



CHEMCO inc.

CANADIAN LEADER IN
ENVIRONMENTAL EXPERTISE
& SPECIALIZED PRODUCTS



Oxidant Selection and Activation - Keys to Successful Contaminant Destruction

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Presentation Outline

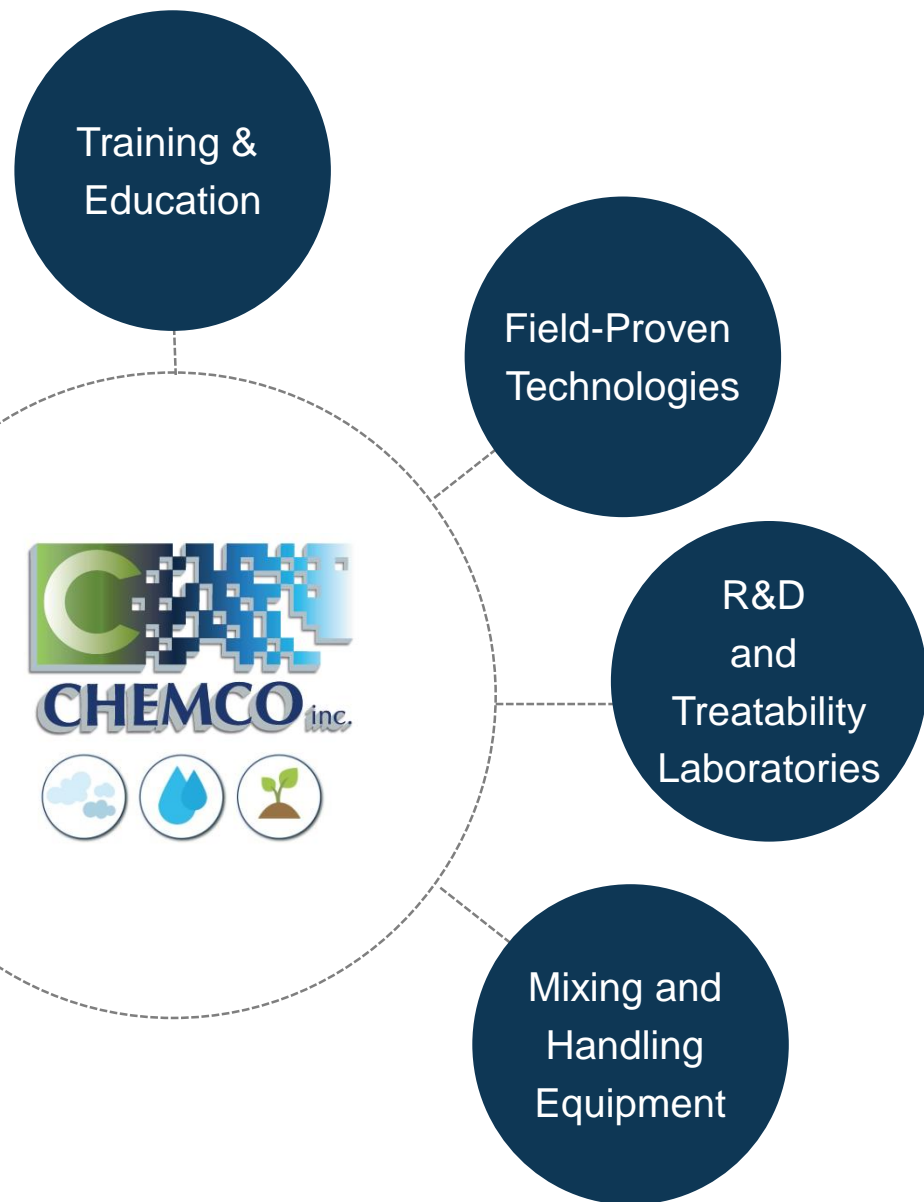
- *About us*
- *Chemical Oxidation – Technology Review*
- *Common Oxidant & Activation Mechanism*
- *Principle and Applicability*
- *Design and injection parameters*
- *Case Study*



About us

- Canadian Company founded in 1988
- **Production and warehouses throughout Canada**
 - Quebec
 - Ontario
 - Alberta
 - British Columbia
- **Sectors of activity:**
 - Industrial and Municipal Potable & Waste Water
 - Contaminated Soil and Groundwater
 - Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
 - Process Water & Thermal Exchange Fluids (Glycols)
 - Drilling Fluids (Oil and Gas & Diamond exploration)
 - Aircraft De-icing Fluids





CANADIAN LEADER IN
ENVIRONMENTAL EXPERTISE
& SPECIALIZED PRODUCTS

- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant Washing
- Enhanced Bioremediation

