



LIFE09/ENV/B/000407

**HEALTH AND SAFETY PLAN FOR FULL SCALE
REMEDIATION**

**Points of interest regarding the safe application of ISCO by perozone
on EX-rated sites**

18/05/2017

VOPAK-EXPERO3

**Using ISCO with perozone for the remediation of a cocktail of
organic contaminants at an EX-rated industrial site in operation**

Table of contents

Executive summary	4
1. Introduction.....	6
2. Problem definition.....	6
3. Selection of the applied technology	8
4. The reagents within Perozone	8
4.1. Legal framework	8
4.2. Ozone.....	8
4.3. Hydrogen peroxide	10
4.4. Combined injection of ozone and peroxide.....	11
5. Site characterization	12
6. Approach and evaluation of risks	14
6.1. Uncontrolled emission	14
6.2. Corrosion.....	20
6.3. Temperature.....	22
6.4. Fire/explosion	23
6.5. Stability of existing constructions.....	28
6.6. Material properties.....	29
6.7. Construction/placement underground infrastructure.....	29
6.8. Modi operandi of the Perozone-equipment.....	30
6.9. Failure of the Perozone-equipment itself	31
7. Conclusions.....	32

List of abbreviations

BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene, xylene
CAH	Chlorinated aliphatic hydrocarbons
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
EC	European Commission
EX	Explosion sensitive
H&S	Health and safety
HDPE	high density polyethylene
ISCO	In situ chemical oxidation
LEL	Lower explosion limit
MPE	Multi phase extraction
m-bgl	Meter below ground level
OVAM	Openbare Vlaamse Afvalstoffenmaatschappij
PID	Photo ionisation detector
PPE	personal protective equipment
SVE	Soil vapour extraction
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
VOC	Volatile organic chlorocompounds

Executive summary

European soils contain many legacies from a less sustainable industrial past: soils, sediments and groundwater are sinks for many contaminating substances.

Major sources of contamination are chlorinated aliphatic hydrocarbons (CAH), BTEX (benzene, toluene, ethylbenzene and xylene) and total petroleum hydrocarbons (TPH). These contaminants all have different chemical and physical characteristics, and aberrant paths of biodegradation. This makes remediation of a site that is contaminated with a mixture of these various contaminants very difficult, expensive and time-consuming.

Furthermore, applying a remediation technology on an industrial land where Ex-rated operations cannot be interrupted causes a supplementary challenge. This is especially the case when oxidising agents are applied, since these are not compatible with stored flammable materials.

Both the complex contamination situation and the restrictive safety rules at an Ex-rated facility had to be confronted at the site selected for this project.

A specified mixture of ozone and hydrogen peroxide, referred to as Perozone, was selected to be used because of its very high oxidising capability compared to the alternatives. This quality makes it an efficient agent to breakdown even recalcitrant organic chemicals.

The project started with a pilot test on an isolated part of the contaminated area. As this spot was less polluted and located just outside the Ex-restricted zone, it was suitable to build up experience with the ISCO-technology.

The observations and experience during this test led to the drafting of an initial health & safety plan, which was gradually upgraded for the full scale remediation project within the Ex-zone and with higher contamination levels.

It was also a useful basis for the final design of the injection and extraction system and the determination of the required capacity of the ISCO-equipment to conclude the project within a pre-set time lapse and at a targeted cost estimate.

All relevant risk fields were identified and followed during the project.

The 2 major challenges appeared to be:

- containing the oxidising agents from manufacturing and dosing until release in the soil;
- preventing the escape of excess gaseous oxidiser and stripped contamination towards locations where human exposure could occur or chemical storage or handling takes place.

During the project it was demonstrated that all risks could remain managed at all times, however the main conclusion is that the progress of the remediation largely depends on a proper risk management.

This document aims to provide a tool to users of this or similar technology to help them evaluate the feasibility for the particular project they are facing.

1. Introduction

The purpose of this health and safety plan is to summarize and to transfer the knowledge acquired during the EC funded LIFE project LIFE/BE/ENV/000407 for the remediation of a mixture of organic contaminants in the groundwater. The remediation technique is based on using ISCO with peroxone at a EX-rated industrial site in operation. This document will answer the question on how to manage process risks and safety. Risks are identified and prioritised and preventive and mitigating measures that need to be considered are defined. Special attention is given to the safety measures related to the EX-rated environment of the chemical storage plant and potentially occurring emergency situations.

This document is established through a combined effort of the beneficiaries of the LIFE project:

- BADECO is acting as the safety coordinator according to the European legislation on temporary and mobile construction sites.
- RSK is the Flemish accredited soil remediation expert.
- VOPAK is responsible for the operation of the chemical storage plant where the project has been executed.

The document gives a general description of the health and safety issues related to in-situ chemical oxidation. **Specific project risk related working instructions are listed in the annex.**

2. Problem definition

In the past decades, great progress has been achieved in the development and optimisation of applied soil remediation technology, resulting in a number of readily available and meanwhile well documented approaches.

For certain situations, traditional remediation techniques such as excavation or bioremediation may be difficult, expensive and time consuming.

The main parameters that matter in selecting the best available solution for a specific soil contamination problem are:

- nature and appearance of pollution
- soil characteristics and physical reachability of the contamination
- site conditions (infrastructure, activities)
- time lapse required (how urgently is action required?)
- final results to be achieved
- resources available (materials and funds).

The finally retained technology for a specific situation will be obtained after assessing and weighing the above data, concluded in a feasibility analysis and cost estimate.

It may well be the case that certain methods need to be combined, depending on their effectiveness and a potential leverage effect in different stages of the soil decontamination project.

Especially when industrial land is still in use, it can be difficult or even impossible to physically remove and replace the contaminated soil without interfering too much with the ongoing economical activity. Alternatively, desorbing the harmful chemicals from the soil by extracting contaminated groundwater and soil vapour is very often a slow and less predictable process in terms of achievable results.

In those situations, it may be favourable to consider the soil itself as a reaction vessel and to target the breakdown or immobilisation of the contaminants in the environment soil compartments. The process can be based on a chemical reaction or on a stimulated microbiological degradation or transfer to less harmful products.

As the knowledge of in situ remediation is evolving progressively, the application and management of more challenging technologies, such as the injection of highly reactive chemicals in the soil, is becoming more feasible.

Non- or difficult biodegradable organic pollutants can be treated by a high-performance technique such as in situ chemical oxidation (ISCO). An interesting side-effect when applying ISCO is the effervescing effect it generates in the soil matrix, which enhances the mass transfer of absorbed contaminants to groundwater and thus make them more available for chemical destruction. This can turn out in a faster and better result.

The main benefits of using ISCO over other conventional treatment technologies are:

- no generation of large volumes of waste material
- project clean-up realized in a shorter time frame.

Both of these advantages result in savings on material, monitoring and maintenance.

A potential drawback of ISCO lies in the fact that the oxidant demand of the soil matrix in many cases will exceed the stoichiometric contaminant demand resulting in increased remediation costs. Because of its non-selectivity, the oxidizing chemicals can also deteriorate structural layers such as peat, making the soil less stable.

Most ISCO-applications involve the use of water soluble, low toxic oxidising reagents

Most ISCO-applications involve the use of water soluble, low toxic oxidising reagents. However, Perozone, being a mixture of ozone and hydrogen peroxide, distinguishes itself as a reagent with a very high oxidising capacity, but on the other hand also with a considerably high toxicity to man.

In-Situ Chemical Oxidation (ISCO) using perozone, being a mixture of hydrogen peroxide and ozone, is a highly performing remediation technology since many kinds of organic contaminants can be treated.

The presence of these strong oxidants however potentially causes major issues with regard to health and safety at explosion sensitive (EX-rated) sites. Contact between the oxidant and inflammable/explosive products at the site must be avoided. Therefore, it is crucial to draw up an extensive health and safety plan to define the safety measures that are necessary during the remediation activities.

These specific characteristics require a profound site related risk analysis and the elaboration of a safety plan.

