



20 years using Persulfate in remediating Soil and GW – Do's and Don'ts

Remtech 2023

Banff, AB, Canada

Presented by

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Presentation Summary



- ✓ **About us**
- ✓ **Oxidation Chemistry Fundamental**
 - *Persulfate Activation Mechanism*
 - *Targeted Contaminant*
- ✓ **Evolution of Persulfate and Lessons Learned**
 - *Combining In situ soil stabilization with In situ chemical oxidation*
 - *Low solubility Oxidant used as PRB Media*
 - *Combining ISCO and Bioremediation*
- ✓ **Conclusions - Do's and Don'ts**



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



Our Services



Specialized Products

- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant soil Washing
- Enhanced Bioremediation
- Permeable Reactive Barrier Amendments
- Metals Stabilization
- Activated Carbon Technologies





Excellence & Science through proud Suppliers & Partners



ADVANCED OXIDATION TECHNOLOGY (AOT) *Since 2005*





Typical site remediation technique



- ✓ Dig & Haul
- ✓ Pump & Treat
- ✓ Soil Vapour Extraction under vacuum with or without air/steam injection
- ✓ Chemical Oxidation In Situ/Ex Situ
- ✓ Chemical Reduction In Situ/Ex Situ
- ✓ Monitored Natural Attenuation
- ✓ Activated Carbon Sorption & Treatment Technology
- ✓ Enhanced Bioremediation
- ✓ Risk Analysis
- ✓ Stabilization/Solidification
- ✓ Soil Washing
- ✓ Phytoremediation
- ✓ Reactive Barriers
- ✓ Thermal degradation/desorption



In Situ Technologies – Key Drivers



- ✓ **Improvement of contaminant removal rate** versus natural attenuation
- ✓ Remedial objectives - **Time versus Money**
- ✓ **Access to the contaminant** of concern (underground infrastructure, public utilities, building, road, etc.)
- ✓ **Polishing step to meet low remedial objectives or Risk-Based Criteria**
- ✓ **Sustainable Development** Contribution versus remote off-site disposal, environmental footprint, air emission from trucking, etc.)

In Situ / Ex Situ Chemical Oxidation



In Situ Chemical Oxidation: Introduction

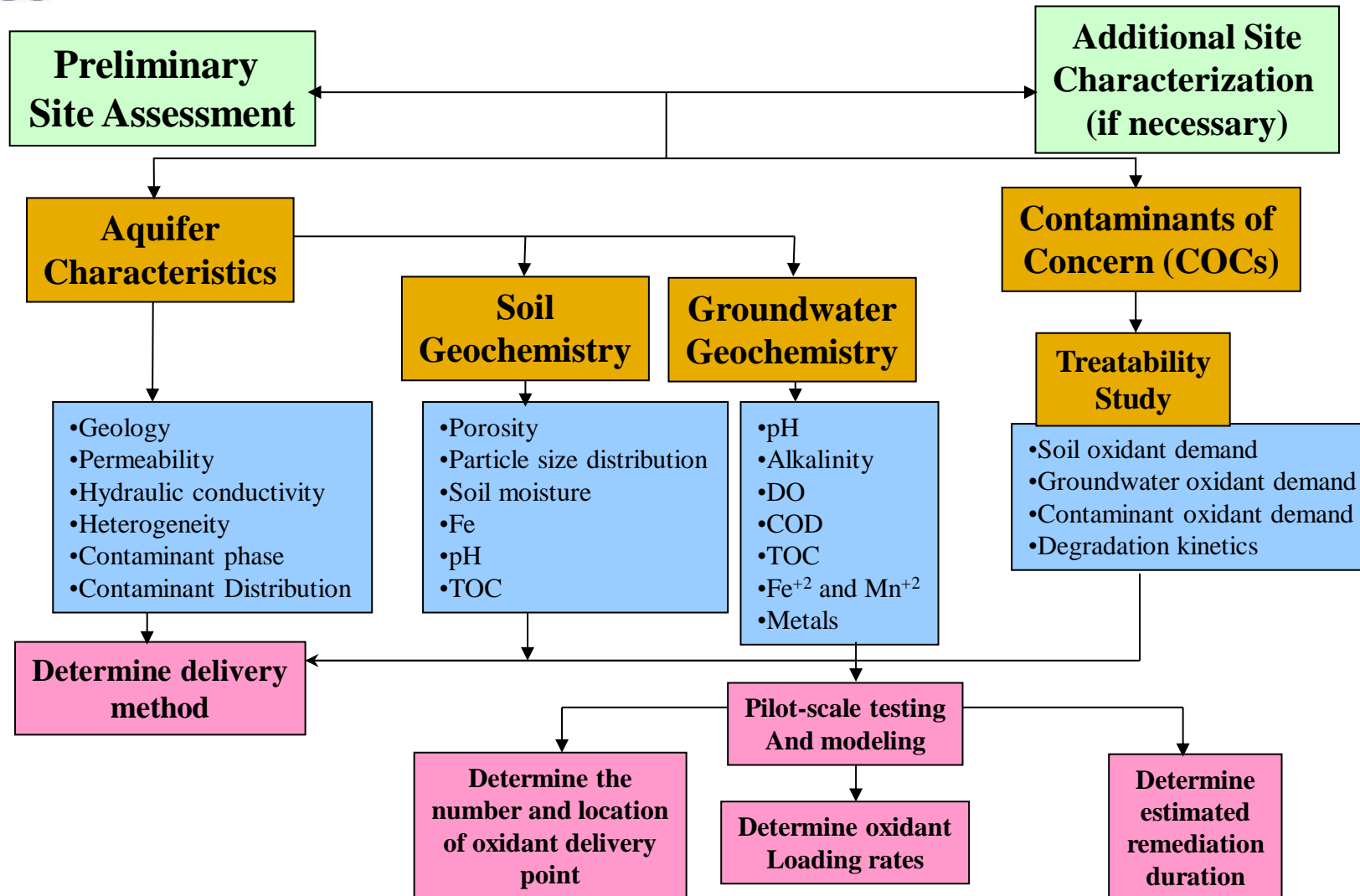
- ✓ In Situ Chemical Oxidation (**ISCO**) commonly refers to remedial technologies that **react and destroy** organic contaminants primarily using an abiotic oxidative **chemical pathway**.
- ✓ Oxidants are introduced or mixed into the contaminated soil and/or groundwater to attack the organic contaminants
- ✓ Typically, ISCO reagents include **hydrogen peroxide, ozone, percarbonate, permanganate, and persulfate**
- ✓ **Water is the carrier** for the oxidants used in chemical oxidation (except for ozone)
- ✓ **Contaminant solubility** might limit rate of destruction (S-ISCO)
- ✓ **Oxidants are non-specific** and will react with the targeted contaminants AND with the soil organic and/or mineral soil matrix content Soil Oxidant Demand - SOD).
- ✓ Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- ✓ If you have enough oxidant present and sufficient time you will push the destruction toward to **FULL mineralization (CO₂, H₂O, Cl⁻)** of the contaminant of concern

