ISCO

In-situ chemical oxidation

Netherlands Centre
for Soil Quality
Management and
Knowledge Transfer

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1. Introduction

In the Netherlands, in-situ chemical oxidation has been applied in soil remediation for a number of years now. This technique is abbreviated to ISCO. In the event of soil remediation involving in-situ chemical oxidation, a strong oxidant is inserted in the soil. When the oxidant comes into contact with the pollution, it is broken down chemically (oxidized). This produces harmless compounds. Thanks to the relative simplicity of the technique and the fast degradation of the pollution, the technique is becoming increasingly popular as a means to treat the source of the pollution. Its popularity is further based on the large mass of pollution which can be removed from the soil in a short period of time. In addition, the so-called aftercare phase, the period in which the remainder of the pollution must be monitored to establish the scope and the development thereof, is reached quicker and often involves lower levels of residual pollution compared to other in-situ techniques.

Five years ago, in-situ chemical oxidation was relatively new and still in its experimental phase, with only a few specialist contractors applying the technique in the Netherlands. Today, in 2006, multiple contractors are active in the market offering a wide range of applications of in-situ chemical oxidation for the removal of small and large-scale soil pollution. The technique has become fully-fledged in the Netherlands and forms a standard part when considering the remediation options. In spite of this, the technique is still largely unknown among the public. The objective of this document is to increase its familiarity and to answer important questions with regard to the ISCO technique. In addition, the document must provide sufficient information to start working with this technique as part of in-house practice. The document translates knowledge often locked up in complex and localised reports at a readable and applicable level. It was decided to describe the different subjects on the basis of common issues. The subjects and questions are geared to the different target audiences that may be confronted with the technique. The target audiences that have been chosen for the document are:

- the problem owner or the commissioning party;
- the assessor or the competent authority;
- the consultant at a small consultancy agency.

The part of the document intended for the first target audience, the problem owner or the commissioning party, discusses general matters surrounding the technique. An example thereof includes the possible effect which soil remediation using in-situ chemical oxidation can have on operational management. The part aimed in particular at the competent authority focuses on the various assessment aspects involving soil remediation using in-situ chemical oxidation, including the verifiability of the results that have been achieved. The third target audience, consultants at smaller consultancy agencies, discusses the technical aspects of the technique more. That does not mean that a reader from a certain target audience is restricted. The document as a whole offers a comprehensive picture of the technique and can help explaining as to why a decision to use in-situ chemical oxidation is made, or why it is decided against.

This document does not claim to be complete. As a result of research and experience, gained when applying the technique at strongly varying locations and pollutants, knowledge is still growing. This document does provide an overview of the main aspects and knowledge at this moment in time and the application thereof in the field of soil remediation in the Netherlands.

Each time the document discusses different applications of the technique within in-situ chemical oxidation (ISCO), it will specifically state which application and thus which oxidant it involves.

Book marker

This document consists of three parts detailing information on the technique, each differing in information density and specifically geared to the three aforementioned target audiences. The first part is suitable for all target audiences in order to gain an overall picture of the technique. The parts written for the commissioning party and the competent authority are intended to provide a general picture of what is and what is not possible using in-situ chemical oxidation. The part for the consultant is a more in-depth discussion on the theory, the practice and the subject matter. Hence this part is three-tiered with the objective of providing sufficient information, so that the consultant is able to apply the technique in-house.

Flow charts

Figure 1

Decision chart for a fast, indicative assessment as to which ISCO remediation technique can be applied for a small to medium-sized source area;

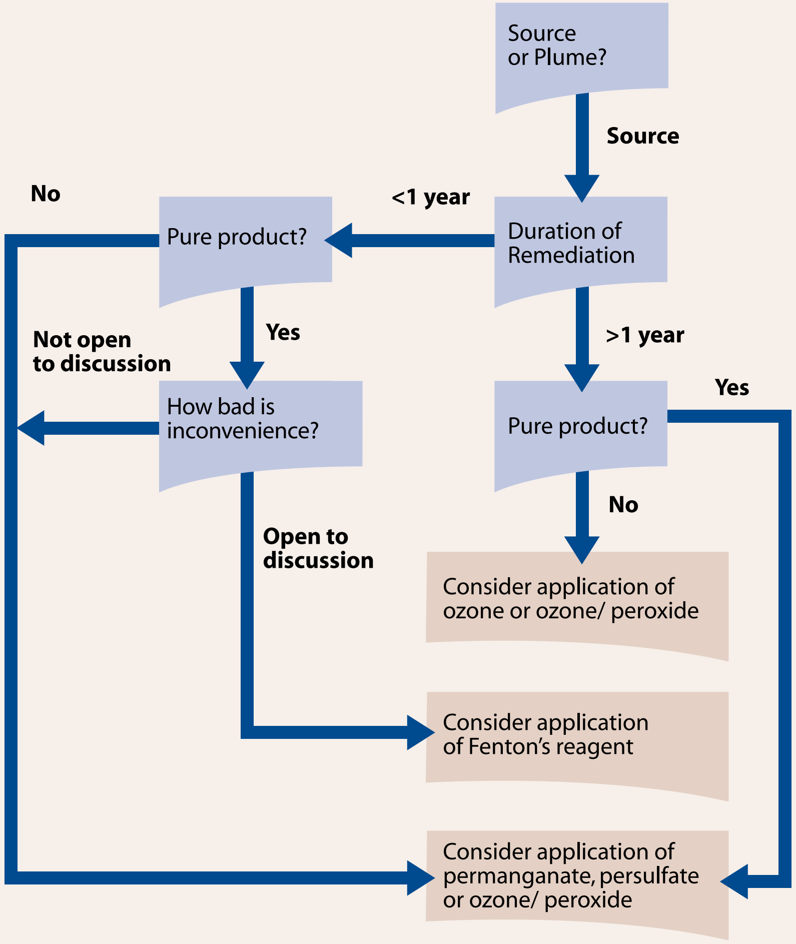
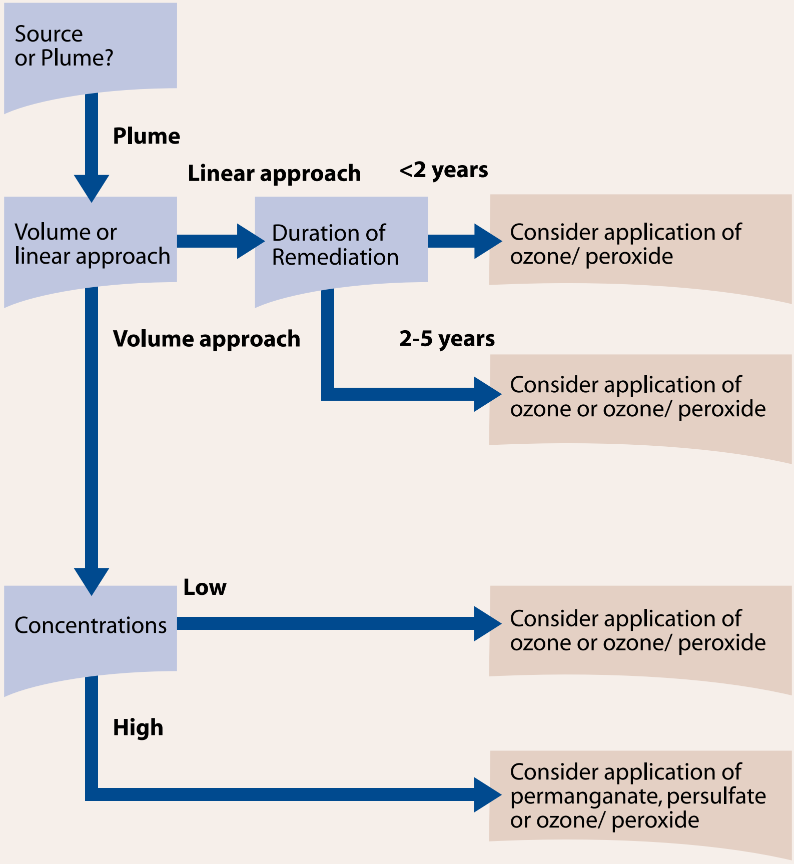


Figure 2

Decision chart for a fast, indicative assessment as to which ISCO remediation technique can be applied for a small to medium-sized plume area;



A linear approach means that on a line at right angles with the plume, where the source area turns into the plume, a screen is placed with the stated ISCO technique.