Our product and services



*Excellence & Science through proud
Suppliers & Partners*

ADVANCED OXIDATION TECHNOLOGY (AOT) *Since 2005*



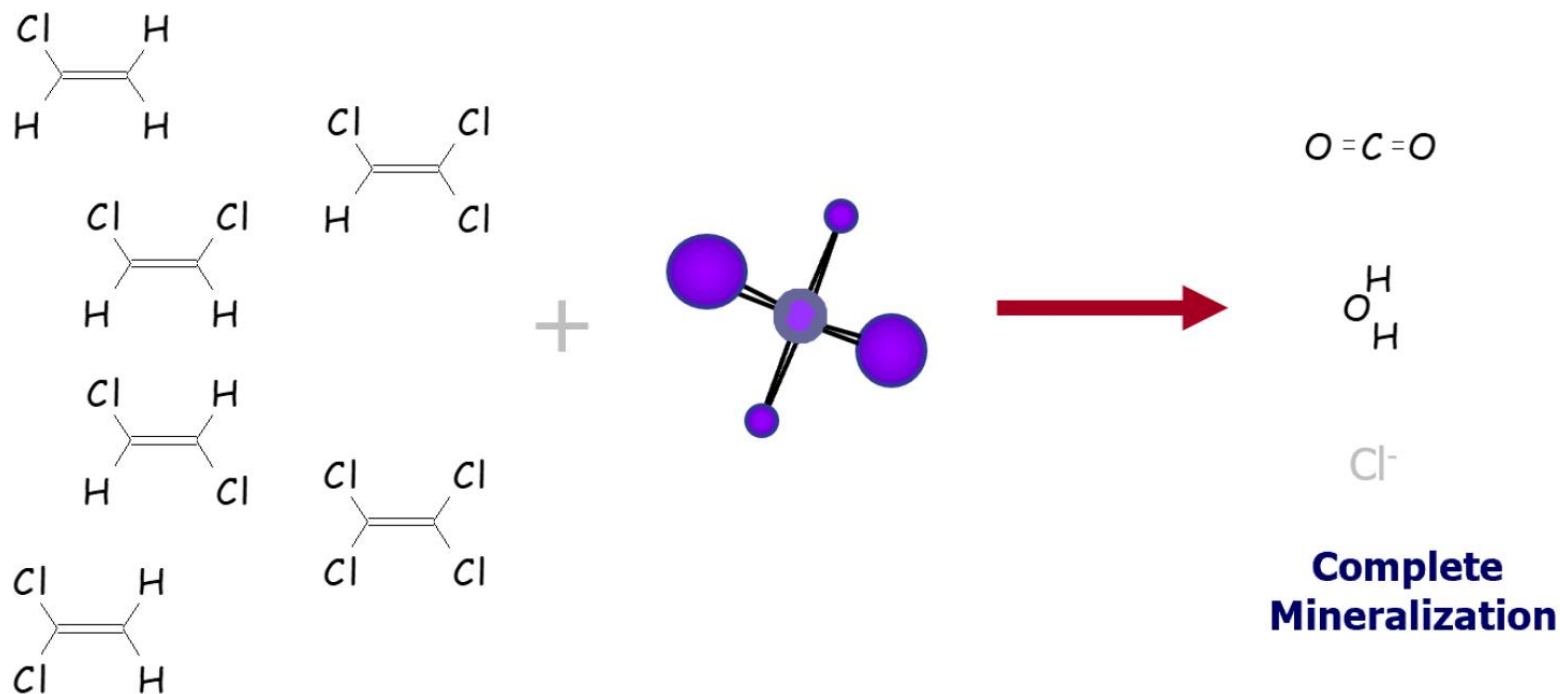
Chemical Oxidation – Technology Review

- Oxidants are introduced or mixed into the soil and groundwater to attack the organic contaminants
- Chemical oxidation treatments are commonly used in potable and wastewater applications
- Oxidants are non-specific and will react with the targeted contaminants AND with the soil organic content called Soil Oxidant Demand - SOD).
- Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- Water is the carrier for the oxidants used in chemical oxidation (except for ozone)
- If you have enough oxidant present and sufficient time you will push reaction to FULL mineralization (CO_2 , H_2O , Cl^-) of the contaminant of concern



Breaking of chemical bond

Chlorinated ethene destruction using permanganate



Chemical Oxidation – Limitations

- All chemical oxidation reactions occur in the **WATER** or moisture phase (except for ozone)
- Kinetics of the chemical oxidation reaction is thus influence by the **contaminant** of concern **solubility** and **availability** in the groundwater or moisture phase
- Sorbed phase contamination might be challenging to remediate (less available)
- In NAPL containing sites, contamination can persist because of the highly hydrophobic properties of the chemicals that make up the NAPLs
- Injection technique must induce **proper contact** between the contaminant and the oxidant for a proper **duration** for the required reaction to occurs (kinetics)



Additional considerations

- All oxidants can change the oxidation state of metals and thus increase their solubility and mobility
- Metals of particular concern are: chrome, lead, uranium, selenium, vanadium
- In most of these cases, the metals will come back in their reduced state once all of the oxidant has been consumed by the environment
- Impurities contained in the oxidant must be evaluated based on oxidant quality & site specific aquifer characteristics (Manganese, Sulfate, Sodium, etc.)
- In the case of arsenic, oxidation will help immobilizing the metal by reducing its solubility



Chemical Oxidation – Technology Review

Common Chemical Oxidants

- Potassium or sodium permanganate
- Hydrogen Peroxide
 - alone
 - with catalyst
 - with Retarding agents
- Ozone & Per ozone (hydrogen peroxide and ozone mix)
- Potassium or Sodium Persulfate
 - Requires activation to generate free sulfate radicals.
 - Heat, chelated metal, high pH, hydrogen peroxide, surface can be used to activate the persulfate. Activation method can be adapted to site conditions.
- Sodium Percarbonate



Compounds Degraded by Oxidants

Example Contaminants Treated by Oxidation

(not all ISCO reagents treat all compounds listed)

Chlorinated Solvents

PCE, TCE, DCE
TCA, DCA
Vinyl chloride
Carbon tetrachloride
Chloroform
Chloroethane
Chloromethane
Dichloropropane
Trichloropropane
Methylene chloride

Others

Carbon disulfide
Aniline
1,4-Dioxane

TPH

BTEX
GRO
DRO
ORO
creosote

Oxygenates

MTBE
TBA

Perfluorinated

Freon
PFOA, PFBA

Chlorobenzenes

Chlorobenzene
Dichlorobenzene
Trichlorobenzene

Phenols

Phenol
Chlorophenols
Nitrophenols

PAHs

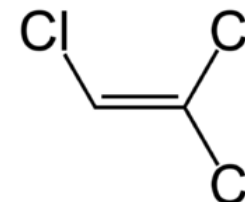
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
Trimethylbenzene

Pesticides

DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

Energetics

Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



Radical Formation Upon Activation

- Kinetically faster reacting radicals that are:
 - More powerful oxidants ($\text{SO}_4\bullet$ and $\text{OH}\bullet$) than persulfate itself
 - Reductants ($\text{O}_2\bullet^-$)
 - Nucleophiles ($\text{O}_2\bullet^-$ and HO_2^-)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($\text{OH}\bullet$)	2.59	Siegrist et al.
Sulfate radical ($\text{SO}_4\bullet^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($\text{O}_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Conditions for Selecting Chemical Oxidation