3. Selection of the applied technology

Among the existing technologies that are based on Advanced Oxidation Processes and that are available on the market, it was decided to select the Perozone system. Perozone is an ISCO-technique built around a multifunctional gas-liquid injection system, referred to as Laminar Spargepoints (LSP). The LSPs are designed to obtain the thorough mixing of gas and liquid only at the point of release in the soil. This will result in a maximum possible yield of radicals directly in the environment where the chemical activity of these very unstable, short-living molecules is desired.

The Perozone-technology has been used on many occasions to remediate various organic compounds such as VOCL, mineral oil, BTEXN and PAH, but also with capacity to break down specific compounds like pesticides and medicins.

4. The reagents within Perozone

4.1. Legal framework

Depending on the nature and quantities, the onsite storage and production of chemicals may be submitted to environmental and legal conditions or restrictions. Industrial sectors where handling of chemicals is an inherent part of the licensed activities, the site permit may already hold regulations that are also applicable to the production of Perozone.

In other cases, a project-related license to perform ISCO-based decontamination work may specifically deal with the chemical related risks.

4.2. Ozone

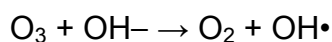
Oxidizing process

Ozone (O₃) is one of the strongest oxidants applied to ISCO.

Because ozone is a gas, aberrant from other oxidizers, it can also be used to remediate vadose zone contamination. Also, ozone provides oxygen to the microbial community when decomposing, which can benefit bioremediation. However, because of its sterilizing properties when applied in high concentrations or when long residence times are applied, ozone must be carefully controlled if bioremediation is to be enhanced.

Direct oxidation involves the opening of double carbon bonds by ozone itself. In addition to this, by reacting with hydroxide ions at neutral to basic pH ranges, ozone may produce hydroxyl radicals (OH•).

Basic reaction:



Hydroxyl radicals are nonselective and powerful oxidizers, which rapidly break down carbon-to-carbon bonds of many organic compounds.

The behavior and life-time of the unstable hydroxyl radicals depends on the nature of the soil matrix and its organic constituents. In particular, non-intended radical scavengers may occur, such as naturally occurring carbonates and humic acids. These scavengers will increase the ozone demand due to the non-selectivity of ozone and the hydroxyl free radicals and thus limit the effectiveness of the oxidant.

Resulting products of ozone oxidation are usually nonhazardous, naturally occurring compounds such as aldehydes, ketones, carboxylic acids, carbon dioxide and water.

Since the mass transfer of ozone to groundwater is limited, ozonation is typically sustained over a longer period of time than with other oxidants. To maximize mass transfer to groundwater, ozone is commonly delivered via sparge screens with very small orifices such that fine bubbles are being formed.

Availability on site

As the ozone-molecule is unstable, possibly decomposing within minutes, it cannot be stored as such, so it is necessary to produce it on-site at the moment of demand. The common way to produce ozone is by corona-discharge, in which process ozone is generated as a result of electrical discharge applied to a dry pure or enriched oxygen flow. The excessive heat of the electrodes needs cooling, often achieved by cooling water.

This happens starting from pure oxygen that is obtained by molecular sieving of ambient air, after which the oxygen is transferred on line to ozone by exposing it to a high voltage electrical field. The ozone is then mixed with a dry air stream before being fed to the injection system.

Safety

Ozone is a highly biotoxic chemical, which causes acute health problems when persons are exposed to it, mainly by inhalation.

The threshold limit value for the safe use of ozone in a professional working environment is set at a relatively low 0.1 ppm (may vary, depending on local legislation).

High concentrations (>1 ppm) of ozone can cause irritation or damage to the eyes and respiratory tract.

When used for ISCO, ozone-levels are brought to specification grade required for injection by mixing it with air. However, before this point high levels of ozone and also pure oxygen may be present in the generating apparatus or build up in the enclosure containing the equipment in case of leakage.

Ozone, being a strong oxidizer, also promotes fire and reacts heavily with organic and other reducing compounds.

In addition to being an oxidizer, ozone - even mixed with air - is an explosive gas. Oxygen is not combustible itself but enhances combustion of other substances.

Therefore, adequate ventilation of all enclosures where enriched oxygen or ozone may be present due to leaks or any kind of calamity is necessary.

The oxygen is produced on site up to the rate at which it is consumed, limiting the stored quantity of it at any time to the volume that is determined during the design engineering phase. Use of liquid oxygen presents a high risk situation and should be avoided. The risks can be reduced to a large extent by applying in-line oxygen production, where no storage is needed.

Special attention is required to keep the enriched oxygen contained. The quality of the technical equipment, the connecting pieces of the different parts, the housing of it all and the regulating instrumentation must meet tight safety standards and be built together with great care.

All parts of the oxygen containing system that are susceptible to wear and tear need to be placed in a well ventilated area, away from any sources/receptors that can react with oxygen enriched air.

All ignition sources should be kept away from the equipment, such as switches, fuse boxes, lights, heating devices.

ATEX - regulation has to be followed where appropriate.

All materials that can catch fire should be excluded as much as possible from the production facility, including papers, polymeric insulation materials, plastic piping, wooden paneling.

Frequent and periodic control of any leakage should eliminate or at least reduce unexpected oxygen escape from the above ground part of the system.

Continuous monitoring of the oxygen level in critical places should warn for oxygen leaks during the mainly unattended operation of the system.

For more detailed information: see the appropriate msds.

4.3. Hydrogen peroxide

Oxidizing process

Similar to ozone, the oxidizing process with hydrogen peroxide (H₂O₂) involves direct oxidation and free radical (OH•) generation.

Dissolved iron, known as Fenton's reagent, can be used as a catalyst to promote the formation of the powerful hydroxyl-radicals and thus realize oxidation in a much shorter time.

Basic reaction:



The contaminants are treated in situ, converted into innocuous and/or natural occurring compounds.

Availability on site

As hydrogen peroxide - commonly a 35% solution in water - can be stored as a semi-stable chemical, it will be brought on site by truck load. A buffer storage needs to be available on site in order to receive the product and to assure the consumption over a certain time.

Safety

Hydrogen peroxide is a water-soluble oxidizing reagent, decomposing easily when brought into contact with organic materials and with metallic ions at pH above 7.

Hydrogen peroxide is not combustible itself, but the substance may ignite combustible materials, increasing the risk of fire. Many reactions may cause fire or explosion, esp. in contact with heat or metal catalysts.

The peroxide itself can irritate the skin, the eyes and the respiratory tract.

As hydrogen peroxide has a very low vapor pressure, personal protection primarily needs to focus on avoiding any direct contact with the fluid.

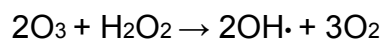
The delivery, storage and user specification of the hydrogen peroxide reagent takes place in conformity with good practices and local legislation.

For more information: see the appropriate msds.

4.4. Combined injection of ozone and peroxide

Combined ozone–hydrogen peroxide reactions result in enhanced generation of hydroxyl radicals. Formation of hydroxyl radicals during ozone–hydrogen peroxide treatment involves direct hydrogen peroxide and ozone reactions (see above) and intermediate ozone and hydrogen peroxide reactions.

Basic reaction:



This makes ozone–hydrogen peroxide injection much more aggressive for the removal of e.g. petroleum-based pollutants than ozonation and Fenton's reagent used alone.

Chain propagating reactions can produce other radicals such as: $\text{HO}_2\cdot$, $\text{O}_2\text{---}\cdot$ and $\text{R}\cdot$.

These radicals also contribute to the breakdown of organic pollutants, but these intermediate products can be readily scavenged by Fe_2^+ or Fe_3^+ . This makes the excess presence of iron adverse and perhaps problematic leading to an important yield loss.

The Perozone-technique targets the formation of a thin film of hydrogen peroxide around the ozone containing air bubbles released in the soil, using a static mixing device that is placed at the outlet side of each injection well.

The efficiency of Perozone oxidation reactions will be affected by several variables that must be considered simultaneously for each soil aquifer, with both supportive and antagonistic results for timing and cost. This includes temperature, pH, concentration of the reactants, catalysts, reaction by-products, and system impurities (e.g., natural organic matter, oxidant scavengers especially carbonate ions, etc.).