Volume approach means that the entire plume is subjected to the so-called ISCO technique.

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ISCO and the commissioning party

This part of the document is intended to provide a general picture of the technique. General questions such as: how does the technique work, what applications are categorised under ISCO and where can the technique be deployed are discussed in brief. Whilst writing this document, it has been taken into account that a company with a pollution problem may also be the possible commissioning party for ISCO remediation, hence subjects have been included that may affect operational management.

How does in-situ chemical oxidation work?

In the event of in-situ chemical oxidation (ISCO), a strong oxidant is inserted in the soil in the form of a solid substance, diluted with water or in conjunction with air. When the oxidant in the soil comes into contact with the pollution, it is broken down chemically (oxidized) producing harmless compounds, such as water and carbon dioxide. Different oxidants are applied within soil remediation, for which the process of degradation is either indirect, involving highly powerful oxidation particles, or direct with the pollution, depending on the oxidant. The different oxidants are discussed later in this document.

Which pollutants can be tackled?

A large number of pollutants can be broken down using ISCO. Which pollutants depends on the oxidant. The overview table (table 1) shows which pollution can be removed using which oxidant. Less common pollutants have not been included in the overview table, but may be suitable for remediation by means of ISCO. A feasibility test conducted by a specialised laboratory can offer a solution here.

Pollution in the soil often involves two different zones: a source area and a plume area. A source area is characterised by high concentrations of pollution in the soil and groundwater. Sometimes a source area of pollution also includes a pure product in the form of a so-called LNAPL (Light Non-Aqueous Phase Liquid), a layer that floats on top of the groundwater table, or a DNAPL layer (Dense Non-Aqueous Phase Liquid), that is heavier that water and that accumulates below the groundwater table., Compared to the source area, the plume area is characterised by lower concentrations in the groundwater and hardly any or no pollution in the soil. ISCO can be applied both in a source area of the pollution and in the plume area. The choice to use a certain oxidant in a source or plume area depends on the location of the pollution in the soil, the presence of pure product (NAPL), the duration planned for a remediation and the costs. Some oxidants are too expensive to use for low concentrations in a plume area. The overview table (table 1) shows a summary which oxidant can be used where. An overall assessment to establish this can be conducted by means of the two flow charts (figures 1 and 2).

Which oxidants are used?

A number of oxidants are used for the remediation of soil pollution. In table 2, the different oxidants used for soil remediation in the Netherlands to date have been ranked according to relative strength, on the basis of the oxidation potential. The overview table (table 1) includes a more extensive overview detailing the specific application areas as well.

Persulfate has been included in both tables, as it offers a number of advantages compared to the other oxidants. It has not yet been used in the Netherlands. In addition, there are so-called fixed peroxides, mainly originating from the detergent industry, which are used in soil remediation on a gradually increasing scale. Both persulfate and the fixed peroxides are not described in this document due to the limited experience with these substances in the Netherlands.

Table 2

The relative strength of the different oxidants.

Oxidant	Relative strength	Oxidation potential (mV)[1]	Condition
Fenton's reagent	Very strong	2.800	Liquid
Ozone/peroxide		2.800	Gas
Persulfate		2.700 (activated)[2]	Solid / Solution
Ozone		2.600	Gas
Persulfate		2.010 (not activated)[2]	Solid / Solution
Peroxide		1.800	Liquid
Permanganate		1.700	Solid / Solution
Fixed peroxides	Weak	-	Solid

[1] *This is the standard oxidation potential applicable at a pressure of 1 atmosphere, a temperature of 25°C and for 1 mol.*

[2] *Persulfate can be activated by increasing the temperature or by using a catalyst.*

Some oxidants also require certain auxiliary substances to be inserted into the soil in order to ensure that the reaction produces to best possible result. For example, in the event of Fenton's reagent, an iron solution is inserted in the soil, either as a salt, or as part of a compound in an organic complexing agent. Persulfate performs better when activated, i.e. the oxidation reaction needs a driving force to gain momentum. Here too auxiliary substances are used. As a result of the production process, permanganate contains small amounts of impurities, particularly heavy metals. The concentrations of both the auxiliary substances and the impurities are proportionally small, so there is no renewed risk of pollution.

What is the effect of ISCO remediation on aboveground activities?

Whether ISCO remediation affects aboveground activities depends on the oxidant that is used, the manner in which the oxidant is inserted into the soil and whether it involves remediation of a source or plume area. In general, the inconvenience caused in the event of a remediation of a source area is more intense compared to that of a plume area. Fenton's reagent can cause some inconvenience in the event of remediation of a source area, as the location which is injected must be fully fenced off for multiple days securing access thereto. This is done in connection with the possibility of violent underground reactions occurring at the beginning of an injection. The other oxidants offer multiple possibilities of inserting these in the soil. For example, parts can be completed underground and with that the inconvenience can be limited to a shorter period of time.

How long does ISCO remediation take?

An attractive advantage of ISCO is the short period of time it takes to complete the remediation, this in contrast to a number of alternative soil remediation techniques. The time needed for an ISCO remediation depends on the amount of pollution, the polluted soil volume, the oxidant and the speed at which the oxidant can be injected. The first two factors are site-specific . However, on the basis of the oxidant, it is possible to indicate an average remediation time. An ISCO remediation of a source area takes three months to two years. An ISCO remediation of a plume area often takes longer. The overview table (table 1) shows the average time period per oxidant in relation to a remediation for pollution on a small to medium-sized scale.

How much does ISCO remediation cost?

The general time needed to complete an ISCO remediation is difficult to indicate. Assessing the costs of an ISCO remediation, without taking into account the amount of pollution and the polluted soil volume, is even harder. Per oxidant, the costs are determined by different factors. With regard to permanganate, the main cost item is the oxidant itself. More or less the same applies to ozone and ozone/peroxide. In the event of Fenton's reagent, the execution costs account for the main cost item. Later in this document, the costs of ISCO remediation are discussed in greater detail.

Does ISCO involve substances that constitute a hazard?

Yes, unless the contractor who carries out the ISCO remediation is competent to do so. ISCO remediation does constitute potential safety risks, as it involves working with strong oxidants, strong acids or other chemical substances. All these risks can be controlled well, provided the contractor is competent, complies with all safety regulations that reduce the risks to an acceptable level and acts accordingly. Supervision by an objective third party with regard to compliance with the safety measures is part of the safe working practice during an ISCO remediation. Once injected, the oxidants are used up in the reaction which produces mainly water and carbon dioxide. Later in this document, the safety aspects are discussed in greater detail.

Is it possible to be insured against ISCO remediation?

Yes. The executive contractor must in any case have taken out liability or CAR insurance. In addition, so-called BOSA insurance can be taken out for any type of soil remediation, including ISCO remediation. This insurance reimburses specific soil remediation elements of the activities. However, it is possible that the insurer sets additional requirements with regard to the insurance. A case has been reported that an insurer refused to insure remediation due to the presence of cables and pipelines and the possible damage caused to them by the oxidant.

ISCO remediation of pollution involving chlorinated hydrocarbons underneath industrial premises

Within the corporate grounds of a metal processing company in the Dutch part of De Kempen (province of Noord-Brabant), pollution involving tri-chloroethene (TCE) and 1,2-cis-dichloroethene (Cis) has been detected. The corporate grounds include industrial premises for production as well as storage. The industrial premises are used very intensively. The pollution underneath the premises is diffuse and present in concentrations of up to 1,000 $\mu g \cdot l^{-1}$ and in a number of source areas up to a maximum of 30,000 $\mu g \cdot l^{-1}$ TCE. The pollution is serious. Only Cis is present as a degradation product of the pollution. Other degradation products which may demonstrate biological degradation, vinylchloride, ethene and ethane, are not detected onsite. No pure product is present.