	Chemical Oxidation Applicability	Limitation / Disadvantages	Possible Alternative Options
Mobile NAPL	Probably not the best choice	High oxidant requirement (\$)	Multiphase Extraction Thermal degradation Soil Washing
Residual NAPL (higher than 10,000's mg/kg)	Yes, but difficult	High oxidant requirement (\$)	Extraction with air/steam injection Thermal degradation Soil Washing
High conc. in soil & groundwater (10's – 10000's mg/kg)	Yes, good conditions	Normal considerations	Extraction with air/steam injection Bioremediation
Dissolved plume (< 1 mg/kg)	Yes, but could be costly	Higher cost due to SOD	Bioremediation, Reactive barriers

Chemical Oxidation - Tools, testing and tricks

Before you get to the field

- Validating the qualification and quantification of the selected oxidant or amendment with bench scale lab study
- Soil and Groundwater Oxidant Demand validation and treatability study are ALWAYS recommended

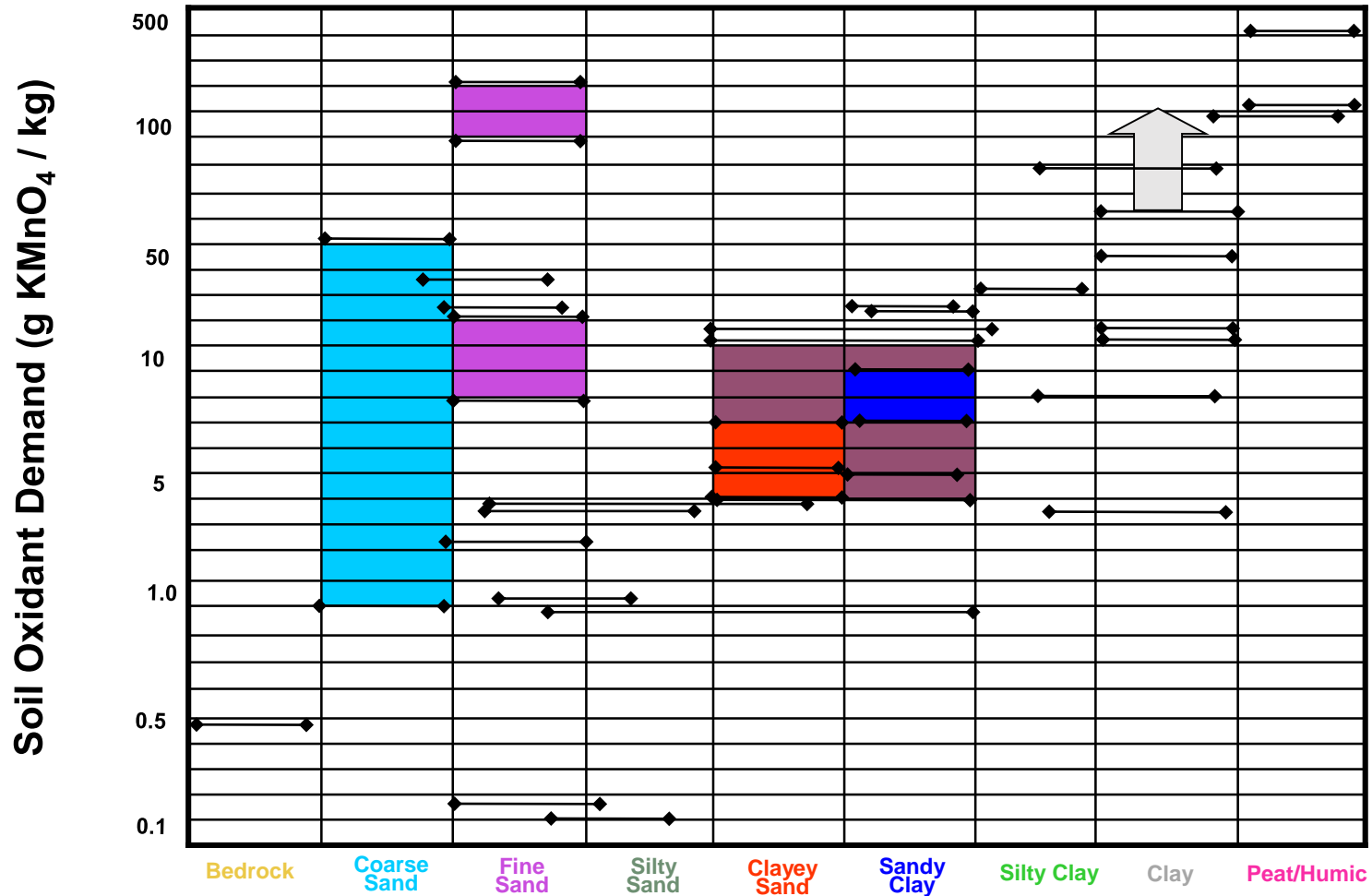
(If it doesn't work in the lab in ideal contact conditions it WON'T work in the field)

- Make sure you have all the necessary data and your injection plan is set properly



