatures above 30°C, e.g. in combination with or after a steam injection)
- hydrogen peroxide
- a highly basic pH (pH > 10,5).

Side effects

The most important change in the quality of the groundwater is an increase of the sulphate content and a decrease of the pH. When 1 mol of sodium persulphate is added, 1 mol of sulphuric acid and 1 mol of sodium sulphate are formed. The pH effect is cancelled out if the buffering capacity of the soil is sufficiently large. The acids produced can be attenuated by reaction with carbonates and clay minerals if these are present in the soil in sufficient amounts. Moreover, the concentration of the produced sulphate will decrease considerably as a result of a reaction with calcium minerals to gypsum. The effect is also buffered by the dilution effect. The elevated sulfate concentrations are also a point of consideration in an eventual biological post treatment.

An additional effect of the lowering of the acidity of the soil is the possible release of metals into the soil.

2.1.4 Ozone

General

Ozone (O₃) is one of the most powerful oxidants that can be used for ISCO. Ozone has been used for more than 100 years in the water treatment industry. More recently, ozone has also been used for the remediation of organic soil and groundwater contamination. To this end, a gas mixture of compressed air with ozone is injected into the soil. The volatile compounds go from the aqueous phase to the gas phase, in which these compounds are oxidised by the ozone present. Part of the ozone also easily dissolves in the aqueous phase to oxidise the contaminants there.

Due to the relatively short half-life of ozone, ozone is always generated on site using an ozone generator. Ozone is usually generated from the following two methods: using UV light or by corona discharge. Ozone generation via corona discharge is most common today. The ozone generator contains the corona discharge element. Inside, ozone is produced from oxygen by creating high tension (10-20 kV) between the electrodes, which results in an electric discharge (corona discharge). Through collision with electrons, this corona discharge splits the molecular oxygen into atomic oxygen. Some of these oxygen atoms together form an ozone molecule, while others come together to form molecular oxygen again. For the production of ozone ambient air can be used (supplied by a compressor) or pure oxygen. In order to condition this air it is passed through air dryers and dust filters. Advantages of the corona discharge method include a higher durability of the unit, a greater ozone production and cost efficiency. A disadvantage is that a lot of energy is needed for the generation of ozone.

During ozone generation energy is released in the form of heat. At higher temperatures oxygen molecules are formed again and the efficiency of the ozone production decreases. In order to limit the disintegration of the ozone formed, the temperature in the discharge space must not be higher than approximately 25°C. In order to sufficiently cool the generator a considerable amount of cooling water is necessary (200 liters/hour)

The generated ozone concentration directly depends on the capacity of the generator (typically a few kilograms ozone / day). With ozone production from oxygen maximum ozone volume concentrations of 8-10 % are generated; with production from atmospheric air concentrations are 1 to 2 %. When using ozone as an oxidant the injected quantity of oxidizing agent per day is much smaller (order of magnitude a few kilograms) compared with other oxidants, so that the duration of the decontamination of an ISCO remediation with ozone takes considerably more time.

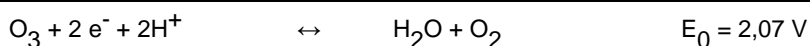
	Ozone O ₃
molecular weight (g/mol)	48
physical appearance	light blue to colourless gas
solubility (1,5 weight percent in air at 20°C (g/l))	0,06
density (g/cm ³)	0,0021

Table 5: physical properties of ozone

Reactions

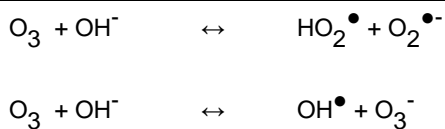
The chemical reactions are complex and take place both via direct electron transfer and via the formation of radicals, and this both in the aqueous phase and in the gas phase.

Direct oxidation half reaction:



The direct oxidation reaction (Criegee oxidation⁴) is quite selective (C=C bond).

Two of the different possible radical reactions (these reactions are not very selective):



The final degradation products of the reaction (H₂O, CO₂ and O₂) are harmless; they are naturally present in the soil.

⁴ d Due to the dipolar structure of ozone, the ozone molecule is able to enter into a 1-3 dipolar cyclo addition with saturated bonds (double or triple bonds). This results in the formation of an unstable bond called ozonide.

Characteristics

Ozone is highly reactive and oxidises most organic contaminants. With a low pH especially a more selective direct oxidation (larger radius of influence) will take place, which will not be able to break down all contaminants. In a neutral or basic environment mainly the rather unselective radical reactions (limited radius of influence) will occur. As a result of the presence of the hydroxyl ion in groundwater the half-life of ozone in the groundwater (20 minutes) is much shorter than the half-life of ozone in the gas phase (3 days).

A limitation of ozone is that its supply is limited and that the costs of its production are relatively high.

Ozone is a highly toxic gas. Proper safety measures for operators are an absolute necessity.

Side effects

Ozone is added to the soil as a gas. Consequently, the reaction with the contaminants will take place at the liquid-gas and the solid-gas interphase. An important point to keep in mind is the escape of unreacted ozone and the volatilisation of reaction products. With ISCO using ozone an additional soil vapour extraction system could be necessary to prevent the release of ozone and other volatile components into the atmosphere.

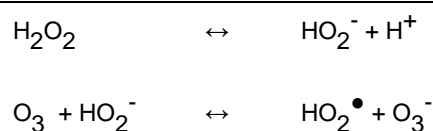
Attention must be paid to the use of ozone underneath impermeable layers. The danger exists that ozone will accumulate underneath this layer or that the ozone gas will spread via preferential flow paths and be released into the atmosphere in places where one initially had not expected this. Therefore, extensive research into the geology of the site is fundamental.

As ozone is highly corrosive, caution must be exercised if ozone sparging is applied in the immediate surroundings of pipes, tanks, etc. A minimum distance of 5 metres must be kept from underground constructions to avoid damage.

Ozone decomposes into oxygen; consequently, aerobic biodegradation of organic contaminants can be additionally stimulated.

Ozone in combination with hydrogen peroxide

Ozone is sometimes combined with hydrogen peroxide. By the reaction between hydrogen peroxide and ozone various radicals are formed, which has a very high oxidation power.



Oxidation with ozone and hydrogen peroxide is possible via laminar sparge units (e.g. perozone[®] process). These sparge units consist of a central cylinder surrounded by a hydrophobic gas filter and a microporous coating. Via two dosing pipes, on the one hand, a mixture of air and ozone under pressure (1-4 bar) and, on the other hand, diluted hydrogen peroxide are passed to the filter. The mixture of air and ozone is blown into the microporous coating via the central channel and the gas filter, where the diluted hydrogen peroxide is located. The gas bubbles percolate through this medium and are coated with a layer of diluted hydrogen

peroxide. The outer filter has very fine pores. This results in tiny bubbles (10-50 μm) consisting of ozone-enriched air enveloped by a thin layer of diluted hydrogen peroxide. The gas bubbles spread rather fast in the groundwater and move to the soil surface. During this movement, the various radicals are formed, and the organic contaminants are mobilized and oxidized.

The unreacted hydrogen peroxide and ozone decomposes into oxygen (and water). The concentration of dissolved oxygen will rise.

With the current technology it is possible to inject maximum of 2,500 kg O_3 / year (300 g O_3 / h), and consequently based on the stoichiometry of the decomposition reaction, 5,000 kg PCE or TCE can be degraded per year. Breaking down DNAPL's is therefore possible but slow and therefore not cost-effective.

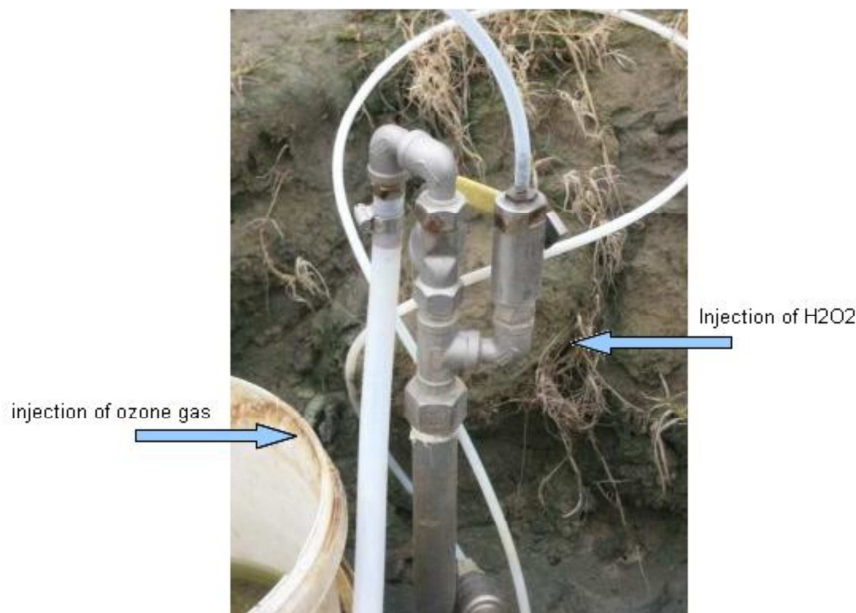


Figure 2: ozone / hydrogen peroxide injection filter

2.2 A few points of attention related to ISCO

2.2.1 Incomplete degradation

The degradation of contaminants via natural processes is a dehalogenation process in which one chlorine atom at a time is separated (tetrachloroethene \rightarrow trichloroethene \rightarrow dichloroethene \rightarrow vinyl chloride \rightarrow ethene). Chemical oxidation, on the other hand, follows a totally different course than degradation by natural attenuation. Therefore, with ISCO there is no risk of accumulation of intermediate products, such as dichloroethene or vinyl chloride, because these products are not formed. In theory, with ISCO the contaminants are broken down fast into harmless products which are naturally present in the soil. In practice, it can be seen that with chemical oxidation intermediate products are formed (momentarily) as well. For

instance, when oxidising tetrachloroethene with Fenton's reagent, dichloroacetic acid and formic acid are formed.

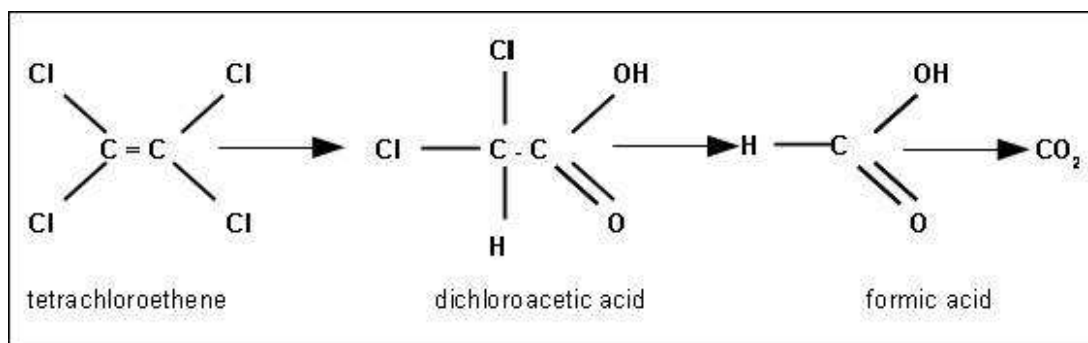


Figure 3: oxidative degradation of tetrachloroethene

When the oxidation is incomplete, for instance due to a lack of oxidants, these intermediate products can persist. They are usually less toxic and also better suited for biodegradation.

2.2.2 Oxidation of metals

Each soil is characterised by a certain concentration of metals. The nature and amount of metals that are found in the soil are the result of the pedological and geological processes in the soil. Generally speaking, metals are present in the soil in reduced form and/or adsorbed to both the mineral and the organic part of the solid phase of the soil.

When oxidants are added to the soil, the metals present will oxidise, for chromium, this means an oxidation to a more toxic form (Cr³⁺ to Cr⁶⁺).

The change in the redox potential (and the possible change in the pH for example, by the acidification of the soil) has a great influence on the solubility (Pourbaix diagrams)⁵ of the metals. In addition, the ionic strength of the soil solution is increased by the application of the oxidant and the reaction products of the redox reactions (for example chlorides), which will have an impact on the solubility. As a consequence of these processes, the concentration of heavy metals in the groundwater increases.

The oxidation of heavy metals is a reversible process. Once the redox potential of the soil is back to a natural value, the heavy metals will go back to their insoluble, reduced form. Based on 23 case studies conducted in the United States, in 10 cases (43%) no increase in the concentration of heavy metals in the groundwater was detected. In the remaining 13 cases (57%) a higher metal concentration was found in the groundwater during and immediately after the injection, compared to before. However, the increased concentrations were always lower than the applicable standards. Arsenic, chromium, manganese and nickel were the metals with

⁵ Pourbaix diagram, or pH - Eh diagram, which schematically shows the appearance of the metal as a function of pH and redox potential. On the diagram it is possible to see what the effect is when the redox potential increases or decreases or as the pH changes. It is, however, not yet known how quickly the reaction proceeds.

the most increased concentration. The period during which these increased concentrations were found strongly depended on the site and varied from less than one month to more than 36 months.

If necessary, the reduction of the oxidised metals can be boosted, once the effect of the oxidant has worn off, by injecting reductants, such as zerovalent iron or a carbon source.

2.2.3 Rebound effect

Just like with other in-situ soil remediation techniques, with ISCO there is always – to a greater or lesser extent – a rebound effect. The rebound effect implies that the measured concentrations of contaminants in the groundwater go up again after the active remediation has been completed.

The three main reasons for rebound with ISCO are:

- discharge into the groundwater due to remaining pure product that goes into solution (DNAPL);
- diffusion of contaminants from less permeable layers;
- oxidation of organic material to which the soil contaminants were adsorbed (the greater the affinity of the soil contaminants for the solid phase of the soil, the greater the rebound effects);

Despite the fact that the concentrations in groundwater go up again, it is found that substantial pollutant loads are removed from the soil (based on a study in the United States the average is 84%). To get an accurate picture of the effect of chemical oxidation it is important to know the total pollution load for the injection (including the contamination present in the solid part of the earth in the saturated zone). Given the possible rebound it is insufficient to only monitor the groundwater, especially in the source zone.

A solution to the rebound effect is to carry out another injection round or to combine ISCO with another remediation technique.

2.2.4 Combination with other remediation techniques

Monitored natural attenuation

Chemical oxidation has been used frequently and successfully on different soils to remove considerable pollutant loads. ISCO offers the possibility to quickly reduce pollutant loads, but chemical oxidation will rarely (at a reasonable cost) eliminate the contamination entirely. Experience shows that ISCO technology is a technically sound and possibly cost-effective approach for a considerable mass reduction of contaminants in a relatively short time. To obtain very low concentrations, it is advisable to combine ISCO with enhanced natural attenuation. Furthermore, chemical oxidation will not always manage to completely oxidise the contaminants present (e.g. function of the molecule structure of the contaminants) but incomplete oxidation usually results in daughter products that are more biodegradable.

Over the past twenty years during which chemical oxidation has been applied, there has been discussion about a possible sterilisation of the soil as a result of the oxidants. Laboratory tests have shown that the bacteria populations present are eliminated as a result of the use of chemical oxidants. Today, this idea has generally been refuted now that an increasing amount of research and experience have proved the contrary.

Unlike in laboratory tests, where the oxidant and the soil sample are mixed very well, the soil always contains (micro)pores in which bacteria do not come into contact with the oxidant. From here, within a few weeks or months after the injection of the oxidant, the soil will again be completely colonised by bacteria. Bacteria counts on different sites before and a few months after the injection show little difference in bacteria populations.

Surfactant enhanced ISCO (S-ISCO)

Chemical oxidation is mainly limited to the aqueous phase. The degradation of pure product zones (LNAPL or DNAPL) is limited by the small contact surface of the pure product and the limitations of mass transfer. As a result, usually several injections are needed to remediate an area where contaminants are also present in the form of undiluted pure product.

With S-ISCO, in addition to a traditional oxidant (hydrogen peroxide, persulphate or permanganate) and catalysts, a mixture of co-solvents and non-ionic surface-active substances from plant origin will also be injected (e.g. coconut and castor oil and citrus extracts). The technology is best suited for heavy hydrocarbon (PAHs, coal tar, creosote) or fuel (BTEX) contamination.

Surface-active substances are partly hydrophilic and partly hydrophobic. The hydrophobic part usually consists of a long hydrocarbon chain and forms, as it were, the tail of the molecule. The head, on the other hand, is hydrophilic. When surface-active substances are present in water, these will not mix evenly with the water. With a concentration higher than the critical micelle concentration, the molecules will position themselves in such a way that the hydrophobic 'tails' sit together and the hydrophilic heads are surrounded by water molecules as much as possible. This gives rise to micelles⁶ of the surface-active substances that contain pure product particles.

⁶ A micelle is a microscopically small structure of a number of molecules of a surface-active substance in water. These molecules usually form a small ball with sizes varying from a few to hundreds of nanometers. In the central part (the hydrophobic tails) of such a micelle hydrophobic substances can settle. When the critical micelle concentration is exceeded, the micelles will form.

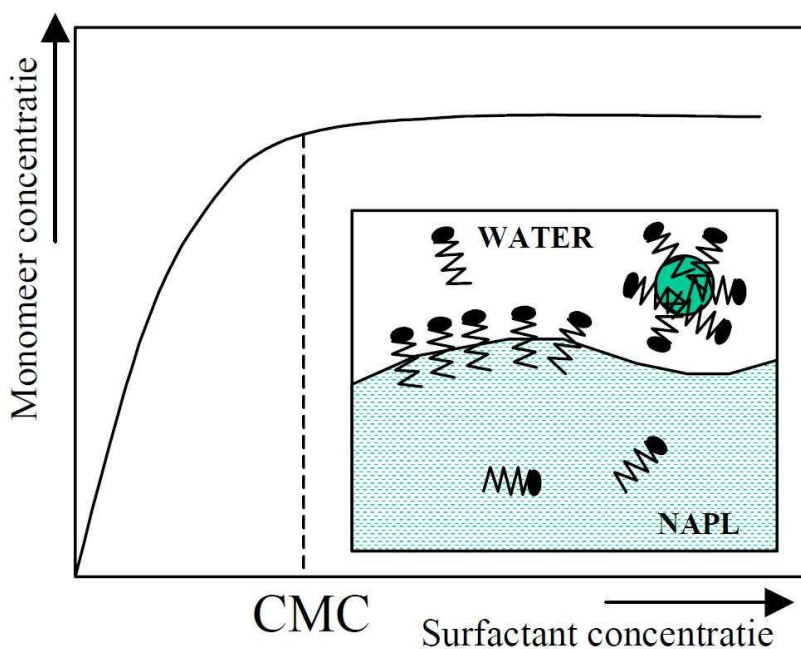


Figure 4: principle of micelle formation according to surfactant concentration

An important parameter in the use of surfactants is the critical micelle concentration (CMC). This is the threshold surfactant concentration at which micelles are formed. The CMC is normally rather low (between 0.01 and 2 g/l) and depends on the type of detergent, water hardness and temperature. In soil remediation applications the amount of surfactants to be applied must be chosen in such a way that the applied concentration (to be determined via laboratory research) is higher than the CMC. In this way, an optimal increase in the apparent solubility of the DNAPL is obtained (in practice, an increase in solubility by a factor of 10 to 100 is mentioned). By increasing the solubility of the pure product and by increasing the potential contact surface, pure product zones could be handled much more efficiently.

An important remark is that the injection of vegetable substances will lead to a higher oxidant demand.



2.3 Overview table

The following table gives an overview of the most used oxidants in ISCO applications and their main properties. The retention time and loss per day are indicative values and will depend on the soil characteristics and the injected oxidant amount.

Oxidant	Hydrogen peroxide	Potassium/sodium permanganate	Sodium persulphate	Ozone	Perozone	Sodium percarbonaat
formula	H_2O_2	$\text{KMnO}_4 / \text{NaMnO}_4$	$\text{Na}_2\text{S}_2\text{O}_8$	O_3	$\text{H}_2\text{O}_2 + \text{O}_3$	$2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
Appearance	liquid	solid/liquid	solid/liquid	gas	gas	solid/liquid
Oxidation Potential (V)	1,8 – 2,8	1,7	2,1 – 2,6	2,1	2,1	1,7
Activator	none, Fe(II), Fe(III)	none	none, Fe(II), Fe(III), heat, pH	none	O_3	Fe(II), pH
Reactive part	$\text{OH}^\bullet, \text{O}_2^{\bullet-}, \text{HO}_2^\bullet, \text{HO}_2^-$	$\text{MnO}_4^{\bullet-}$	$\text{SO}_4^{\bullet-}$	$\text{O}_3, \text{OH}^\bullet$	$\text{O}_3, \text{OH}^\bullet$	HO_2^\bullet
Loss (%/day)	10 - >95	0,1 – 1,0	1 – 3	1 – 5	1 – 5	1 – 3

	Hydrogen peroxide	Potassium/sodium permanganate	Sodium persulphate	Ozone	Perozone	Sodium percarbonaat
Retention time	minutes to hours*	weeks to months	days to weeks	hours to days	hours to days	days to weeks
Retention time	minutes to hours*	weeks to months	days to weeks	hours to days	hours to days	days to weeks
H phrase**	H 302 / H315 H 318 / H 335	H272 H302 H410 (KMnO ₄) H272 H314 (NaMnO ₄)	R8 R20 R22 R36 R37 R38	R5-R6-R23- R36/37/38		H272 H302 H318
P phrase**	P 261 P305+P351+P338 P310 / P 321 P 405 / P 501	P220 P273 P501 (KMnO ₄) P220 P280 P310 P305+P351+P338 (NaMnO ₄)	S17 S26 S36			P220 P280 P305+351+358
Common injectionmethod	filters	direct push	filters	sparging	sparging	direct push

Table 6: overview of a few frequently used oxidants

* Experience shows that the retention time of modified fenton's can vary between days to several weeks

**Phrases indicating hazards (H phrases) and precautionary measures (P phrases) that are used in the European Union (see appendix).