In order to verify site compatibility, laboratory or pilot testing may be required.

Both peroxide (diluted to 5-10% in the process) and ozone-enriched air are jointly fed to the injection system, strategically positioned in or underneath the targeted contaminated soil layer.

The realization of the synergetic effect caused by simultaneously introducing ozone and peroxide in the soil largely depends on the configuration and position of the 2 separate release devices at the end of both ducts that transport the oxidizing reagents. As gas (ozone) tends to follow a mainly vertical path of lowest resistance to the surface, liquid (peroxide) will show a more three-dimensional distribution promoted by the displaced volume.

Therefore it is obvious that the point of ozone release needs to be chosen in order to get the generated gas bubbles to travel through the liquid oxidizer within the soil matrix, resulting in a maximum contact surface between the two phases. Moreover, reducing the size of the bubbles will enlarge this surface, ultimately benefiting the spontaneous yield of radicals.

It is at this point that providers of this specific ISCO-technology are aiming to reach a distinctive added value.

5. Site characterization

ISCO is a technology generally applied in the aqueous-phase, so - except for ozone - the oxidant must be introduced in a (near-)saturated soil matrix.

The oxidant must be evenly dispersed throughout the contaminated soil matrix, avoiding forced migration of the contamination or oxidizing reagent outside of the treatment area.

Low soil permeability usually limits all forms of in situ soil remediation. However, the gaseous ozone will take advantage of the much higher gas-phase permeability.

Other site conditions such as subsurface heterogeneities, preferential flow paths and the extent of the vadose zone can cause an unequal distribution of the oxidant, hampering the effectiveness of any ISCO-technique.

Gaseous and liquid reagents can migrate to undesired spots, resulting in pockets of un- or less treated contamination.

When investigating heavily affected sites, it is almost certain that sorbed material will represent an important fraction of the total contamination. As the natural organic matter in the soil will also be consumed by the non-selective reagents applied, any sorbed contamination will gradually be released.

Because the ISCO-process generates micro gas bubbles (mainly O₂, but also CO₂ resulting from the destruction of organics) at the surface of the solid fraction within the soil, there will be a further desorbing and releasing effect of the pollutants. This makes them better available to oxidation reaction but at the same time it may also create a new environmental problem.

When monitoring and understanding the evolution of the groundwater quality during and perhaps even for some time after the ISCO, the phenomenon of delayed contaminant release to the groundwater needs to be considered. Therefore it is important to investigate the sorbed contaminant mass as part of the site characterization.

The influence radius of an injection well in an undisturbed soil is mainly determined by the hydraulic conductivity, providing an upfront basis for the required spacing of wells to achieve an optimal distribution of the injected oxidant.

Many industrial sites may show altered surface levels, reached after excavation or embankment for former building purposes, but also subsurface infrastructure such as (abandoned and current) conduits (utilities, sewer, former boreholes). All of these may disturb the natural and locally expected hydraulic gradient.

The less permeable the subsurface geology may be (i.e. silts and clays), the more these anomalies can contribute to contaminant and perhaps oxidant and reaction products migration pathways.

Because of the often disturbed subsurface of industrial areas and on the other hand the considerable financial resources needed to decontaminate the soil through ISCO, feasibility of the remediation technique should be demonstrated in advance by performing a pilot-scale test.

Considerations to be addressed for a pilot-scale test of ISCO are:

- selection of a restricted location that is sufficiently representative for the overall site conditions, with no inconvenience for the other site activities and that will ideally not become contaminated again after successful completion of the test;
- ability for calculation and design of the system in order to be able to upgrade to the full scale;
- presence of an appropriate groundwater monitoring network.

Some of the more recalcitrant contaminants can be oxidized only with the stronger oxidants, but these same reagents also tend to be consumed quickly in the subsurface, limiting the distance the oxidant can travel. This means that the density of the infiltration system will also be influenced by the nature of the contaminant.

Once it is decided to further investigate the application of ISCO-technology, a site survey is needed to specifically reveal possibilities and threats in order to properly design and implement ISCO.

This includes:

- determination of the nature and concentration of the contaminants, their distribution in the soil and their appearance (sorbed, dissolved, free-product phases);
- documenting of the subsurface (hydro-)geology;
- presence of (sub-)surface structures that might influence the soil vapour pathways, including underground utilities and sewer systems, cable/pipe trenches, recent or perhaps redundant foundations, building basements and giving potentially rise to unexpected migration pathways;
- locating potential receptors within the area to which soil vapour and contaminants or chemicals may migrate, focusing on spots where release to the atmosphere is less hampered such as uncovered spaces.

When evaluating the situation, following points of attention need to be considered:

- minimize distance between the oxidizing reagent-generating equipment and the injection wells, thus reducing the chance of pipe leaking or damage and also facilitating a quick emergency response;
- find out how a regular inspection of the integrity of the piping tracks can be performed easily;
- determine protected or shielded places for putting the piping, where it can be expected that the normal industrial activity of the site and e.g. weather conditions will not cause any damaging;
- think ahead that piping should be put preferably without any connection pieces, so it needs to be possible to overcome any physical obstruction and to bridge voids on the targeted track;
- place oxidizing reagent generating equipment in an outside and well ventilated area, away or at least protected from regularly used passage ways.

6. Approach and evaluation of risks

Specific project risk related working instructions are listed in the annex.

6.1. Uncontrolled emission

When considering the application and implementation of an in-situ soil remediation, the moment or time span during which the contamination could take place generally lies way back in time. This allowed for the establishment of a certain equilibrium of the contaminants between the vapor, liquid, and sorbed phases.

Because of the reactivity of the oxidants and the physical aspects of their carrying media that are introduced to the soil, there will be a change in both concentration and

distribution of the contamination. This will potentially result in significant changes in a site's equilibrium of contaminants between the different phases.

The Perozone mixture consists of a gaseous and a liquid phase.

This gas and liquid injected into the soil will distribute and migrate through the matrix following a pattern gradually shaped by the lowest resistance. Furthermore, the gas volume will increase because oxygen and CO₂ will be formed as a result of the oxidation process and the gas will also expand due to decreasing pressure when moving towards the groundwater surface.

Compared to groundwater migration, soil vapour travels much more swiftly, esp. through sandy soils. As a result, significant movement of soil vapour will already be induced by low air pressure differences, which are often too small to quantify or monitor properly.

As a result of this, every even minor underground disturbance can and will have an effect on the consequential air flow pattern, giving it a rather unpredictable character, thus making it hard to calculate conclusively beforehand.

To effectively degrade contaminants, the oxidant obviously must come into contact with the contaminant on a molecular level, meaning that the interphasing surface should be as large as possible. Ideally, the oxidant delivery technique should ensure that it is evenly dispersed throughout the area to be treated.

Subterranean structures or artifacts that need to be considered are:

- remaining relicts from previous activities, quite often not or poorly documented for land with a large industrial history;
- foundations or pipe/cable tracks/embedding;
- irregularly formed, thin or interrupted soil layers with relevant deviant permeability such as clay and peat pockets;
- *dense or light non aqueous phase layers (dnapl/lnapl)* that may act as a resisting barrier for vapour migration depending on the viscosity of the compounds.

Utility surveys should be conducted to account for the effect of underground piping, utilities or trenches on preferential pathways and/or pockets for organic decomposition, explosive liquids, vapors or oxygen.

Incomplete degradation of the injected oxidizing reagents and stripping of volatile substances that are dissolved in the groundwater can lead to the migration of a chemically heavily polluted air phase through a less polluted vadose zone.

The chemical oxidation of hydrocarbons can lead to the formation of toxic intermediate products, often showing increased mobility. E.g. ISCO-treatment of chlorinated hydrocarbons may initiate the highly toxic and mobile gaseous vinyl chloride.

The presence of existing infrastructure (e.g. large storage tanks, liquid tight containment of a tank farm facility) can limit the space that is available or easily accessible for the emplacement of the subsoil in-situ treatment devices, making it difficult to achieve the optimum soil vapour extraction design.