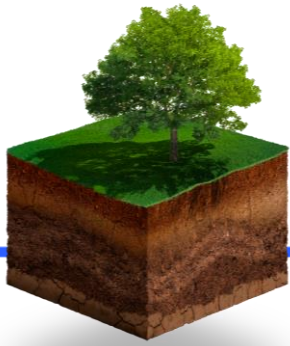
Conditions for Selecting Chemical Oxidation

	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 or 1 ug/l)	Yes, but could be costly	Higher cost due to SOD	Bioremediation, Reactive barriers



Carus Haz Rem Assessment Process





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^-)

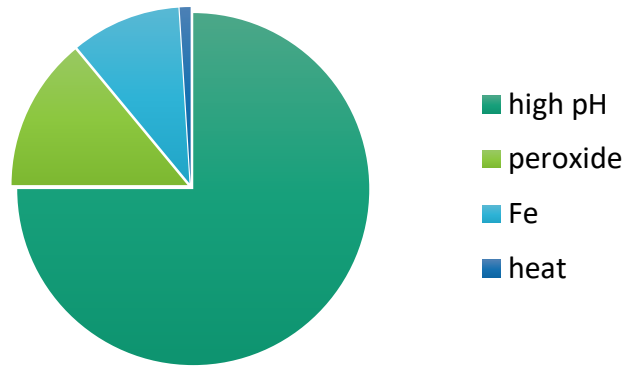
Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($\text{OH}\bullet$)	2.59	Siegrist et al.
Sulfate radical ($\text{SO}_4\bullet^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist 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)

Persulfate activation methods

Adaptive activation mechanism



Estimated Activator Usage



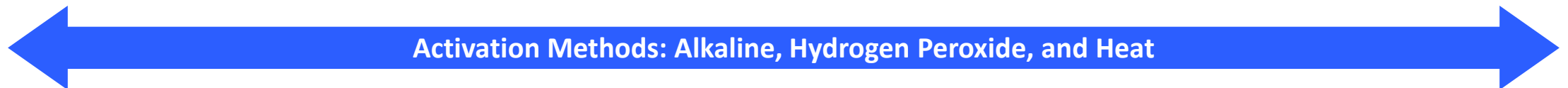
Purchase of Klozur persulfate includes with it the grant of a limited license under Peroxychem' S patents covering the use of Klozur persulfate for environmental applications at no additional cost to the buyer

- **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
 - Possibility to use Zero Valent Iron (solid state activator)
- **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 Contaminant Degradation Pathways