Natural Oxidant Demand (NOD) Variability

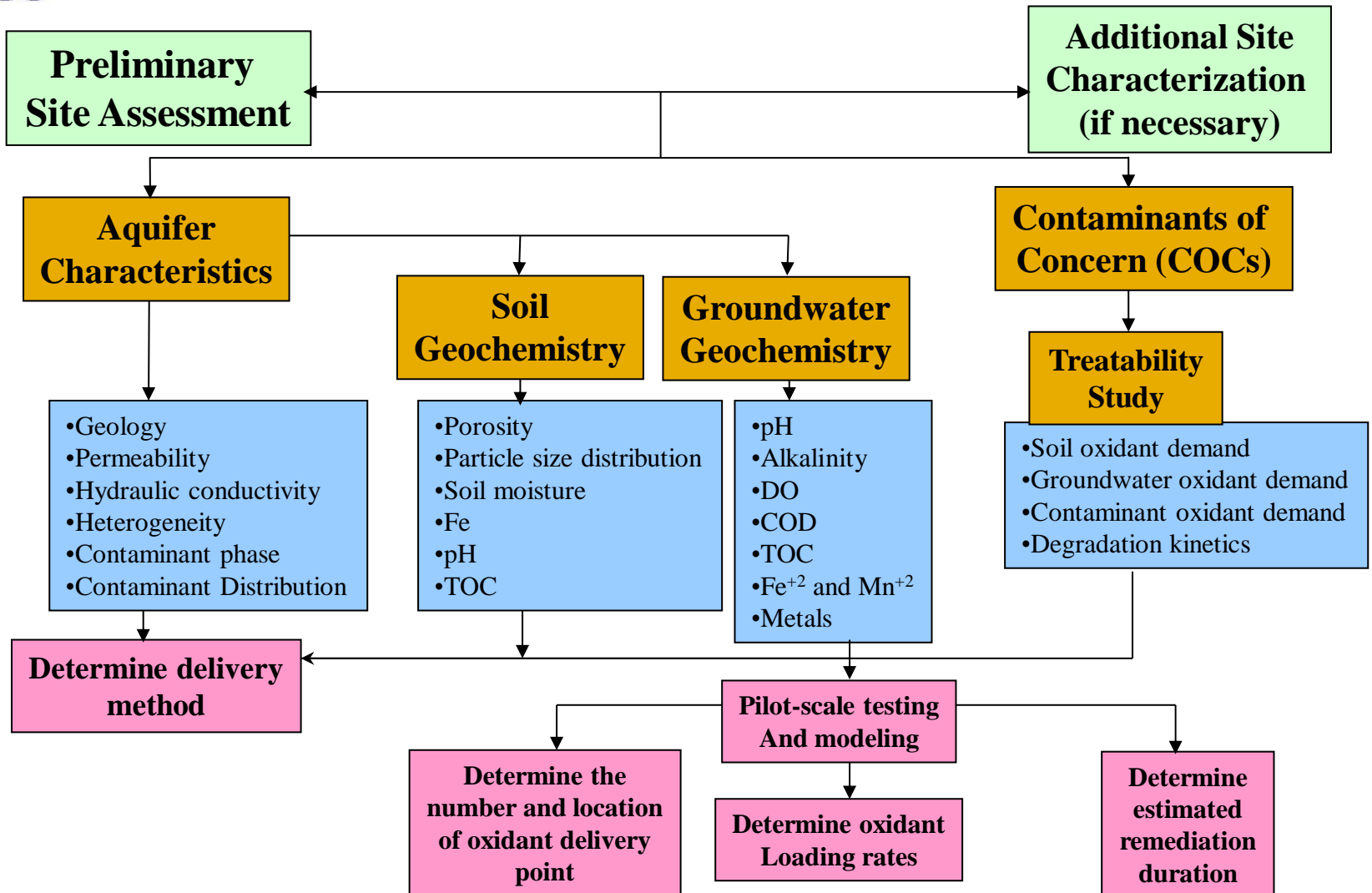
(adapted from Shaw E & I presentation - 2003)