3 Application methods

3.1 General

The choice of the application method is at least as important as the choice of the oxidant. Direct contact between the oxidant and the contaminant is necessary in order for ISCO to be successful. The description of the application methods is limited to a short description of the technique together with the main advantages and disadvantages.

Method	Description	Disadvantages	Advantages
Injection via filters	Injection of the oxidant into the soil under pressure via (existing) vertical filters.	Cost of the material of the injection filters (must be resistant against the oxidants used).	A second injection round (e.g. after rebound) is very simple.
Injection via direct push methods	Injection of the oxidant into the soil under pressure via direct push methods (e.g. Geoprobe® probe). The maximum depth is limited to approx. 20 m bgl.	If a second injection round is required, a new mobilisation is necessary as well, which strongly increases the cost. Usually the radius of influence is slightly smaller than with fixed injection filters.	Relatively simple to treat specific areas at a certain depth.
Recirculation	Combination of direct injection or infiltration and groundwater abstraction.	Higher cost.	Good hydrological control and spread possible with a minimal amount of oxidant.
Infiltration	Passive infiltration of oxidant through horizontal or vertical filters.	Only possible in highly permeable soils.	With vertical filters the filter configuration can be adapted to the specific conditions of the site. Horizontal filters are less recommended if there are heterogeneities in the soil.
Soil mixing	Mixing contaminated soil or sediment with oxidant using auger drills.	Limited to shallow soil (< 2 m bgl). Loss of soil structure.	Good contact possible between oxidant and contaminants.
Sparging ⁷	Injection of ozone into the saturated zone.	Only applicable for ozone.	

Table 7: overview of application methods

The limiting factor of ISCO is still the contact between the soil contaminants and the oxidant. If these do not come into contact, no reaction can take place. In order for the reaction to take place, first of all sufficient oxidant (and additives) must be injected into the soil. Secondly, the design must take into account a sufficient overlap between the different application areas. It is important to quantify both aspects in time. To this end, it is best to use laboratory tests and pilot tests.

Technological progress will lead to the development of new application methods. Moreover, some application methods can be combined. Sometimes ISCO is also combined with the remediation technique 'excavation with drainage'. After the excavation (which may be limited in depth due to technical limitations or for cost reasons) oxidants are applied to the soil of an excavation area in the form of slurry or powder to treat possible (residual) contamination.

3.2 Injection via filters and the direct push method

The oxidant is pumped into the soil by means of injection tubes or filters. In the case of injection via filters, the existing infiltration media (probes, filters, drains) can be used to apply the oxidant. The use of these media will depend on the radius of influence and the number to guarantee sufficient coverage of the contaminated area. If necessary, additional injection media must be installed.

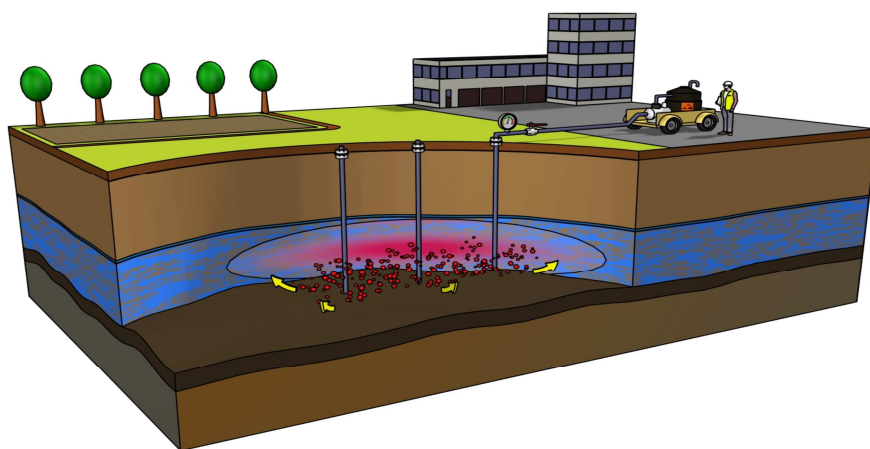


Figure 5: principle of direct injection via vertical filters

The advantage of using a direct push method is that selectively contaminated areas can be treated according to the presence of contaminants. However, if several injection rounds are required, this method can be expensive. If contaminants are present at depths greater than 20 m bgl, the use of a direct push method is technically no longer feasible.

As liquids are injected under pressure, there needs to be sufficient counterpressure from the soil and the groundwater column (Terzaghi's principle / Hubbert & Willis⁸) in order to prevent breakage and tearing.

⁸ If the injection pressure is greater than twice the effective soil tension, this can give rise to breakage and tearing.

The shape and dimensions of the oxidant plume of one injection point depend on the injection rate and pressure, heterogeneity, permeability and the speed with which the oxidant is consumed (which depends on the amount of contaminant, the soil oxidant demand and the stability of the oxidant). It is very important for injections to be carried out with a good injection pump. To this end, it is best to use pumps which can handle a rate of at least 20 litres/minute and a pressure of at least 1,500 kPa (sandy soils) to 5,500 kPa (loam soils). An important factor is permeability. The lower the permeability of the soil, the more difficult the injection of liquids will be. This means that either a higher injection pressure is needed, or more time to add the same amount of oxidant to the soil. A stable oxidant will over time migrate with the groundwater flow. This way, the radius of influence will increase further.

In order to be sure to avoid an uncontrolled spread during the injections, it is best to start the injections at the edges of the area to be treated and then inject more towards the centre of the area. When injecting an amount of oxidant under pressure, one must also take into account the spread of oxidant via preferential flow paths (e.g. sewer system), the oxidant coming to the surface (e.g. not properly sealed monitoring wells) and a possible spread of the groundwater contaminants. The possible spread as a result of the injection is usually not much larger than the radius of influence of the oxidant (taking into account the retardation and the exponential increase of the pore volume depending on the distance). With direct injection via filters, especially in heterogeneous soils, the filter length must not be too long, because otherwise the oxidant will mainly spread in the most permeable layers. The use of cutting filters is not recommended either because then the oxidant will mainly spread in the unsaturated zone, as resistance is lower there. Given the potential pressure build-up, the injection filters must be finished with cement or cement-bentonite groutstop.

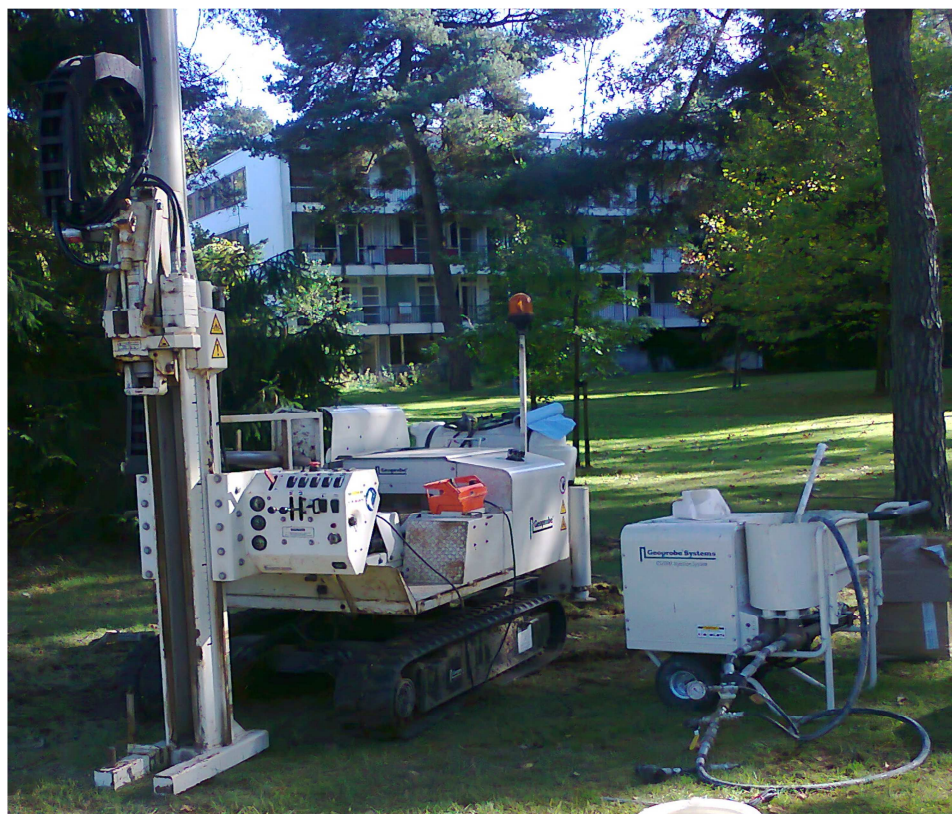


Figure 6 example of injection using direct push method

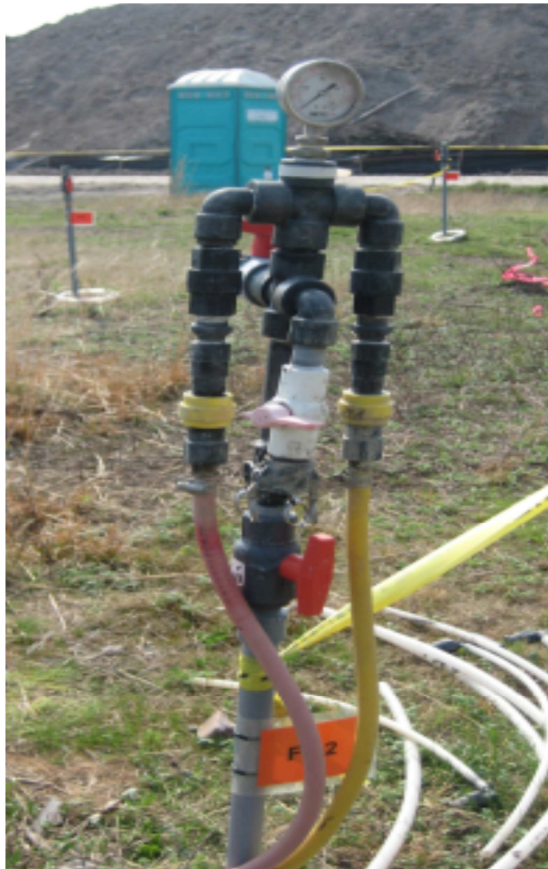


Figure 3: detail of direct injection via vertical filters



Figure 4: example of direct injection via vertical filters

Injection

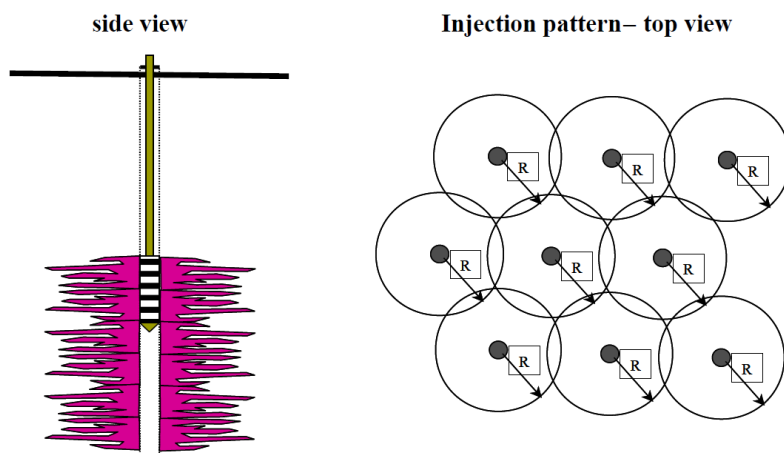


Figure 5: schematic view injection

Injection

Injection pattern - side view

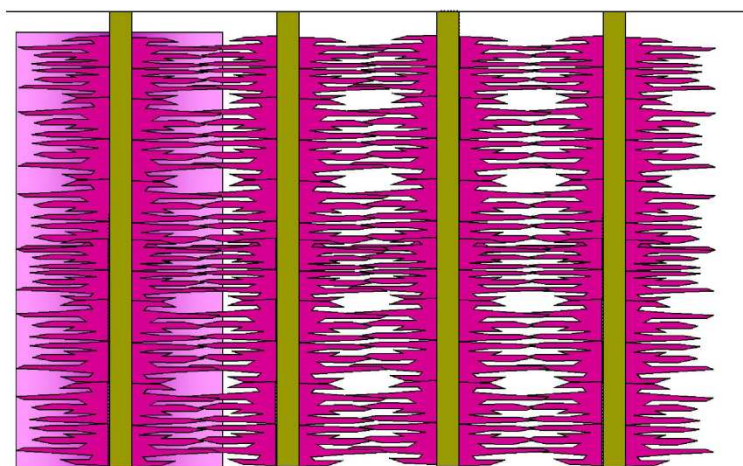


Figure 6: schematic side view injection

3.3 Recirculation

Recirculation is the process whereby in a (closed or open) system oxidant is injected at one location and groundwater is abstracted at another. The method is a combination of a classical groundwater remediation technique, namely 'pump and treat', and ISCO. This process offers the following advantages:

- Via the process of infiltration and extraction a larger hydraulic gradient is created within the contaminated area. The gradient ensures that the remediation can take place faster than with only an injection system.
- As a result of the hydraulic gradient the area of influence of the application is larger.

However, the application of recirculation depends on the local geology, the appearance of the contamination, the local hydrogeology and the local geochemistry.

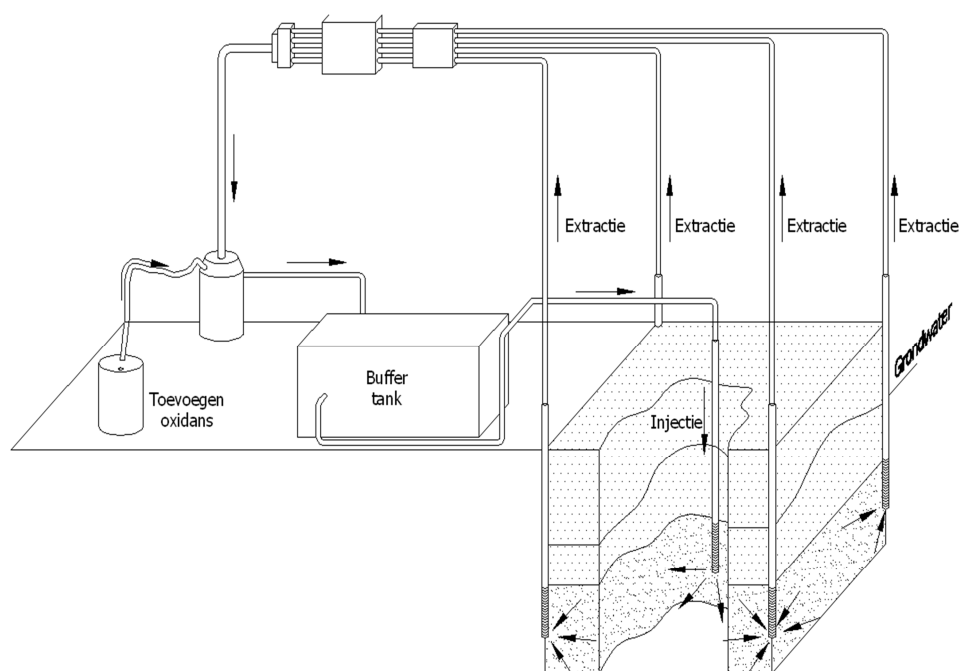


Figure 7: diagram of the recirculation principle

3.4 Infiltration

With this method the oxidant is applied to the soil via infiltration drains or probes. The oxidant is injected into the soil without the help of mechanical actions or pressure. With a passive system, one needs to take into account the infiltration capacity of the soil, the groundwater level, the groundwater flow rate and the life of the oxidant. The infiltration capacity of the soil is closely connected to the soil type. When dimensioning the infiltration set-up, it is important to estimate the infiltration capacity as accurately as possible. The values mentioned in the table below are a rough estimate of the infiltration capacity.

Soil type	infiltration capacity
rough sand	500 mm/u ($= 1,4 \cdot 10^{-4}$ m/s)
fine sand	20 mm/u ($= 5,6 \cdot 10^{-6}$ m/s)
loamy fine sand	11 mm/u ($= 3,1 \cdot 10^{-6}$ m/s)
loam	2,1 mm/u ($= 5,8 \cdot 10^{-7}$ m/s)
light clay	1,5 mm/u ($= 4,2 \cdot 10^{-7}$ m/s)
medium heavy clay	0,5 mm/u ($= 1,4 \cdot 10^{-7}$ m/s)

Table 8: infiltration capacity according to soil type

Infiltration tests can provide help in making a more accurate estimate of the infiltration capacity of the soil. It should be mentioned here that it does not make much sense to test the infiltration capacity in soils which already have a much too low permeability from a theoretical point of view.

The use of an indirect application method requires a groundwater flow which is greater than 0.05 m/day. If the groundwater flow is lower than 0.05 m/day, it is less easy to apply passive infiltration as the oxidant will spread insufficiently.

Infiltration is only a valid injection technique if the following conditions are fulfilled:

- The oxidant must remain reactive in the soil long enough to oxidise the contaminants. Rule of thumb: the half-life of the oxidant in the soil is greater than twice the reaction time.
- The oxidant must remain stable in the soil for long enough to obtain a sufficiently large radius of influence. Rule of thumb: the half-life of the oxidant in the soil is greater than the time in which the oxidant travels 10 metres. When injecting the same volume with a higher injection rate, the radius of influence of an (unstable) oxidant will also be larger.
- The injection of an oxidant must not have any harmful consequences for people or nature. With infiltration the risks of a long-term presence of an oxidant on the site and the effects of a longer injection period must be accurately estimated.

Infiltration

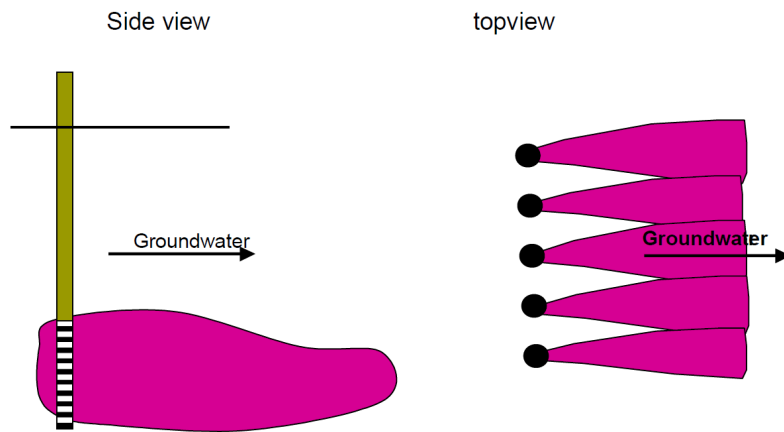


Figure 8: principle of infiltration

3.5 In-situ soil mixing

With the help of an auger drill with a large diameter (typically 1 to 3.5 metres) the soil is mixed with the oxidant. The auger enters the soil and turns it up. Via a dosing system in the auger, oxidant is added to the soil.

This technique has a few important limitations. For instance, at greater depths its use is limited. The price of soil mixing increases exponentially with the application depth. Hence, soil mixing is less interesting financially for depths greater than 2 m bgl. A second important limitation is that the soil loses its structure as a result of the mixing, leading to the loss of the civil-technical characteristics of the soil. A plus of this method is that the technique guarantees an optimal contact between the contaminated soil and the oxidant.

In certain cases, part of the source is excavated and the oxidant is directly applied to the soil of the excavation area in the form of powder or slurry, after which it is filled again.

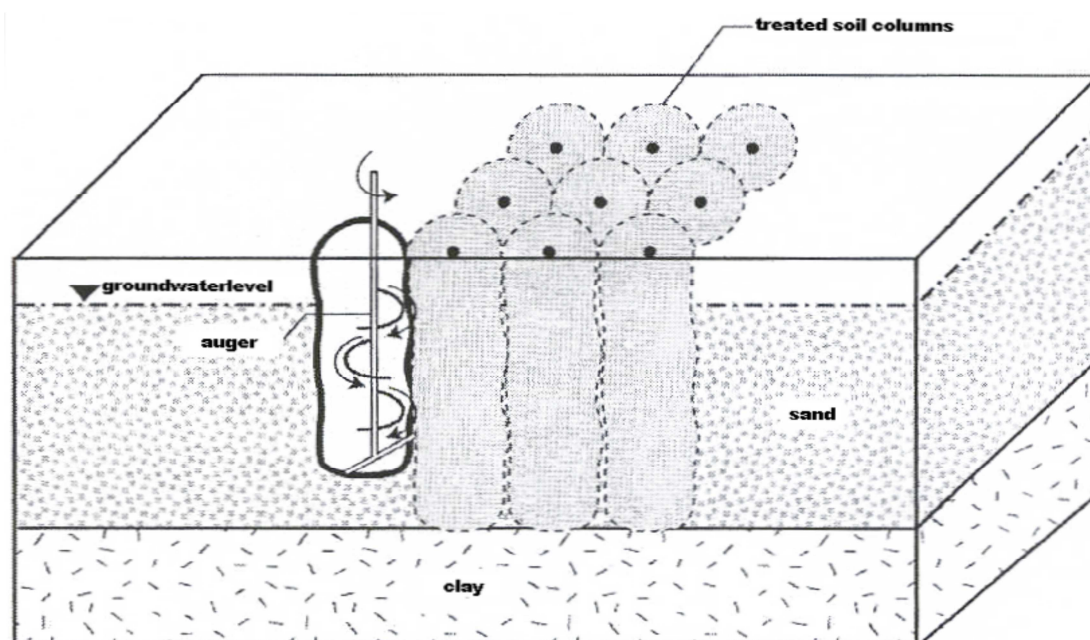


Figure 13: principle in-situ mixing

3.6 Ozone injection (sparging)

As ozone is a gaseous oxidant, the application method is different from the other application methods. The application methods for ozone have been derived from conventional compressed air injection techniques. However, the big difference with these techniques is that more stringent requirements apply to the material. Due to the corrosive nature of ozone, relatively expensive materials, such as stainless steel, teflon, etc., have to be used.