Petroleum Hydrocarbons	PCE, TCE, DCE and VC	Carbon Tetrachloride
MGP Residuals	Chlorobenzenes	1,1,1-Trichloroethane
BTEX	Chlorophenols	Dichloroethanes
PAHs	Select Pesticides	Select Pesticides
Oxygenates	Select Fluorinated Compounds	Select Energetics
1,4-Dioxane	PCBs	
	Select Energetics	





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

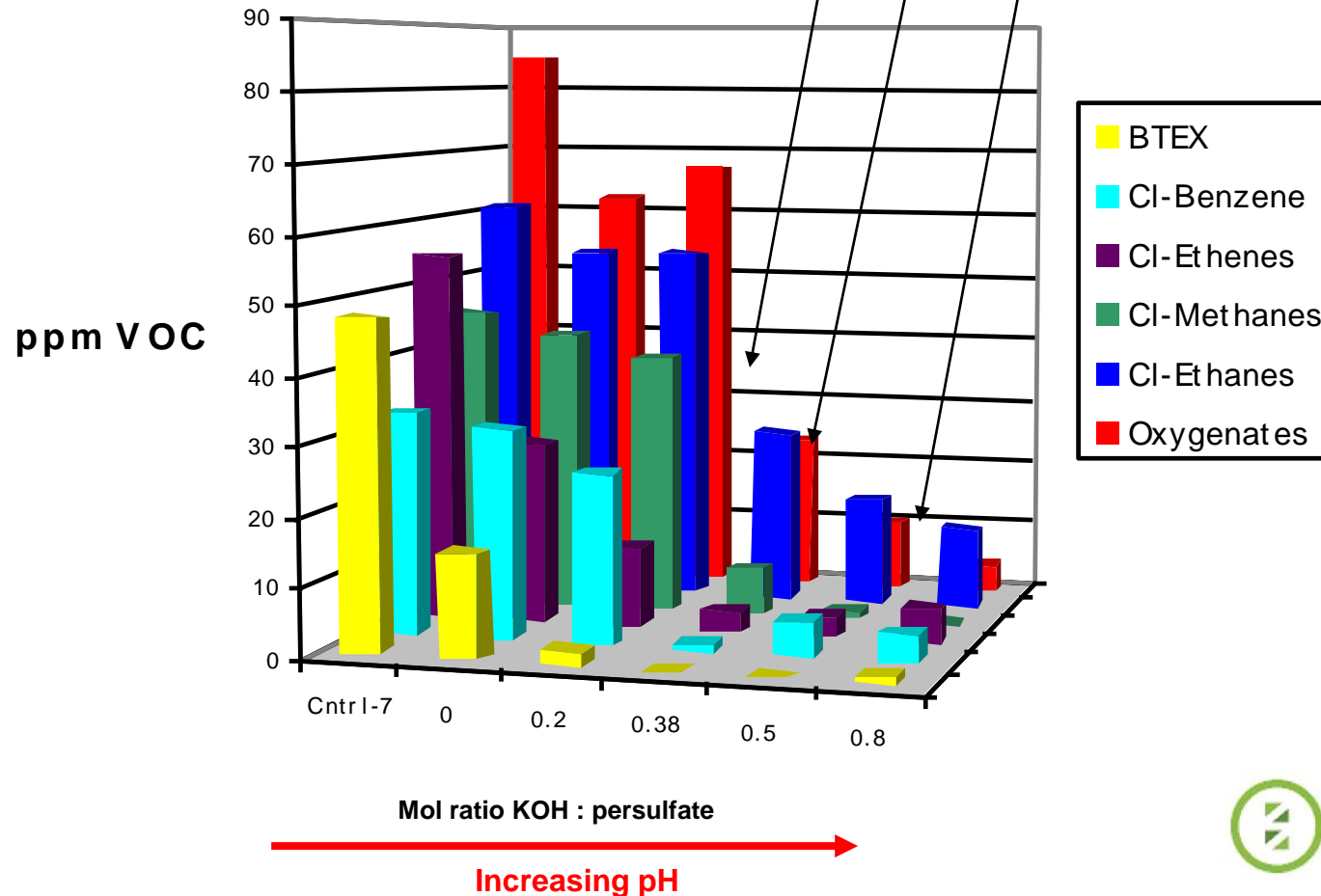


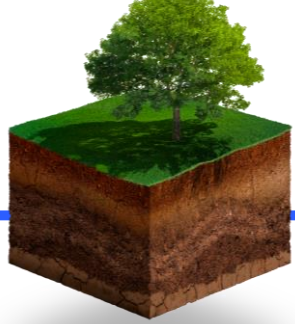
Persulfate Alkaline Activation Mechanism