Source: adapted from Shaw E & I presentation - 2003



Carus Haz Rem Assessment Process



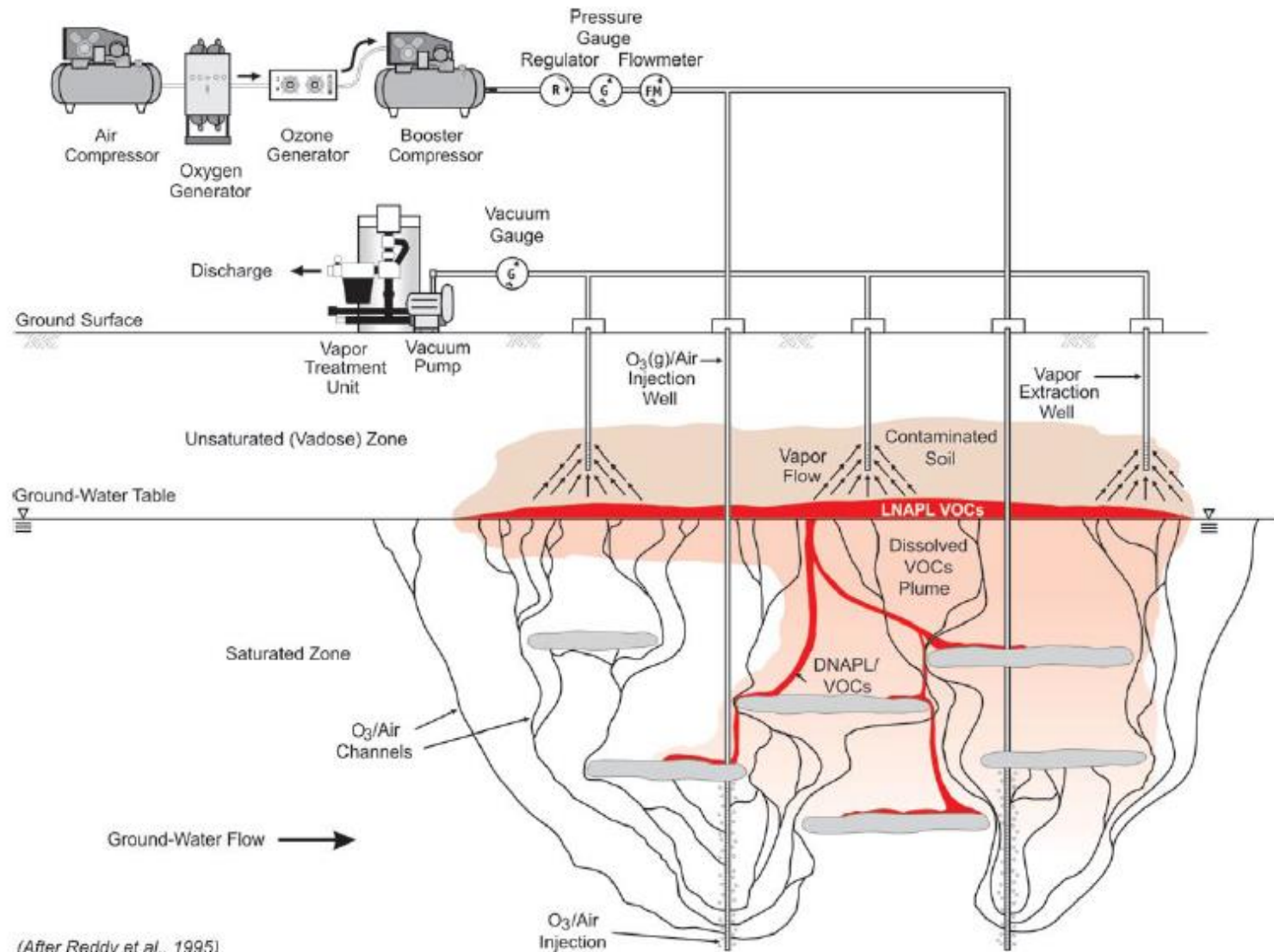
Ozone & Per ozone

Ozone Oxidation

- Ozone (O₃) is a gas that is generated On-Site
- Ozone is a very powerful Oxidizer
- Applicable Contaminants :
 - Chlorinated Solvents
 - PAH's, Chlorinated phenols
 - PCB's, pesticides
- Ozone is generated from Oxygen and degrades to Oxygen
- Since Ozone is a gas it is most ideal for Vadose Zone treatment vs. liquid oxidants
- Ozone/per ozone persistency is minutes to days



Ozone Oxidation



(After Reddy et al., 1995)

Ozone Oxidation Implementation

- Ozone generation systems
 - Continuous Pressure, output and flow
 - Pulsed Injection
 - Multi-level wells help ozone distribution
- Optimization of biodegradation co-process
 - Improve aerobic conditions
 - Co-metabolic microbial process enhanced by partial ozone oxidation (reducing toxicity)



Hydrogen Peroxide

Hydrogen Peroxide activation methods

Process:

- Hydrogen peroxide and Iron catalyst (or other species) can react to produce OH• (hydroxyl radical)
- Research showing that other radical species produced (super oxide anion, hydro peroxide, etc.) may be more active than the hydroxyl radical.

Basic Fenton reaction :



- Hydroxyl radical are non-specific oxidizing agents
- Contaminants are converted to H₂O, CO₂ and halides (Cl⁻)

Non desired reaction

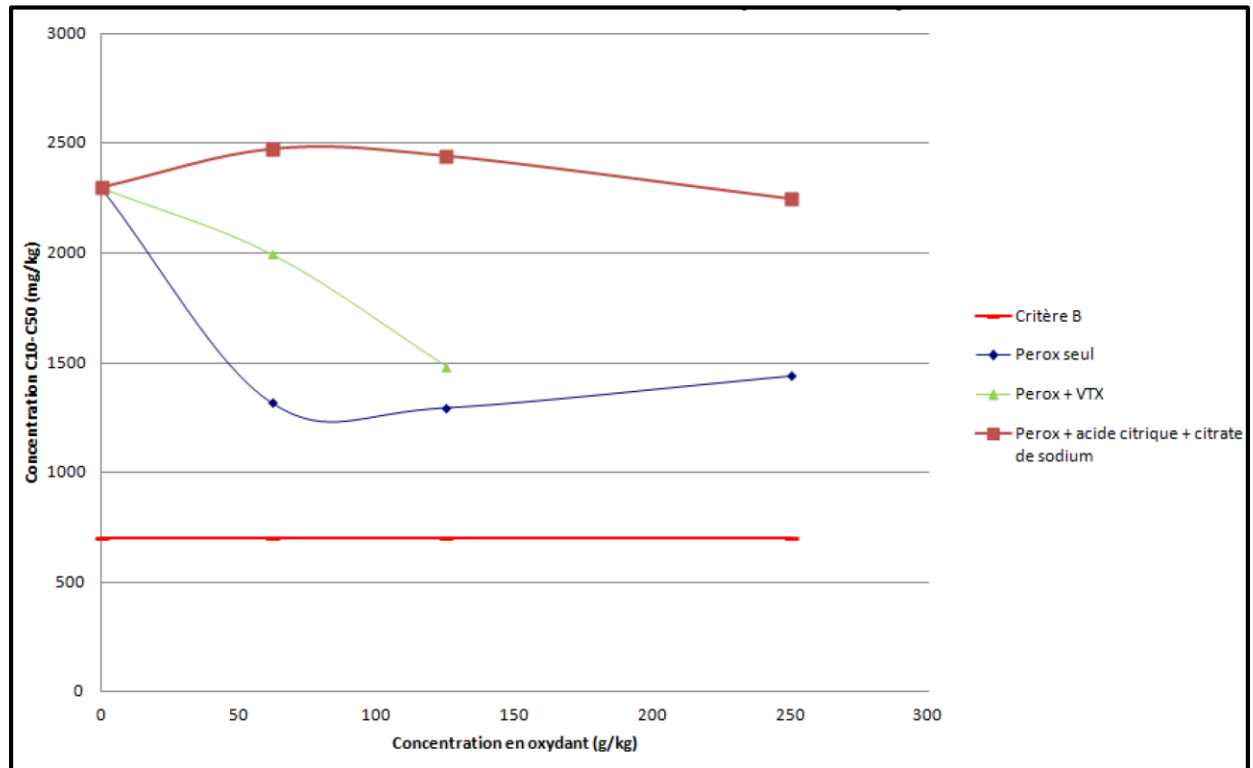


- This reaction can be induced by temperature, soil organic or mineral species (SOD dependant)

Hydrogen Peroxide activation methods

Variations:

- Hydrogen Peroxide with iron (regular Fenton reagent reaction)
 - Need to establish acidic conditions (ideal pH between 4 and 6)
 - Might enhanced metal mobilization
- Modified Fenton Reagent with chelated metals (neutral pH)
- Use of Retarding agent to help minimize heat and oxygen degradation pathway
- Treatability Bench Scale study always recommend



Source: ITRC, 2004

Chemco, 2017

Sodium & Potassium Permanganate

Sodium and potassium permanganate

Sodium Permanganate

- Liquid
- Available up to 40 %
- Less complex injection equipment
- Smaller injection volumes
- Lower injection time
- Higher cost than potassium

Potassium Permanganate

- Powder (dust issue)
- Soluble to 3 % (field)
- More complex injection equipment
- Higher injection volume
- Longer injection time
- Less expensive than sodium