Venting or negative pressure systems will be appropriate for most ISCO-projects to accommodate off-gasses and relieve pressure and buildup of volatile organics. This consideration is especially important if the ground surface is paved or when preferential pathways could lead soil vapour towards places where people are present.

Establish a field monitoring and sampling program that will adequately monitor both the dispersion of the oxidant and the effectiveness of the treatment.

Monitoring wells must be located near and downgradient of each injection point. So supplementary monitoring wells, additional to the ones that have been placed previously for the conducting of the environmental site investigation, may have to be installed.

Ideally, the monitoring wells should be located at differing distances from the injection points so that dispersion of the oxidant can be tracked and adequate monitoring data can be collected. As a minimum, the perimeter of the contaminant plume must be monitored to ensure no off-site migration of oxidant and/or contamination.

For gas injection systems, pilot testing should be performed to substantiate the radius of influence of the injection point. This can be performed by evaluating pressure influence, dissolved oxygen increases, water table mounding, and dispersion of the injected gas (e.g. via helium gas tracing).

For liquid-injection systems, the pilot test should substantiate the dispersion of the solution into the groundwater (and should be performed separately from any gas-injection testing) to ensure that there is an appropriate influence area at varying injection flow rates. This can be performed by evaluating dissolved oxygen increases, water table mounding, or concentration of the injected fluid.

A good understanding of the generated air/gas volume and their pathways through the soil are the basis of all further design calculations for the soil vapor extraction (SVE). Both the volumes of the injected ozone-enriched air, expanding when moving upwards through the groundwater, and the CO₂ generated by oxidation of organic material should be included in the evaluation.

Equal to the similar threats that exist for the injection system, the inherent subsurface heterogeneity that can cause unexpected elevated pressure losses in the extracting system needs to be taken into account. This reflects on the configuration and the feasible spreading of the extraction system throughout the site. Placing the SVE-system close to the extraction filters, reducing pressure loss, will increase the efficiency.

When designing the desired soil vapour extraction and treatment capacity, following aspects have to be taken into account:

- The overall soil resistance to vapour movement.

For a proper understanding, one has to consider the nature of the activities of (petro-)chemical plants, with often considerable pressures put to the ground by the weight of large storage tanks and facilities (up to 1000's of tons) and perhaps intense heavy duty traffic for (off-)loading. Over the years, this may have resulted into a strongly and presumably asymmetrically compacted soil. Hence, the soil vapour extraction system (SVE)-system must be sufficiently performant and implanted on well chosen locations in the field to compensate for this phenomenon. The final target is to create a directional soil vapour displacement still on all edges of the covered surfaces towards the SVE-system.

- Safety margins.

On the basis of a non-ideal flow pattern caused by different ground layers, the presence of trench shaped, good permeable zones (such as sand bedding for cables, pipelines, sewers) or lesser permeable zones (compacted areas, subsurface massifs such as screed and foundations, ...), an excess capacity needs to be foreseen. How large this should be depends on the risk analysis for the specific situation, but it seems advisable to take at least an overall extra 30% above the injected and generated gas volume (atmospheric reference).

- Positioning of the SVE.

The contact-zone of the system that will extract the soil vapour must be put in strategically chosen places. When operated, it needs to be entirely in the vadose zone of the soil, in order not to be hampered by water locking. Otherwise, this might cause subareas that are unexpectedly not or not properly ventilated.

Take care that a raised water napkin during winter time can make water to enter the SVE-system. Also, the injection of air/liquid will locally produce a water mound. When water needs to be evacuated from the drainage system, this will make a waste water handling or even on-site treatment necessary, complicating and making the overall treatment technology more expensive.

- Absorption of volatile materials.

The air filter polishing the extracted soil vapour before discharge to the atmosphere needs to be performant and adequate to remove the gaseous contaminants and any potentially remaining ozone. The logic choice will be the use of activated carbon, with a quality grade and volume adapted to the kind and quantity of compounds to be absorbed. Two activated carbon filters should be installed in a serial line. Any excess ozone normally will simultaneously be removed efficiently by activated carbon.

- Air pump capacity.

Both the required flow rate as well as the necessary vacuum pressure need to be determined, based on the actual field situation. The vadose zone where vapours resulting from the Perozone-injection can arrive needs to be flushed properly not to let contaminated air escape to the atmosphere. Also, all height differences in piping need to be mapped, since they could become condensate traps when the air pump is not designed to overcome the resulting pressure drop. A pressure monitor placed on the suction side of the air pump can detect a potential problem and eventually produce an alarm.

- Winter conditions.

When part of the air pipes are exposed to cold temperatures during winter time, vapour condensate may lead to clogging due to icing. Especially in an intermediately operated system with periods of no flow rate, this phenomenon may occur more easily.

In this case it is advised to develop a winterization program, detailing the possible problems and the actions to be taken to overcome them.

Wherever possible, it is advised to check a good distribution of the air bubbles rising from the injection wells. Whenever a hard covering of the surface is locally taken away to place the SVE-system, the opportunity should be taken to perform this check before its restoration. This applies mainly for soils with shallow ground water level, because an inspection can only take place with a visual on a free water phase. When eventually feasible, saturate the top layer with water for this test. The test makes it possible to check on short circuiting, a phenomenon that becomes difficult to detect once the physical situation of the site is restored.

Fissures in the top layer within the radius of influence of the injection points can be addressed with an appropriate sealant, improving the tightness of the covering floor.

When placing groundwater monitoring wells in the reaction zone, it is advised to limit the height of the slit area of the well tube and the drainage material around the tube. As vapour is following the way of the least resistance, the slit zone forms a by-pass for the adjacent soil layer, which will consequently receive less of the active Perozone-mixture.

As long as there is no certainty about the safe human exposure within certain zones, they need to be clearly marked as potentially high risk areas. Depending on the risk assessment, only competent persons can enter the dedicated areas, equipped with the necessary personal protection gear and monitoring equipment (pid, ozone-detector). Efforts must be made to limit the time during which this uncertainty can last, by demonstrating the irrelevance of the actual risk or by taking measures to reach this latter situation.

As the concentration of the contamination decreases during the soil treatment, the injection rate of oxidizers needs to be lowered, thus preventing escape of the redundant chemical agents to the atmosphere. The consequence is that the progress of decontamination inevitably will become slower in the final phase.

After having installed the injection and extraction system, it is advised to run a preliminary service test of the complete system, without the ozone being added. Once the air flow pattern in the soil becomes steady, potential leaking points can be checked for the presence of VOC being stripped and/or increased oxygen levels.

For larger projects, a stepwise activation of the different subsystems until full operation should be considered.

During operation, further specific measurements should be performed on those spots in the field where incomplete or failing SVE could cause emission/accumulation of remaining gases (ozone, VOC, oxygen). These include subsoil spaces (sewers, access shafts, etc.), fissures or interruptions in or even absence of a hard soil covering, interiors of nearby buildings, etc.

Monitoring of ozone in the atmosphere can show a certain instability, producing drifting results. In that case it is advised to standardize the measuring method, e.g. by using a headspace in a closed sampling container or putting the device in a controlled and reproducible air stream.

Process follow up needs to include measurement of any possible remaining ozone in the extracted soil vapour. This would indicate an incomplete reaction of ozone in the soil, increasing the risk of emission of this highly toxic chemical to the environment in case the soil vapour is incompletely extracted by the SVE-system. At the same time, it can be a useful tool to adjust the process parameters when necessary.

Also, the extracted vapour needs to be monitored by photo ionization detector (pid) for the presence of any volatile chemicals, in order to understand the stripping effect in the soil and the potential risk of emission not being caught by the extraction system. Knowledge of the vapour quality will also enable the design of a proper air treatment before safely venting to the atmosphere.

Measuring the (very low) vacuum in the existing monitoring wells (filter slits must make contact with the vadose zone) can help understand if and how the soil vapour is flowing. This may detect soil vapour not being caught by the extracting system, in which case the need to adjust the operating rules before the toxic ozone is being added.