Alkaline Activation
pH > 10

pH 10, pH 11, pH 12

Degradation of COC Utilizing
Alkaline Activation





Persulfate activation methods

ALL IN ONE – SELF ACTIVATING PRODUCT

✓ **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**

Evolution of Persulfate chemistries

Combining In situ soil
stabilization with In situ
chemical oxidation
ISS-ISCO



In Situ Solidification-Stabilization (ISS)

- Contaminant **immobilization or mass flux reduction** (used for metals and organic leachable species)
- **Stabilization** - Decreases the hydraulic conductivity of soils
- **Solidification** - Compressive soil strength influenced by type and dose of reagents
- Applied via soil mixing/blending

ISS is commonly used to immobilize highly contaminated petroleum hydrocarbon sites (MGP sites, etc)



In Situ Chemical Oxidation (ISCO)

- In situ chemical oxidation (ISCO)
- Powerful destructive remedial technology
- Applied via injection, recirculation, backfill amendment, and soil mixing
- Alkaline activated persulfate
 - Thousands of successful applications
 - Oxidative and reductive destructive pathways
 - Complex comingled plumes
 - Minimized corrosivity on carbon steel equipment & underground infrastructure
 - Little to no heat or gas evolution

ISCO works by establishing contact between a sufficient mass of activated persulfate and the mass of contaminant



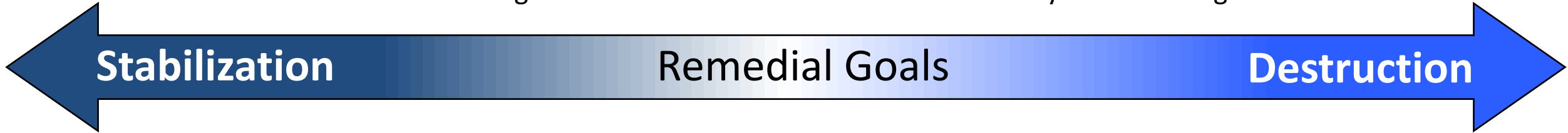
ISCO applied via Soil Mixing

- **ISCO with Soil Mixing**
 - Establishes contact
 - More rapid treatment
 - Homogenizes soil and contaminant
 - Minimizes impact of heterogeneity
 - Low permeable soil
- Some sites have reported **very soft soils** post soil mixing



ISS-ISCO Reagent Ranges

ISCO and ISS reagent doses can be varied to achieve a variety of remedial goals



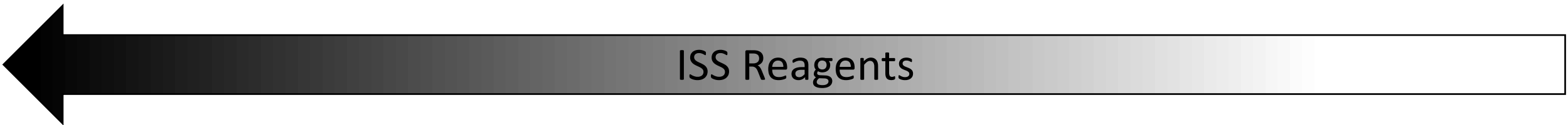
ISS

ISS with ISCO

ISCO-ISS

ISCO with ISS

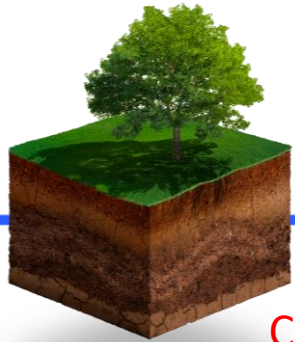
ISCO





Remedial Objective - Where to Use ISS and ISCO

- **Source zones**
 - Very highly contaminated sites (NAPL)
 - Petroleum hydrocarbon (MGP, etc.)
 - cVOC
- **To create hydraulic barriers**
 - Lower hydraulic conductivities observed in ISS with ISCO rather than ISS alone
- **Soil mixing application strategy**
- **Enhanced Site soil characteristics**
- **Balance contaminant destruction, solidification, and post application**