Sodium and potassium permanganate

Single Component Oxidant

- Complete mineralization of chlorinated ethenes and others
- Complex mixing and distribution of multiple compounds is not necessary
- No activation or catalyzing
- Total volume of fluids injected reduced
 - Potential reduction of injection costs and/or short circuiting

pH

- No need to adjust pH for application
- Reduced corrosion effects in injection equipment and utilities and structures

Chemical Persistence

- Advection and diffusion main transport mechanism
 - Not pressure and reaction dependent
- Long-lasting oxidant
 - Treat compounds desorbing from matrix
 - Diffuse into tight matrices

Color

- No tracer required



Permanganate (sodium or potassium)

Implementation

- Effective from pH (3 to 12, optimum 7) for desired chemical interaction
- High density (around 1.3) helps distribution and penetration
- Long reaction times allow higher distribution distance and better desorption processes thus low contaminants residual value obtainable
- Applicable in many soil types.
- Possibility to sequester the solid Manganese Dioxide (MnO_2) by pre-mixing polyphosphate & permanganate prior injection.

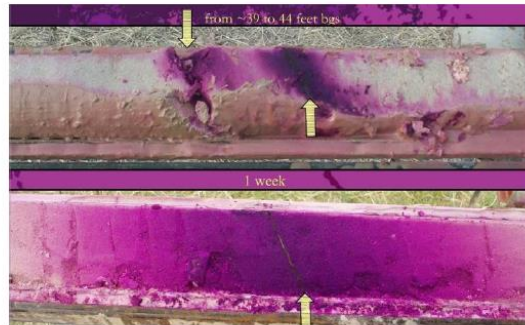


Permanganate (sodium or potassium) Application

Injection



Hydraulic Slurry Emplacement



Soil Blending



Permanganate Benefits

More Effective

- Low treatment endpoints (e.g. MCLs)
- Rapid treatment (< month)
- High density enhances delivery
- High stability
- Longer transport distances
- Effective in all geological media
- Diffuses into low permeability zones
- Easily scalable
- Reaction not pH sensitive

Safety

- Avoids DNAPL remobilization
- No heat generation
- Non-corrosive
- No hazardous gas generation
- Less intrusive/impact
- Non-hazardous by-products
- Spent solution may be sent to WTP
- Not harmful to bio-systems (non-toxic)
- Color indicator (Un-reacted solution is purple)



Sodium Percarbonate

Sodium Percarbonate (RegenOx)

- Requires activation to generate free radicals
- Patented technology using an activated sodium percarbonate
- Applicable to many type of contaminant (petroleum hydrocarbon, chlorinated solvents, ethanes)
- Minimal heat and gas generation
- Extended pH application range (alkaline solutions around pH 10 for initial injection)
- 2 components injection – one of them a slurry
- Low solubility for the sodium percarbonate

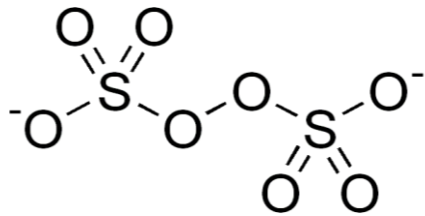
Source: Regenesis



Sodium & Potassium Persulfate

Sodium or Potassium Persulfate Portfolio

All Klozur products release the persulfate anion:



Key Characteristics:

- A strong oxidant
- Activation results in the formation of radicals
- Applicable across a broad range of organic contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no heat or gas evolution
- Potential low corrosivity on carbon steel (alkaline activation)
- Applicable in an Oxidative Permeable Reactive Barrier

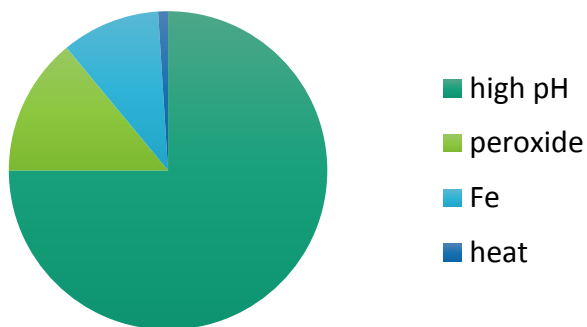
Persulfate activation methods

- Activation method can be adapted to site conditions. Proper activation for your contaminant vs. site lithology and hydrogeology
- Possible one system injection with the mixing of the activator and oxidant prior to the injection



Persulfate activation methods

Estimated Activator Usage



- Zero Valent Iron
 - Solid state activator
 - Oxidative pathway

Purchase of Klozur persulfate includes with it the grant of a limited license under Peroxychem's patents covering the use of Klozur persulfate for environmental applications at no additional cost to the buyer

- Alkaline Activated Persulfate
 - Well suited for most applications
 - More compatible with carbon steel
 - Reductants, oxidants and nucleophiles
- Iron-Chelate Activated Persulfate
 - Chlorinated ethenes and hydrocarbons
 - Oxidative pathway
- Heat
 - Complex sites
 - Polishing step after thermal treatment
 - Reductants, oxidants and nucleophiles
- Hydrogen Peroxide
 - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate
 - Reductants, oxidants and nucleophiles
- Surface Activation
 - Silica Gel matrix
 - Could be injected as a slurry

Persulfate Heat Activation Mechanism

Heat



Compound with > 90% decomposition treated with persulfate

20 °C	35 °C	45 °C
Toluene	Benzene	1,1,1-TCA
Ethylbenzene	Chlorobenzene	Chloroform
Xylene	1,2-DCE	Methylene Chloride
1,1-DCE	PCE	
1,2-Dichlorobenzene	TCE	
1,3-Dichlorobenzene	1,1-DCA	
1,2,4-Trichlorobenzene	1,2-DCA	
	MTBE	
	Vinyl Chloride	
	Carbon Tetrachloride	