As with the injection of compressed air, a soil vapour extraction system may be necessary to eliminate any released soil gases and surplus ozone gas.

For the generation of ozone an ozone generator is used. Ozone production is expressed in kg/day. Ozone production does not take place in batches, but continuously.

When applying ozone injection, the radius of influence of the injection and the radius of influence of the extraction are important. Both aspects can be determined by pilot tests.

Injection filter	Recirculation well	Perozone
Only microporous injection filter	Two injection filters and an underwater pump	Combination gas/liquid injection
The air/ozone mixture is injected into the soil in very small bubbles. These microbubbles spread relatively far into the soil.	A recirculation well consists of 2 injection filters and an underwater pump. The injection causes an upward flow of the injected gas which, together with the pump, creates a circulation effect. This results in a larger radius of influence.	A coating has been applied around the injection filter with glass beads along which H_2O_2 is passed. The result is a mixture of ozone and hydrogen peroxide which is injected into the soil.

Table 7: application possibilities for ozone

4 Selection of the oxidant and feasibility study

4.1 Introduction

Before being able to remediate soil contamination, a BATNEEC study must be made of the different relevant technical possibilities. Depending on the contaminants and the specific characteristics of the site, one can consider selecting ISCO as a relevant remediation technique. A thorough preliminary study is required to provide the necessary proof that ISCO is feasible and can be regarded as the Best Available Technique.

In this chapter we will describe the procedure for studying the feasibility of chemical oxidation. This procedure explains the different steps that need to be taken to this end:

1. First of all, it must be studied which oxidant is able to oxidise the contaminants. This can be done based on data from the literature and/or laboratory tests
2. If it is clear from the previous step that there is an oxidant that can oxidise the contaminants at hand, the applicability of the oxidant has to be checked. The applicability of the oxidant depends on a number of factors, including contaminant concentration, the amount of oxidant needed, the remediation objective proposed, acidity and buffer capacity, organic content, the presence of metals, the presence of electron scavengers, the appearance of the contamination.... Many of these factors are site-specific and it is often difficult to predict in advance what the effect of the combination of these parameters on the required quantity of chemicals (oxidant, catalysts, acids) will be. This requires the necessary laboratory tests like determination of buffer capacity, determination of soil oxidant demand and determination of the reactivity.
3. Once the previous steps have shown that an applicable oxidant is available for the corresponding soil, the application method needs to be chosen. When doing so, one needs to take into account factors such as the type of oxidant, the structure of the soil, the expected radius of influence and the appearance of the contamination.
4. Finally, it needs to be checked whether the application method can be used on the site in question. Here, site-specific characteristics need to be taken into account and it is advisable to carry out a pilot test.

In the next paragraphs attention will be paid to the determining factors for the selection and the applicability of the oxidant.

4.2 Selection oxidant

The following preconditions are important in the selection of an oxidant:

- the properties of the oxidant;
- the relative density of the oxidant;
- the concentration and oxidizability of the soil contaminants;
- the local geology;
- the local hydrogeology;
- the local geochemistry;
- the cost price of the oxidant.

4.2.1 The properties of the oxidant

Oxidation potential

ISCO can be considered for the remediation of soil contamination which can be oxidised with chemical oxidants. The table below gives a few examples of contaminants that can and cannot be degraded by means of ISCO.

Contaminants that can be degraded very effectively by chemical oxidation	Contaminants that can be degraded by chemical oxidation, but the effectiveness of which is less certain (often site-specific)	Contaminants that cannot be degraded by chemical oxidation
chloroethenes (e.g. PCE, TCE) BTEX mineral oil PAHs chlorobenzenes phenolen MTBE alcohols free cyanides	chloroethanes (e.g. TCA) TNT pesticides / herbicides PCBs dioxins	heavy metals salts nutrients (nitrate, phosphate)

Table 8: oxidizability of different contaminants

It is clear that not all oxidants are suitable for the oxidation of all kinds of contaminants. The oxidation potential of the contaminant and the oxidant are the determining factors for this. Only if the oxidation potential of the oxidant is higher than that of the contaminant will a reaction take place and will the contaminant be oxidised. Based on the following table a first indication can be obtained of the applicability of an oxidant for a certain case of contamination.

Contaminant	MnO ₄	H ₂ O ₂	2Na ₂ CO ₃ ·3H ₂ O ₂	Na ₂ S ₂ O ₈	O ₃
Light mineral oil	+	++	++	+++	++
Heavy mineral oil	-	+	+	-/+++	+
Benzene	--	+++	+++	+++	+++
Toluene, ethylbenzene, xylene	++	+++	+++	+++	+++
MTBE	-	++	++	+++	++
TBA	--	+	+	+ /+++	+
PAHs	++	++	++	++	++
Chloorethenes	+++	+++	+++	+++	+++
Chloroethanes	--	+ /+++	+	+ /+++	++
PCBs	--	+	+	+	--
Chlorobenzenes	-	+	+	++ /+++	+
Dioxins	--	+	+	+	--
Pentachlorophenol (PCP)	++	++	++	++	++

Table 11: Indicative amenability of contaminants to oxidation by commonly used oxidants

Legend:-- = not applicable, - = low effectiveness, + = medium effectiveness, ++ = high effectiveness, +++ = very high effectiveness

Relative oxidant density

The relative density of the oxidant indicates whether the substance is heavier or lighter than water. Preferably an oxidant solution should be chosen that approximates the physical properties (density) of the contaminant as much as possible. As a result it is more likely that the injected solution will spread along practically the same pathway as the contaminant.

4.2.2 Contaminant concentration

The concentration of the soil contaminants and the location where one wants to use ISCO for soil remediation (contamination plume or source) will also influence the choice of the oxidant.

In the source zone (area with relatively high contaminant concentrations and pollution load) an oxidant with a high reactivity or a high oxidation potential must be chosen. If an oxidant is chosen with a reactivity or oxidation potential that is too low, it is possible that not all contaminants are oxidised. In the source zone

there may be a DNAPL. Soil remediation by means of ISCO often requires an adapted method for DNAPLs because the oxidant demand is very high.

To treat a contaminant plume (downstream from the source, lower concentrations) generally a stable oxidant is chosen. The pollutant load present is lower than in the source zone. The use of a stable oxidant will result in a longer retention time in the soil. As a result, there is a bigger chance of contact with the soil contaminants because the oxidant will spread further following the natural groundwater flow. For this reason, unstable oxidants have a smaller radius of influence, which is why more injection points are required, thus increasing the costs of the treatment of the plume.

A consideration here is that for the remediation of larger plumes with lower concentration of pollution, even with a stable oxidant, you will have to inject much oxidant (the oxidant must come in contact with the pollution). This increases the cost greatly and other remediation techniques are often more efficient.

Characteristic	MnO ₄	H ₂ O ₂	2Na ₂ CO ₃ ·3H ₂ O ₂	Na ₂ S ₂ O ₈	O ₃
Very low concentration	-	-	-	-	+
Low concentration	++	++	++	++	++
Moderate concentration	+++	+++	+++	+++	+++
High concentration	++	+++	++	+++	+
Very high concentration	-	++	+	++	-

Table 12: oxidant choice versus concentration

Legend: - = low effectiveness, + = medium effectiveness, ++ = high effectiveness, +++ = very high effectiveness

4.2.3 Local geology

The geological structure of the soil also greatly influences the spread of the oxidant. Transport of dissolved substances in the saturated zone is mainly caused by the groundwater movement (advective transport⁹ and dispersion¹⁰). Diffusion is important mainly in case of a weak groundwater flow and for the dissolution of pure product. In turn, the groundwater flow is strongly influenced by the nature of the soil. A distinction is made between 3 different soil types according to their most dominant transport processes:

1. Highly permeable formations (sand and gravel)

In highly permeable formations, oxidants can spread relatively easily after the injection. The spreading of oxidant through the soil takes place mainly via advection processes. Advection processes are fast processes. Both stable and unstable oxidants can have good results. Due to the fast advection transport processes, the possible spread of the oxidant to adjoining plots must be taken into account.

2. Low-permeable formations (clay and silt)

⁹ Advective transport is driven by the difference in groundwater potential over a certain distance (gradient) and is further determined by the hydraulic permeability according to Darcy's Law.

¹⁰ Dispersion is not a separate physical process. It is basically advection. However, due to the different lengths of the flow paths, even in homogeneous soils, a fanning effect is created.

In low-permeable soils, mainly diffusion processes are responsible for the spread of the oxidant. The transport of the oxidant is much slower. Therefore, the use of stable oxidants, such as permanganate, is advisable. These remain reactive long enough to be able to enter the formation via diffusion and then oxidise the contaminants. In comparison with highly permeable formations, these processes are much slower, which is why ISCO is considered less applicable.

3. Moderately permeable soils.

These encompass all remaining soil types (loam, heterogeneously structured soils). Transport through these soils takes place both by advection and by diffusion, neither of which can be considered dominant. The choice of the oxidant will therefore depend to a great extent on the specific permeability at the site in question. A thorough preliminary study and the performance of feasibility tests will have to determine which oxidant is most suitable.

Soil characteristic	MnO ₄	H ₂ O ₂	2Na ₂ CO ₃ .3 H ₂ O ₂	Na ₂ S ₂ O ₈	O ₃
Highly permeable	+++	+++	+++	+++	+++
Low permeable	+	-	-/+	+	-
Moderately permeable	++	-	+	++	-

Table 13: geology versus oxidant choice

Legend: - = low effectiveness, + = medium effectiveness, ++ = high effectiveness, +++ = very high effectiveness

The injection of ozone is possible in soils with a permeability from 0.2 - 0.5 m / day. In soils with a lower permeability there is a risk of breakthrough of ozone to the surface.

4.2.4 Local hydrogeology

Besides the local geology the local hydrogeology is also important. Most oxidants are added in solution or slurry, which makes them extremely suitable for the treatment of the saturated zone. Where the unsaturated zone is concerned, attention must be paid to the contact and the retention time of liquid oxidants in the unsaturated part of the soil. If the ISCO treatment is aimed at the unsaturated zone, this should be considered carefully when designing the ISCO. A gaseous oxidant, such as ozone, on the other hand, is more easily applicable in both the saturated and the unsaturated zone.

Similarly to what was described in the previous paragraph, a stable oxidant is more suitable on a site with a relatively slow groundwater flow.

4.2.5 Local geochemistry

The local geochemistry will play an important role in the choice of the oxidant. It mainly concerns the following aspects:

— Acidity or pH:

ISCO can have a substantial impact on the pH of the soil, either through the injection of an oxidant together with an acid or through the production of protons or hydroxyl ions during the reaction. The use of permanganate as an oxidant can influence the pH depending on the substance to be oxidised. For instance, with oxidation of PER and TRI the pH can drop as a result of the release of H^+ , with oxidation of DCE and VC the pH will rather rise as a result of the creation of OH^- (see table 3):

tetrachloroethene (PCE):	3 mol PCE \rightarrow 8 mol H^+
trichloroethene (TCE):	1 mol PCE \rightarrow 1 mol H^+
dichloroethene (DCE):	3 mol DCE \rightarrow 2 mol OH^-
vinyl chloride (VC):	3 mol DCE \rightarrow 7 mol OH^-

The impact of this on the soil depends on the buffering capacity of the soil. To a large extent, carbonates are responsible for the pH buffering capacity of the soil. From the general reaction kinetics of the redox reaction it is clear that the proton concentration will play a role in defining the reaction equilibrium. Given that the carbonate system in the soil steers the soil pH, the carbonate system in the soil will indirectly be co-responsible for the reaction kinetics with ISCO. Carbonates are also radical acceptors. Hence, it is clear that the carbonate concentration in the soil will influence the SOD by directly accepting radicals and/or indirectly modifying the redox reaction kinetics.

Characteristic	MnO_4	H_2O_2	$2Na_2CO_3 \cdot 3H_2O_2$	$Na_2S_2O_8$	O_3
pH					
< 5	+++	+++	--	+++	+++
5 – 6	+++	+++	+	+++	+++
6 – 7	+++	++	++	+++	+++
7 – 8	+++	+	+++	++	++
8 – 9	+++	-	+++	+++	++
> 9	++	--	+++	+++	+

Table 14: pH versus oxidant choice

Legend :-- = not applicable, - = low effectiveness, + = medium effectiveness, ++ = high effectiveness, +++ = very high effectiveness

— Natural organic matter:

Most oxidants have a significant affinity for organic matter. In other words, they do not only have a redox reaction with the contaminants, but also with the organic matter in the soil. Of the most frequently used oxidants permanganate is the most reactive with natural organic material and persulphate is the least reactive. In addition to an increased SOD, the elimination of organic matter in the soil through the reaction can also have significant secondary effects on the soil structure, such as subsidence, peat fires, etc. Moreover, other contaminants might be released from the organic matter, which might give rise to new contamination.

Characteristic	MnO_4	H_2O_2	$2Na_2CO_3 \cdot 3$	$Na_2S_2O_8$	O_3
----------------	---------	----------	---------------------	--------------	-------

			H ₂ O ₂		
Organic carbon fraction f _{OC}					
> 3 %	--	--	-	+	--
1 – 3 %	-	-	+	++	-
0,3 – 1 %	++	++	+++	+++	++
0,1 – 0,3 %	+++	+++	+++	+++	+++
< 0,1 %	+++	+++	+++	+++	+++

Table 15: organic carbon fraction f_{OC} versus oxidant choice

Legend: - = low effectiveness, + = medium effectiveness, ++ = high effectiveness, +++ = very high effectiveness

4.2.6 Cost price of the oxidant

On the one hand, the cost price depends on the unit price of the oxidant per kilogram and, on the other hand, on the oxidant 'consumption' for the ISCO. In turn, the oxidant consumption depends on the stoichiometry of the reaction, the SOD, the stability and the specific density of the oxidant.

- By stoichiometry the reaction equivalent of the oxidant is meant. A redox reaction is, in fact, a reaction by which the oxidant accepts electrons from the contaminants. By accepting electrons the oxidant is reduced and as a result of the loss of electrons the contaminants are oxidised.
- To a significant extent, the oxidant consumption can be influenced by the SOD. Oxidants do not only react with the contaminants present, but also with uncontaminated organic and inorganic materials (such as humus and metals). This may lead to an increased oxidant consumption.
- The cost price of a substance is also determined by its stability. The more stable the oxidant, the smaller the amount that needs to be added to the soil in comparison with an oxidant that is characterised by a small half-life or low stability.
- Where the specific density of the oxidant is concerned, the following applies: the lower the specific density of one reaction equivalent, the lower the price per kg of the oxidant.

More important factors for the cost of an ISCO remediation (approximately 75% of total costs) are the injection method, the injection time (the time necessary to inject the desired amount of oxidant) and the fact whether several injections (mobilisation/demobilisation) are required.

Cost	NaMnO ₄	H ₂ O ₂	2Na ₂ CO ₃ ·3H ₂ O ₂	Na ₂ S ₂ O ₈	O ₃
(euro/kg)	4,0 - 5,5	1,0 - 2,0	3,5 - 5,0	1,5 - 2,5	1 – 2 euro/m ³

Table 16: range cost oxidant

4.3 Feasibility tests

The site-specific data gathered during soil surveys are usually insufficient to make a proper remediation design. This is especially the case for in-situ techniques, such as chemical oxidation. Therefore, in order to

make a proper remediation design, the feasibility of ISCO must be studied by carrying out laboratory and/or pilot tests. When doing so, all site-specific characteristics must be taken into account (CSM).

Hence, a first step in the study of the feasibility of ISCO is to carry out laboratory tests. Based on the results of the laboratory tests and the dosage calculations a first estimate can be made of the feasibility and total amount of oxidant needed. From this, it will already be clear whether chemical oxidation with the tested oxidant is (economically) feasible. In case of a positive result of the laboratory tests, it is best to carry out a pilot test.

4.3.1 Laboratory test

Dosage calculations and evaluation

The oxidant use per mass of soil is calculated based on the difference between the initial added amount of oxidant and the remaining amount of oxidant after the reaction. The difference is calculated per mass of soil.

$$\text{Oxidant use} \left(\frac{\text{mg}}{\text{kg}_{\text{soil}}} \right) = \frac{(\text{Oxidant}_{\text{begin}} - \text{Oxidant}_{\text{end}})}{\text{Mass}_{\text{soil}}}$$

During the test oxidant is consumed by the reaction with the soil and by degradation. The degradation of the oxidant is also determined during the test by looking at how much oxidant reacts in a sample which has not been brought into contact with the soil but is subjected to the same treatment as the other samples. The effective oxidant consumption by the soil is then calculated as follows:

$$\text{Effective oxidant use} \left(\frac{\text{mg}}{\text{kg}_{\text{soil}}} \right) = (\text{Oxidant use} - \text{decomposed oxidant})$$

Additionally, the decrease of contaminant levels is determined. The soil oxidant demand (SOD) can be calculated as follows:

$$\text{SOD} = (\text{Effective oxidant use} - \text{oxidant used by pollution})$$

The soil oxidant demand is expressed in litres of oxidant solution per volume of wet soil (l/m³). The SOD is usually much higher than the amount of oxidant required for the oxidation of the soil contaminants. The applicability of the oxidant on the site in question follows directly from the definition of SOD. A high SOD implies that a large volume of oxidant needs to be added to the soil. In such case, one must ask oneself whether ISCO is still the best available technique.

The injection of an oxidant will also modify the characteristics of the soil. Hence, the SOD will change compared to the initially calculated SOD as the injection process progresses. In heterogeneous soils or soils in which the contaminants are spread unevenly, the SOD may differ according to the sampled area.

The aim of these laboratory tests is:

- To study the oxidisability of the contaminants, including the effect of any pure product present (mobile and/or residual) and any other soil components or contaminants that may react with the oxidant.
- To determine the reaction kinetics and formation of intermediate products, incl. gases that can be formed and heat that is produced.
- To determine the stoichiometry and the amount of oxidant necessary per unit of soil volume or weight (SOD).
- To determine the buffering capacity of the soil.
- To determine the possible effects of changes in pH and redox potential on the presence and the mobility of any (heavy) metals that may be present.
- To determine possible side reactions, for instance in case of the use of permanganate as an oxidant: to determine the effect of the formation of MnO_2 precipitation on the permeability of the soil (column set-up with aquifer sample).

When designing the laboratory or batch test, one must take into account the specific characteristics of the chosen oxidant and the specific characteristics of the site and the soil in which the contaminants are present. The SOD is also best determined based on several aquifer samples because even in a relatively homogeneous soil medium the SOD may vary strongly. As the SOD also depends on the concentration of the oxidant used, this must be taken into account already during the laboratory test.

Laboratory test for hydrogen peroxide, permanganate en persulphate

A laboratory test usually takes place in 4 phases:

1. Soil and groundwater sampling.
Representational soil material is sampled at the site (soil/aquifer material and groundwater).
2. Initial characterisation of the contaminant in soil and groundwater.
The soil is pretreated, homogenised and then analysed for the relevant contaminant(s), Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD), other soil components, texture, pH, etc.
3. Determination of the effectiveness of the oxidant.
To determine the effectiveness both samples with and samples without added oxidant are tested. Based on the initial and final concentrations the effectiveness can be studied.
4. Determination of the soil oxidant demand or matrix demand (SOD) and side reactions.
The oxidant does not only react with the contaminants present, but also with uncontaminated organic and inorganic materials (metals, sulphides). In most cases the oxidant consumption to oxidise these compounds is considerably larger than the oxidant consumption to oxidise the groundwater. For this reason the SOD of the soil is determined

Two examples of laboratory tests to determine SOD with permanganate

- The aquifer material is put in plastic tubes (20 ml) with distilled water in a 1:1 solid-liquid proportion. Increasing amounts of KMnO_4 are added to the tubes. The tubes are then closed and shaken with a rotating movement for 2 weeks at room temperature in the dark. Based on the purple colouring the SOD can then be determined.
- The soil sample is first heated at 105°C for 24 hours and allowed to cool down, then passed through a sieve (2 mm). For each sample, three reactors are filled with 50 grams of soil and 100ml of 20 g/l KMnO_4 solution (40 g KMnO_4 / kg dry soil). The reaction vessels are inverted once to mix the reagents. The residual permanganate is determined after 48 hours¹¹.



Figure 9-15: example of dilution series with permanganate and persulfate

Example of laboratory test to determine buffering capacity and SOD with persulphate

One method to activate persulphate is to increase the pH. A parameter that is important for this is the buffering capacity of the soil. If the buffering capacity of the soil is very high, a lot of base is required to increase the pH of the soil sufficiently to activate the persulphate. With a high buffering capacity it is possible to choose to activate the persulphate using a catalyst with which the pH does not need to be increased. To determine the buffering capacity, aquifer material is titrated with diluted base, while continuously measuring the pH. In this way, a titration curve is made, based on which the buffering capacity can be determined.