In-situ chemical oxidation is quickly considered in view of the absence of biological degradation. Within the framework of assessing the remediation options, two remediation tests have been conducted involving different ISCO techniques and in different source areas. The techniques applied are the classic Fenton's reagent and ozone/peroxide. In addition to the feasibility of the ISCO technique, a lot of attention has been paid to the inconvenience caused to the company, staff safety whilst the techniques are applied and monitoring the progress of the remediation. In the remediation test using the classic Fenton's reagent, the groundwater pollution concentrations have been reduced by 63 to 99%. The reduction has been established after a period of approximately six months, after ending the active phase of the test remediation. With regard to the ISCO test remediation using ozone/peroxide, the groundwater pollution concentrations have been reduced by 78 to 90%. After both test remediations have been carried out, the groundwater concentrations appear the gradually increase again. This indicates diffusion from the soil emerging from parts in the ground which were not reached by the oxidant. The inflow of polluted groundwater from other parts at the location causes the groundwater concentrations to increase. The inconvenience caused to operational management during both test remediations has remained limited to a small surface area which did not affect corporate activities. Staff safety too was sufficiently guaranteed during both test remediations thanks to intensive process and risk monitoring.

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ISCO and the competent authority

This part of the document mainly discusses the ISCO remediation aspects which are important to the competent authorities. The competent authorities are particularly interested in finding out whether an ISCO remediation is feasible and whether the agreements entered into regarding the remediation are enforceable.

In order to assess the feasibility as well as the enforceability of a remediation plan on the basis of ISCO, the following needs to be taken into account:

- Is there sufficient insight into the amount of the pollution?
- Have laboratory tests been carried out demonstrating the feasibility of the technique?
- Has a remediation test been carried out? Or is this still to be carried out to determine the final dimensions of the ***full-scale*** remediation?
- Is the monitoring process sufficiently geared to the end result?

On the basis of the above questions, the competent authorities can determine whether the feasibility and the technical options onsite have been carefully considered. The questions do not specifically apply to ISCO remediation alone, but more or less apply to all soil remediation operations. When the technique is applied to reduce the pollution load in a source area, ISCO deviates from other in-situ techniques in terms of feasible remediation reduction values. Monitoring is of vital importance for the feasibility. It is important for the competent authority to carefully check the monitoring process, as well as where and when monitoring takes place. In addition to these two important aspects, a number of other issues are discussed in brief.

Is ISCO remediation feasible?

The feasibility of ISCO remediation is determined by a multitude of factors, as are all other in-situ techniques. Some of these factors cannot be influenced, e.g. the soil structure. However, the influence these factors have on the feasibility can be assessed prior to the remediation being carried out. With regard to the different ISCO applications, a laboratory test can assess whether the application of a certain oxidant breaks down the pollution in a certain soil type. On the basis of the laboratory test, an onsite remediation test can provide insight whether the selected oxidant can indeed be brought into contact with the pollution. In addition, realistic remediation reduction values are sometimes overstated in the light of a new technique and people's enthusiasm about it. The same applies to ISCO. Since ISCO remediation is often aimed at the removal of the pollution load, it is better to think in terms of the pollution load rather than in remediation reduction values. The remediation reduction value must be derived on the basis of the load removal which is deemed feasible. With regard to all ISCO applications, the feasible load reduction ranges between 70 and 95% or higher. However, in the event of a volume reduction of e.g. 95%, the groundwater concentrations can still exceed test or intervention values. Prior to the ISCO remediation, there needs to be a general consensus on the load present in the remediation area.

A feasible remediation reduction value?

Is it possible to determine a feasible remediation reduction value for ISCO remediation? Yes, however, traditional remediation reduction values as target or intervention value are out of reach for nearly all oxidants within the context of acceptable costs or efforts. This particularly applies to the use of ISCO in source areas. A feasible remediation reduction value can be derived on the basis of the load removal which is deemed feasible, preferably on the basis of a remediation test. Using the residual content value in the ground, the groundwater concentration can be computed on the basis of balance calculation. Using ISCO in plume areas involves much lower starting concentrations and it is therefore easier to derive a feasible remediation reduction value on the basis of a test remediation. Here too a target value is highly unlikely to serve as a feasible remediation reduction value.

Even here, the remediation return value cannot be reached in some areas of the remediation area, despite all efforts. In that instance a so-called polishing step can be applied. By using an alternative oxidant, which stays in the ground longer, the pollution can be broken down gradually. Permanganate can be used after the application of a Fenton's reagent ISCO remediation in order to break down any residual chlorinated hydrocarbons. In the event of pollution with mineral oil, fixed peroxides can be applied. This results in oxygen being produced followed by biological degradation of the residual pollution.

More information on the different aspects with regard to the laboratory tests and the remediation tests are included in chapter 4, ISCO and the consultancy agency.

Is the ISCO remediation enforceable?

ISCO remediation can be enforced by the competent authority by carefully checking the monitoring data. Within this respect, the final concentrations achieved must be noted in particular, as diffusion from the soil may still occur.

It may be the case that during the remediation not all onsite pollution has been reached by the oxidant. This may be the result of incomplete dimensioning; too little oxidant may have been injected in order to remove the load, or the pollution has partly shifted as a result of the injection. It is these points that the competent authorities can enforce. In addition, it is important to the competent authorities that safety is taken into account. To this end, continued process monitoring can be used.

The competent authorities are able to enforce at the following points:

- In order to check whether all pollution in the remediation area has been removed, measurements must not be conducted in the injectors alone. Particularly in the injectors, contact between the oxidant and the pollution has been intense, hence monitoring must be performed predominantly in newly placed monitoring wells ;
- In order to determine whether the pollution has shifted, monitoring must be effected both upstream and downstream during injection and rest periods of ISCO remediation operations. It is further recommended to check the edges of the pollution.
- During the injection of the oxidant, for reasons of security, the groundwater level must be measured, the temperature and the formation of explosive gases expressed as the LEL value (lower explosion limit). If it appears that gas formation is excessive, any risks can be assessed on the basis of indoor air measurements within surrounding buildings.
- When measuring the diffusion from the soil, the stability of the different oxidants in the ground needs to be taken into account. In the event of Fenton's reagent, the diffusion from the soil can be quickly checked as peroxide will disappear from the soil fast. Permanganate is much more stable in the ground, as a result of which the effects of diffusion from the soil will manifest itself much later. Also, in the event of agreements on when to determine whether remediation reduction values have been achieved, the stability of the different oxidants in the ground needs to be taken into account.

Chapter 4 details further information on the different aspects with regard to monitorin

Is inconvenience caused to other aboveground activities?

One of the tasks of the competent authorities is to find out whether an ISCO remediation causes inconvenience to other aboveground activities in the direct vicinity of the remediation site. Practical examples:

- Threatened activities, such as groundwater extraction, can be negatively influenced by ISCO remediation. For example, permanganate colours the groundwater dark purple, a harmless yet often undesired side-effect.
- Construction. Evaporation of hazardous substances, including both reaction products and pollution, towards surrounding buildings, is possible. The set-up can take this into account and reduce any potential risks, e.g. by installing a ground air extraction system.
- Production process. Disruption of the production process can occur if remediation takes place within a company. The commissioning party is not always the owner of the company where the remediation is to be carried out.

- Other possibilities of contact with the surroundings. This, for example, is possible due to the quick rising of the groundwater level whilst the oxidant is being injected. In the event of a rise in the groundwater level, the surrounding area may come into contact with the polluted groundwater or the oxidant itself.
- Diversions. When, for example, the pollution is located underneath a road surface, traffic during the injection period is not desirable from a safety point of view.
- Ecology. When at a remediation site flora or fauna are protected, additional protective measures may be taken. In a case involving protected trees near the remediation site, additional ground air extraction filters were placed in combination with intensive monitoring to prevent any damage.

Does chemical oxidation require specific permits?

No. In the event of short-term remediation operations (less than six months) within grounds for which no permit has been issued within the framework of the Environmental Management Act, the installation used to insert the oxidant in the soil is not deemed a facility. However, since ISCO remediation involves the storage of hazardous substances, remediation operations that take longer do require a permit. When the installation is used on corporate grounds for which a permit has been issued within the framework of the Environmental Protection Act, a written notification of the activities by the permit holder suffices. This must be done at least one month in advance.