Note: generally the number and location of monitoring wells is determined by what is necessary for environmental follow up and therefore merely not intended for the mapping of soil vapour movement. Furthermore, there is reluctance to puncture protective floors unnecessarily or too much, as this creates potential future points of

concern to maintain the integrity of the covering plate, e.g. for retaining chemical spills.

The vacuum produced in the soil matrix itself is very low, which goes at the expense of the measurement accuracy. Furthermore, for larger areas, a rotation system of successively extracting different zones can be applied, depending on the peroxide-injection cycle, provoking a dynamic and continuously evolving pattern. This makes the measurement results even harder to interpret.

The measurement of specific field parameters, such as oxygen, carbon dioxide, and LEL, are useful in establishing a safe monitoring program. The monitoring of VOC and ozone at sensitive locations remain an important and indispensable control tool to guard and secure the ISCO-process.

Conclusion: a reliable control of the pattern of air movement in the soil in order to check on the performance of the extraction system is not easy to achieve, making the prior design an important and indispensable step to ensure proper functioning.

Aside from the obvious emission caused by residual oxidants in the soil vapour and stripped volatiles, there is also a risk related to the production of ozone.

When producing pure oxygen prior to turn it into ozone, the redundant enriched nitrogen gas will be drained into the atmosphere.

Like oxygen, nitrogen is a colourless and odourless inert gas, it is therefore impossible to notice any level-changes without a suitable monitoring device. Nearby the release point, the oxygen percentage will decrease, producing a hidden danger for human exposure to a low oxygen-level. Oxygen percentages inferior to 17% can cause acute health-problems and provoke unconsciousness when this drops to below 15%.

It is advised to fence the flush point of nitrogen gas and provide hazard pictograms.

6.2. Corrosion

Corrosion processes in the soil can be oxygen-driven or pH-driven.

The redox-balance in an undisturbed and covered soil tends towards anoxic conditions, thus spontaneously slowing down natural corrosion due to oxidation.

Forced oxygenation of the soil is a logic result of injecting natural air, additionally enriched within ISCO with highly active oxidizing agents.

On the other hand, the oxidation of chlorinated organic compounds results in the formation of chlorohydric acid (HCl), potentially increasing the acidity of the groundwater by reducing the pH or at least consuming the buffering capacity of the soil. As oxidation of organic compounds finally results in the production of carbon dioxide CO₂, this latter chemical will also contribute to the acidification of the soil.

Earlier experience shows that the pH does not change appreciatively by applying ISCO, because many reactions are occurring at the same time, generating both H⁺ and OH⁻.

Generally, the direct attack mechanism tends to lower the pH, while the radical pathway tends to increase it.

(Per-)ozone is a powerful, non-selective oxidizing reagent, reacting with both the organic pollution in the soil (intended effect) and other corrosion sensitive materials such as unprotected tank bottom plates and underground cables/pipelines (unwanted effects). Many of the customary metal storage tanks in the chemical industry are made of carbon steel, making them vulnerable to aggressive corrosive substances. This is especially the case where tanks or other receiving vessels are buried in or resting on the soil.

Very often, the large tank storage facilities and (petro-)chemical plants are located near waterways, in which case there is a presence of adjacent surface water (docks, river) inducing a shallow groundwater level at nearby facilities. Moreover, as the soil is compacted through carrying heavy equipment, the capillary zone is expected to be more prominent than it would be in undisturbed circumstances. As a result, any pH-alteration of the groundwater will more easily affect any structure that is touching the soil.

In case tanks do not have a protective, supportive layer or coating shielding them from the environment, potential contact from non extracted soil vapour containing residual oxidizing gas cannot be excluded.

It is essential to make an inventory of all underground pipes/cables/other structures and determine or estimate the resistance level of these materials against (per-)ozone, but also against the mobilized volatile organic compounds. These latter ones, some of which will be readily stripped from the polluted matrix thus making them migrate through the soil matrix, can exert a dissolving activity on this track.

A proper design of the SVE-system needs to restrict the escape of any air injected and capture it well before reaching places it should to be kept away from.

The dosing of the oxidizing reagents (ozone and peroxide) needs to be aligned closely to the current level of remaining pollution, taking into account the half life expectancy of any inadvertent excess of gaseous oxidizer.

The material of which the perozone containing piping is made of needs to be chemically sufficiently inert to prevent any leakage for the planned injection period, in some cases being multiple years. Each pipe leading from the perozone generator to the injection points will ideally consist of 1 integral piece, in any case without

underground connections that could fail over time. In case this is not feasible, the use of electric welding is advised so that no other materials can weaken the integrity of the whole system.

Leak tests must be performed before permanently covering the piping and making it inaccessible unless perhaps disturbing and expensive action is taken.

Depending on the local climatic conditions, protection measures against frost damage have to be taken.

SVE-wells need to be located in between peroxide injection points and corrosion-sensitive equipment/facilities, forming a barrier for soil vapour that might flow towards those places.

The SVE-system must be set up in order to remain operational even some time after the peroxide-injection has been stopped. Hence, this will also be part of the shut down procedure.

Cathodic protection of the steel tanks or any other equipment/material may be considered as a protective measurement.

In case of doubt when trying to estimate the resistance of certain materials or constructions to be safeguarded, samples of them can be brought into the active area when performing a pilot test. Evaluation of any degradation can indicate the effect caused during full scale.

A witness piece made of material equal to less accessible and potentially vulnerable construction parts may be buried in the reaction zone, so that intermediate inspection can reveal or predict any corrosion effect.

Although the establishment of an oxygenated soil matrix during ISCO, reducing environments are usually rapidly restored as the oxidant is consumed by the aerobic bacteria, natural organic matter and the contaminant targeted for oxidation.

Follow up of groundwater-pH changes will indicate the potential effect of acidic corrosion. If necessary, start/increase acidic groundwater extraction to neutralize/mitigate this effect.

Follow-up of redox-potential in ground water, preferably in the vicinity of sensitive structures, will indicate the possible effect of oxygen driven corrosion.

When performing the periodic inspection of the tank bottoms, depending on local legal obligations, the attention should also be targeted on any corrosion that might be related to peroxide-injection in the soil.

6.3. Temperature

Chemical oxidation of organic compounds is an exothermic reaction. This can increase the temperature in the soil - mainly in the core of the reaction zone where the highest level of contamination is located.

Even a limited temperature increase of just some degrees may already have a noticeable impact on the evaporation rate esp. of highly volatile substances, which finally affects the probability of uncontrolled emission and the performance of the SVE and the in-line treatment of the extracted vapour.

Elevated temperatures can also lower the physical resistance of thermoplastic materials, often used for the construction of the injection and extraction infrastructure.

When applying the perozone-technique, the oxidizing reagents added to the soil are injected gradually and in low concentrations, unlike other in-situ chemical oxidation remediation techniques where high concentrations of chemicals are injected within a short time. This allows a better dissipation of the heat produced, avoiding strong and sudden temperature increases.

Soil vapour extraction will also carry away heat from the soil.

Monitoring of the temperature in the air coming from the SVE and perhaps in the soil/groundwater itself will map this effect.

Nevertheless, when temperature increases would need to be addressed for, the dosage of oxidizing reagent can be adjusted accordingly to control this effect.

6.4. Fire/explosion

Site characteristics

Fire hazard and explosion risks represent a major safety issue in any industrial setting where flammable goods are stored or handled.

Areas intended for the storage/treatment and (off-)loading of flammable liquids by the site operating company are clearly defined and legally restricted as a safety zone (e.g. EX-rated area). For any work performed in such a zone, tight measures to exclude or shield energy sources that could induce ignition have to be taken. In case this is not feasible, proper monitoring of the ambient air near the temporary work spot must secure the situation. All work within the safety zone needs to be screened against these conditions, with definition of appropriate preventive and fire abating measures.

In case the piping for the SVE extracting-system of Perozone is installed under a larger liquid-tight hard covering, it is very unlikely that any spill originating from the operational activities could be readily caught by it, hence existing safety monitoring equipment will indicate a potential risk well before this could become a threat to the Perozone-equipment.