To determine the SOD, as for permanganate, a dilution series is set up in which each time 15 g of aquifer material is brought into contact with $\text{Na}_2\text{S}_2\text{O}_8$ in different concentrations, after which the liquid volume is diluted to 15 ml. The bottles are shielded from the light and shaken with a rotating movement (shaking table) for 3 weeks. After this period H_2SO_4 , $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and KSCN are added. If persulphate is present there will be a colour reaction (orange) that allows for a visual assessment of whether or not the persulphate has been completely eliminated by the reaction.

Example of laboratory test to determine buffering capacity and reactivity with Fenton's reagent

Traditional Fenton's reagent is best used with a low pH. The amount of acid that needs to be added to the aquifer material depends on the acid buffering capacity of that aquifer material. If the buffering capacity of the soil is high, a lot of acid is required to lower the pH of the soil sufficiently to make a traditional Fenton's reagent possible. With a high buffering capacity it is better to opt for 'modified'

¹¹ ASTM D7262-method

Fenton's with which the pH does not need to be lowered. This buffering capacity should also be determined during the feasibility study. To determine the buffering capacity, 15 g of aquifer material is titrated with diluted sulphuric acid or phosphoric acid, while continuously measuring the pH. In this way, a titration curve is made, based on which the buffering capacity can be determined.

A reactivity test is similar to a SOD-determination, however rather than to quantify this, one will check the amount of iron and other transition metals present and available in the soil to react with the hydrogen peroxide. The pH is generally lowered by the addition of phosphoric acid or sulfuric acid to a pH of 4 to 5. In first instance, no catalyst is added. The degree of reaction of the diluted hydrogen peroxide with the soil can visually be monitored.

In addition, possible side reactions (concentrations of dissolved heavy metals, decrease in organic matter) can be quantified.

Laboratory test for ozone

For ozone a different type of test is possible, as it concerns a gas. A laboratory test for ozone takes place in different phases:

The first two phases are the same as the laboratory tests mentioned above. After the characterisation of the soil and the groundwater four different parallel tests are carried out for a number of weeks:

- Ozone (~ 5%) is passed over the fraction of contaminated groundwater.
- Ozone (~ 5%) is passed over a slurry of soil and demineralised water.
- Ozone (~ 5%) is passed over annealed soil and demineralised water.
- Oxygen is passed over a slurry of soil and demineralised water.

Based on these tests insight is gained into:

- the estimated ozone demand of the groundwater;
- the estimated ozone demand of the soil matrix;
- the estimated degradation of ozone;
- mass balance (chemical degradation, volatilisation, biodegradation).

The evolution of the soil and groundwater quality is monitored by means of regular measurements of the gas volume and analyses of the eliminated ozone and contaminants.

4.3.2 Pilot test

The extrapolation of data from a laboratory test to a large-scale remediation design involves certain risks. Generally speaking, the results of a pilot test give a more representative image and are more suitable for a large-scale design. Unless ISCO is used as an after-treatment (e.g. addition of oxidant to an excavation zone) it is very strongly recommended to carry out a pilot test in order to get the most accurate image possible of the efficiency and the effectiveness of ISCO soil remediation taking into account the site-specific circumstances. The pilot test will also provide important information on the practical conditions for implementation in the site-specific circumstances, namely:

- the amount of oxidant that can be injected and the feasible injection pressure and rate;

- the radius of influence of the injection points, both horizontal and vertical, and hence the distance required between injection points;
- the spread of the oxidant and the influence of the soil structure, e.g. the appearance of preferential flow paths;
- the volumes and dosage of the oxidant and possible auxiliary substances;
- the injection pressures and flow rates to be achieved;
- the pollutant load reduction to be achieved, and possible post-remediation values to be reached;
- the possible rebound after a (first) injection.

A pilot test is best performed in an area close to the source but upstream so that the area of the pilot test is not immediately contaminated again by inflowing contaminated groundwater. Preferably with at least three injection points to make it possible to also follow up the pilot test via monitoring wells within the circumference of the injection points, so that the above-mentioned edge effect is reduced. A good location of the monitoring wells is necessary to determine the efficiency. When performing pilot tests, specific safety and health aspects of ISCO must be taken into account.

The next paragraphs comprise a non-exhaustive list of different types of pilot tests.

Push-pull test

The purpose of the push-pull test is to determine the degradation of contaminants in the groundwater. With the push-pull method an oxidant (and possibly a tracer) is added to the groundwater. The oxidant is not injected but mixed above the ground with groundwater that is pumped up at the site. Then the mixture is injected into the soil under pressure. Compared to other methods, this way of working offers the advantage that a relatively large amount of water is quickly given the right composition or circumstances for degradation, and that this amount of water moves as fast as the groundwater itself. After this, the evolution of the groundwater quality and the spread of the oxidant in the immediate surroundings of the injection point is monitored by means of several wells.

In this way, it can be studied how much oxidant has been eliminated by the reaction in a certain amount of time and how much contamination has been eliminated in that time. This provides information on the SOD in field conditions and on the speed with which the contaminants can be broken down in the soil.

Circulation test

With circulation tests a certain oxidant volume is injected on one side of the test set-up. At the same time, contaminated groundwater is extracted on the other side. The extracted groundwater is analysed at different moments in time. Based on the composition of the extracted groundwater, the design parameters can be estimated. The groundwater quality is followed up by monitoring groundwater from wells located between the injection and extraction filter(s).

An advantage of this test compared to push-pull tests is that a larger aquifer volume is tested. A better image is obtained of oxidant amounts and dosage, flow rates and pressure. In addition, the test allows us to determine the radius of influence of the application method as the set-up also serves as a pump test. A disadvantage is the higher cost due to the substantial installation work, the longer duration and the treatment of the pumped up contaminated groundwater, if necessary.

Injection test

In this test, a certain oxidant volume is injected by means of a direct injection method. The impact of the injection is monitored in surrounding wells.

Sparge test

This test only applies to the injection of gases (ozone). The purpose of the test is to gather information about:

- the effectiveness of the chemical oxidation;
- the volume/mass proportion of the injected gas;
- the radius of influence of oxidation;
- the extraction rates required of the extraction system;
- the monitoring of gases that are released (important for the safety aspect).

Carrying out a sparge test for ozone is comparable to a 'normal' air sparging test. However, for ozone sparging additional safety requirements apply.

4.4 Remediation design for chemical oxidation

Once a certain oxidant has been selected and the feasibility has been studied by means of a laboratory test and/or a pilot test, the design for a large-scale application needs to be developed. To allow for proper evaluation against other remediation techniques and/or variants, a complete design (including the application method) needs to be developed.

When making the remediation design, knowledge of the site characteristics (geology, hydrogeology, potential preferential flow paths...), the land use (cellars, old boreholes, drains) and the presence of soil contamination (the conceptual site model) is extremely important. The better and more accurate the insight into the conceptual site model, the bigger the chance of success of the remediation technique. Important points to keep in mind with all in-situ remediation techniques are:

- The establishing of the exact depth and appearance of the contaminants to be treated, with specific attention to the presence of pure product.
- The local soil structure, with specific attention to permeability, stratification, the presence of (thin) more permeable layers and the groundwater flow (direction and speed). In the context of an ISCO soil remediation it is extremely important to know the different potential pathways along which the oxidant may spread (this should include attention to the possible spread of emissions through the soil air).

Extra for ISCO soil remediation there must also be a solid knowledge of the local soil chemistry:

- the soil oxidant demand;
- the presence of potential activators (Fe^{2+} , Mn^{2+});
- the presence of radical acceptors (CO_3^{2-});
- pH, TOC and redox potential.

LNAPLs can be treated with chemical oxidation, depending on the accessibility, the type of product and the ease with which contaminants go into solution. However, it is often more cost-effective to treat a LNAPL with a thickness of more than 5 cm with a different technique than ISCO.

DNAPLs can be treated with in-situ chemical oxidation in moderately to highly permeable soils. When a DNAPL is located partly in a low-permeable layer, other techniques are preferred. However, residual pure product that is present in the pores can be treated with ISCO.

For the field implementation a distinction is made between the different injection techniques.

parameter	filters	direct push	recirculation	infiltration	soilmixing
hydraulic conductivity					
$> 10^{-3}$ cm/s	+++	+++	+++	+++	+++
10^{-4} tot 10^{-3} cm/s	++	+++	+	++	+++
10^{-4} tot 10^{-5} cm/s	+	+	-	+	+++
10^{-5} tot 10^{-6} cm/s	-	-	--	-	+++
$< 10^{-6}$ cm/s	--	--	--	--	+++
depth to be treated					
< 5 m-bgl	+++	+++	+++	+++	+++
5 tot 10 m-bgl	+++	+++	+++	-	+++
10 tot 25 m-bgl	+++	++	+++	--	-
25 tot 50 m-bgl	++	+	++	--	--
> 50 m-bgl	++	--	++	--	--

Table 17: hydraulic conductivity and depth versus injection technique

Legend: -- = Not applicable; - = low effectiveness; + = medium effectiveness; G = high effectiveness; +++ = very high effectiveness;

5 Follow-up and end of remediation

In an ISCO remediation 5 stages can be distinguished:

1. Definition of the contamination situation and post-remediation values.

2. ISCO implementation and monitoring period.
3. End of ISCO once the post-remediation values have been reached.
4. Check after a certain amount of time of whether the post-remediation values are maintained. If this is not the case, the soil remediation works must be resumed (e.g. additional injection round) and it must be studied whether changes to the system are required.
5. Delivery of the remediation if repeated samples show that the set post-remediation values have been reached. It should be noted that the proof of a stable result involves more than the maintaining of the post-remediation values. Other parameters which were monitored during the performance of the ISCO must also be included in the monitoring plan to review the soil remediation works performed.

The monitoring during the ISCO soil remediation is very important, because it provides more information about:

- the remediation design and the application method;
- possible effects on safety, health and the environment;
- the efficiency and effectiveness of the soil remediation.

As soon as the soil remediation is started, the monitoring must be started as well in order to check whether the remediation is going according to expectations. A distinction must be made between the follow-up of the soil quality, on the one hand, and the follow-up of the technical aspects on the other. The follow-up of the soil remediation works takes place before, during and after the injections.

5.1 Follow up technical aspects

In order to get a good insight into the impact of the ISCO remediation on the aquifer and the course of the remediation, and in order to correct the process in due time if necessary, at least the following aspects (if applicable) must be periodically monitored:

- the injected volumes and concentrations of oxidant per injection point;
- the injected volumes and concentrations of catalyst/stabiliser per injection point;
- the injection rate and pressure per injection point;
- the injected volumes per injection interval per injection point;
- the radii of influence of injection (and extraction);
- the spread of the tracer, if applicable (bromide, SF₆¹², fluoresceine...);
- temperature and pressure build-up in the soil;
- groundwater levels;
- inspection of the ground level (e.g. detection of contaminants coming to the surface)
- continuous measurement of ozone in container with ozone generator (with ozone injection).

5.2 Follow-up of soil quality

¹² sulphur hexafluoride

In order to be able to correctly monitor the course of the soil remediation, it is important to determine the zero level (soil properties, pollutant load present and its distribution) shortly before the injection of the oxidants.

To this end, on the one hand, a number of samples need to be taken from the solid part of the earth using soil probes, and these must be analysed for the specific contaminant (and degradation products) and organic content.

On the other hand, new measurements need to be made for the parameters below in a number of relevant probes (with attention to different filter set-ups):

- the specific contaminants (including any daughter products) in the different sections;
- site-specific redox-sensitive metals;
- the main ions (Na, K, Ca, Mg, Fe, nitrate, sulphate, chloride, phosphate);
- TOC;
- redox potential (field measurement);
- dissolved oxygen (field measurement);
- acidity (pH) (field measurement) and/or alkalinity (CaCO₃);
- electrical conductivity (field measurement);
- groundwater levels (field measurement).

When monitoring the groundwater quality during and after the injection, it is best to periodically monitor the following parameters (Table 18: parameters to be monitored during remediation) in various relevant probes (with attention to different filter set-ups). Hereby the use of field kits can be recommended. Many of these parameters can be determined quickly and in sufficient accuracy using field kits. Not all parameters need to be monitored equally frequently.

The quality of the solid part of the earth must also be checked from time to time, and especially on completion of the soil remediation, by means of samples using soil probes for the relevant parameters. This requires analytical testing.

Parameter	H ₂ O ₂	NaMnO ₄ KMnO ₄	Na ₂ S ₂ O ₈	O ₃
contaminants in different compartments	X	X	X	X
groundwater levels and flow (+tracer)	X	X	X	X

Oxidant (+ catalyst and/or stabiliser)	X	X	X	X
redox-sensitive metals	X	X	X	X
redox potential	X	X	X	X
TOC	X	X	X	X
acidity (pH)	X	X	X	X
iron	X		X	
electrical conductivity		X	X	
dissolved oxygen	X	X		X
sodium or potassium		X	X	
phosphate	X		X	
soil vapour measurements (volatile pollutants, O ₂ , and CO ₂)	X			X (+O ₃)
manganese		X		
sulphate			X	
colour		X (purple)		

Table 18: parameters to be monitored during remediation

When sampling, it must be ensured that samples do not contain any remaining oxidant, as the oxidant may interfere with the analysis or continue to break down contaminants after the sampling. If necessary, a reductant (e.g. sodium thiosulphate) must be added to the sample to eliminate any excess oxidant.

When using Fenton's reagent, more intensive monitoring must be carried out for the parameters above immediately after implementation of the remediation due to the possible explosion hazard (heat generation). When using ozone, for safety reasons, a permanent monitoring system must be set-up to check for the presence of ozone and oxygen.

Contaminant concentrations often vary considerably during the chemical oxidation process, with concentrations initially rising, and dropping afterwards. As the reaction kinetics of the oxidant with organic carbon (TOC) are usually faster than those with organic contaminants, organic contaminants desorb during

the first phase of treatment. As a result, concentrations will initially – for a short period of time – increase, after which they will decrease permanently as the contaminants are oxidised. The groundwater monitoring programme should take this into account.

An additional possibility to monitor the effectiveness of the ISCO is through analysis of the carbon isotopes. In addition to the most common isotope, carbon-12, all carbon also contains the stable isotope carbon-13 (around 0.1%). With chemical oxidation the carbon-12 atoms are transformed slightly faster than the carbon-13 atoms present. As a result of the degradation by ISCO, the carbon isotope ratio (C13/C12) will increase.

5.3 Recommendations

5.3.1 Hydrogen peroxide or Fenton's reagent

Recommendations regarding soil structure and contamination load

- Fenton's reagent is best injected in very permeable soils. Injections into sand, loamy sand or sandy clay are indeed possible. Permeability greater than 10⁻⁶ m/s is suggested.
- The heterogeneity of the soil must be known as well as possible ahead of time. In a strongly heterogeneous soil there are preferential channels, as a result of which the injected oxidant will not reach all contamination. The pilot test must provide a definitive answer concerning the feasibility of ISCO remediation in strongly heterogeneous soils.
- Less permeable soils can be treated with 'modified' Fenton's instead of with the traditional Fenton's reagent. The acid buffering capacity of the soil specified during the lab test is determinative for the ultimate choice.
- In soils with high organic content (e.g. peat), the use of Fenton's reagent is not recommended because of the high matrix demand, potentially heavy reactions in the subsoil and the potential setting of the peat.
- Fenton's can be applied to source remediation where DNAPL is either present or not. The source zone and the zone(s) with DNAPL must be mapped out as well as possible before the injections are started. The contamination load must be known as well as possible ahead of time.

Recommendations concerning the injections

- The injection of Fenton's reagent always takes place based on fixed injection filters (no direct push). The material for the fixed injection filters consists of stainless steel, HDPE or C-PVC.
- The injection with catalyst always precedes the injection with the actual oxidant. The reaction must take place in the soil. A mixture of the catalyst and the oxidant above-ground is not permitted.
- The injections preferably occur discontinuously and are guided in function of temperature measurements.

- The following process parameters must be observed during the injection: injection rate, injection pressure, pH, Cl⁻ (in the case of chlorinated solvents), excess of peroxide, oxygen, CO₂ and temperature.
- The injection of Fenton's reagent occurs with a maximum 10% solution.

Recommendations concerning working with Fenton's reagent

- The delivery of the Fenton's reagent occurs in a concentration of a maximum 50% solution, preferably delivered in HDPE storage tanks (no storage in iron drums or containers).
- During storage, the Fenton's reagent may not come in contact with UV light.
- Storage in high-temperature areas must also be avoided.
- Stabilized peroxide must be used in order to avoid auto-oxidation during storage.
- An automatic injection system is not permitted. Injections must be guided by a team of at least two trained technicians.

5.3.2 Permanganate

Recommendations concerning soil structure and contamination load

- Permanganate is best injected into very permeable soils but can also be applied in less permeable soils considering it is a stable oxidant with a long after-effect.
- The heterogeneity of the soil must be known as well as possible ahead of time. In strongly heterogeneous soil there are preferential channels, as a result of which the injected oxidant will not reach all contamination. The pilot test must provide a definitive answer concerning the feasibility of a permanganate injection.
- Permanganate is a weak oxidant and is preferably used in plume areas or as after-treatment (polishing step) of a source remediation.
- The use of permanganate is not recommended for handling DNAPLs because of the possibility of crust formation of MnO₂ around the pure product.

Recommendations concerning working with permanganate

- Injections with permanganate can take place by means of fixed injection filters or by direct push.
- The injection of permanganate takes place with solutions between 4% and 10%.
- Permanganate is preferably administered as sodium permanganate (in fluid solution). This is more easily manageable than potassium permanganate which is delivered in the form of a powder.
- The mix and injection material must be resistant to the oxidizing agent.
- The injections occur preferably with low concentrations in the start-up phase of the project. The concentration will be increased gradually during the course of the project.
- Permanganate cannot be mixed with peroxides during injection. This leads to heavy reactions in the piping.

5.3.3 Persulphate

Recommendations concerning soil structure and contamination load

- Persulphate is best injected into very permeable soils but can also be applied in less permeable soils considering it is a stable oxidant with a long after-effect (shorter than permanganate).
- The heterogeneity of the soil must be known as well as possible ahead of time. In strongly heterogeneous soil there are preferential channels, as a result of which the injected oxidant will not reach all contamination. The pilot test must provide a definitive answer concerning the feasibility of an ISCO-based remediation in a strongly heterogeneous soil.
- Activated persulphate is a strong oxidizing agent and can be applied in source areas where DNAPL is either present or not. The source area and the areas(s) with DNAPL must be mapped out as well as possible before the injections are started. The contamination load must be known as well as possible ahead of time.
- Activated persulphate can also be used for oxidizing DNAPLs. Taking the cost into account (and the high matrix need in the case of oxidation of the DNAPL), the persulphate can best be used as a polishing step after, for example, an injection with Fenton's reagent.
- Non-activated persulphate is applicable to BTEX contamination, but less suitable for remediation of contamination with diesel or chloroethanes. It is applicable for chloroethanes.
- Injections with persulphate can take place based on fixed injection filers or with direct push.
- The injection of persulphate takes place with solutions of between 20 and 70 g/l.

Recommendations concerning working with persulphate

- Persulphate must be stored in dry, closed containers.
- Persulphate is mixed as a powder prior to injection. Persulphate presents a risk for inhalation.
- The mixture and injection material must be resistant to the oxidizing agent. Steel injection rods, connections and valves corrode! Chemically resistant material must be used in all of the pipework.
- Injections preferably take place with low concentrations in the start-up phase of the project. The concentration will be increased gradually during the course of the project.
- Injecting near concrete constructions is not recommended due to possible impact on the concrete.

6 Effects on safety and health

As with other soil remediation techniques, with ISCO safety and health aspects are very important. In addition to the general safety and health requirements, there are some extra aspects to take into account when performing ISCO. These aspects can be divided into two groups:

- Safety and health requirements for the handling and storage of chemicals.
- Safety and health requirements referring to the thermodynamic aspects of ISCO.

The safety and health requirements discussed in this chapter are certainly non-exhaustive, the safety aspect dealing with ISCO is a large and important field and has a lots of aspects. The intention in this chapter is only to give a general idea of these special aspects. Prior to the soil remediation a risk assessment must be made. This should include all safety and health risks associated with:

- the site-specific circumstances;
- the civil engineering works;
- the different chemicals used.

6.1 Safely designing ISCO

Safety and health start with a good design and proper planning of the soil remediation project. When evaluating the different soil remediation techniques to be carried out, safety for man and the environment will occupy a dominant position. If the soil remediation requires safety measures (e.g. soil vapour extraction in the case of ozone sparging, measures to prevent a fire and explosion hazard...) the cost of these should be taken into account in the assessment of the different soil remediation techniques.

Before carrying out the soil remediation works, a safety coordinator has to be appointed. The appointed safety coordinator, the soil remediation expert and possibly also the operator or owner of the site will impose specific safety measures for ISCO soil remediation. These must be strictly observed by all the parties carrying out the remediation.

Important aspects to take into account are:

- Material Safety Data Sheets (MSDS). There are MSDS for all chemicals used in ISCO. The data of the MSDS must be assessed by a qualified person prior to the design and planning of the soil remediation works. In this way, all possible risks are clearly identified prior to the design and the works.
- The P and H phrases, as mentioned on the packaging of the oxidant;
- Prior to the soil remediation a risk assessment must be made. Based on this risk assessment all potential dangers are identified and quantified, e.g. site-specific aspects, utilities, preferential flow paths, contaminants and the injected oxidant. In the next step the procedures are developed and protective measures are proposed. A specific monitoring programme for migration to off-site receptors is drawn up.
- The resistance of all the material used must be assessed in light of the oxidant in question.