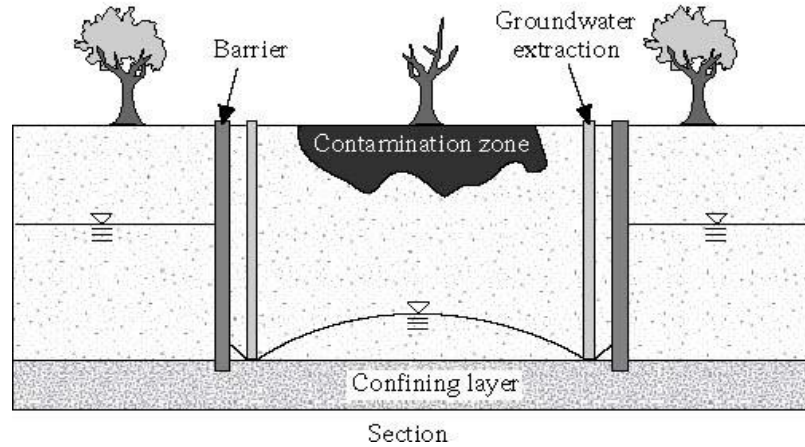


ISS & ISS-ISCO - Deployment Options

Circumferential



Plan view

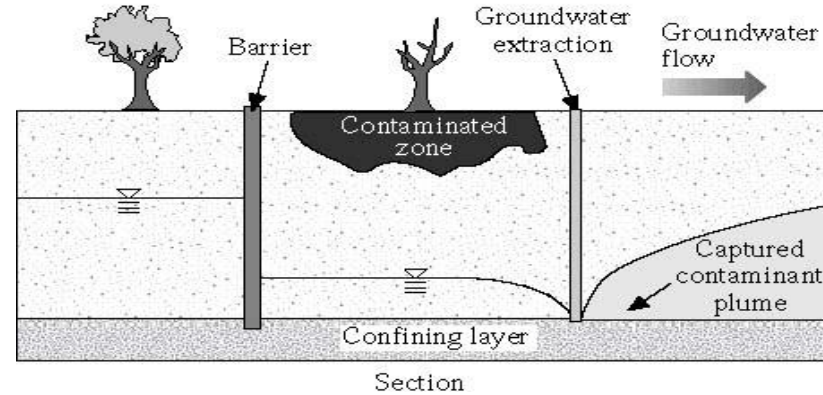


Section

Upgradient

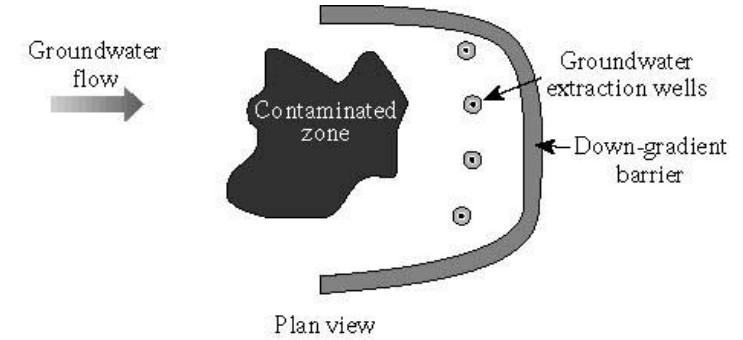


Plan view

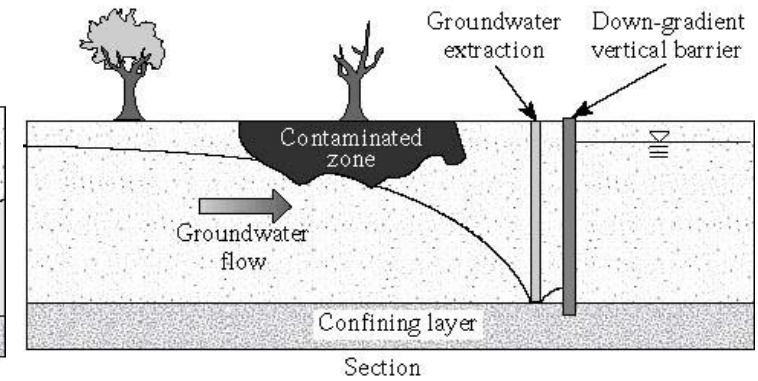


Section

Downgradient



Plan view



Section

TECHNOLOGY EVOLUTION - ISS and ISCO



ISCO-ISS
Bolzano, Italy
Courtesy of Ladurner



Technological Synergies of ISCO and ISS

Combining ISCO and ISS can make each technology better

ISCO benefits:

1. Alkalinity from ISS reagents can be used to **activate** Kloxur SP

Soils can have their geotechnical characteristics enhanced with low amounts of ISS reagents

ISS benefits:

3. **Contaminant destruction** by ISCO can enhance stabilization from ISS

Helps the cementitious process

Less contaminant to immobilize = lower leachate concentrations

4. Less overall mass of reagents results in **less excess soil generation**

5. Better **balance between hydraulic conductivity and compressive soil strength**

Contaminant destruction and immobilization in single soil mixing application (combined remedy)