In addition to the Environmental Protection Act, other permits may apply in the event of ISCO remediation. Experience shows that the permits have been requested in some of the following cases:

- Exemption from the Water Board or the Higher Water Board for the installation of monitoring wells and injectors.
- Exemption from the Water Board or the Higher Water Board for the injection of a liquid.
- Permit under the Pollution of Service Waters Act when extracting and discharging groundwater at the same time.
- A permit for the storage of chemicals within public grounds.

An ISCO remediation must of course also be reported to the competent authorities prior to the start of the remediation. In some cases the same applies to remediation tests.

ISCO remediation involving aromatics/ mineral oil pollution underneath two residential homes

In the past, an oil tank was once stored near two residential homes in a city in the province of Overijssel. Although the oil tank was removed prior to the houses being constructed, part of the pollution remained in the soil. The soil contained mineral oil pollution causing high concentrations of volatile aromatic hydrocarbons (BTEX) in the groundwater of up to 26.000 $\mu g \cdot l^{-1}$. Since BTEX groundwater pollution involves a direct risk to public health and thus the residents, it was decided to carry out a specific remediation of the soil. When considering the different remediation options, during which an in-situ remediation was preferred with a view to the presence of the houses, an ISCO remediation using the classic Fenton's reagent proved to be the most favourable choice. During the assessment, the short remediation time and with that the short period of inconvenience for the residents played an important role. The remediation plan linked a load removal of at least 80% to a desired groundwater concentration of 65 $\mu g \cdot l^{-1}$ or lower per individual component.

It was decided not to do a test remediation, but to carry out a full remediation directly. In addition to the elaborate system for the injection of the oxidant, a ground air extraction system was installed against the front of the houses. Approximately 3 m^3 of 50% peroxide was injected during two injection periods. After the first injection period, the groundwater concentrations with pollution were reduced by more than 90%. Following the second injection period, approximately 4 weeks after the first period, the groundwater concentrations were reduced to the desired concentration of 65 $\mu g \cdot l^{-1}$ for benzene. Intensive risk monitoring was carried out during the active remediation period. During those periods, the LEL value was not exceeded and no increased concentrations of oxygen, mineral oil or volatile aromatic hydrocarbon were measured in the crawl spaces underneath the houses. After twelve weeks, a monitoring round was conducted to determine the diffusion from the soil. It was found that the BTEX concentrations had increased as a result of diffusion from the soil. The overall reduction of the groundwater concentration was still more than 90%. Immediately after the ISCO remediation, a positive side effect was detected in that the redox conditions in the groundwater had risen from low oxygen content to high. This is favourable to the biological degradation of the residual pollution. A final monitoring of the crawl spaces to determine any public health risks is still to be carried out.

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ISCO and the consultancy agency

4.1 ISCO in theory

Previous parts of this document outlined the principles of the techniques, the different oxidants and applications and the type of pollutants that can be removed with it. This part of the document elaborates on this information and describes the chemical operation of the different oxidants. An overview of this information is detailed in table 1. In table 2, the oxidants are arranged according to relative strength. The choice as to where to deploy the oxidant, either in the source area or the plume area, can be made on the basis of the two flow charts (figures 1 and 2).

Which oxidants are used?

Fenton's reagent

Fenton's reagent is the strongest oxidant currently used within soil remediation. Fenton's reagent is a combination of hydrogen peroxide and iron (II). The iron (II) serves as catalyst and can be added to the soil in two different ways. In what is commonly referred to as the classic or acid Fenton's, iron (II) is added in the form of an iron sulphate solution, whilst the soil must be acidified with a strong acid in order to maintain the iron (II) solution. During the application referred to as modified Fenton's, the iron is added together with an organic complexing agent. In this instance, it is not necessary to acidify the soil. This at the same time prevents the risk of heavy metals being mobilised, which risk is present within the classic application. The complexing agent used in the United States is called EDTA. Its use is banned in the Netherlands. In the Netherlands, a number of contractors use citrate as complexing agent. The peroxide in either ISCO application with Fenton's reagent is a concentrated solution of 35 to 50%, which is diluted to a peroxide solution of 5 to 15%. Degradation of pollution using Fenton's reagent takes place

on the basis of a direct chemical reaction or via so-called hydroxyl radicals. As a result of this combination of reactions, the degradation is fast and effective, yet not particularly specific. Everything in the soil that can be oxidized is oxidized. Therefore, Fenton's reagent is able to break down a wide range of organic compounds. Since the reaction is fast, the injection of the oxidant and the auxiliary substances often take only a few days or weeks. The amount of Fenton's reagent injected on a site depends on the oxidation potential of the soil, the pollution and the load. An ISCO remediation with Fenton's reagent is carried out on the basis of at least a laboratory test in which both factors are determined. In the event of the classic reagent, it is also determined which acid must be injected and the amounts thereof. Once injected in the soil, the stability of the oxidant lasts less than a day.

Ozone/peroxide

Oxidation of pollution on the basis of a combined injection of liquid, peroxide and a gas, ozone, has been applied in the Netherlands since only recently and is marketed as Perozone^{TM}. The mixture of peroxide *and* ozone is a stronger oxidant compared to either individually. The ozone/peroxide mixture, within which ozone is first mixed with air, is injected in the soil via specially designed injection nozzles. As is the case with Fenton's reagent, degradation takes place via hydroxyl radicals causing a fast, yet not specific breakdown. Hence ozone/peroxide can be used for a wide range of pollutants. Once injected in the soil, the stability of the oxidant lasts around a day, maximum two days.

Persulfate

The application of persulfate is two-tiered: non-activated and activated. Non-activated persulfate is a mild oxidant and not applied in soil remediation. However, in its activated form, it is as nearly as strong an oxidant as ozone/peroxide and Fenton's reagent. Activation means that the chemical oxidation reaction is catalyzed forming both hydroxyl and sulphate radicals. Activation can be done in four ways: 1) adding heat (up to 45°C), 2) adding a catalyst such as iron (II), 3) adding a complexing agent such as EDTA or 4) strongly alkalyzing the ground (up to a pH of 11.5).
Persulfate in the ground is very stable and stays in the ground for a number of months, depending on the ground and the pollution. In addition, persulfate can be used to break down a wide range of pollutants. These possibilities are already applied in the laboratories and in the United States too the oxidant is already in use. Persulfate is listed in the overview table (table 1) and table 2, despite the fact that it has not been used in the Netherlands to date. Persulfate has a number of advantages over other oxidants and expectations are that in the Netherlands too it will be applied within the foreseeable future. Since there is not much experience with the use of persulfate as yet, this oxidant is not discussed any further.

Ozone

As is the case with Fenton's reagent, ozone can react with the pollution directly or via hydroxyl radicals that have been formed. Oxidation by radicals is faster than oxidation by ozone itself. However, the reactive potential of ozone is such that it may not be transported. Hence all oxidant that is used at the location must be produced onsite. However, this is compensated by the fact that ozone (because it is a gas) is the only oxidant that can be used in unsaturated parts of the soil. The stability of the oxidant in the ground is one to two days, comparable to that of ozone/peroxide. Ozone has been on the market as an oxidant as the C-Sparge^{TM} technique in the Netherlands for some years now. As is the case with ozone/peroxide, during this application the ozone is mixed with air prior to being injected.

Permanganate

Permanganate is a mild oxidant, but in contrast to the aforementioned oxidants, the degradation reaction is very specific. For example, to break down double carbon compounds found in many polluted grounds, such as tetrachloroethene (also known as perchloroethene, PCE) and degradation products in the ground. In addition, the stability of the oxidant in the ground is high. Depending on the ground and the pollution, permanganate can continue to be reactive for multiple weeks and break down the pollution.
Permanganate can be applied in multiple formats. The most common forms are potassium and sodium permanganate. The advantage of sodium permanganate is that it can be supplied as a solution.
A standard 40% solution is available to the soil remediation market, with low concentrations of heavy metals and impurities (RemOx™).
Potassium permanganate is cheaper, yet only available as a solid. Therefore, in order to inject it, it needs to be dissolved which brings a number of adverse side effects such as dust formation. Also, the maximum solubility of potassium permanganate is lower (solubility of approximately 6%) compared to that of sodium permanganate.
All permanganate solutions are dark purple in colour.