- In accordance with the legal requirements, all persons taking part in the soil remediation works must previously have been sufficiently trained in the established safety procedures and protective actions and measures. Moreover, personnel must receive training on actions with chemicals used during the ISCO soil remediation.

The proposed safety plan is non-exhaustive. The design and planning of the ISCO remediation is an iterative process aimed at determining the best remediation technique in which efficiency, costs and safety aspects are optimised. Moreover, during the performance of the ISCO soil remediation risks which had not been identified up to then may surface.

6.2 Safety and health requirements for the handling and storage of chemicals

Oxidants for ISCO are, by definition, highly reactive. This means that they oxidise all substances that come into contact with them, including tissues. In fact, inhalatory exposure entails the biggest risk. The oxidant may enter the lungs as a gas or in the form of dust or mist in the case of a solid oxidant. The alveoli are oxidised, leading to suffocation. Ozone is particularly dangerous because it is an odourless, colourless gas which is not blocked by gas masks. On site, exposure can be minimised by the use of personal protective equipment (PPE). During the injection of liquid oxidants two operators must always be present.

Due to their high reactivity, oxidants can cause damage to underground infrastructure (cables, pipes, etc.).

In most cases, ozone is produced on site. This avoids specific actions and transportation measures. The main data on ozone can be found on the MSDS for ozone. High ozone concentrations (> 2 ppm) cause irritation and permanent damage to the eyes and lungs.

Off site, the risk can be managed through monitoring and by neutralising the oxidant when it leaves the site (or when this is possible).

6.3 Safety and health requirements referring to the thermodynamic aspects of ISCO

ISCO is a relatively fast reaction. This also means that energy (in the form of temperature and / or pressure) is released very quickly. Besides energy, oxygen is formed as a result of the ISCO reaction as well.

Oxidants themselves are not flammable, but due to the release of oxygen they can increase the possibilities of fire. Peroxide in high concentrations can give rise to accelerated self-degradation through contact with catalysts (metals) or fire, in which case oxygen and even more heat are released. This could create an explosive situation. The degradation speed is managed by applying lower concentrations, smaller amounts, lower pressure, a lower temperature or by using inhibitors. When treating contaminated soil with flammable liquids, such as mineral oil, extra care must be taken. The heat developed and the stripping of the contaminants, e.g. with Fenton's reagent, can give rise to a flammable or explosive vapour mix. For hydrogen peroxide it is recommended to work with relatively low oxidant concentrations (lower than 11%).

What is special about oxidants is that they can usually also supply their own oxygen, which means that they cannot be extinguished with the conventional methods. Dust explosions may also occur with oxidants in powder form.

Part 2: A few cases

1. ISCO with activated sulphate in Brussels (Belgium)
2. ISCO with ozone in Utrecht (the Netherlands)
3. ISCO with permanganate and hydrogen peroxide in Gelderland (the Netherlands)
4. ISCO with hydrogen peroxide in Mechelen (Belgium)
5. ISCO with hydrogen peroxide in Zele (Belgium)
6. ISCO with hydrogen peroxide in Papendrecht (the Netherlands)

1 Chemical oxidation with activated sulphate – example

1.1 Introduction

Starting in 1920, a number of varied industrial activities were conducted on the site situated in Brussels (Belgium). These industrial activities ranged from the production of hats to metal working (e.g., the manufacturing of metal components). As of 1996, second-hand car repair shops and spray-painting cabins were located on the site. Early 2000, such industrial activities were discontinued. The old buildings on the terrain were demolished in 2010.

The contamination of groundwater with chlorinated solvents was to be remedied by means of chemical oxidation. This remediation of the groundwater was started in 2011 and has continued until the present day. Ultimately, the terrain will be redeveloped as a housing site for residential dwellings and apartments.

1.2 Conceptual site model

1.2.1 Geology

The site is located in the alluvial plain of a river and characterized by a 1-metre thick layer of rubble in the uppermost stratum, followed by a moderately to hardly permeable loamy layer down to a depth of 9 to 10 mbgl. This loamy stratum is a deposit from the Quaternary Period (Q1-stratum). Below the Q1-stratum there is a readily permeable sandy stratum mixed with gravel. This layer is also a deposit from the Quaternary Period (Q2-stratum) and in situ has a thickness varying from 2 m to 5 m. Below the Q2-stratum, we find the Kortrijk Formation (Tertiary Period) with at the top a hardly permeable layer.

1.2.2 Hydrogeology

The groundwater is found at a depth of 2.0 to 3.5 mbgl. The hydraulic conductivity of the Q1-stratum lies between 10^{-6} m/s and 10^{-7} m/s. The hydraulic conductivity of the Q2-stratum measures 10^{-4} m/s. The groundwater is slowly moving in an easterly direction.

1.2.3 Description of the contamination

In the groundwater of the Q1- and Q2- strata, we observed contamination by chloroethenes and chloroethanes. No pure product was observed on site. The volume of the contaminated groundwater amounts to 13000 m³. The contour of the groundwater contamination by chloroethanes lies entirely within the contamination zone with chloroethenes. The following maximum groundwater concentrations were recorded:

- trichloroethene (TCE): 4000 µg/l
- dichloroethene (1,2 DCE): 2000 µg/l
- trichloroethane (1,1,1 TCA): 60000 µg/l

— dichloroethane (1,1 DCA): 20000 µg/l

It was proposed to remedy the groundwater contamination in the Q1-stratum via chemical oxidation, given that the owner wanted a quick remediation technique (hence, no stimulated natural attenuation). The groundwater of the Q2-stratum will be remedied with pump and treat.

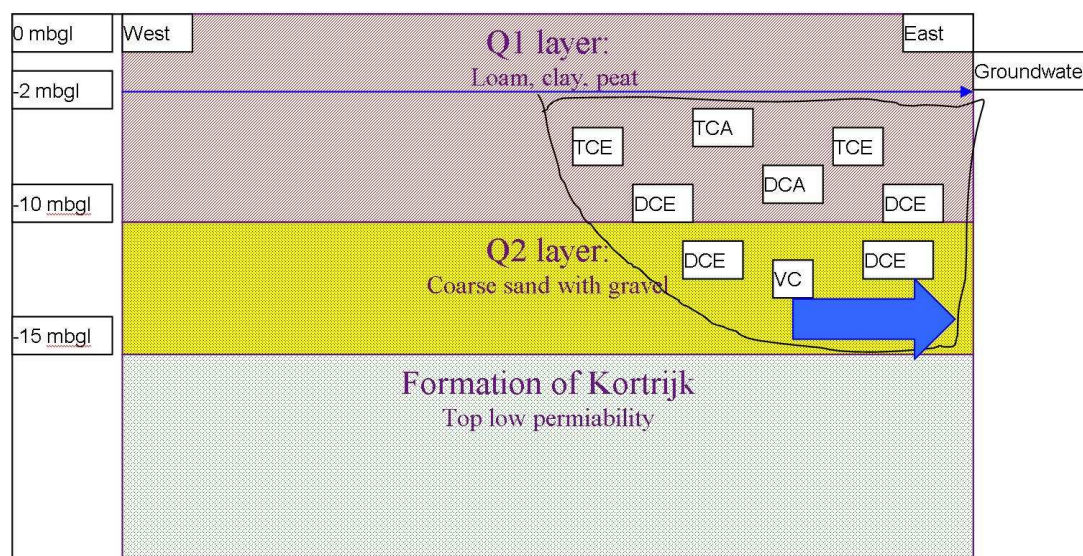


Figure 16: conceptual site model

1.3 Choice of the oxidant

Since we find on the site chloroethanes that are difficult to oxidize, it is necessary to proceed with a strong oxidant such as Fenton's reagent, ozone, or activated persulfate. Other oxidants such as permanganate or percarbonate are deemed unsuitable because of their inadequate oxidizing potential for the oxidation of the chloroethanes.

Ozon and Fenton's reagents are strong oxidants but unstable and they disappear quickly in reaction. This limits the possibility for contact between oxidants and the contamination. Contamination that does not come in direct contact with the oxidant is therefore not being remedied and will adversely impact on the effectiveness of the remediation in heterogeneous soil. In the Q1-stratum, we furthermore find local layers of peat. The application of Fenton's reagent can - in contact with the peat - lead to uncontrolled side reactions (settling of the peat, exothermal reactions).

It was decided to resort to ISCO with activated persulfate, given that persulfate combines the positive properties of Fenton's reagent or ozon (strong oxidants but unstable) and permanganate (stable but weak oxidant). In activated form, persulfate is a strong oxidant (+2700 mV) and, non-activated, it is stable with a higher oxidizing potential than permanganate. The technique of persulfate injection can be applied under different pH conditions. Persulfate, moreover, displays less reactivity with the soil matrix than, for instance,

permanganate of Fenton's re-agent; hence, a greater variety of contaminations can be treated with persulfate (BTEX, MTBE, chloroethenes, chloroethanes, and chlorobenzenes).

The activation of the persulfate is to be carried out applying heat rather than on the basis of pH enhancement. A pH enhancement would (likely) be rejected by the competent authority. Activation by steam or with electrodes would prove too expensive. For such reason, it was opted to conduct the activation by using warm water.

1.4 Safety

The persulfate needs to be stored dry in a closed container. Aside from the conventional personal protective equipment, eye-wash liquid must be ready at hand. Persulfate presents a high contact risk, especially to the eyes. It is essential that skin contact with persulfate be avoided at all times.

1.5 Labtest

Given the limited experience with activated persulfate, a lab test was carried out. The purpose of this test was to determine whether or not activated persulfate would be capable of oxidizing chloroethenes and, especially, chloroethanes and of determining the soil oxidant demand.

1.5.1 Test set-up

All lab tests were conducted at a temperature of 45°C in order to imitate as closely as possible the injection on the terrain. At a temperature of 45°C, persulfate radicals are created that ought to be able to oxidize chloroethanes.

Part 1 of the lab test was carried out with soil material and contaminated groundwater collected from the terrain. The soil material came from the depth layer between 6.6 and 8.0 mbgl (Q1-stratum). 100 g of soil material was mixed with 400 ml of groundwater and treated with persulfate in a measured applied concentration of 20g/l. The incubation period was 1 week. After 1 week, groundwater samples were taken of the blank test material and of the treated samples. The measured concentrations were compared with one another.

Part 2 of the lab test (the determination of the soil oxidant demand) was conducted by exposing a series of soil samples to increasing persulfate concentrations. The soil samples were shaken and the lab test was conducted within a nitrogen atmosphere (to prevent oxidation by oxygen). The excess of persulfate (persulfate not removed in the reaction) was measured at the conclusion of the lab test with a spectrophotometer.

1.5.2 Results

Part 1 of the lab test showed that after the treatment with activated persulfate, the parameters 1,2 DCE, TCE, and 1,1 DCA had completely disappeared from the groundwater solution. 1,1,1 TCA appeared to be the most persistent parameter. 99.2% of the 1,1,1 TCA present was removed in the lab test.

Part 2 of the lab test demonstrated a soil oxidant demand of persulfate of 16.63 g/kg dry weight. In the calculation of the soil oxidant demand, account was taken of auto-oxidation of the persulfate (50% after 7 days).

1.6 Pilot test

1.6.1 Set-up

In total, 6 fixed injection filters were placed for the conducting of the test on the terrain (field test). The permanent filters were prepared and readied with an enveloping filling of filter gravel and subsequently grouted up to ground surface with cement bentonite.

Four injection filters were positioned crosswise around 1 monitoring probe pit (PP105) at a horizontal distance up to the probe pit of 1.0 to 1.5 m. Two injection filters were positioned with the filtering part between 6.0 and 9.0 mbgl, and 2 injection filters were positioned with the filtering part between 3.0 and 6.0 mbgl.

Two additional shallow injection filters (situated near the probe tube 114) were positioned with the filtering part between 2.0 and 4.0 mbgl.

On 13 November 2007, a start was made on the field test. A watery solution of sodium persulfate (5%) was mixed above-ground. The solution (500l) was pumped across an electric boiler and heated to 50°C. Next, the solution was injected across the 4 injection filters near probe tube 105. The injection was invariably conducted simultaneously across 2 injection filters situated at an identical depth.

During the days following, the injection volume was increased to 2m³ per day (total period, 5 days of injections). At the end of the test period, for another 4 days injections were made of a volume of 1m³/day across the 2 shallow filters situated near probe pit 114.

The injection temperature at the injection point was always above 45°C. In total, a volume of 14.5 m³ of persulfate was injected during the entire period of the pilot test.

At regular intervals, samples were taken from probe tubes 105 and 114, namely at 1 week after the conclusion of the injection and 1.5 months following the injection. The parameters monitored were redox potential, pH, EC, sulfates, chloroethenes and chloroethanes. The results are shown in the following table.

1.6.2 Results

	PB 105				PB 114			
	01.06 2005	18.10 2007	29.11 2007	03.01 2008	01.06 2005	18.10 2007	29.11 2007	03.01 2008
Redox potential		102	344	126		97	348	103
pH		7	6	6,3		7,6	6,5	7,2
conductivity ($\mu\text{S/cm}$)		1435	6340	5330		987	5380	1265
sulfates (mg/l)		170	3600	2100		49	3500	340
VOCL's ($\mu\text{g/l}$)								
trichloroethene	1200	990	330	370	68	35	<1,5	22
1,2 dichloroethene	1100	1900	830	410	59	31	<d	26
1,1,1 trichloroethane	15000	6100	7400	2600	9300	240	4600	1600
1,1 dichloroethane	5600	4100	8100	2500	21000	11000	8500	5700
1,2 dichloroethane	<20	<15	9,2	2,2	50	44	36	26

Table 19: results pilot test

- Following the injection, a distinct increase of the redox potential inside probe tubes 105 and 114 was recorded
- Following the injection of the persulfate, a distinct increase of the EC and of the sulphate content was recorded
- The pH level dropped only slightly, probably because of the soil's strong buffering action. 1.5 months following injection, a renewed increase in the pH was recorded, from which it appears that the pH fairly quickly reverts to its initial value.
- A significant drop in the concentration of chloroethenes was recorded 1 week following the injection.
- The drop in chloroethane concentration was less pronounced yet present. Seeing that the chloroethane concentrations in January 2008 continued to drop compared to the readings at the end of November 2007, it may be held that the persulfate still remained active more than 1 week after the injection.

The pilot test was deemed a success. It was recommended that, during the full scale remediation processes, the injection temperature be increased to 60°C and the injection dosage raised to a 10% sodium persulfate solution in order to enhance the impact of the persulfate on the sanitation process.

1.7 Full scale execution

1.7.1 Phase 1: set-up

In the spring of 2011, the first phase of the full scale remediation was performed. Use was made of the direct push technique for the injection of the persulfate. During the first injection round, a total of 4275 kg of persulfate was injected, divided over 83 injection points over in total 670 metres of injection with a 5% sodium persulfate solution. The advice to make use of a 10% sodium persulfate solution was not followed because of cost considerations.

1.7.2 Phase 1: results

The results of the first injection round showed no drop in concentrations of chloroethenes and chloroethanes compared to the zero base line. The sulfate concentration had not, or barely, increased and the redox potential remained low.

The disappointing results are attributable to problems encountered during the persulfate injection process:

- Use of too low dosage (5% solution)
- Surface mixing and heating with temporary above-ground storage
- Serious time loss was encountered between the mixing and heating of the solution and the final injection. As a result, the reaction already started above ground and persulfate radicals, which only have a limited lifespan (from a few seconds to a few minutes), are already largely spent at the moment of the injection
- The use of iron injection probes that are readily affected by the aggressive persulfate. The persulfate reacts inside and with the piping and its effect is largely spent before it is being injected into the soil
- Prevention of uncontrolled spread mainly in the shallow layer (present rubble layer).

1.7.3 Phase 2: set-up

A second (limited) phase of the injection was conducted during the spring of 2012, with the following adjustments made to the injection method:

- The injection dosage was raised to a 10% solution
- The injection volume was raised to 500 liter solution per running meter
- All injection material was made of galvanized steel
- The interval between mixing and heating, on the one hand, and the injection, on the other, was reduced to an absolute minimum
- Injections were conducted at a distance of 1 m from the monitoring probe tubes 500, 501, 504 and 505 over a depth trajectory between 3.0 and 9.0 mbgl

1.7.4 Phase 2: results

	PB 500	PB 501	PB 504	PB 505
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	(2-4 mbgl)		(6-9 mbgl)		(2-4 mbgl)		(6-9 mbgl)	
	voor injectie	na injectie	voor injectie	na injectie	voor injectie	na injectie	voor injectie	na injectie
redox potential	-27	270	-124	90	-19	445	-97	36
pH								
conductivity (µS/cm)								
sulfates (mg/l)	1400	6400	230	2200	1800	5400	300	140
V OCL's (µg/l)								
trichloroethene	130	39						
1,2 dichloroethene	140	70	4100	2100	15	2,3	88	62
vinyl chloride			15	1,5	9,8	0,6	1800	950
1,1,1 trichloroethane					12	10		
dichloroethane					390	300	6600	5400

Table 20: results full scale

It appears from the table that the injection has exerted a demonstrable effect on the geo-chemistry and on the contamination of chlorinated solvents. The sulfate concentrations rose significantly in most of the probe tubes, as did the redox potential. The chloroethenes concentrations demonstrated a clear drop. The chloroethanes concentrations likewise showed a drop but to a lesser extent.

1.8 Conclusion

Based on the findings of the conducted lab test and the pilot test, the oxidation of chlorinated solvents (chloroethenes and chloroethanes) with activated persulfate appears feasible. During full-scale application, special attention needs to be paid to the injection method. Usage of correct injection material, injection dosage, injection time is absolutely necessary to achieve any kind of success. Several injection sessions need to be scheduled to remove the greater part of the contamination. At the end of the injection period, the monitoring of the results needs to be continued in order to determine if there is evidence of rebound effects.

2 Chemical oxidation with ozone - example

2.1 Introduction

A study was carried out in the municipality of Utrecht (the Netherlands) into possible techniques for remediating chlorinated solvents in central urban areas. One of the tested remediation techniques involved ozone injection near a former laundry facility. The source of the pollution was an old sump.

2.2 Conceptual site model

2.2.1 Geology

The soil is built up as follows:

- – 2.0 m below ground level: clay;
- 2.0 – 20.0 m below ground level : fine to coarse sand, gravelly.

The groundwater table is at approximately 1.5 m below ground level.

2.2.2 Description of the contamination

The solid part of the soil and the groundwater on the terrain are contaminated with chlorinated solvents. The contaminated soil around the sump was excavated. The following maximum groundwater concentrations were established:

- shallow: max. 110 000 µg/l (mainly tetrachloroethene);
- deep: max. 15 000 µg/l (mainly tetrachloroethene).

The project was started as a test and then continued full-scale. The pilot area is situated on the transition from source to plume area and contains mainly PCE in concentrations of approximately 14 000 µg/l.

2.3 Pilot test

For a period of 24 days, ozone was injected into spargepoint SP6A (10.3-11 m below ground level). A carrier gas (air) was used to inject the ozone into the soil. The entire gas flow rate (mainly air) amounted to approximately 8 to 10 Nm³/hr. The injection occurred intermittently (25 minutes on; 25 minutes off) and for a net period of approximately 222 hours. The actual amount of injected ozone was calculated based on ozone measurements in the gas stream, the injection flow rate ((Nm³/hr) and the net amount of hours involved. During the pilot test a total of 7.8 kg of ozone was injected, i.e. an average of 35 g of ozone per hour. Based on monitoring results the radius of influence was established at 10 metres. The calculated stoichiometric

ozone consumption amounts to 6 kg. The difference of 1.8 kg can be explained from soil oxidant demand and self-degradation.

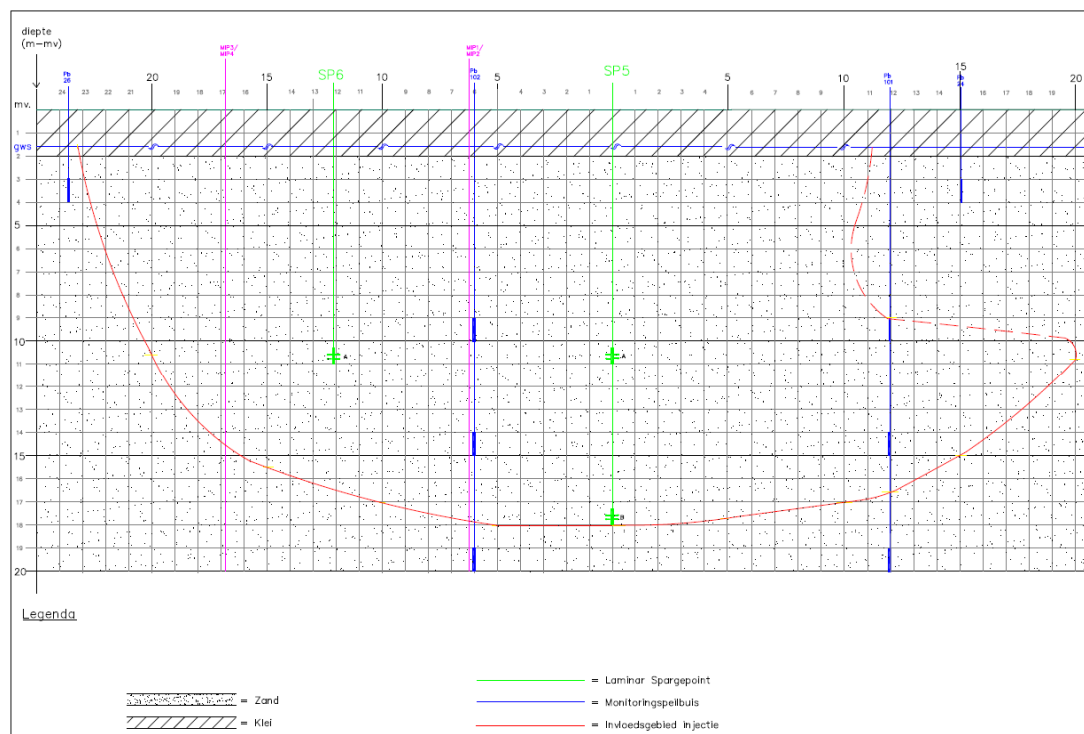


Figure 17: conceptual site model

2.3.1 Pilot test results

At the start of the pilot test a positive redox potential was found of approximately 100 mV. Probe tube measurements taken during the pilot test (and during remediation) showed a clear increase of the redox potential to values of 400-500 mV. Measurements carried out four months after the start of the pilot test show a slightly reduced, yet still higher (approx. 300 mV) redox potential as compared to the situation at the start.

	pollution load (kg)		% pollutant load reduction
	before injection	after injection	
VOCL's			
tetrachloroethene	18,55	9,04	51
trichloroethene	0,15	0,08	47
1,2 dichloroethene	1,52	0,73	52
vinyl chloride	0	0	0
total	20,22	9,85	51

Table 21: results pilottest ozone injection

The above table demonstrates that within the influence area of the injection, as compared to the baseline a considerable load reduction was realised for all the components present. The load reduction was confirmed by MIP (membrane interface probe) screenings. Neither the concentration measurements in the probe tubes, nor the MIP screenings displayed any up- or downward spread or mixing of contamination. DELCD and PID peaks in the MIP screenings are found before and after the injection in the same area.