It is advised that upon any alarm of chemicals spilled nearby any part of the Perozone-system, the equipment is shut down, taking into account that the SVE-system will still remain active a given time. Therefore adequate training must be provided to the company's staff who is responsible for emergency intervention or alarming the fire brigade.

Risks related to increased oxygen levels

Oxygen itself is not flammable or explosive, but in places where it can accumulate it will lower the flashpoint of many substances and it makes materials that do not burn in air susceptible to catching fire. Also the intensity of the flame temperature and the speed of the fire are much higher compared to atmospheric conditions, turning it quickly into an uncontrolled situation. Part of this effect is due to the absence of nitrogen which would normally absorb part of the heat released and provide an energy buffer that slows down the combustion.

This may transfer the incineration of materials like oils, fats, synthetic materials and even products that are fire retardant such as protective clothing, from a normally burning into an explosive-like process.

A large contact area may induce a spontaneous ignition more easily, as this can be the case where e.g. oils or other flammable substances are present as a thin film or coating absorbed to a large surface, especially when this concerns materials with poor heat transfer properties. In this latter case, self-ignition will be inhibited.

It is generally accepted that oxygen levels exceeding 23% are dangerous. As oxygen is colourless, odourless and has no taste, the presence of an oxygen enriched atmosphere cannot be detected by normal human senses.

The 23%-threshold can easily be reached in case of leakage or oxygen resulting from chemical processes such as decomposition of ozone. The latter process can occur in the soil matrix, creating related risks in this rather unexpected environment.

There are literature references of such cases where in-situ chemical oxidation caused the soil catching fire, fueled by residual pollution and perhaps peat.

Although very unlikely to happen, the effect could be dramatic in terms of risks and abating costs.

Persons that have been exposed to increased oxygen levels need to vent their clothing thoroughly for about 15 minutes. Lighting a cigarette within this period could still lead to spontaneous ignition of any clothing.

Breathing of air with increased oxygen level will normally not give rise to any health issue, although the uncontrolled inhalation of pure oxygen may lead to complications.

Applying Perozone-technology, with continuous but low injection of oxidizing agents, a sudden release of large quantities of oxygen is less probable.

Influence of temperature to the explosion risk

Oxidation of hydrocarbons is an exothermic process, thus generating heat. Elevated temperatures facilitate the stripping of volatile compounds, which makes them better available for ignition.

Due to the continuous but low dosage of oxidants in the Perozone-approach, no sudden or large soil temperature rise is to be expected, which makes a sudden excess of the flashpoint in the soil much less likely.

Measuring the temperature in the SVE-system and the groundwater will give an indication of the heat that is being produced in the soil matrix itself. Unexpected increase of the temperature or aberrant values for specific sub locations may give valuable input to adjust the process.

Presence of volatile hydrocarbons in the soil vapour

The extracted soil vapour during Perozone-operation contains residues - mainly carbon dioxide - resulting from the targeted oxidation of the organic pollution and the non targeted but inevitable co-oxidation of any naturally occurring organic substances. This gaseous phase will also contain volatile substances that are stripped from the groundwater or extracted from the vadose zone. Especially at the early phase of the chemical oxidation treatment, being the period during which the highest soil pollution is being encountered, the concentration of hydrocarbons in the vapour flow can be considerable. As high vapour tension and flammable substances will be readily volatilized, the level of hydrocarbons in the gas can make the lower explosion level getting exceeded.

Absorption of gaseous hydrocarbons to activated carbon is an exothermic process, producing heat. When heavily polluted air passes through a carbon bed, the flashpoint temperature of highly flammable compounds could be exceeded, possibly setting fire to the carbon filter bed. Especially in the initial stage where high levels of gaseous substances can be extracted from the soil, the temperature increase in the carbon bed might become a concern.

The use and configuration of activated carbon filters as soil vapour polishing filters need to be checked against this risk.

Monitoring the CO content in the exhaust air stream from the activated carbon filters will initiate an early alarm indicating a possible starting fire inside the carbon bed. This alarm should activate the safe shut down of the Perozone-equipment and perhaps extinguish the combustion in an early stage by automatic filling the carbon filter bed with water.

The dry activated carbon filter, where the exothermic absorption of hydrocarbons can make the temperature significantly increase, should be placed in a well considered, less critical place, at a safe distance to the storage of oxidizing (peroxide, oxygen) or

any combustible compounds, expensive equipment and facilities of the site operating company.

Care should be taken to monitor the explosion level of the SVE-gases during the treatment program to ensure that the conduit atmosphere is maintained at all times at a nonexplosive level.

When monitoring of the quality of the SVE-gases reveals high levels of hydrocarbons, measures need to be taken to control this e.g. by altering the operating conditions or by adding ambient air at the air pump's inlet side to dilute the gases.

Stability of ozone-containing air

Concentrated O₂/O₃ – gas mixtures readily explode spontaneously. Such explosions can be initiated by small quantities of organic matter, shocks, electric sparks, or sudden changes in temperature and pressure.

Particle filters, slowing down progressive clogging of Perozone-releasing filters, can be considered as spots with such higher risk.

All equipment, including any metal housing on which surfaces static electricity could build up, needs to be earthed properly, avoiding any unexpected sparks.

Integrity of the technical equipment

All equipment, vessels, piping, etc. that can contain or transfer enriched or pure oxygen at any point should be made and kept gastight using high quality and appropriate materials. The same applies for the sealing of these components when being built together. Vulnerable parts such as nozzles, sampling points, etc. must be shielded to protect them from unintentional physical damaging.

All piping and vessels holding oxygen/nitrogen/ozone/peroxide must be labeled properly.

A continued periodic check to detect leakage already at an early stage is recommended.

Individual parts, such as pressure vessels, that are subjected to legal controls must be certified by notified bodies. The complete assembled machine must be in accordance with the applicable legislation.

Process safety

The performance of a multi-functional hazop safety check of the equipment is advised before it is being assembled, focusing on:

- material properties;
- methods to stop the oxygen flow at a readily reachable place before the gas enters critical parts of the facility, for reasons of maintenance or in case of emergency;
- filters or parts within the equipment where particles can be retained, creating a point where ignition might occur;
- volumes and pressures, understanding the flow conditions and methods to limit the flow velocity;
- sudden temperature changes (e.g. caused by adiabatic compression, friction, electrical sparks);
- overall electricity and powered steering devices;
- containment of the equipment;
- firefighting measures;
- the need for application of ATEX-regulations.

A protocol including a check list describing how the technical maintenance and intervention on the oxygen producing facility must take place should be made up.

Emptying any device with enriched oxygen or nitrogen, e.g. for maintenance or repair, should be done with proper care and preferably with gas release outside any containment or housing. Flushing should be performed with inert gas until the air-quality at the ventpipe shows that the oxygen level inside the equipment has turned to normal.

The contained equipment for the production of oxygen should be kept physically separated from any other devices. A sufficient ventilation of the production room needs to be put in place, also taking into account that oxygen is heavier than air. Within the housing, a room monitoring of the oxygen content will alarm any significant release of oxygen, initiating a call for appropriate technical intervention and eventually automatically shutting down the entire system when a preset safety threshold is exceeded or when the time between alarm and necessary intervention gets too long.

If feasible, all electrically powered equipment is placed outside the EX-zone of the site, thus excluding the risk of explosion due to the ongoing industrial site activities.

If possible, the carbon filter for the polishing of de extracted soil vapour should be placed in the area that is within visual reach of e.g. surveillance cameras.

Continuous and in line LEL-monitoring of the extracted air is an important safety device, inducing shut down of the Perozone-equipment when a preset safety threshold is exceeded.

Frequent monitoring of the concentration of volatile compounds in the extracted soil vapour will support the overall management of the remediation system.

Regular monitoring of VOC's (PID and LEL), ozone and oxygen on locations where vapours might accumulate, such as sewers, technical rooms in the area, any subsurface spaces, has to be organized,. Depending on the results, the Perozone installation needs be shut down until the situation is adjusted.

6.5. Stability of existing constructions

Due to the nature of the industrial activity of many companies, physical stability of the constructions (storage tanks, piperacks, process installations) is of the utmost importance to preserve the good and safe functioning of the facilities. Asymmetric subsidence of the carrying underground may induce increased tensions in the structure, causing deformation and weak spots in it.