6. **Saving project time and overall cost**

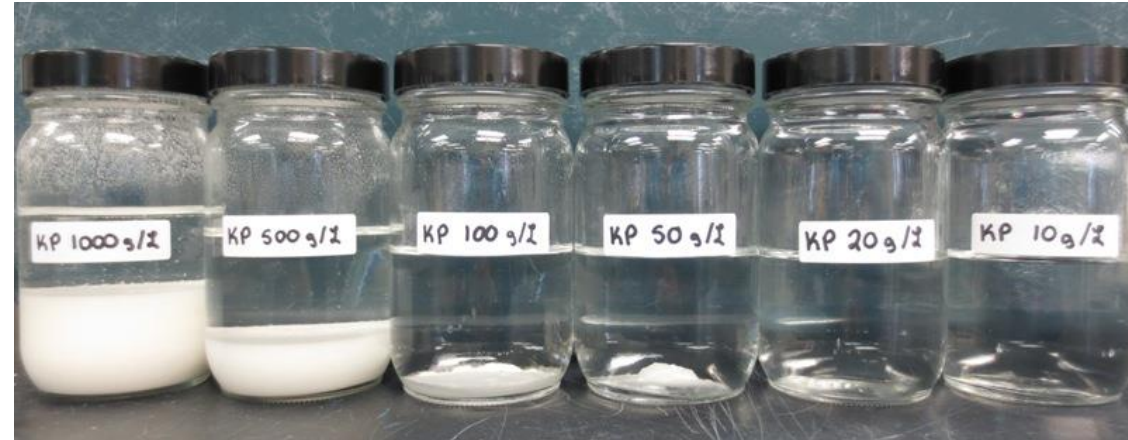
Low solubility Oxidant
used as PRB Media



Solubility Limited Release Static System

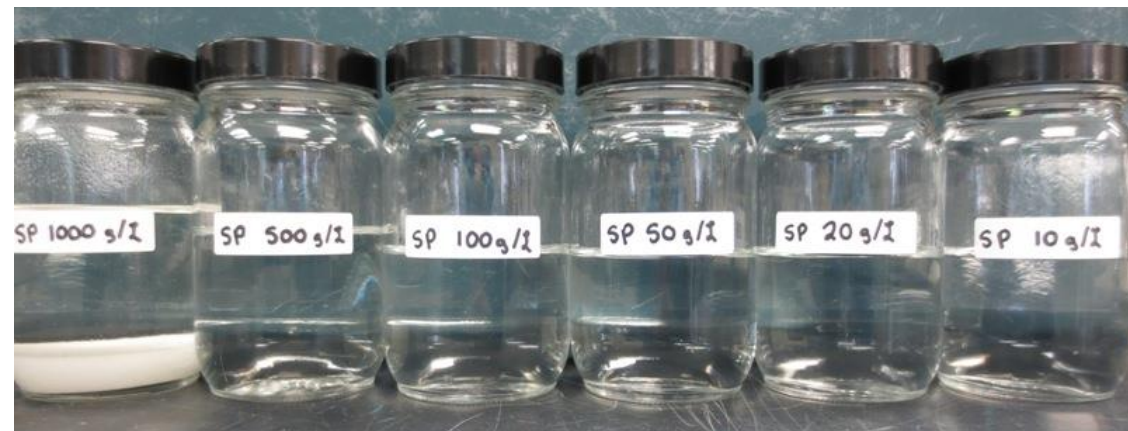
Reactors at 20°C

**Klozur KP Solubility
= 47 g/L**



Reactors at 20°C

**Klozur SP Solubility
= 570 g/L**





Solubility Limited Release - Dynamic System

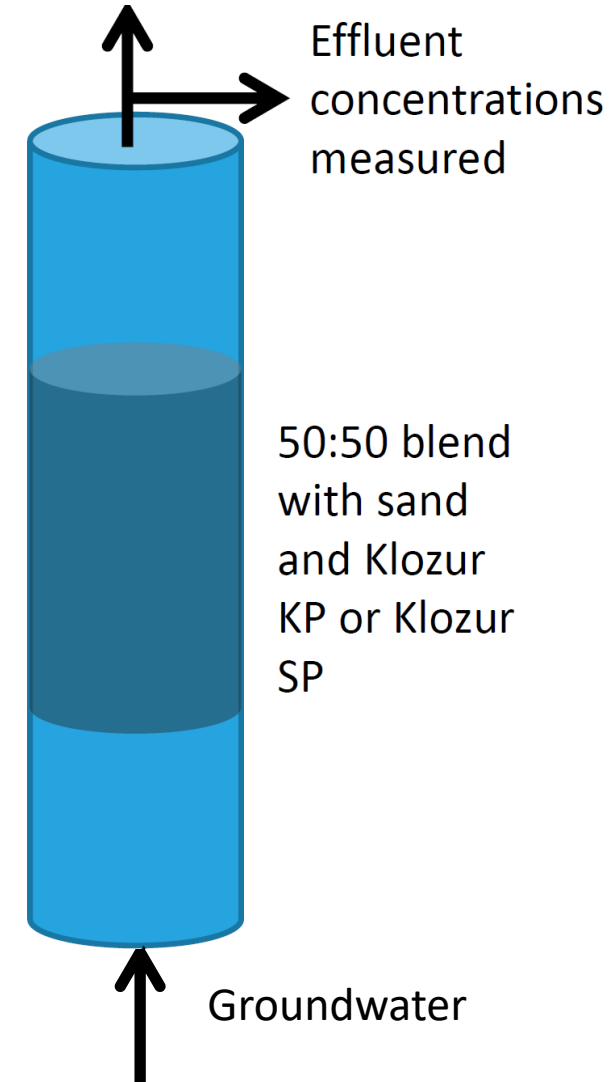
- Column Study:

- 12 inch columns

- 6 inch section of 50:50 blend of sand and either Klozur KP or Klozur SP
- Targeting 300 g of oxidant
- 3 inch sand above and below

- Four columns

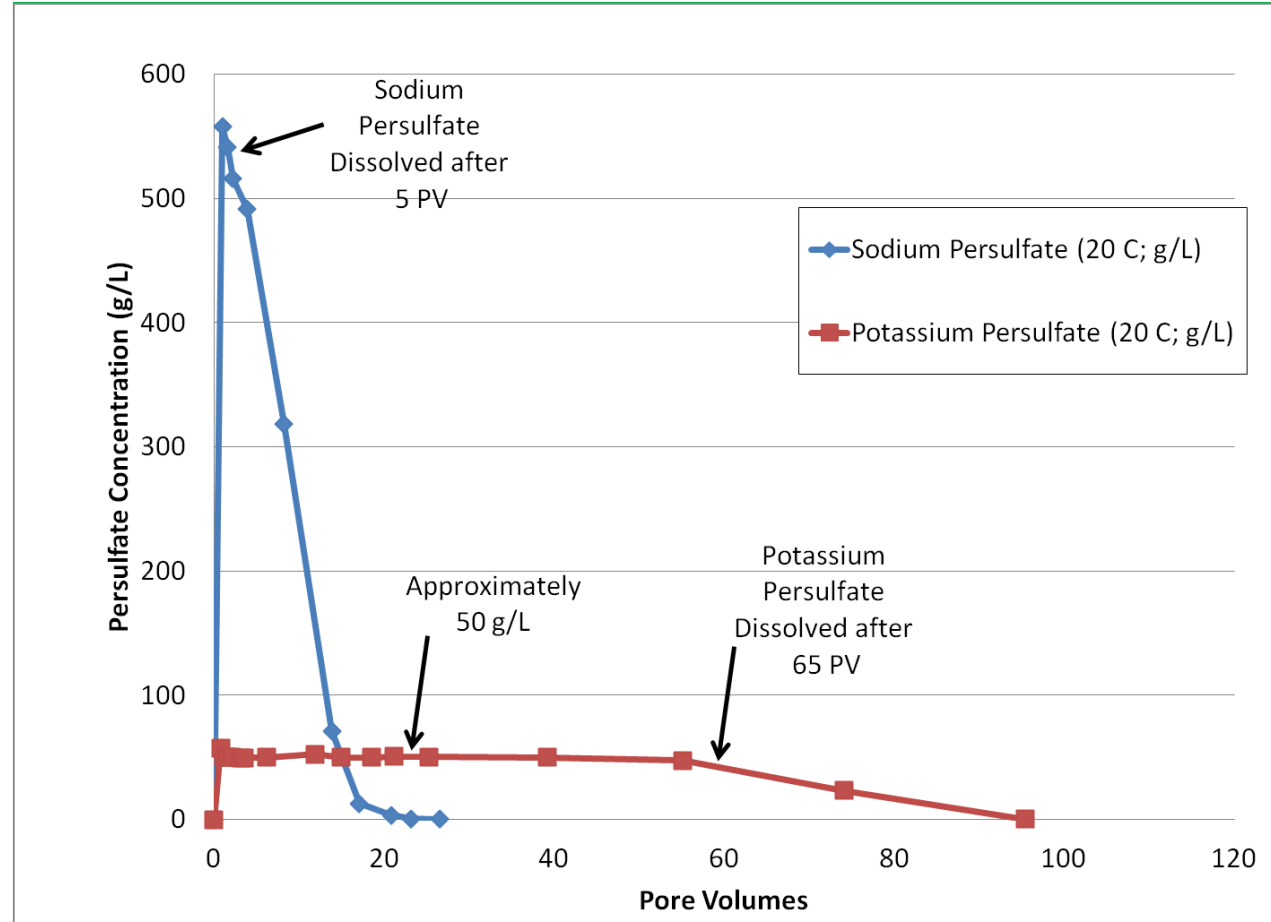
- 2 °C :
 - SP
 - KP
- 20 °C
 - SP
 - KP