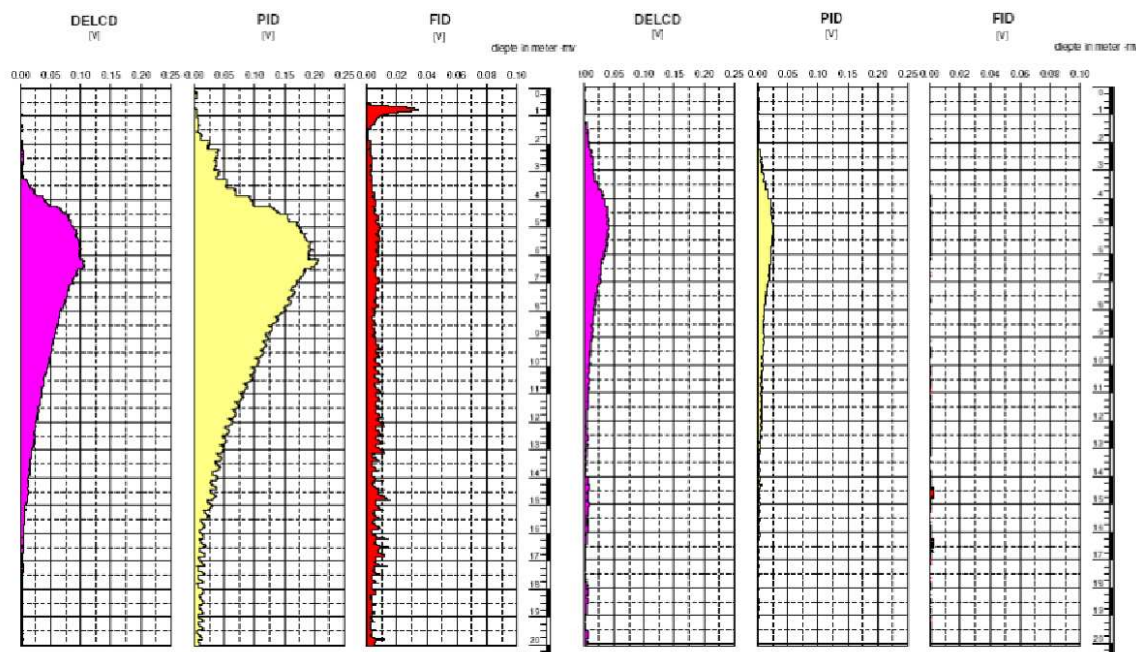


Figure 18: results MIP-screenings

2.4 Full-scale execution

2.4.1 Set-up

Full-scale remediation was started after completion of the pilot project and involved ozone injection over a larger area (15 injection points). At the location of the pilot project, injections into SP6A were made intermittently (30 minutes on; 90 minutes off). During injection into SP6A, the flow rate was 12.8 Nm³/hr. During the intermittent regime, the average injected compressed air volume was approximately 3 Nm³/hr. The ozone injected into the compressed air of SP6A amounted to 2.5 g of O₃ per hour.

The introduction of injection air via microsparging may cause contaminants in micropores to mobilise and can lead to desorption of contaminants. As a consequence, an increased concentration of contamination in the groundwater often is perceived at the start. During this remediation, no clear concentration increases were observed after the start of the injection. Desorption/mobilisation during the injection did not lead to concentration increases because the mobilised contamination immediately oxidised as a result of the injected ozone.

2.4.2 Results

The diagram below shows the concentration process established during the combined pilot phase and full-scale remediation. T = 0 days represents the start of the pilot project. T = 23 days represents the start of the full-scale remediation.

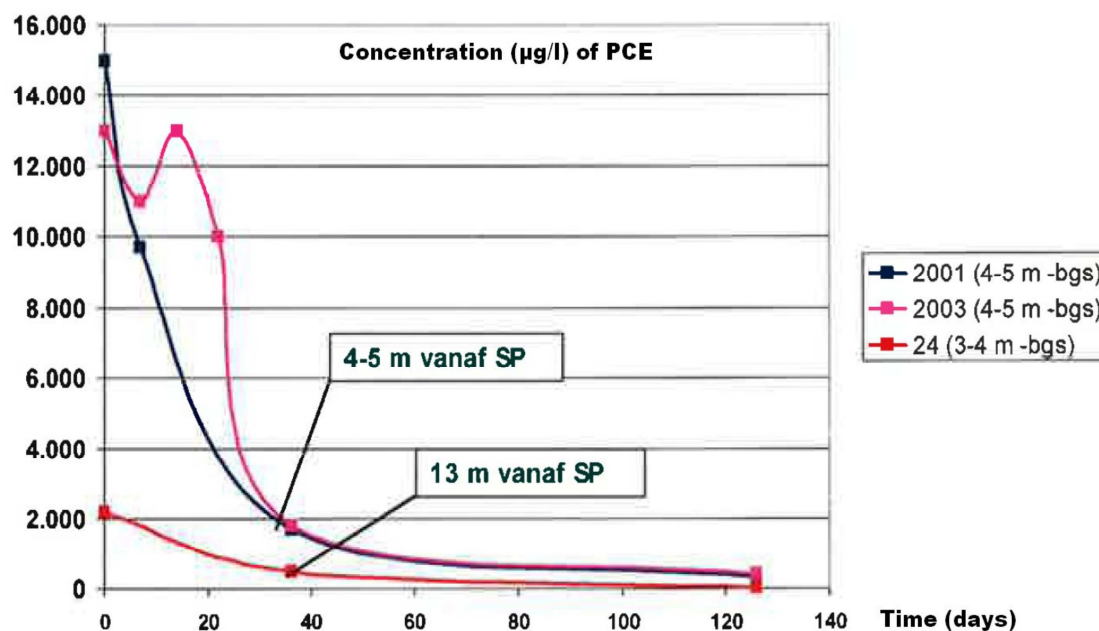


Figure 19: concentration gradient perchloroethene

After one year of injections, the PCE concentrations in probe tubes 2001-1 and 2003-1 amount to approx. 25 µg/l. At a concentration at the start of 14 000 µg/l, this involves a yield of 99.8%. Much of the reduction already took place during the pilot test, which can be explained from the higher probability of finding contamination (higher volume of contamination present) and the higher ozone dosage (35 g/hr during the pilot vs. 2.5 g/hr during the full-scale remediation).

2.5 Conclusions

Using microporous injection filters, very tiny air bubbles (10 – 50 µm) containing air/ozone are injected into the soil. Any contamination is stripped and immediately oxidised by the ozone. The use of microporous injection filters offers the following advantages:

- optimum contact between contamination and oxidant as a result of a large specific surface covered by the tiny bubbles;
- the bubbles penetrate even the tiniest soil pores, ensuring mobilisation and oxidation of contamination even in those places;
- the bubbles rise at a limited speed; the time it takes for them to travel through the package ensures optimum contact between contaminant and oxidant.

3 Chemical oxidation with permanganate and hydrogen peroxide - example

3.1 Introduction

The site in Gelderland (the Netherlands) has been used for a variety of industrial activities. There is soil and groundwater contamination with chlorinated solvents present on the terrain. This was caused by various operational activities prior to 1987, including the storage of trichloroethene.

First a soil remediation was conducted whereby the source of the contamination was removed. Remediation of the groundwater has been delayed for a few years on account of the redevelopment activities on the terrains next to the terrain concerned. For remediation of the groundwater, it was opted for gradual implementation of chemical oxidation. The first phase of chemical oxidation consisted of injection of the Fenton's reagent followed by an injection of sodium permanganate for treating the remaining concentrations.

3.2 Conceptual site model

3.2.1 Geology

The local soil structure is as follows:

Layer depth (mbgl)	composition	geo-hydrological
0.0 – 1.5	fine to moderately fine sand	non-saturated area
1.5 – 6.5	fine to moderately fine sand, local peat layers	phreatic aquifer
6.5 – 11	peat, local sand layers	separating layer
11 – 25	fine to moderately fine sand	unconfined aquifer
25 – 34	clay	separating layer

Table 22: local soil structure

3.2.2 Hydrogeology

The groundwater level is located approximately 1.5 mbgl. Under dry conditions, the groundwater is subject to seepage. The phreatic groundwater moves locally underneath a slight gradient in the southwest direction

toward the nearby canal. The deeper groundwater flows regionally with a slight gradient in the northwest direction.

There is an extraction within the area of the groundwater contamination. With this, groundwater is extracted from the second unconfined aquifer. Because of the presence of the first separating layer, extraction from the second unconfined aquifer has no influence on the shallow groundwater contamination with chlorinated solvents.

3.2.3 Description of the contamination

Soil remediation has been conducted at the location of the former storage area of trichloroethene. In so doing, the contaminated soil was excavated over a surface of approximately 170 m² to a depth of approximately 2.5 mbgl. Approximately 400 tonnes of contaminated soil was excavated. The excavation was conducted with the help of a drainage pump, whereby a total of approximately 800 m³ of groundwater was extracted.

After excavation, the groundwater in the phreatic aquifer across a surface of approximately 4,000 m² to a depth of approximately 6.5 mbgl still contained slight to strongly elevated concentrations of trichloroethene, cis-dichloroethene, and vinyl chloride, in which cis-dichloroethene and vinyl chloride occur in (relatively) high concentrations. The core of the contamination is located in a surface of 1,000 m² with concentrations higher than the intervention value. The volume of the groundwater contamination is approximately 18,000 m³, approximately 3,000 m³ of which is contaminated with concentrations above the intervention value.

The course of the concentrations of chlorinated solvents in the different monitoring wells after conducting the soil remediation always showed a downward trend. Due to the presence of peat layers in the soil, there is naturally an elevated content of DOC (dissolved organic carbon) present in the groundwater. Due to these conditions, anaerobic biodegradation occurs more easily, which can explain the downward trend of concentrations.

3.3 Selecting an oxidant

The terrain will be redeveloped, for the benefit of the remediation objective it is assumed that it will be used for residential purposes. A fast remediation technique is preferred. Chemical oxidation is a relatively fast and effective remediation measure with high removal yield. Chemical oxidation is implemented in the phreatic aquifer above the peat layer at a depth of approximately 6.5 mbgl.

For the trichloroethene, cis-dichloroethene, and vinyl chloride contamination at the site, several oxidizing agents are suitable. At the time of implementation of this remediation, the Fenton's reagent and permanganate were the oxidants used most often.

The advantage of Fenton's reagent is that this reaction is very strong; when the contamination comes into contact with the Fenton's reagent, it reacts immediately. Active friction in the soil is also generated (by the creation of gas bubbles) which promotes the potential for contact. A point to be aware of is that Fenton's

reagent's duration of action is very short (hydrogen peroxide only remains active in the soil for a couple of days at most), and therefore the Fenton's reagent must be injected over several days spread across a few weeks.

Permanganate is also suitable for disintegrating the contaminants present. This is a milder oxidant, but is active over a longer period (a few months). There are two forms to select from when using permanganate: potassium permanganate (solid) and sodium permanganate (liquid). Sodium permanganate is preferable considering that it can be safely handled more easily (no dust) and contains no secondary pollutants.

There is a combination of Fenton's reagent and permanganate provided at the location, concerning the presence of peat layers in the aquifer to be treated. The first phase of remediation is implemented with the Fenton's reagent (a first, fast load removal) with later treatment with sodium permanganate in phases.

The use of both oxidants can easily be combined with biological degradation of the residual contamination on location. Through chemical oxidation, the highest concentrations are removed (source removal), after which the lower concentrations can be broken down through biological degradation. By means of chemical oxidation, an oxidative environment is created, which in theory can impede anaerobic biological decomposition of VOCI. From research, however, it has appeared at several remediated locations that the reductive environment recovers within a few months after chemical oxidation.

3.4 Laboratory test

Preceding implementation of the remediation, laboratory tests were conducted to determine the effect of the oxidizing agents on the soil. During these tests, the capacity for oxidation of the contamination was not investigated, as it is known that these contaminants can be removed by means of chemical oxidation.

The objective of the laboratory tests was to gain more insight into the buffering capacity of the soil, the reacting agents' level of response to the soil, and whether the soil naturally contained catalyzing substances. The tests included indicative tests in which the soil samples are fully in contact with the added substances. The results could therefore not be calculated directly into field conditions, but were used to guide the remediation.

Research showed that the soil has a rather high buffering capacity, whereby the buffering capacity of soil samples at a depth of 4.5 to 5 mbgl was lower than the soil samples in the layer above it (3.0 to 3.5 mbgl). This was caused by the high limestone content, up to 6.7%. The soil samples also naturally contained only a few catalyzing substances. This led to a slight adjustment of the amount of reacting agents injected during implementation (more acid and catalyst with the Fenton's reagent).

The organic matter content in the soil samples was low (< 0.5%). This resulted in a low matrix need for sodium permanganate; 1.6 grams NaMnO_4 per kg of soil. The reaction of hydrogen peroxide with the soil samples also was mild and could be slowed or stimulated by adding various additives.

3.5 Implementation of soil remediation

Soil remediation is implemented in phases such that implementation of subsequent remediation could be adjusted on the basis of results from the prior phase. The first phase of remediation was implemented with the Fenton's reagent. 18 injection filters were placed in the two source areas (a total of 150 m²). A total of 6,600 litres of 50% hydrogen peroxide was injected, distributed across the different filters. Between 210 and 480 litres of 50% solution was injected in each injection filter, diluted to lower concentrations.

PID measurements¹³ were conducted prior to and during implementation of remediation. The PID values are overall measurements of the amount of volatile contaminants (indicative measurement). From these measurements it appeared that the PID values of the soil vapour in first instance sharply increased through mobilization of the contamination (with gas bubbles). The PID values then decreased. This is a normal process during ISCO remediation and is caused because gas bubbles are created during Fenton's reaction. A soil vapour extraction system is installed to collect contamination which could possibly dissipate.

During implementation of remediation, the distribution of oxidant, catalyst and pH is determined in the surrounding filters. These parameters show the extent of the spreading of the reagent. In addition, the concentration of oxygen, carbon dioxide, PID and LEL (lowest explosion level) in the headspace of the filters and monitoring wells are measured a few times a day. By following these values, the effectiveness of the process can be monitored. During implementation of remediation, a maximum carbon dioxide concentration of 13.8 was measured, which is indicative of efficient disintegration. Furthermore, the concentration of free chloride is monitored (disintegration product of VOCl), but no elevated values were measured because this is only visible when there are very high concentrations of chlorinated solvents (> 40 mg/l).

The second phase provided for a larger injection area, whereby the areas with lower concentrations would also be treated. During implementation of the first injection phase, however, it appeared that the contamination had migrated further to the south than was earlier thought. In order to treat the area properly, during the subsequent injection phase, the number of injection filters was increased by 17 fixed injection filters and 39 injection rods so that injection could take place at four different depths. In this way, the surface of the treated area was enlarged to approximately 1,000 m².

The figure below shows the areas treated during the various phases. The red line is the intermediate value contour¹⁴ prior to remediation. The areas shown in blue are the areas treated during the various phases. Left are the areas treated during the first phase (Fenton's reagent), right are the areas treated during the second phase (sodium permanganate). The expansion of the remediation system to the south, which was necessary because the plume turned out to be larger than thought, can be clearly seen in the figure more to the right.

¹³ PID measurements were conducted with a Photo Ionization Detector. This is a type of gas detector which is used for measuring volatile organic compounds.

¹⁴ The intermediate values (T values) from the Soil Protection Act indicate the average of the target and intervention values, or (T+I)/2.

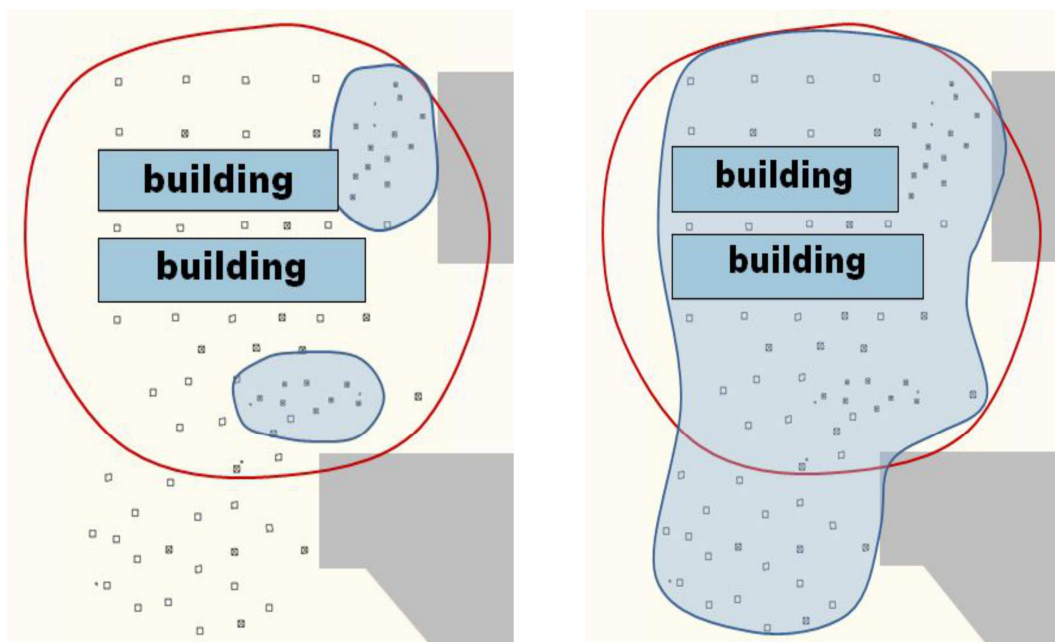


Figure 20: treated areas during the remediation

During the second phase, 1,600 kg of sodium permanganate was injected with a concentration of 0.5-1%, distributed across all the available filters. In doing so, no soil vapour extraction was used because no oxygen was created by this process. The distribution of permanganate is measured on the basis of a colorimetric specification (colour change).

There is a chance during ISCO remediations that by lowering pH during remediation, heavy metals are mobilized, or that heavy metals are present in the injected liquid (as secondary pollution/trace element). Because lowering the pH is only temporary, and it was decided to use sodium permanganate (purer than potassium permanganate), an elevated concentration of heavy metals in the groundwater is not expected. Still, prior to and after the remediation, the content of heavy metals was tested in two monitoring wells. No elevation was measured.

3.6 Safety

A safe working situation must always be achieved for employees of the contractor as well as local residents and workers before a job can be implemented. Working with substantial amounts of chemicals deserves special attention and above all experienced personnel.

When designing a process unit, the oxidation strength of the peroxide and permanganate is taken into consideration. In the pipework, every few metres there are various safety valves built in so that no peroxide can flow out of the process installation, or contaminants into it, without being controlled. The installations are always tested in the development phase by experts from the producer of the hydrogen peroxide.

Exposure to contaminated substances during the injection works will be very minor. The contaminants are in the subsoil. The quality of the soil vapour that comes out of the filters is measured several times a day and is established as a component of the monitoring programme. In order to further minimize risks, a soil vapour installation has been installed.

Considering that work is being carried out with chemicals and the process installation, the use of gloves, safety glasses and safety shoes are required. The injection area is not accessible for third parties. Injections only take place in the presence of two professional process operators. After the daily work is completed, everything is cleaned up and closed off. Generally, no work is conducted in the evening, at night and during the weekend. If no operators are present, oxidizing agents are only present in the designated storage tanks.

3.7 Results

After implementation of the first round of chemical oxidation (Fenton's reagent), the concentrations of contamination decreased significantly. Concentrations of trichloroethene, cis-dichloroethene, and vinyl chloride dropped by 83, 44 and 98% respectively.

After implementation of the second round of chemical oxidation (permanganate), the post-remediation value had been reached on the majority of the terrain. The remediation objective was only not achieved in the southern direction. It appears that subsequent delivery from the peat layers is making attainment of the remediation objective difficult.