Fixed peroxides

Fixed peroxides include all compounds such as calcium and magnesium peroxide and magnesium percarbonate. They are compounds that have been used in cleaning products and detergents for some time now. In the soil remediation sector, fixed peroxides are often referred to under the generic term of oxygen release compounds (ORC®).
Fixed peroxides are often mild or even weak oxidants and generally used to add oxygen to groundwater to stimulate aerobic biological degradation. The oxidation potential of fixed peroxides is often not enough to oxidize pollution directly. The principle and application possibilities of fixed peroxides are not discussed any further in this document.

What is the effect of ISCO remediation on the soil?

During ISCO remediation pollution is broken down, or in other words: oxidized. As a result, the soil conditions become more oxic, meaning the oxygen content increases, whereas in the Netherlands, particularly a few metres underneath groundwater level, the soil is often anoxic or low in oxygen content. When using Fenton's reagent, peroxide and ozone, the oxygen concentration in the groundwater rises to the extent that it can have a positive effect on the biological degradation processes. However, downside is that bacteria also consist of organic material and are thus also oxidized. Yet after ISCO remediation, the soil is not biologically dead. Within the soil, extremely small pores cannot be accessed by the oxidant and bacteria are able to survive therein.
In addition to the soil becoming more oxic, the application of any oxidant involves the formation of acid causing the pH of the soil and the groundwater to fall. In the event of pollution involving chlorinated hydrocarbons, this effect is more intensive as hydrochloric acid (HCl) is formed. However, in the event of classical Fenton's reagent, the pH is reduced in order to improve the chemical oxidation reaction. The reduction of the pH has an unfavourable effect on the behaviour of metals, as at low pH values the mobility increases. These processes need to be taken into account, particularly so when in addition to organic pollution, the pollution includes heavy metals. The mobilisation is often short-lived, after the active phase of the ISCO remediation the mobility falls again. In the event of permanganate, you need to be vigilant for heavy metals in the oxidant itself as a result of the production process. Special permanganate, with low contents of heavy metals, is available for soil remediation applications. The application of permanganate in laboratory tests has led to a reduction in permeability of the soil as a result of the formation of manganese oxides (also referred to as black manganese). This has not been detected in the field with regard to the use of permanganate solutions of up to 4%.
In the field, it has appeared that the use of Fenton's reagent can considerably increase the permeability of the soil. The Fenton's reagent oxidizes organic substances and thus increases porosity, which leads to a higher permeability of the soil. The advantage is

that the oxidant distributes better in the soil. Disadvantage is that in a soil with a high content of organic substances, violent reactions can occur, causing an excessive increase in soil temperature and unacceptable safety risks. All oxidants oxidize organic substances and thus in addition to violent reactions, there is also the risk of subsidence in the presence of layers of peat. However, subsidence can also occur in the event old wooden foundations are present in city centres. Other underground infrastructure too, such as cables and pipelines can be affected.

4.2 ISCO in practice

A consultancy agency only needs to know how a technique works and for which pollution it can be used. There is a wide range of techniques, including in-situ remediation techniques which offer the same solution. This section of the document describes practical matters required to compare the application of ISCO with other remediation options.

Which soil parameters determine the feasibility of ISCO?

In order to answer the question whether remediation with ISCO in a certain location is feasible, we need information about the soil parameters listed below.

- **Soil structure**
  The most important aspect in ISCO remediation is bringing the oxidant and the pollution into contact with each other. Although there is no such thing as homogenous soil, soil consisting mostly of highly permeable sand is more suitable for an in-situ remediation than soil that consists of a succession of sand and clay.
  The more varied or heterogeneous the soil structure, the easier the application of ISCO. Preferred channels are created quicker in heterogeneous soil, so the oxidants injected will not reach part of the pollution.

- **Permeability of the soil**
  The more permeable the soil, the better. In highly permeable soil, the oxidant will distribute better and more evenly than it would in low permeable soil.

- **Groundwater level**
  Since liquids or gases are injected during ISCO, the injection requires a certain counter pressure due to the soil and groundwater column. If the groundwater level is below 1.5 m -mv, there is not enough counter pressure, making injection impossible. If groundwater levels are low, there is also a chance of the groundwater rising as a result of injection, increasing the risk of a flood. If there is a cover, e.g. paving, at ground level, it may be possible to work even though the groundwater level is low.

- **Oxidant consumption of the soil**
  The oxidants used in soil remediation are usually not very specific as to what they oxidize. It is important to know how much oxidant the soil will consume, so that a sufficient amount can be injected in order to oxidize the pollution as well. With any oxidant we recommend determining the soil consumption on the basis of a laboratory test prior to ISCO remediation. Soil parameters that are important to determine ISCO remediation in advance are: the level of organic material, chemical oxygen demand (COD), and natural soil oxygen demand (NOD). Not all parameters are of importance to all applications of ISCO.

- **Buffer capacity**
  Especially when using classic Fenton's reagent it is important to know how much acid must be injected to create the best possible circumstances for the oxidation reaction. This buffer capacity is determined by the presence of carbonate and the pH level of the groundwater.

- **Underground infrastructure**
  In the Netherlands, especially in urban areas, this forms part of the soil parameters. The risk of preferent flow paths is larger and the chance of reaching the pollution diminishes along underground infrastructure such as cables/pipes, but also concrete foundations.

Within the framework given below, the range within which certain soil parameters can occur in order for them to be applied is given for all different oxidants.

Fenton's reagent

Oxidation with the classic version of the Fenton's reagent is the most effective under acidic circumstances, - pH between 2 and 4 - but can be used up to a pH of 7. If the pH is higher than 8 it is not useful to use the classic form of Fenton's reagent. This is due to the iron(II) that acts as a catalyst in classic Fenton's reagent and which must be kept soluble. If the pH exceeds 7, peroxide breaks down and too little is used for the oxidation reaction. If the pH is even higher, combined with high carbonate concentrations in the groundwater, the hydroxyl radicals are absorbed by the carbonate. In the neutral version of Fenton's reagent, the pH levels and presence of carbonates play a less determining role, since the iron(II) is kept soluble by the complexing agents. Before starting ISCO remediation with Fenton's reagent, you must determine the oxidant consumption of the soil.

Ozone and peroxide/ozone

Like the classic Fenton's reagent reactions, ozone reactions are the most effective in an acidic environment due to the formation of radicals. Since ozone is injected as a gas, oxidation with ozone is also an option for ISCO in the unsaturated zone. When applying in the unsaturated zones, it is important to take note of the humidity levels. In the unsaturated zone, ozone distributes better in low humidity levels compared to high humidity levels. When applying ozone in the saturated zone, preferent flow paths caused by underground heterogeneous activities are created quicker, because the gas moves upwards and soil usually has a horizontal stratification. For both ozone and ozone/peroxide, the oxidant consumption by the soil is of minor importance, and in general no laboratory tests are carried out to determine this. As a rule, every m^3 of soil consumes approx. 15 g of ozone. The ideal pH level is between 5 and 8. A pH level of 9 is regarded as the upper limit.

Permanganate

Permanganate can be applied in a broad pH range. However, permanganate is susceptible to the soil structure, since the oxidation with permanganate creates manganese dioxide (also called brownstone), as a result of which permeability can decrease if the pollution load is high. With permanganate it is essential to carry out a laboratory test prior to the remediation in order to determine how much oxidant the soil consumes. This is a so-called natural soil oxygen demand (SOD or NOD) test. The NOD of soil depends on the permanganate concentration under which the test is carried out. This means the test must be carried out under multiple permanganate concentrations, including the concentration under which the remediation is carried out. A rule of thumb is that when the NOD value exceeds 2 g $MnO_4 \cdot kg^{-1}$ of soil, the application of permanganate is no longer cost-effective. In the United States, the results of a laboratory NOD test are often corrected, because the contact between oxidant and soil is often better than it is in the field. Such a correction does not seem justified in the Dutch situation.

- **Pollution load**
  Strictly speaking it is not a soil parameter, but it is important when determining whether ISCO remediation is worth considering. Since most oxidants are extremely suitable for removing the bulk of the pollution, it is important to know what the pollution concentrations are and whether there is any pure product or not.