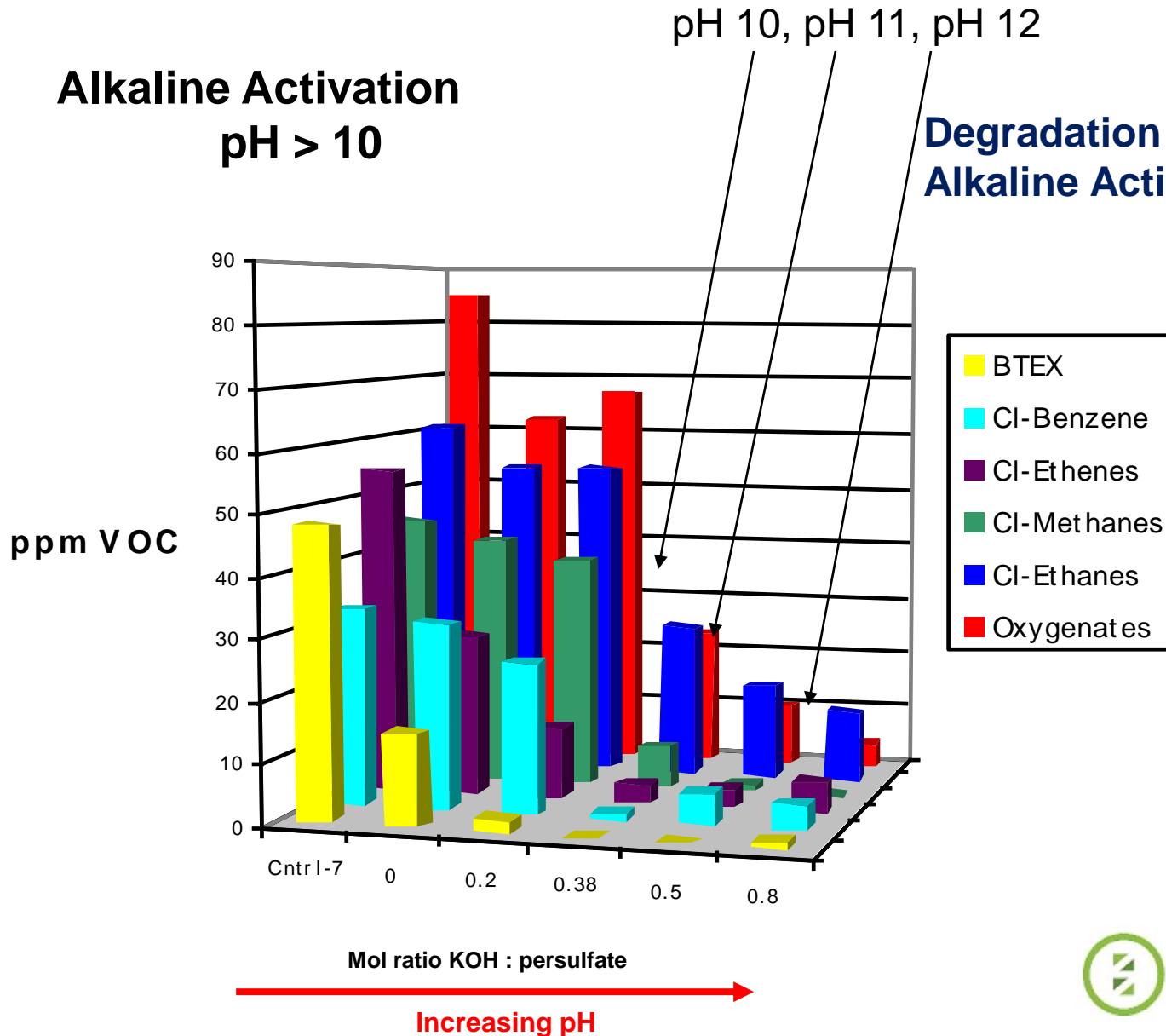
Aqueous solutions - lab data; 72 hour

- **Advantage:** high oxidation potential with many compound with enough energy supply
- **Disadvantage:** might be costly in field application

Persulfate Alkaline Activation Mechanism

Alkaline Activation
pH > 10

Degradation of COC Utilizing
Alkaline Activation



Persulfate activation methods

- **Klozur CR (Combined Remedy)**

50 % sodium persulfate with 50 % Perme-Ox Ultra (alkaline activation) with enhanced bioremediation

- **PersulfOx**

90 % sodium persulfate with 10 % Silica Gel (surface activation)

- **Klozur One**

95 % sodium persulfate with 5 % activator package (multiple activation method)

Klozur One is the only fully water soluble all-in-one product

- **Source: Peroxychem / Regenesis**

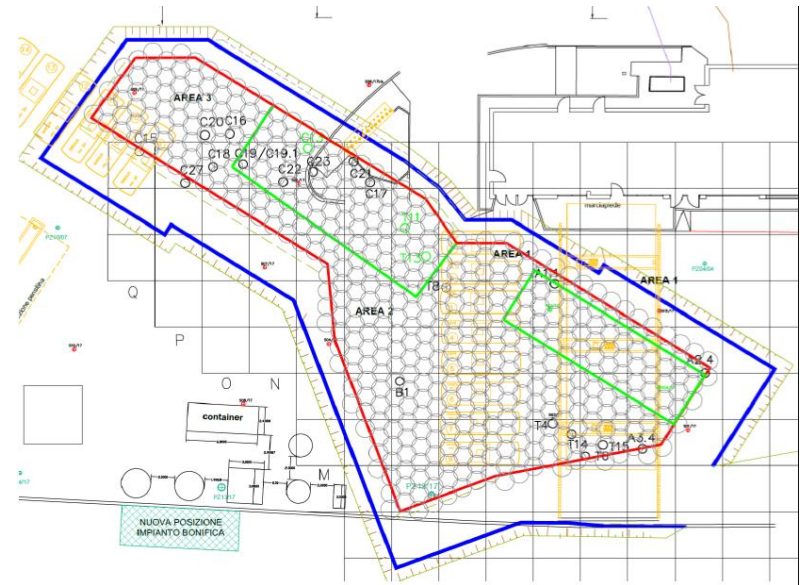


Case Study 1

Combining ISCO with ISS

Case Study: Bolzano, Italy

- Treatment volume:
 - 3,500 m³ (~4,600 yd³)
- Depth:
 - 3 to 8 m bgs (9.8 to 26 ft bgs)
- 556 columns
- Excavation could have caused slope stability issue because of nearby structure
- Reagents
 - 0.7 to 1% Klorox
 - 4 to 8 percent Portland cement
- Treatment speed:
 - 37 MT/hr