Results from the various phases are represented in the following graphs. Figure 21 shows the concentration of cis-dichloroethene before and after the various phases. Figure 22 shows the concentration of vinyl chloride before and after injection of permanganate in the injection filters which were installed after the increase in the number of injection filters. These filters are spread out across the site.

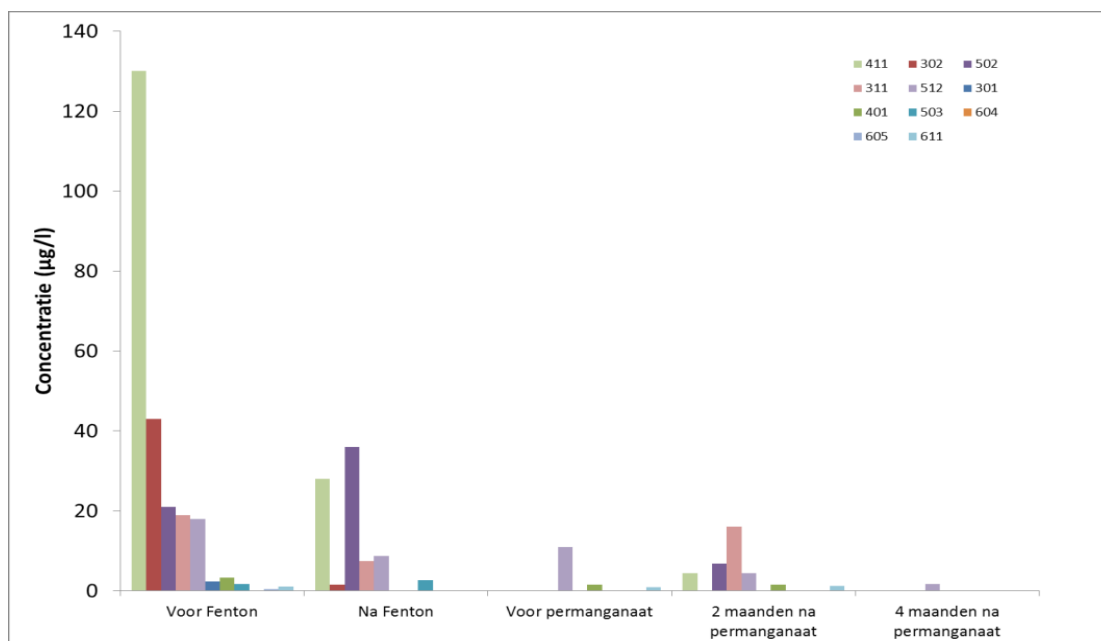


Figure 21: concentration cis-dichloroethene before and after different phases

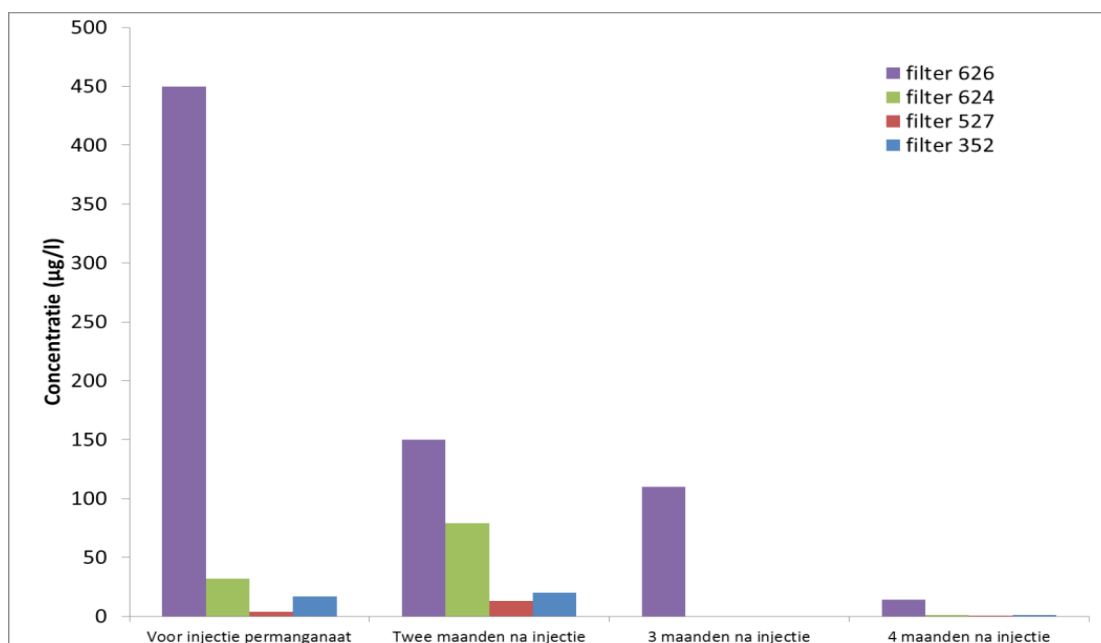


Figure 22: concentration vinyl chloride before and after the injection of permanganate

4 Chemical oxidation with hydrogen peroxide - example

4.1 Introduction

The terrain for Practical example 4 is located in Mechelen (Belgium). It was the scene of industrial activity from 1964 to this date, encompassing the production of calculators, disc brakes and brake systems. The soil became contaminated with chlorinated solvents as result of a leak in an underground storage tank (storage of PCE and TCE). The soil remediation project suggested a combination of several techniques for remediating the chloroethene contamination:

- Shallow excavation to a depth of 3 m below ground level; excavation of the old storage tank and of the contamination in its immediate surroundings.
- Chemical oxidation using Fenton's reagent for remediating the pure product.
- High-vacuum extraction and compressed air injections as post-remediation for the shallow and dissolved phase of chloroethenes (zone 4 – 10 m below ground level).
- Pump and treat and monitoring of the natural degradation for the contamination at deeper levels (> 10 m below ground level).

4.2 Conceptual site model

4.2.1 Geology

Located in an alluvial plain, the terrain is characterised by a sandy loam layer with added peat to a depth of approximately 7 m below ground level. Below is a permeable gravelly sand layer to a depth of 9 to 10 m below ground level. Both upper layers originate from the Quaternary period. Below the gravelly sand layer is another less permeable layer (tightly packed sand, Tertiary sediment) to a depth of approximately 30 m below ground level, and below that is the separating clay.

4.2.2 Hydrogeology

The groundwater is found at a depth of 1.5 to 2.0 m below ground level. The hydraulic activity of the first Quaternary stratum is approximately 10-6 m/s; that of the gravelly sand layer is 10-5 m/s. The groundwater flows in a north-western direction.

4.2.3 Description of the contamination

In the core zone, the peaty top layer shows PCE and TCE groundwater concentrations that suggest the presence of pure product. Some of the contamination is located underneath an adjacent industrial building. There are two source zones: one near the underground PER tank and one near the former galvano department.

The following maximum groundwater concentrations were established in the shallow groundwater:

- tetrachloroethene (PCE): 22 000 µg/l
- trichloroethene (TCE): 290 000 µg/l
- dichloroethene (1.2 DCE): 35 000 µg/l
- vinyl chloride (VC): 5 600 µg/l

The contamination containing chlorinated solvents has spread to the deep groundwater. Near the former PCE tank, the contamination is confined to a depth of approximately 30 m below ground level (just above the clay layer). No pure product was found. The deep groundwater contamination was horizontally confined at 18 m below ground level within the boundaries of the parcel. Spreading beyond these boundaries was only found in the gravelly sand layer at a depth of 7 to 10 m below ground level.

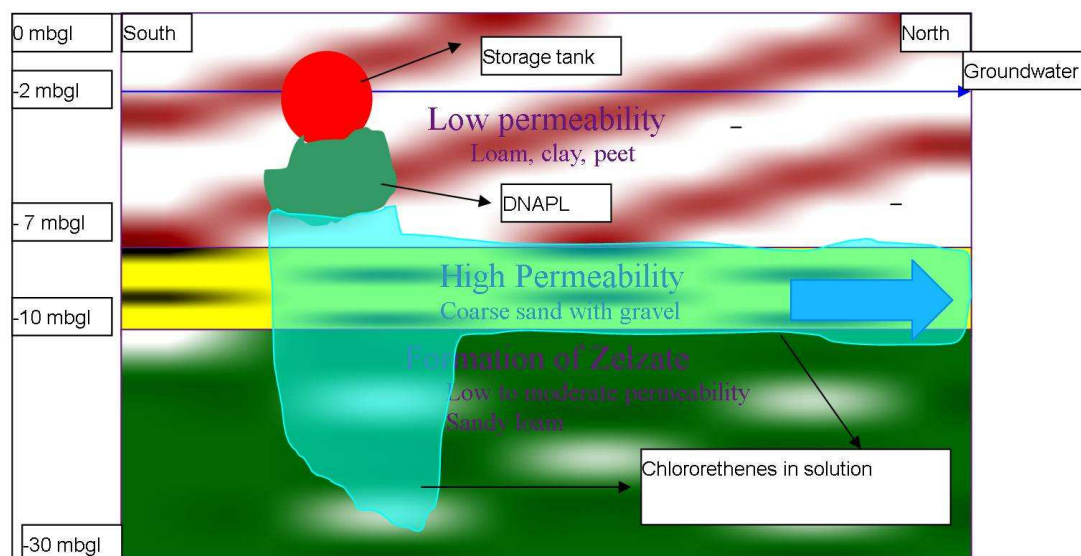


Figure 23: conceptual site model

4.3 Lab test

4.3.1 Execution of the lab test

Due to the poor permeability of the soil and the presence of peat layers, feasibility of the Fenton's reagent must be tested in advance via a lab test and a pilot test. The purpose of the lab test was:

1. to find out whether Fenton's reagent is capable of oxidising the chloroethenes
2. to determine the Soil Oxidant Demand
3. to test gas development during the chemical reaction

4. to test the effect of the Fenton's reagent (pH reduction) on the release of heavy metals.

After delivery to the lab, the soil samples were homogenised in an inert atmosphere. Upon delivery, a ground water sample was analysed for pH, acidic buffer capacity to pH 4, volatile chlorinated hydrocarbons, dissolved iron, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC), and chemical oxygen demand (COD).

4.3.2 Lab test results

To achieve the first goal of the lab test, the groundwater was treated with Fenton's reagent for 24 hours at 12 °C and at room temperature. The results were compared to a blank test. The lab test demonstrates high feasibility of chemical oxidation of chloroethenes in groundwater with full removal of PCE. We note that in this test, almost 40% of the DOC has disappeared from the groundwater after oxidation.

	sample 1 room temperature	sample 2 room temperature	sample 3 12°C	staal 4 12°C	blanco	blanco
DOC (mg C/l)	9		8		10	19
VOCL's (µg/l)						
tetrachloroethene	<	<	<	<	33.7	43.1
trichloroethene	<	0.6	<	0.8	187.9	215.2
1,2 dichloroethene	<	21.1	<	38.3	2522.4	2625.6
dichloroethane	1.0	1.6	0.8	1.2	8.3	8.3

Table 23: oxidizability chloroethane by means of Fenton's reagent

Legend: < = less than detection limit

The second purpose of the lab test (determining the matrix demand) was performed on the soil sample supplied. The pH was reduced to 4-5 by adding sulphuric acid. Hydrogen and iron(II) sulphate were added next. The residual peroxide concentration was determined at several intervals. This test was repeated several times with various concentrations of Fenton's reagent. The reaction at room temperature shows a matrix demand for the Fenton's reagent between 5.7 and 11.3 g of oxidant per kg of aquifer. The reaction is considerably lower at groundwater temperature (12 °C): between 0.7 and 1.4 g of oxidant per kg of aquifer. For oxidation at groundwater temperature, after five days the amount increases to 5.7 g of oxidant per kg of aquifer.

Peroxide	roomtemperature	at 12 °C	at 12 °C
----------	-----------------	----------	----------

(g/kg aquifer)	(1 day)	(1 day)	(5 days)
0.177	-	-	-
0.353	-	-	-
0.706	-	-	-
1.413	-	+	-
2.825	-	+	-
5.650	+ / -	+	+
11.300	+	+	+
22.600	+	+	+

Table 24: results determining matrix demand

Legend: – = hydrogen peroxide is not present in excess , + = hydrogen peroxide is present in excess

Determination of gas development (purpose 3) was established via a VOCl destruction efficiency test for which Fenton's reagent was added to soil/groundwater slurry. The gases evaporating during the oxidation test were captured in a gas bag and analysed for VOCl. After 24 hours almost all VOCl's had completely oxidised. Under both test conditions, all peroxide had vanished after four days. A matrix demand of 6.0 g/kg as determined proved correct. Gas production during the test was relatively limited (1,7m³ gas for 1 m³ aquifer material (at 0.5 x MB) and 2.0 m³ gas for 1 m³ aquifer material (at 1 X MB)).

For the fourth purpose, a pH neutralisation was performed on the soil/groundwater slurry. After pH neutralisation, the heavy metal concentration in the groundwater was compared to the concentration before neutralisation. The heavy metal content in the soil as well as the iron and aluminium hydroxide content were determined (the latter via oxalate extraction). Iron hydroxide content and aluminium hydroxide content are important since they play a role in the fixation of heavy metals. The heavy metal content had increased strongly as compared to the situation at the start. A neutralisation step was carried out which showed that the heavy metal content in solution again decreased after completion of the neutralisation step.

4.4 Pilot test

4.4.1 Set-up of the pilot test

For the pilot test, eight fixed injection filters, six venting and fourteen soil vapour extraction filters were installed. The eight injection filters were positioned crosswise relative to each other, in two parallel lines at a horizontal distance of 3.5 to 5.0 metres. The filter position of these filters was between 6.5 and 8.5 m below ground level with a maximum filter length of 1 metre (filter path 6.5 – 7.5 m below ground level or 7.5 – 8.5 m below ground level). The soil vapour extraction filters were tested in the unsaturated zone (< 2 m below ground level). The results of the pilot test were monitored using six probe tubes that were located in the immediate vicinity of the injections.

4.4.2 Execution of the pilot test

The injections with Fenton's reagent were carried out in two phases, while applying a pre-injection with primer (strong acid and catalyser Fe(II)SO₄) in each phase. Primer and oxidant were injected separately at every

stage. The total quantity of peroxide injected during the pilot test was 12 m³ (10% hydrogen peroxide solution).

The main process parameters observed during the injection were as follows:

- pH
As a general observation, the pH in all injection filters decreased as a result of the primer solution injection. This general fall in pH indicates that the primer solution spread over a relatively large surface. The decrease in pH was more prominent in the injection filters, which showed pH values below 3. In the surrounding probe tubes, positioned at some distance from the injection filters, pH decreased by one unit on average as compared to the initial pH value (decrease to pH 5 or 6).
- Temperature
A slightly higher temperature of the groundwater was established during and immediately after the injection phase. This rise in temperature is the result of the exothermic reaction occurring during the chemical oxidation with hydrogen peroxide. The highest measured groundwater temperature was 21 °C.
- CO₂ production
Increased CO₂ concentrations were observed in the soil vapour extraction filters during injection. CO₂ is a decomposition product of organic matter and of contaminants after oxidation. The measured CO₂ concentration in the influent of the soil vapour extraction increased from 0 volume percent before injection to 1.5 volume percent CO₂ after injection.

4.4.3 Pilot test results

A sharp decrease in VOCI concentrations was observed in the injection filters after the second round of injection with Fenton's reagent. A contamination load reduction of more than 90% was demonstrated in six out of eight injection filters. In the remaining two injection filters, the load reduction exceeded 60% as compared to the initial situation before the injection.

The influence radius of the injection filters in the core zone was relatively low (approximately 1 meter) as a result of the large quantity of pure product in the peaty layer and the moderate to poor permeability of the soil layer. Quick consumption of the oxidant in the core zone prevented it from spreading far from the injection filter. A larger influence radius of up to 3 meters was observed in the underlying gravelly sand layer.

The probe tubes used for monitoring of the pilot test showed a contamination load reduction varying between 70 to 87% after the second injection with Fenton's reagent. A number of probe tubes and injection filters showed rebound effects one month after the injection.

4.5 Full-scale execution

4.5.1 Full-scale setup

For the soil remediation, it was decided to carry out a combination of high-vacuum extraction and chemical oxidation in alternating cycles. Starting points included cycles encompassing two weeks of high-vacuum extraction, followed by two weeks of chemical oxidation. A total of two of these cycles were carried out. Injection and extraction were performed on the same filters, but separated in time (first extraction, then injection). The reason for performing high-vacuum extraction before the injection was to loosen up as much contamination from the soil matrix as possible, so as to make it easily accessible for the injected oxidant. A total of thirty injection/extraction filters was added in the core zone. Existing injection/extraction filters, placed for the pilot test, were included in the injection/extraction cycle. The injection filters were positioned with their filtering parts at different depths (3.0-4.0 m below ground level; 5.0-6.0 m below ground level; and 7.0-8.0 m below ground level) to maximise coverage of the contaminated package.

The first injection with Fenton's reagent was carried out intermittently over a period of six days and involved 24.3 m³ of peroxide (10%). The second injection of Fenton's reagent was performed over a period of ten days and involved 27 m³ of peroxide (10%). Since the chemical oxidation with Fenton's reagent is an exothermic reaction, the temperature was monitored as well. The highest registered temperature during the first injection cycle was 28 °C. During the second cycle this was 34 °C. Increased concentrations of oxygen (> 20.5%) were observed on the soil vapour extraction filters. CO₂ levels showed an increase on several soil vapour extraction filters at the end of the first and second injection cycle.

4.5.2 Results of the soil remediation

Based on the extracted influent concentrations and the measured water and air flow rates, it was calculated that a contamination load of approximately 1250 kg was removed as a result of the high-vacuum extraction and the soil vapour extraction.

During the remediation process at which a combination of high-vacuum extraction, soil vapour extraction and chemical oxidation were used, a total of three monitoring rounds were held (i.e. of the baseline situation; after the first cycle of chemical oxidation and high-vacuum extraction; and after the second cycle of chemical oxidation and high-vacuum extraction).

Based on the monitoring results after the first cycle, a significant decrease in the concentration of chlorinated solvents was recorded as compared to the baseline measurement. However, a comparison of the results of the monitoring round after the second cycle to those of the monitoring round after the first cycle, showed a less prominent decrease in TCE and PCE concentrations. The first injection/extraction cycle probably quickly removed the easily accessible product, whereas the second cycle had to extract and oxidise the harder to reach contaminants and therefore was less successful.

Significant decreases in chlorinated solvent concentrations as compared to the baseline measurement were, however, observed in the deeper situated package (between 7.5 and 8.5 m below ground level, gravelly sand layer).

For the package situated at medium depth (5.5-7.5 m below ground level) and particularly for the shallowly located peat package it was concluded that, despite the observed decrease in concentrations of chlorinated

solvents, significant residual contamination remained. Measurements performed at a later stage indicated the occurrence of rebound effects in the peat layer (depth between 3.5 and 7.0 m below ground level).

Based on the above results and observations and in conformity with the remediation project, it was decided to continue remediation with a combined system of high-vacuum extraction and compressed air injection as a polishing step.

4.6 Safety

Besides the classical personal protection equipment, an eyewash shower must be available at the site at all times. Primer and hydrogen peroxide are injected separately. Separate conduits must be used for primer and oxidant and they must be marked with separate colour codes.

Process parameters must be monitored closely and the injections must be adjusted in accordance with the measured results to avoid strong exothermic reactions in the subsoil.

4.7 Conclusions

The lab test and pilot test show that chlorinated solvents can be oxidised with Fenton's reagent, both in permeable and less permeable soils.

During the full-scale application, the process parameters (oxygen production, CO₂-production, pH and temperature) must be watched closely in order to control the exothermic oxidation process. Proper safety precautions are indispensable when working with Fenton's reagent.

Several injection rounds must be planned to maximise removal of the contamination. An after-treatment (after chemical oxidation) with a different remediation technique must be provided in cohesive soils.

5 Chemical oxidation with hydrogen peroxide - example

5.1 Introduction

The site is located in a residential area at the town centre of the municipality Zele (Belgium). On the site was an industrial laundry facility (laundry and dry cleaning) active. Activities were started in the 1940s and gradually expanded over the years. The former storage of tetrachloroethene and the processing of dry-cleaning residues (containing tetrachloroethene) were assumed to be the main sources of contamination.

5.2 Conceptual site model

5.2.1 Geology

The soil is built up of fine Quaternary sand with a less permeable layer of loam and loamy sand between 4 and 6 m below ground level. From 13.5 to 14 m below ground level the soil is a loamy clay that turns into heavy clay as from 14 m below ground level.

5.2.2 Hydrogeology

The groundwater is at a depth of 1.0 m below ground level. Slug tests carried out near the source show permeability of 10-5 m/s for both the upper and lower Quaternary sands. The loamy layer of 4-6 m below ground level has a permeability of 10-7 m/s, moderate to poor permeable. Near the plume, the upper Quaternary sands show a permeability of 10-5 m/s; for the lowest Quaternary sands a permeability of 10-4 m/s. In the lowest Quaternary sands the groundwater contamination extends to approximately 350 m outside the source parcel.

5.2.3 Description of the contamination

The VOCI contamination was found in the source across the entire groundwater column up to the top of the clay layer. Downstream from the source, the contamination was found only in the deeper groundwater layer. The maximum PCE concentrations found in the solid part of the soil amounted to 160 mg/kg ds. The PCE maximum observed in the groundwater was 200 000 µg/l. This indicates the presence of pure product. The following contamination loads were observed in the source zone:

contaminant load (kg)	source zone soil	source zone groundwater	plume
-----------------------	------------------	-------------------------	-------

tetrachloroethene	130	45	110
trichloroethene	10	37	104
1,2 dichloorethene		61.5	168
vinyl chloride		1.5	4

Table 25: present contaminant load

5.3 Lab test

The lab test used samples of the soil and the groundwater from the core area. The purpose of the lab test was to determine whether, using a moderate quantity of acid, the pH can be reduced to a value below 6 and whether this value can be maintained for a realistic period of time (determination of the buffer capacity).