The applicability can then be determined on the basis of the following:

- **ISCO remediation is applicable if:**
    - the pollution can be oxidized with one of the oxidants;
    - the hydraulic permeability of the soil exceeds 10^{-6} cm per second;
    - the groundwater is deeper than 1.5 m -mv;
    - It is not a problem if pure product is present, provided any LNAPL layer is not thicker than 15 cm.

- **ISCO remediation is not applicable if:**
    - the pollution cannot be oxidized with one of the oxidants;
    - the soil structure shows that the pollution can mainly be found in a layer of soil with a high level of organic compounds, e.g. peat or highly humous soil;
    - there is a LNAPL layer thicker than 15 cm. If the LNAPL layer is thicker than 15 cm, we recommend removing the LNAPL layer by means of a different technique;
    - there is any pure product in the vicinity of the underground infrastructure, e.g. cables/pipes.

What determines the effectiveness of ISCO remediation?

The effectiveness and success of ISCO remediation are determined by the contact between the oxidant and the pollution. In order to bring the oxidant and the pollution into contact effectively, an injection system geared to the location-specific circumstances is required. A proper characterisation of the location, soil structure and the aforementioned soil parameters and the demarcation of the pollution are very important. In addition, it is important to make a good assessment of the pollution load and the soil's demand for oxidant, since the amount of oxidant to be added depends on this.

In order to obtain clarity about the extent of contact between the oxidant and the pollution and the amount of oxidant required, a number of laboratory tests must be carried out prior to a full-scale remediation. It is also recommended to carry out a test remediation (a small-scale field test), especially in the case of major pollutants. Based on both results, the cost effectiveness of a full-scale ISCO remediation can then be determined.

What is the environmental outcome of ISCO remediation?

The environmental outcome of remediation is determined by a number of factors. In the case of ISCO remediation, the following factors could affect the environmental output:

- **Release of dangerous substances**
  The oxidation of pollution mainly generates water and carbon dioxide. In principle, no dangerous substances are released.
  It is possible that the chemical breakdown of the pollution is accompanied by the production of heat, causing the soil to warm up slightly up to approx. 30°C. This may cause the pollution to evaporate.

- **Production of waste matter**
  In order to prevent exposure to any pollution caused by evaporation, a ground air extraction system is installed for nearly all oxidants (with the exception of permanganate). The extracted air must be purified, during which active carbon is produced as waste matter.

- **Groundwater extraction**
  In order to enable the oxidant to come into contact with the pollution as well as possible, groundwater can be extracted in specific locations. This means that injections are carried out at one point and that a similar amount of groundwater is extracted at one or more other points. This enables one to control the distribution of the oxidant. When extracting groundwater, a drop-out current of polluted groundwater is created. This groundwater must be treated before it can be discharged.

- **Water use**
  The water use - either tap water or extracted groundwater - strongly differs per oxidant. During the injection of Fenton's reagent and permanganate, a relatively high amount of water is used in order to dilute the injection products. However, only small amounts of water are needed for the injection of ozone and ozone/peroxide.

- **Energy use**
  The energy use during ISCO remediation strongly differs per oxidant. Energy use during the injection of Fenton's reagent or permanganate is low. When using ozone and ozone/peroxide, ozone must be generated locally, so the amount of energy used is higher compared to the other versions.

How much does ISCO remediation cost?

In the first section of the document we briefly discussed the costs of ISCO remediation in general. In the case of permanganate, the biggest cost item usually is the oxidant itself. To some degree, this also applies to ozone and ozone/peroxide. In the case of Fenton's reagent, the execution costs are the biggest cost item. Table 3 shows indicative prices, based on a number of large and small-scale ISCO remediation projects using different oxidants. The basic cost price of the oxidant is also included, i.e. without the costs relating to an injection system, execution costs, etc.

Table 3
The indicative price per cubic metre of polluted soil and the cost price for the different oxidants.

Oxidant	Price per m³ of soil (€)	Cost price (€/kg)	Type
Fenton's reagent	15 - 120	0,7 - 1	5 - 15% solution
Ozone/peroxide	2 - 20 plume method 20 - 60 source method	1 - 1,5	Gas/liquid
Ozone	40 - 60	1 - 1,5	Gas
Permanganate[1]	25 - 100	4 - 6	40% solution

[1] *Sodium permanganate-based*

We should emphasise that the prices listed in the table are not fixed. It is merely an estimation of the costs. The actual costs strongly depend on the location-specific circumstances and the type of pollution, and may therefore deviate from the table. The estimated price per m³ of soil does not include the costs for the environmental supervision and management.

How does ISCO compare to other in-situ remediation techniques?

ISCO is an in-situ remediation technique which can be applied both in the source area and in the plume area of the pollution.
In the Netherlands, this technique is mainly used as a source removal technique. Table 4 shows how ISCO remediation compares to other techniques for polluted source areas without pure product.

Table 4

A relative comparison of different in-situ remediation techniques.

	ISCO	Pump and treat	Compressed air injection	Stimulated biological degradation
Remediation period	Short <5 years	Very long >30 years	Long <10 years	Long >10 years
Cost level	Low	High	High	Low
Disruption	Depends on application method	None	Little	None
Environmental output	High	Low	Low	High

The table only serves as an indication as to how the different techniques compare. Compared to the other techniques, the biggest advantage of ISCO is the short remediation period at relatively low costs. The environmental output of the technique is also high compared to for instance groundwater draw-off (pump and treat) or compressed air injection. On the other hand, the level of disruption during ISCO remediation can be higher than the other techniques. However, this does depend on the type of oxidant used. The main argument against quick ISCO remediation is that one is left with residual pollution in the case of remediation of a source area. This must subsequently be reduced in concentrated form by means of a different technique, e.g. stimulated biological degradation.

4.3 ISCO and the design

The knowledge of the technique and the decision whether or not to apply ISCO to a location was discussed in previous paragraphs. Now it is time to focus on the subjects relating to the design. This section of the document describes subjects required to be able to assess the design from a contractor, to supervise the project and to test the results.

What are the main design parameters and how can I determine these?

Many of the design parameters for ISCO remediation are similar to the aforementioned soil parameters to determine the feasibility of the remediation. In addition to these parameters, a number of design parameters must be set for the injection system.

- **Horizontal distance between the injection points**
  The distance between the injection points is determined by the projected effective radius. The effective radius depends mainly on the soil structure and the injection depth. As a rule of thumb, the 15 feet rule is applied, i.e. the injection points are placed at a maximum distance of approx. 5 m. Larger effective radii are used for ozone and ozone/peroxide, ranging from 10 to 20 m.

- **Depth of the injection point filter arrangements**
  This is entirely determined on the basis of previous research data and the soil structure. In addition to horizontal permeability, the soil also has vertical permeability. The filters are to be positioned in such a way that the entire polluted soil section comes into contact with the oxidant.

- **How much oxidant to inject**
  The amount of oxidant to be injected consists of the amount of pollution load present plus the amount of oxidant consumed by the soil. The first can be determined on the basis of the chemical reaction between the oxidant and the pollution when the extent of the pollution load is known. The consumption by the soil can be determined in advance by means of a laboratory test of soil samples. The organic content and COD can also be used for this. For Fenton’s reagent one must also take into account the fact that out of the amount of peroxide injected only 10 to 20% is actually involved in the reactions.

- **Daily injection quantities**
  The amount to be injected daily determines the remediation period and with that largely, the costs. For highly permeable soil, the injection quantities for Fenton's reagent and permanganate are approximately 1 to 1.5 m^3 of undiluted solution.

The design parameters can be obtained:

- by combining chemical analyses and geohydrological data from the preliminary research with a possible additional soil survey, aimed at the execution of the remediation. Based on this data, the general applicability of ISCO can be determined.
- by means of special laboratory test, including column and batch experiments, in order to check the applicability and to verify or substantiate certain assumptions for the application of the technique. This could include an NOD determination prior to ISCO remediation with permanganate.
- by means of a test remediation on location in order to determine the applicability under location-specific circumstances and important parameters for the design of the full-scale remediation.

Is a test remediation required?