Courtesy of Ladurner

Remedial Goals

- Contaminant reduction • Stable (compressive strength)
- Eliminate free product • Minimize waste generation
 - Normal fluff generation will vary between 6 % up to 18 % w/w



Auger Based ISCO-ISS



Bolzano, Italy
Courtesy of Ladurner

Results

ISS Remedial Goals:

- UCS:
 - 215 kPa to 470 kPa
 - ~30 psi to ~70 psi
- Permeability:
 - 2.8×10^{-6} cm/sec to 7.3×10^{-7} cm/sec

**Less than 15% bulking of
Soils**

ISCO Remedial Goals:

- Benzene:
 - 100% sample locations below 2 mg/Kg remedial goal
- TPH (C<12)
 - 100% sample locations below 250 mg/Kg remedial goal
- TPH (C>12)
 - Some free product observed
 - Some TPH (C>12) above goals

Summary

- Remediation and soil stabilization in a single application
- Site was suitable for construction shortly after the application (1-2 weeks)
 - Is now a parking lot with other structures
- ISCO-ISS addresses several issues versus ISS only
 - Less excess soil requiring disposal
 - Carbon footprint decreased
 - Contaminant destruction
 - Contributes to lower leachate concentrations

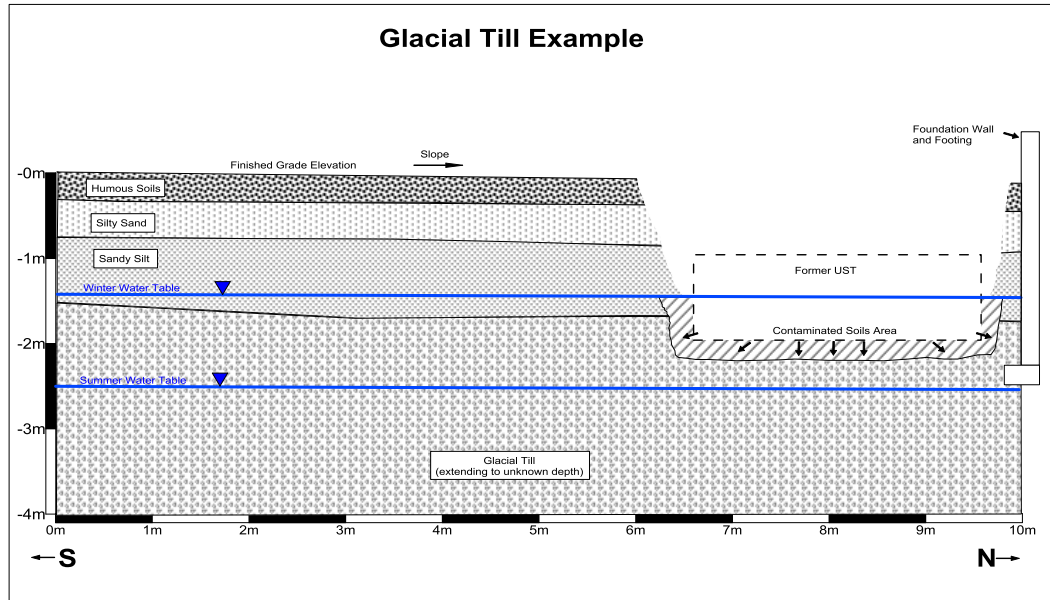
Case Study 2

Tight Geology Application

Insitu Chemical Oxidation (ISCO) and Bioremediation in the Complex Geologies of the Lower Mainland of B.C.



Application of Sodium Persulfate / Calcium Peroxide in Glacial Till



- Given the yearly variation in water table depth there is often a small amount of contaminated soils that are above the water table.
- Holes are drilled into the excavation area for injection after mixing or the sodium persulfate / calcium peroxide can be mixed and poured directly into an open excavation or pressure injected or mixed into the soil.
- This creates an infiltration gallery effect where water is applied, especially in summer when lower water table conditions prevail.

Source: Ventus Consulting

Pressure injection Application



- Ventus employee makes up a soil watering probe with ½ inch steel threaded pipe.
- Holes are probed into the soils above the glacial till while the pressure jet nozzle of the watering probe mixes the sodium persulfate calcium peroxide with soils.

Source: Ventus Consulting

Open Excavation Soil Mixing Application



- Probe holes close up show additional bubbling where compound has contacted soils contamination.
- Often if we want to speed up the reaction of the compound we add additional water with the watering probe.

Source: Ventus Consulting

Borehole Application



- Injection holes are dug on very narrow spacings and overfilled in sandy conditions.
- In all soils conditions a very narrow spacing of injection holes or application to an underground storage tank (UST) nest before backfilling is preferable.

Application of Sodium Persulfate / Calcium Peroxide Least Expensive Option



This \$2500 project was completed with injections April 19, 2018 and final samples May 3, 2018 so the project only took some 3 weeks after application. We were able to obtain a further soils sample from the formerly impacted soils area during construction of a garage onsite, allowing collection of the June 22, 2018 sample.

Concentration reductions in soils by late June would be due to both ISCO and bioremediation, dates much later would have predominant bioremediation occurring.

Source: Ventus Consulting

Summary

Chemical Oxidation Applicability

■ Using Common Oxidants

- Source zone treatment
 - Highly soluble
- Great for GW contamination
- Oxidative and reductive pathways possible
- Aqueous Solution Injection
- Direct Push / Fracking emplacement for slurry
- Soil Mixing for tight geology or open excavation

■ Slow release Oxidant

- Permeable Reactive Barriers set up and low permeable soil treatment
- Solid/slurry injectate
- Oxidative and reductive pathways

■ Oxidation/Bioremediation Combination

- Combined remedy of ISCO followed by bioremediation
- Solid/slurry injectate



Acknowledgement

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