Industrial harbour land is often created by elevating the natural soil with dredged material originating from the nearby river or sea. In case peat layers are part of the soil structure, they will obviously contribute to the overall carrying capacity. As a result, weakening this layer through chemical oxidation will undoubtedly reduce the carrying capacity of the soil, with potential effect to the stability of any structure placed in or on it.

Before designing the Perozone injection-system, a detailed stratification profile of the subsoil has to be made up.

Lowering the groundwater level should not cause peat layers to become drained which could make them subside irreversibly.

Putting setting bolts on critical constructions within the assumed area where stability-effects can occur makes it possible to monitor unwanted effects in an early phase.

Tank shell stress monitoring must be adjusted for the changing load in the tanks, perhaps also affecting simultaneously any subsidence of other tanks nearby.

6.6. Material properties

Because many cases tank storage and (petro-)chemical facilities are located in coastal areas/seaports, groundwater is often brackish. The selection of the proper grouting mixture must ensure a sustainable sealing of injection and extraction wells.

In case of doubt, the selection of the best available materials should be based on appropriate strength testing under simulated field conditions.

The use of the chemically highly resistant hdpe is a common choice for in situ soil remediation projects. On the other hand however, the particular adhesive properties of this material make it difficult to obtain a durable sealing with other materials, e.g. where puncture holes in concrete must be restored.

As much of the material is installed underground, it is not obvious to monitor any possible degrading process. Wherever possible, e.g. visual inspection must be done regularly.

6.7. Construction/placement underground infrastructure

Depending on the site conditions, it may be necessary during the construction phase to temporarily disrupt the integrity of liquid tight floors or contained tank parks. This causes a raised concern to abate environmental damage in case of spills or face any other calamity where liquid chemicals would be released.

To mitigate possible environmental damage resulting from causes outside the remediation project, provision of temporarily protective measures can be considered and perhaps safety surveillance can be adjusted.

When excavating e.g. trenches for installing the underground pipe work, this can eventually make life-saving appliances or existing fire-fighting equipment more difficult to reach. Emergency services such as the fire brigade may be confronted with poor accessibility of certain spots. As part of the project risk analysis, the accessibility of all non-removable on-site prevention tools must be evaluated. When this does not lead to feasible and satisfying solutions, temporary alternative means need to be put in place.

The emergency services have to be consulted whenever any safety intervention could be affected by the works.

The installation phase should be carefully prepared and the proper resources put in place in order to avoid unnecessary waiting time to restore the situation.

During the construction phase, specific field characteristics may hamper the work:

- a high retaining wall around the storage tanks may reduce natural ventilation of the work spot nearby, causing poor dilution in case of any emission from the polluted soil (e.g. when drilling the boreholes), so exposed persons need to carry appropriate personal protection equipment;
- the regular safety requirements applicable for EX-restricted areas within (petro-)chemical plants imply strict conditions for using motorized devices, often limiting the choice of the appliances that can be used;
- the abundant presence of piping, control equipment and other operational devices will constrain the room for manoeuvring, further limiting the use of heavy motorized tools, making at least part of the work to be carried out manually.

This tends to make (part of) the preparatory work potentially unhealthy and physically stressful.

The use of collective protective equipment must be considered (e.g. forced ventilation) prior to the use of personal equipment (PPE).

The selection of PPE must be based on efficiency and user comfort (e.g. pressurized breathing equipment).

Monitoring the air quality at the working place should limit the wearing of uncomfortable PPE to when this is needed or advised.

Persons that are possibly exposed to harmful emissions are subject to medical biomonitoring, according to local legal regulations.

6.8. Modi operandi of the Perozone-equipment

The soil is a semi-contained environment, with evolving conditions as the injection of oxidizing reagents is persisted.

A total control of the chemical reaction within the soil is hard to perform and is mainly based on assumptions and *a posteriori* knowledge that is obtained by analytical follow up. Changes in the operating parameters will thus be based on information that reflects an already past situation.

Injection rates and doses of Perozone should be carefully and gradually increased when starting the remediation process, following a safe and conservative approach.

The frequency of follow-up analyses must be adjusted, based on the progress and clear logging of the past results and observations.

Monitoring of field water quality during and after injection of the oxidant can help understand its distribution and thus the effectiveness of the remediation project. This can include: pH, oxidation reduction potential (redox), dissolved oxygen, dissolved carbon dioxide, temperature, and specific conductance.

6.9. Failure of the Perozone-equipment itself

The Perozone- and its auxiliary equipment form a complex and delicately integrated unit where mechanical or other failure can easily disturb the good functioning of it.

The equipment is running highly automatically and auto-correctively, onsite operator presence for maintenance and verification of the good functioning is limited in time.

When applying Perozone in an active industrial environment, it is very likely that third party and thus untrained persons may be working in the vicinity of the ISCO-machinery and infrastructure.

Chemicals with harmful properties are either produced (oxygen, ozone), stored (oxygen, peroxide) or extracted from the soil (polluting compounds), which needs an overall safe approach.

Because the in-situ treatment is an activity limited in time, the necessary temporary infrastructure and piping for applying Perozone will be installed in an industrial environment with high quality standards for piping and auxiliary equipment. Furthermore, the oxidizing compounds transported through the Perozone-ducting will generally not be compatible with the chemicals that are being stored and transferred in the facility. Therefore, any leakage presents a risk for dangerous chemical reactions.

When starting up the Perozone equipment, intensive surveillance and monitoring of all *modi operandi* need to be organized. Controlling and adjusting the equipment without onsite presence of a skilled operator is only allowed when a safe and stable working regime is attained.

The quality of the piping and its proper construction in the field, especially in the area where other chemicals are being stored or handled, is an important factor to reduce the chance of leaking. Weak spots such as nozzles and fittings should be located in areas with lesser risks in the event of product loss. Also regular visual inspection must be possible in an easy way.

It is a general practice in chemical plants to label any piping that contains utility products (air, nitrogen, steam, water) or specific chemicals. It is advised to adopt this method to mark the piping with ozone and peroxide, on every location where this can be useful.

A pipe burst in the injection system can be safeguarded by sudden pressure drop detection.

As any first emergency intervention will be performed by people that are not familiar with the operation of the equipment, there must be clear instructions clarifying the

risks persons may be exposed to. Accordingly these persons should be made acquainted to perform safely the necessary emergency actions to the equipment when a calamity occurs.

An emergency push-button must be placed on a well-chosen place, although a sudden power cut may damage the ozone-generating equipment.

All critical technical parameters that ensure a good operation are remote controlled and logged. Switching off the equipment is either self-induced or initiated by an operator.

A risk assessment of all possible calamities must be made. Preventive and mitigating measures have to be determined.

A monitoring program must be elaborated and applied, including frequent on-site checks with measuring equipment (pid, ozone, LEL) and inspection walks.

7. Conclusions

ISCO remediation by perozone on a chemical storage facility with EX-rated areas can be conducted safely if following conditions are respected:

- A optimised injection proces of perozone minimising the sparging of ozone and volatile organics to the soil vapour;
- A performant soil vapour extraction system enabling the removal of accidental excess of ozone in the vadose soil zone;
- An intensive monitoring program evaluating weekly to fortnightly the concentration of ozone, volatile organics or oxygen and explosion levels against threshold action values in the subsurface (monitoring wells, sewage system, vapour extraction wells and drains, soil vapour below steel tank bottom..) and ambient air (floor fissures, immision and emission of granulated activated carbon filters, above ground hydrogen peroxide pipes ...).

Applied project specified working instructions related to the health and safety related risks of the perozone treatment at the chemical storage facility of VOPAK are listed in the annex.

ANNEX 1: OVERVIEW OF WORK INSTRUCTIONS

1. INTRODUCTION

This annex summarizes the safety controls and tools applied in the LIFE Project. These controls and tools depend upon the injection and extraction system installed and the environment in which the system is operating. A pilot test has been conducted prior to the design of the full-scale remediation system (f.i. injections rate, radius of influence....)