Yes, in principle one must carry out a test remediation prior to any in-situ remediation technique. No matter how much experience the consultancy agency and the contractor may have, no location is the same and the design parameters can differ considerably per location. Based on the results of the test remediation, the design parameters can be determined and optimised. This will lead to an improved remediation system, optimisation of the costs - including those of the full-scale remediation - and with that to an increased chance of success for the ISCO remediation.

The results of an average test remediation should answer the following questions:

- What is the effective radius of the injection points, both horizontally and vertically, and with that the distance required between the injection points?
- What are the distribution picture and the influence of the soil structure, for instance in the event of preferent flow paths ?
- What is the maximum load reduction to be achieved? Are the remediation reduction values for the full-scale remediation feasible with the intended system?
- How much oxidant and auxiliary substances are required in order to achieve the desired load reduction?
- What is the composition of the pollution after the test remediation? Has the pollution truly been broken down, or has the injection merely shifted it?
- Is there any diffusion from the soil after an (initial) injection phase?
- Is the selected oxidant cost-effective?

For a proper test remediation, the objectives and questions to be answered by the test are to be recorded. Intensive monitoring of the injection system and the results in the soil are vital during a test remediation, because this data provides the answers to the questions. A test remediation does not necessarily have to be successful in order to meet the formulated objectives. A failed test remediation often teaches us more than a successful one. In both cases it can save the commissioning party a lot of money.

As is the case with a full-scale remediation, a test remediation requires a decision and report from the competent authorities.

The risks and safety measures involved in ISCO remediation

No remediation is without risks. However, the risks can be controlled if you have a thoroughly experienced consultancy agency, contractor and possible subcontractors, combined with a proper risk inventory carried out prior to the ISCO remediation. An ISCO remediation can involve a multitude of different risks, with health and safety risks taking absolute priority. In addition there could be ecological and quality risks. We will not discuss the latter two.

Since use is made of chemicals that harm man's health, an ISCO remediation involves certain health risks. As for toxicity, oxidants such as peroxide and permanganate are relatively safe. The dangers involved in oxidizing chemicals must be acknowledged and kept to a minimum. Contact with the skin and inhalation of these substances must be avoided at all times. Furthermore, the oxidants should **never** be mixed with reducing substances and inflammable substances. Oxidants and reducing and inflammable materials react strongly. The reaction generates oxygen, which has fire-inducing powers. High concentrations of ozone in the air - more than 2 ppm - can lead to irritation of and damage to the eyes and airways. Air with high levels of ozone can build up in enclosed areas or in a space where remediation is carried out. It is vital to properly ventilate enclosed areas or spaces. Detection equipment will be installed to detect any early-stage build ups. In addition, all ignition sources are to be kept away from the equipment used.

The safety measures for an ISCO remediation are very similar to any other remediation. The standard safety measures for the execution of a remediation are described in the CROW publication 132. A health & safety plan must be drawn up prior to an ISCO remediation, including the test remediation. Also, the injection equipment is to be tested for any faults and the effects thereof by means of a so-called HAZOP.

Safety measures for a number of ISCO-specific subjects:

- Oxidants are usually diluted on the remediation location itself, using a concentrated solution supplied by a manufacturer. The chemicals must be diluted in a designated process container which can be sealed off properly. The same applies to the production of ozone on location. In the case of permanganate, a special section of the location can be set up for the preparation of the injection solutions.
- The oxidants are to be stored in a properly sealed container fitted with precautions such as drip-trays so that the substance cannot spread in the event of calamities.
- Only appropriately qualified and experienced staff can be deployed for injection activities.
- During the injection of the oxidants, two members of staff must be present at the location at all times.

How do I select a contractor?

A contractor who tenders for an ISCO remediation should first and foremost be able to demonstrate that he has experience with the technique. Working with a chemical oxidant is not without risks. It is therefore important that the level of experience of the contractor, and any subcontractors, is sufficient. The level of experience can be demonstrated by, among other things, reference projects, but also by the required accreditation and certification of the company itself or the equipment to be used. There are a host of other possible things that may be taken into account in the selection including, not least, the price.

A small selection of criteria that may not be obvious, but *are* important:

- The positioning and design of the injection system and the amounts one thinks can be injected. Does it involve one or more injection rounds of oxidant? If so, what criteria form the basis for a new injection round?
- Have the results from the preliminary investigation, including laboratory tests, been included and actually incorporated in the result?

- Has the wish for or necessity of a test remediation been taken into account?
- The monitoring plan. This provides the ideal difference between the various types of monitoring such as process and performance monitoring. How is the load removal to be monitored or determined?
- Are there enough consultation moments? When will the progress and evaluation reports be submitted?

What do I measure before, during and after ISCO remediation?

During each remediation project, there are three measuring moments:

1. before the remediation, in order to determine the point of departure.
2. during the remediation, in order to monitor progress, and
3. after the remediation, in order to record the results thereof.

This document will not discuss the monitoring before the remediation process, the so-called reference monitoring. We will discuss the progress monitoring conducted during the remediation and the monitoring conducted after the remediation has been completed.

Progress monitoring

The monitoring conducted during remediation, also during ISCO remediation, is known as progress monitoring. For an ISCO remediation, this progress monitoring comprises three different elements.

- Process monitoring, to track and check the technical performance of the remediation system;
- Risk monitoring, to track the health and safety risks during remediation;
- Performance monitoring, to track and check the result achieved.

When a remediation plan is executed, a check must be made in order to assess whether the technique and the design can be applied at the location. **Process monitoring** is conducted as a quality control measurement before, during and immediately after injection of an oxidant. The primary elements of process monitoring are:

- The confirmation of injected volumes, flow rates and contractions of oxidant;
- Measuring the stability of the oxidant in the soil;
- Measuring oxidant concentrations in the groundwater or ground air samples.

When oxidants are used, process monitoring comprises the measuring of the pH, temperature, pressure, oxygen and carbon dioxide concentrations. These parameters - to monitor the process - are measured very frequently each day. The pollution in the soil, groundwater and ground air is measured on a less frequent basis. In addition, it is important to find out if there are any preferent flow paths , and to assess how the oxidant and any other substances required distribute themselves. To that end, monitoring wells can be fitted afterwards in order to determine whether the entire remediation area has been treated. Since powerful oxidants are used, so-called **risk monitoring** is to be carried out as a safety measure in built-up locations. Parameters such as temperature, oxygen, pressure, etc. are measured each day on a regular basis, e.g. each hour or every three hours following the last injection of oxidant for that day. The measurement is preferable carried out in the open air. This is especially important during ISCO remediation with Fenton’s reagent. If ozone is injected, the ozone concentration is also measured. If an air soil extraction system is in place, the build-up of hazardous substances (photometric ionisation detector, or PID measurement) and explosive gases (lower explosion limit, or LEL measurement) is checked in the extraction system. Permanganate is a milder oxidant and will therefore carry fewer risks, as a result of which risk monitoring will be simpler.
In some cases, risk monitoring can also comprise the effects of chemical oxidation on the biological life in the soil. To that end, bacteria counts can be carried out.

A couple of weeks after the injection phase, **performance monitoring** or **verification monitoring** is conducted. In order to be able to assess the performance, we must have a good definition of when the remediation is a success. In the case of ISCO remediation, chemical analyses in the soil, the groundwater and the soil are vital, because there are three ways in which ISCO contributes to the reduction of the pollution:

- chemical oxidation, i.e. breaking down of the pollution;
- evaporation of the pollution;
- dilution of the pollution by injecting various solutions.

A groundwater analysis alone will not give you a definite answer of the contaminant load that has been broken down. Since the soil organic matter is also broken down, pollution that relates to the organic matter will be released at the start of the treatment. The result of this is that - and it has been observed during a host of ISCO remediation projects - the concentration in the groundwater increases at the start of the remediation. The concentration then decreases and will continue to decrease once the contaminant load decreases. Monitoring during the oxidant injection period is often unnecessary. As a result of the large quantities of solution to be injected, pollution in the groundwater may be displaced. To prevent this, oxidants are to be injected at different injection points alternately, so that the groundwater is not moved into one direction. Nevertheless, it is wise to check for diffusion on the edges of the injection area.