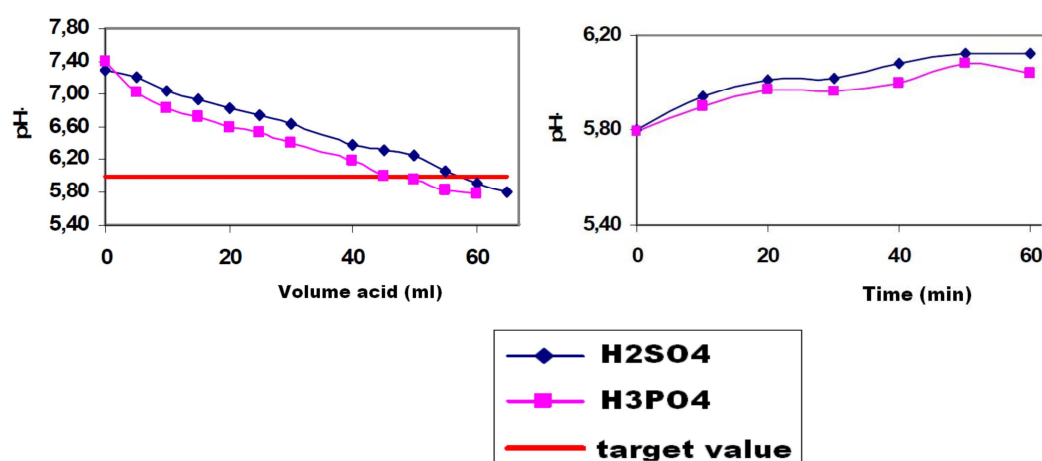


Figure 24: pH evolution during pilot test

A pH value below 6 was obtained quickly; this indicates that the quantity of acid required to reduce the pH in the field will be limited. Due to its triprotic:¹⁵ properties, phosphoric acid often yields better results in a soil matrix containing carbonates than sulphuric acid. After injection of the acid, the pH increased only gradually, indicating that a stable pH reduction is possible.

5.4 Pilot test

¹⁵ The intermediate values (T values) from the Soil Protection Act indicate the average of the target and intervention values, or $(T+I)/2$.

5.4.1 Set-up and execution of the pilot test

Nine injection filters and eight venting filters were installed. In a period of 13 days, a total of 50 000 litres of peroxide (10-12%) was injected. The observed injection pressure was relatively low, which indicates that the reagent easily spreads. After the first two days of injections, the groundwater pH fluctuated between 3.0 and 4.5; iron concentrations reached a maximum of approximately 1125 mg/l. This indicates that it is possible to realise the correct circumstances for ISCO with Fenton's.

The groundwater in the different injection filters, venting filters and two probe tubes was checked and soil samples were taken at three locations. The analyses of the three soil samples show a significant decrease in the PCE concentrations. PCE concentrations in sample 1 reduced by almost 100% (from 133.481 mg/kg to 0.59 mg/kg); in sample two by 95% (from 11.11 mg/kg to 0.59 mg/kg) and in sample 3 by 94% (from 4.72 mg/kg to 0.28 mg/kg).

The groundwater results are shown in the following diagrams.

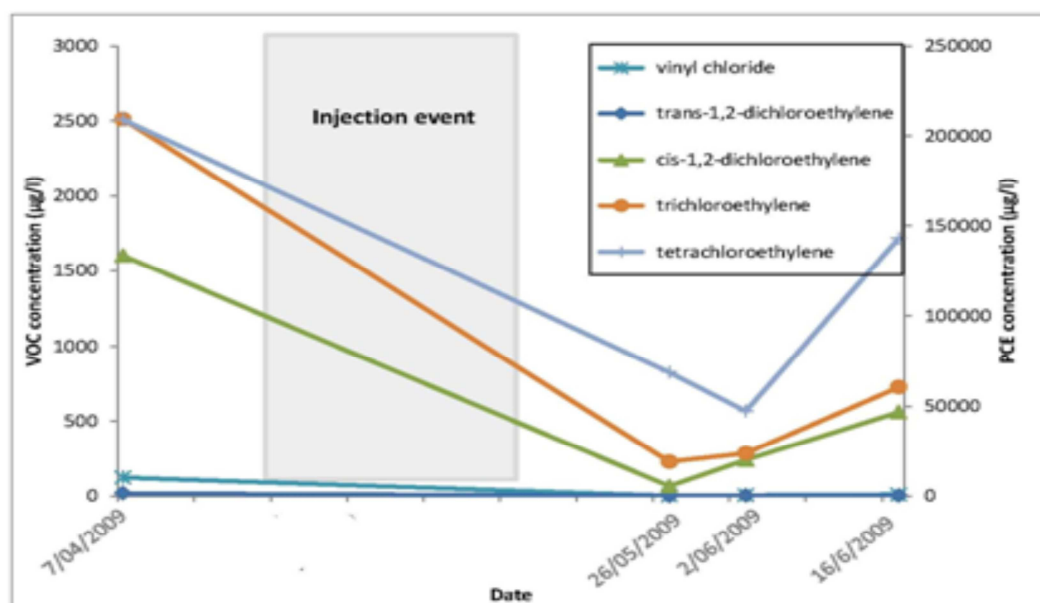


Figure 25: results for the most contaminated monitoring well

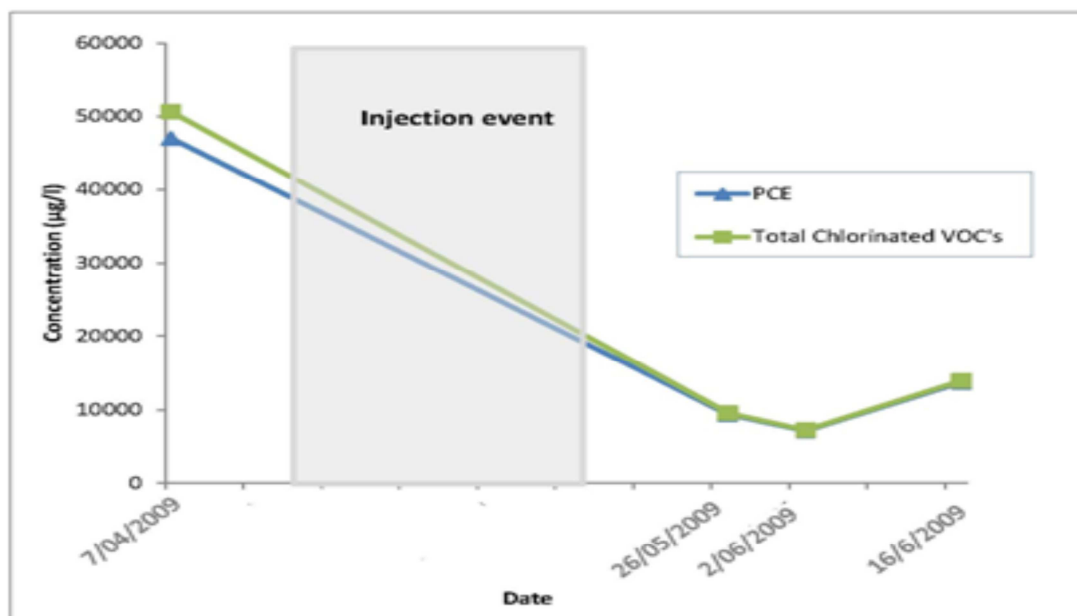


Figure 26: average concentrations on site

In the first sampling round after injection, the total VOCL-concentration showed a reduction to an average concentration of 9,556 µg/l as compared to the average concentration at the start of 50,599 µg/l (81% reduction). The results of the second sampling round after injection proved an additional reduction of the total VOCL concentration to 7,274 µg/l, on average (86% reduction as compared to 50,599 µg/l). The results after the third round of sampling showed a slight increase to 13,916 µg/l. This yields a general reduction of VOCL concentrations by 72%.

The vision behind the planned remediation works is to use the chemical oxidation to realise a strong reduction of the contamination load, and to subsequently tackle the residual contamination via stimulated anaerobic bioremediation. An important point of attention for joining these remediation variants is that after injecting the Fenton's reagent, the acid pH in the groundwater rises back to normal values. After all: too low pH would slow down microbial activity. Monitoring results during and after the injections show that pH in the injection filters reduced to 3.7. 28 days after the last injection, the pH level is back at an average level of 5.96, which indicates that the soil has sufficient buffer capacity to restore pH levels to their natural values.

5.4.2 Conclusions from the pilot test

The pilot test gave rise to the following conclusions:

- Monitoring showed that even in the field, the appropriate circumstances for ISCO can be created.
- The influence radius of the injection filters was 5 meters.
- Analyses of the groundwater and soil samples show that a considerable reduction of contamination load can be realised.
- Due to the presence of pure product, several injection rounds will be necessary in order to realise the planned reduction of contamination load.
- The combination of ISCO with a biological post-treatment is possible.

5.5 Full-scale soil remediation

5.5.1 Set-up and execution of the remediation works

The soil studies revealed two source zones containing pure product. The ISCO process aimed at maximised treatment of these two zones so as to realise a strong reduction of the contamination load. Initially 44 shallow injection filters, 85 deep ones, and 113 venting filters were installed. Some venting filters also revealed DNAPL during injection. Consequently, an additional 12 deep injection filters, 7 shallow injection filters and 4 venting filters were installed. The installation totalled 51 shallow injection filters to a depth of approximately 6 metres below ground level; 97 deep injection filters to approximately 14 m below ground level; and 117 venting filters to approximately 14 m below ground level. During installation, samples were taken and analysed to establish the baseline situation. During these analyses, pure product was found in 62 deep filters and in 1 shallow filter.

Over a period of 119 days, a total of 99 416 litres of 50% hydrogen peroxide was injected (90 554 litres into the deep filters; 8 861 litres into the shallow filters). Prior to injection, the hydrogen peroxide was diluted to a 5% hydrogen peroxide dilution. The amount of hydrogen peroxide to be injected was determined separately for each filter in accordance with the established concentration of contamination.

5.6 Results of the soil remediation

Groundwater samples were taken daily during the injections in order to monitor the process of remediation and adjust where necessary. The samples were analysed for:

- Acidity: most soils are naturally rich in carbonates. Carbonates will act as scavengers for the hydroxyl free radicals. To tackle this problem, pH levels must be lowered sufficiently. During the injections with Fenton's reagent, pH in the groundwater lowered from 7.9 to an average of 4.0.
- Temperature: an increase in groundwater temperature was expected as a result of the exothermic reaction of hydrogen peroxide with the contamination. During the injections, an average 14 °C increase in groundwater temperature was established to a maximum of 25 °C.
- Iron concentration.
- Peroxide concentration: in order to get an idea of the influence radius of the injections.
- PID Headspace: PID measurements were carried out at the gas-phase above a water sample in a closed container. These measurements involve a semi-quantitative measurement of the VOCL concentration in the groundwater. Consistent with Henry's, the VOCL concentration in the headspace is proportional with the concentration in the groundwater sample.



Figure 27: injection head, mobile control unit and hydrogen peroxide storage tank

After the first injection round with hydrogen peroxide, the contamination concentrations were strongly reduced. Of the 63 locations where pure product was found initially, only 3 locations still showed pure product after the first injection. In order to evaluate the temporary results from the first injection round, soil samples were also taken near the same locations as before the injections.

concentration PCE (mg/kg ds)			
	before injection	after injection	reduction (%)
sample 1	280	21	92.5
sample 2	350	74	79.1
sample 3	350	0.28	99.9

Tabel 26: concentration of PCE in 3 soil samples before and after the first injection round

About one month after the first injection rounds, 7 locations still contained pure product. A second injection round will be carried out as planned to remove the remaining pure product. We expect to inject 45,000 litres of (50%) hydrogen peroxide in the second round. After removal of the pure product, the remaining contamination in the core as well as in the plume will be remediated via stimulated biological decomposition.

5.7 Conclusions

The appropriate conditions can be created and maintained at the terrain for chemical oxidation of the contamination with hydrogen peroxide. This shows from the following:

- Groundwater pH remained at a level below 5 during the entire injection phase;
- Monitoring showed a good spread of hydrogen peroxide;
- The observed iron concentrations were higher than the required minimum of 10 mg/l;

Monitoring also showed that an effective reaction had taken place and that the reagent spreads sufficiently;

- The risen groundwater temperature demonstrates the expected exothermic reaction;
- Measured CO₂ concentrations in the soil vapour increased as a result of decomposition of the contamination;
- Hydrogen peroxide was found in the wells located at 3 m distance from the injection filters.

6 Chemical oxidation with hydrogen peroxide - example

6.1 Introduction

The remediation took place at the former production site of an airplane builder in Papendrecht (the Netherlands). The past activities at the terrain led to complex soil contamination with heavy metals, PAKs and chloroethenes and contamination of the groundwater mainly with chloroethenes. Several contaminated zones were found on site, of which zone no. 5 showed the most severe contamination with chloroethenes up to 13 m below ground level.

6.2 Conceptual site model

6.2.1 Geology

The soil is built up of a sandy top layer with a thickness of 2.5 metres; underneath is a clay layer to a depth of 5 metres below ground level. At a depth of 5 to 15 metres, the soil shows a highly layered profile consisting of alternating layers of sand, clay and peat. The groundwater is at a depth of 1.2 m below ground level.

6.2.2 Description of the contamination

Prior to remediation of the most severely contaminated centre, an MIP study was carried out for a better localisation of the contamination. Based on this study, the contamination of the source was characterised as follows:

- The contamination shows a complex, layered pattern due to the layered structure of the soil between 5 and 15 m below ground level and pure product was found.
- The surface of the source zone is confirmed, between 1,500 and 2,000 m².
- The contaminated layer is about 5 to 6 metres thick.
- The total volume of soil and groundwater to be remediated is approximately 7,200 m³.

	depth	PER	TRI	DCE	VC
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well	(mbgl)				
5007	7.5-8.5	1 300	590	8 100	2 300
6007	10.0-11.0	< 0.1	<0.1	0.35	0,4
6008	9.0-10.0	110 000	12 000	10 000	1 100
6009	9.0-10.0	0.5	0.1	460	2 000
6010	9.0-10.0	110 000	1 300	580	< 100
6013	9.0-10.0	26 000	26 000	39 000	3 600
6017	10.0-11.0	85	10	270	35
6027	5.0-6.0	6 800	810	2 000	630
6025	5.0-6.0	2 600	22 000	72 000	8 200
6029	5.0-6.0	130 000	1 900	51 000	4 400
6030	12.5-13.5	3 900	55	9.8	< 1
MIP 12	11.0-11.1	310	1 600	34 000	2 200
MIP 13	6.0-7.0	6.2	5.3	69 000	4 000
Average		27 932	4 734	20 461	2 038

Table 27: concentrations of chloroethenes in the groundwater (µg/l)

6.3 Execution of the soil remediation

A combination of four different remediation techniques was used for remediating zone no. 5:

- Excavation of the contaminated soil to 4.5 m below ground level
- Removal of (mobile) pure product via groundwater extraction
- In situ chemical oxidation in the saturated zone for removal of the high concentrations
- In situ bio-simulation for remediating the residual contamination

6.3.1 Partial excavation to 4.5 metres (phase 0)

In the first phase, about 500 m³ of the contaminated soil – 7,200 m³ in total – was excavated and removed.

After the excavation, the entire in situ infrastructure was installed for remediating the remaining contaminated soil volume (6,700 m³). All the required extraction and injection wells were positioned:

- 2 deep wells (5 – 13 m below ground level);
- 16 extraction and injection pits (11.5-12.5 m below ground level);
- 9 extraction and injection pits (5 – 6 m below ground level);

6.3.2 Removal of (mobile) pure product via groundwater extraction (phase 1)

During a period of three months, 25,000 m³ was extracted at an average extraction flow rate of 7.7 m³/hour. A total of 2 m³ of tetrachloroethene was pumped up.

6.3.3 In situ chemical oxidation with modified Fenton's (phases 2 and 3)

Based on lab tests, followed by a pilot test, it was decided to apply ISCO with Modified Fenton's. The lab test and pilot test were deemed necessary for assessment of the feasibility of the technique.

The injections were realised in 6 injection rounds, carried out over a period of 11 months. Approximately 210 m³ of 5% hydrogen peroxide dilution and about 159 m³ of catalyser were injected in total to achieve the desired concentrations.

A second extraction phase (phase 3) was inserted after completion of the injection activities, for the purpose of quick removal of the significant quantity of mobile contamination (desorbed by the oxidation). After all: strong oxidants, such as Modified Fenton's, have a dual action: on the one hand, the oxidant causes decomposition of the organic contamination in harmless materials such as O₂, H₂O en CO₂. On the other hand, it causes desorption of the contamination absorbed in the soil particles.

Results after phase 3:

- Increase of the oxygen concentration (from 1 to 8.8 mg/l);
- Increase of the redox potential (from -100 mV tot +30 mV);
- A temperature increase during the reaction by 20 to 25 °C

	soil		groundwater	
	concentration (mg/kg)	reduction (%)	concentration (µg/l)	reduction (%)
tetrachlooretheen	20	96	10000	92
trichlooretheen	3	90	6000	77
1,2 dichlooretheen	2	45	20000	72
vinylchloride	0.2	44	3200	61

Table 28: concentrations of chloroethenes after ISCO treatment

6.3.4 In situ biostimulation of the anaerobic decomposition (phase 4a)

Due to the significant quantities of daughter products of the dechlorination of tetrachloroethene found during the soil studies (ethane in the plume; dichloroethene in the source), in situ biostimulation of the anaerobic decomposition was chosen as the remediation technique for the residual contamination.

The injections of the carbon source were realised in 4 rounds over a period of 10 months. A total volume of 28 m³ of 10% carbon source dilution was injected. To avoid blockage of the injection filters and for maximisation of the influence environment, each injection into the carbon source was followed by an injection with plain water. This post-rinsing process involved about 40 m³ of water in total.

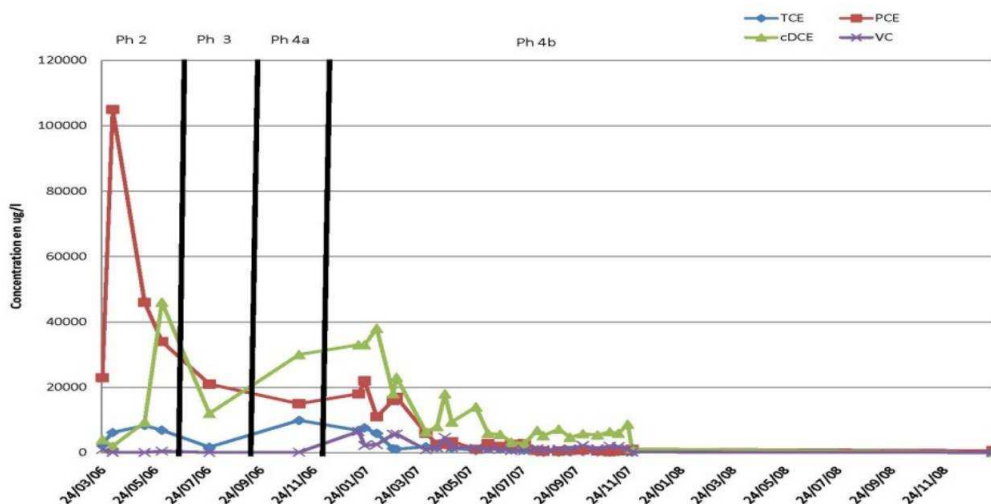


Figure 28: evolution of the concentration of chloroethenes in the groundwater during the remediation

6.4 Conclusions

Opting for the combination of different remediation techniques for treatment of the source zone proved to be the right decision. Despite the delay encountered as a result of locally occurring 'rebound' effects, the remediation yield was 90 to 100%. A stable end situation was obtained after two years of monitoring. A monitoring check is planned in the next few years to confirm the situation.

After the biostimulation, biological activity in the soil increased and dechlorination levels of up to 90% were observed. The following average concentrations were achieved in 2012:

	concentratie (µg/l)	reductie (%)
tetrachlooretheen	600	94
trichlooretheen	50	99
1,2 dichlooretheen	65	99
vinylchloride	35	99

Table 29: concentrations of chloorethenes in the groundwater after the remediation

The intensive contamination load removal at the start of the works (phases 0 and 1), the use of Modified Fenton's (phase 2) and the injection of a carbon source (phase 4a) helped to conquer the stagnation of the dechlorination process (on dichloroethene) found in the source zone.

The effectiveness, speed and specific properties of in situ chemical oxidation with Modified Fenton's make it an ideal technique for tackling this type of heavily contaminated cores. The remediation works can be synchronised perfectly to the redevelopment activities on the terrain. After removal of the largest part of the

contamination load with Modified Fenton's, the residual contamination is tackled with in situ biostimulation. After completion of the in situ chemical oxidation, the redox situation in the soil recovers after three to six months. We did not find any negative effects from the in situ chemical oxidation on the microorganisms present in the soil: after injection of the required quantity of carbon source, there was an almost immediate positive effect on the dechlorination activities in the soil.

This soil remediation, too, proves that in situ oxidation with Modified Fenton's can be combined with in situ biostimulation of chloroethenes. The in situ chemical oxidation does not have a negative effect on the biological decomposition that takes place at a later stage.

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