Gaseous ISCO treatment by injection is always combined with a separate soil vapour extraction system to prevent uncontrolled emissions to the underground structures and ambient air.

2. UNCONTROLLED EMISSION

2.1 Oxidant injection system

Special injection wells (laminar sparge points at 2 m below groundwater level) were installed in a raster of 5 m by 5 m in order to simultaneously inject ozone gas and the fluid hydrogen peroxide.

The efficacy of the ISCO injection during operation is evaluated by periodically monitoring the ozone and VOC concentrations in the soil vapour of extraction wells and drains (see 1.3 monitoring).

Injections tests with the full scale remediation installation are performed in the beginning of the project in order to optimize the oxidant injection scheme. Following results were obtained and applied in the latter three years:

- ISCO Injection rate per 2 or 3 combined filters: 4 m³/hour
- ISCO mass load: 50 Nm³/hour and 120 ml/min 7% H₂O₂
- PLC controlled injection scheme of 10 injection phases of 2 minutes on 20 to 30 injection filters followed by a break of 4 minutes (total injection time per round is 24 minutes)

Provide a protocol for the start-up and shut down of the ISCO and SVE system for every contaminant zone

1.2 Soil vapour extraction

Soil vapour is extracted by vertical extraction wells in the tank park and by shallow horizontal drains on the road and storage facilities. Pavement was made air tight before or during the operation of the ISCO treatment by booting bursts and fissures or by renewing the concrete pavement.

The efficacy of the soil vapour extraction is evaluated by periodically monitoring the ozone and VOC concentrations in the soil vapour and ambient air, the pressure and flow in the extraction wells and drains (see 1.3 monitoring).

1.3 Monitoring

The intensive monitoring is a combined effort of the contractor, the commissioner and the accredited environmental office.

To evaluate field monitoring results, threshold action values for LEL (10%), Ozone (0.3 ppm) and oxygen (22.5%) were established indicating above which levels corrective actions should be undertaken. Exceedance of these threshold action values indicates that there is an uncontrolled emission to the soil vapour and ambient air (due to injection or to leakage of ozone or hydrogen peroxide). These threshold actions values are not based on safety regulations as such and should be determined individually for each specific situation.

Weekly monitoring at the tank park of volatile hydrocarbon concentrations, ozone and oxygen levels, explosions levels (LEL) by measuring with multi gas detection systems (including PID) in

- the soil vapour of groundwater monitoring wells; SVE wells and ISCO injection wells;
- the ambient air at the floor bottom of the casings of SVE wells and ISCO injection wells;
- the soil vapour of soil vapour monitoring wells with filter below above ground storage tank
- the ambient air underneath the monitoring wells covers;
- the influent and the effluent of the granulated activated carbon filters treating extracted soil vapour
- the soil vapour of the soil vapour extractions wells

Fortnightly monitoring at the concrete paved midway volatile hydrocarbon concentrations, ozone and oxygen levels, explosions levels (LEL) by measuring with multi gas detection systems (including PID) in

- the soil vapour of groundwater monitoring wells and ISCO injection wells;
- the ambient air underneath the monitoring wells covers;
- the head space of the sewage system traversing the contaminant plume
- the soil vapour in the extraction drains

Fortnightly monitoring at the extraction and injection control unit of the volatile hydrocarbon concentrations, ozone and oxygen levels, explosions levels (LEL) by measuring with multi gas detection systems (including PID) in

- the ambient air of the container with soil vapour extraction system
- the influent and the effluent of the granulated activated carbon filters treating extracted soil vapour

Fortnightly monitoring pressure and discharge flow in soil vapour extraction systems (SVE wells and drains) using pressure gauge and (manual) flow meters

Biannually monitoring the VOC concentrations in the groundwater of monitoring wells at the different contaminant zones;

3. CORROSION

The groundwater level in the injection zone is shallow (half a meter below surface). The project inventoried the known underground structures and the materials used in order to identify the risk of potentially damaging these pipes; conduits; (electrical and other) utilities or subsurface structures (f.i. steel bottom of the above ground storage tank)

Leak detection test of all installed piping for the injection of gaseous ozone and hydrogen peroxide solution.

Starting the ISCO injection is always proceeded by the soil vapour extraction with monitoring during at least one day.

The soil vapour extraction is maintained operational during at least one day following the shutdown of the ISCO injection.

Weekly monitoring of ozone concentrations in the vadose soil zone below the (steel) bottom of the above ground storage tank. Specially inclined vapour monitoring filters at the tank terp were installed.

On the occasion of the demolition of a very nearby stainless steel tank after some 3 years since the injection of Perozone started in this area, the bottom was inspected visually but revealed no asymmetric or even increased corrosion.

4. TEMPERATURE

ISCO Injection is plc controlled both limiting the ozone and peroxide load (50 mg/hour and 120 ml/min of 7% solution) and the injection time (2 minutes every 24 minutes);

5. FIRE/EXPLOSION

Increased concentrations of oxygen; ozone and organic compounds could result into spontaneous inflammation.

Conduct a multi-functional hazop safety check at an early stage of the project.

Application of ATEX guidelines where appropriate

Provide firefighting equipment on site

Optimisation of the perozone injection by conducting injection tests (see 1.1 oxidation injection system)

Indispensable to operate a remediation zone covering soil vapour extraction system and shut down immediately the injection and extraction system if ozone or hydrogen peroxide is leaking. (see 1.2 soil vapour extraction system)

Accurately monitoring the oxygen, ozone and VOC concentration in the soil vapour and ambient air of the treatment zone (see 1.3 monitoring)

Accurately monitoring the oxygen, ozone and VOC concentration in the soil vapour and ambient air of ISCO injection and vapour extraction equipment (see 1.3 monitoring)

Accurately monitoring the oxygen, ozone and VOC concentration in the influent and effluent of the GAC vapour treatment (see 1.3 monitoring)

The GAC vapour treatment is installed away from the ISCO injection unit and storage

Provide a protocol including a check list describing how the technical maintenance and intervention on the oxygen producing facility must take place

Provide a protocol on how burning GAC filters should be extinguished

Provide a protocol discussed by the commissioner, the contractor, the supplier on how hydrogen peroxide has to be delivered.

Continuous and in line LEL-monitoring of the extracted air

An in-line CO-monitoring device was installed on the exhaust-pipe of the GAC filters, to detect fire of the carbon bed at an early stage. The alarm would shut down the equipment and fill the filter body with water.

6. STABILITY OF EXISTING CONSTRUCTIONS

Trimestral monitoring of the potential subsidence of the above storage tank and infrastructure by an accredited land surveyor due to groundwater lowering or peat oxidation.

7. INSTALLATION AND OPERATION OF REMEDIATION INFRASTRUCTURE

Injections and extractions wells at the tank park are equipped with above ground casings to prevent infiltrations of chemicals to the subsurface if spills or (large) leakages are occurring.

Carefully perform risk analyses on the installation works of the remediation infrastructure taking into account potentially emergency situations in this project phase (such as accessibility of firefighting equipment at the tank park),

Strictly application of the regular safety requirements of EX-restricted areas such as presence of fire warden in EX rated zones during installation works or at deliveries of goods (f.i. GAC; hydrogen peroxide, ...)

Strictly wear personal protective equipment (PPE) according to regular safety protocols and remediation protocols (Chemical resistant hand gloves, hard hat, safety glasses, full body covering clothing etc)

8. MODI OPERANDI OF THE PEROZONE-EQUIPMENT

The progress of the project was discussed in recurrent meetings, participated by all parties involved. The settings of the equipment were adjusted based on the conclusions of these meetings.

9. FAILURE OF THE PEROZONE-EQUIPMENT ITSELF

The equipment was operated with remote control. Any failure or exceeding of a set threshold value initiated an alarm or induced a safe shut down of the unit when considered critical.

The equipment was placed within sight of camera surveillance.

A training was given to the company fire department how to approach the Perozone- and soil vapour treatment equipment in case of calamity.

An emergency switch to shut down the equipment was foreseen in an accessible spot, with safety consignments explaining what to do and who to contact.

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