Performance monitoring serves to assess whether an ISCO remediation actually does what it is supposed to do. A number of performance monitoring elements can be measured directly in the field:

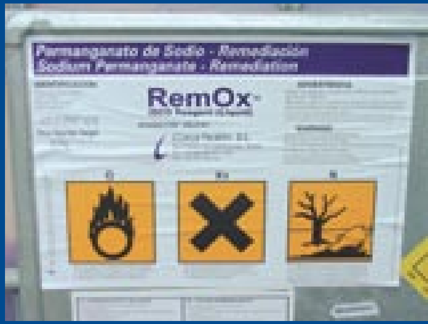
- the pollution and any degradation products of the pollution, e.g. chloride as an indicator for the breakdown during the remediation of chlorinated hydrocarbons;
- the oxidant - for permanganate for instance, a quick, simple colour assessment is available;
- auxiliary substances, e.g. the iron(II) concentration and pH in Fenton’s reagent.

After remediation

First, the scale of the pollution and the concentrations must be determined. In the case of ISCO remediation with Fenton’s reagent, ozone and ozone/peroxide, the final monitoring should be conducted shortly after the final injection round due to the poor stability of the oxidant in the soil. In the case of permanganate, the period until the final sampling can be longer. Following the ISCO remediation, the soil conditions should ideally return to the initial situation. Parameters that help us in determining this include: temperature, the presence of an oxidant residue and redox conditions.

During each in-situ remediation, diffusion from the soil will occur. As a result of diffusion from the smaller and poorly accessible pores, the concentration of the pollution in the groundwater slowly increases again. It is therefore wise to analyse groundwater samples for a long period of time following the last injection phase. These periods are three and six months long. In the case of permanganate one is advised to observe these periods after the purple colour has disappeared from the cleared up area.

ISCO remediation with permanganate of residual pollution at a dry cleaner



The activities of a chemical laundry cause the soil and groundwater to be polluted with tetrachloroethene (PCE). Due to the relatively low levels of the groundwater at approx. 4 m -mv, the pollution occurred in high concentrations, both in the unsaturated and saturated zones of the soil. The remediation plan therefore intended to tackle the pollution by means of a ground air extraction system for the unsaturated zone, and groundwater draw-off for the saturated zone. Both systems were started in 1997. Remediation of the unsaturated soil was halted in 2000. In 2004, the groundwater draw-off yielded an average of 200-300 $\mu g \cdot l^{-1}$. In the source area, occasional concentrations of 5,000 $\mu g \cdot l^{-1}$ were found. The estimated surface area of the residual pollution amounted to approx. 75 - 100 m^2.

It was then decided to apply ISCO. Due to the small amount of biological activity, the oxygen-rich conditions in the groundwater, the commissioning party's wish for a minimum amount of disturbance and the low NOD value (0.5 - 1.9 g $MnO_4 \cdot kg^{-1}$ of soil), it was decided to tackle the residual pollution with permanganate. The injection system comprised three injection points and two extraction points. This configuration made it possible to specifically aim the oxidant through the residual pollution. The extracted groundwater, including any traces of permanganate, was treated with a purifying agent containing active carbon. During two injection periods, 2,700 kg of permanganate were injected as a 4% solution with an output of 1 $m^3 \cdot u^{-1}$ and a groundwater extraction of 5 $m^3 \cdot u^{-1}$. The verification monitoring process comprised field measurements for pH, temperature, redox conditions, conductivity and permanganate concentrations, plus chemical analyses for PCE and heavy metals. Following injection, an obvious effect was observed on the redox conditions and conductivity. Based on the permanganate measurements in the field plus drillings, it was found that the permanganate stopped having an effect at 10 m of the injection filters. This could be a result of the soil's demand for oxidant. During the active phase of the ISCO remediation, the PCE concentration in the groundwater fell below the detection limit. Between the first and second injection phase, the PCE concentrations quickly returned to concentrations between 1,000 and 2,000 $\mu g \cdot l^{-1}$. Following the second injection phase, diffusion from the soil was observed, but the groundwater concentrations in the source area remained between 280 and 360 µg·l-1. In the source area, a load reduction of more than 90% was observed three months after the active remediation phase had ended.

5

Additional information

This document was written on the basis of our own practical experience and a wealth of literature, such as excerpts from conferences, scientific articles, magazine articles, and reports on different ISCO remediation projects. We also consulted various Internet sources, including those of specialist contractors. Below is a selection of the various sources that provide additional information on ISCO.

Conferences are the perfect opportunity to stay up-to-date on the latest developments in the field of in-situ remediation. Specific conferences that focus entirely on ISCO, or conferences that have ISCO remediation as a permanent item on the agenda include:

- the biennial FZK/TNO conference Contaminated Soil, or ConSoil. Focuses mainly on developments in Europe. See also www.consoil.de;
- Another biennial conference, this time in the United States: The International Conference on Remediation of Chlorinated and Recalcitrant Compounds. This conference often deals with the latest developments in the field of soil remediation, including ISCO. See also ww.battelle.org/conferences;
- The annual European Conference on Oxidation and Reduction Technologies for Ex-Situ Treatment of Water, Air and Soil and In-Situ treatment of Soil and Groundwater (ECOR) in Göttingen, Germany. ECOR specialises in ex-situ and in-situ oxidation and reduction remediation techniques, including ISCO and its applications. See also www.terratech.com.

There are a number of specialist Dutch magazines that publish the most significant developments in the field of the environment, such as: *Bodem, Land + Water en Milieumagazine*. Other scientific journals, such as the *Technisch Weekblad* and *Cobouw,* often publish interesting articles on in-situ remediation, including ISCO. For the in-situ remediation company that wants to find out more, we recommend the following scientific magazines: Environmental Science and Technology (ES&T), Groundwater Monitoring and Remediation (GWMR) and Water, Air and Soil Pollution (WASP).

During the past few years, the Internet has become a source of information for technical developments in the field of in-situ remediation. Apart from contractors publishing detailed information on the techniques they offer, the websites of various governmental institutions (especially those in the USA) are very good sources of information, where you can also find the very latest details on ISCO. Here is a small selection:

- **www.bodemrichtlijn.nl** - the digital version of the Soil Remediation Techniques Handbook includes a section on ISCO. See the chapter Library;
- **bodem.pagina.nl** - the ultimate home page in the field of soil, also in the field of remediation techniques;
- **www.epa.gov** - US Environmental Protection Agency (EPA);
- **clu-in.org** - Hazardous Waste Clean-up Information (also from the EPA, but specifically aimed at the technical element) offers a wide range of documents on ISCO applications and developments;
- **www.frtr.gov** - Federal Remediation Technology Roundtable technology website. Like the clu-in website, it contains lots of up-to-date information;
- **www.itrcweb.org** - Interstate Technology and Regulatory Council website. Contains documents about different techniques and what is feasible, also from the point of view of the competent authorities.

Apart from these sources, there are of course a number of books that discuss ISCO as a remediation technique. Here is a small selection:

- CGJM Pijls, ThJS Keijzer, ECL Marnette, M Sumann, F Volkering, M van Zutphen (2005). *In-situ bodemsanering, theorie en praktijk. Tauw, Deventer;*
- RL Siegrist, MA Urynowics, OR West (2001). Principles and practices of in-situ chemical oxidation using permanganate. Battelle Press, Monterey CA, USA;
- ITRC (2005). Technical and regulatory guidance for in-situ chemical oxidation of contaminated soil and groundwater. Interstate Technology & Regulatory Council, USA.

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We extend our thanks to:

Twan Kanen	*Mourik Groot-Ammers*
Rudi Pelgrum	*In Situ Technieken*
Charles Pijls	*Tauw*
Bert Scheffer	*Verhoeve Milieu Oost*
Roland de Wit	*Mateboer Milieutechniek*

Design	Van Lint Vormgeving, Zierikzee
Printer	Hoorens Printing, Kortrijk
Images	Tauw (pages 10, 15, 18, 20, 23, 25, 27, 28, 46, 50, 53 and 57) KBBL (pages 15 and 25) IST (page 17 and 38) Verhoeve (page 30) SKB (pages 7, 46 and 54)

September 2007