Column Study (20°C) Effluent Persulfate Concentration

- Dissolution of Persulfate
 - 20-25 °C
- Klozur SP
 - Peak at theoretical maximum
- Klozur KP
 - Sustained at theoretical maximum

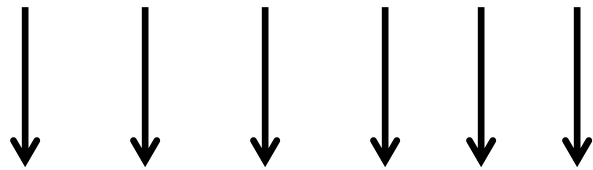




Conceptual Permeable Reactive Barrier

- Permeable Reactive Barrier (PRB)
- Conceptual Design of Gate
 - 50 ft wide, 10 ft high, 5 ft deep
 - ~50% w/w KP
 - 150,000 lbs KP

Groundwater Flow



KP PRB



Activator PRB

Conceptual “Ideal” Persistence of the Extended Release KP

Conceptual Klozur KP Persistence (months)					
Temp (°C)	0	10	20	25	
Solubility (g/L)	17	29	47	59	
Groundwater Velocity (ft/yr)	5	679	398	246	196
	10	339	199	123	98
	20	170	100	61	49
	50	68	40	25	20
	100	34	20	12	10
500	7	4	2	2	

Does not consider potential “site” factors

Case Study

Klozur® KP In Situ Chemical Oxidation Reactive Barrier for the treatment of 1,4-Dioxane



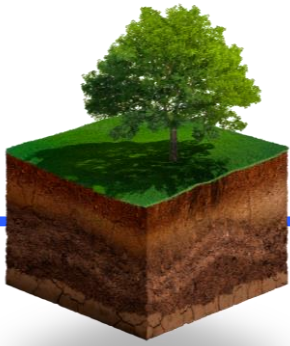
Location: Confidential Former Industrial location
in New York State

Lead Consultant: AECOM

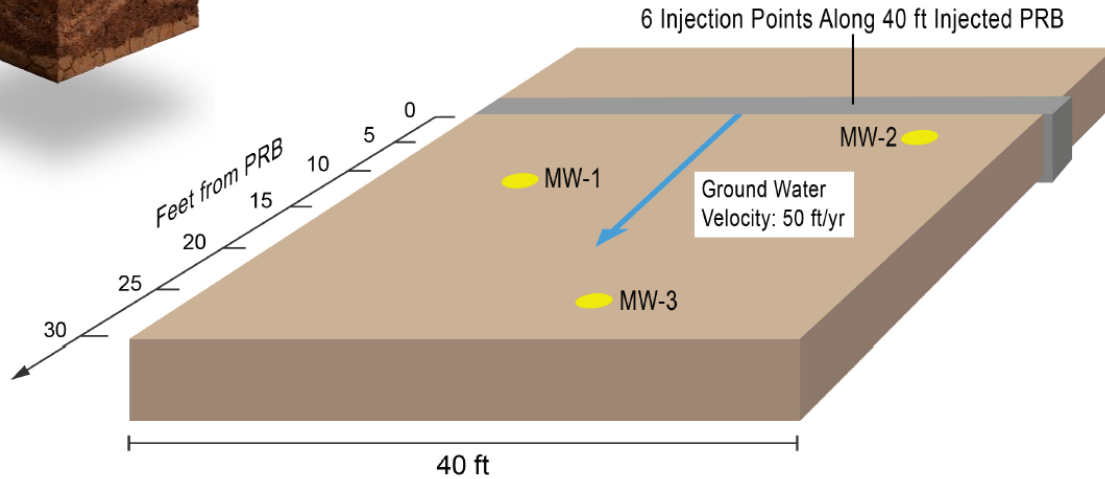
Technical Support: Evonik

Contaminants: 1,4-Dioxane, 1,1,1-TCA, 1,1-DCA, 1,2-DCA, and 1,1-DCE
Oxidant: Klozur® KP w alkaline activation

Strategy: In Situ Applications of Klozur KP
- Slurry injection



Pilot scale KLOZUR KP PRB Results



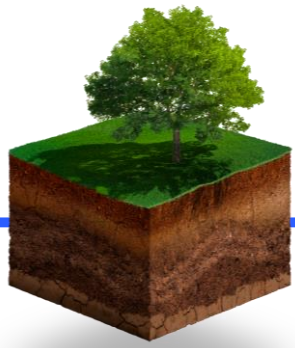
- Data from (MW-1) demonstrated a **99.8% reduction** for all contaminants and treatment of **1,4-dioxane to non-detect**.
- Residual persulfate and alkaline conditions persisted for up to eight months** after the pilot test application within the PRB. This indicated that the geochemical conditions for alkaline activated persulfate were maintained at the PRB for longer than the designed 6 month time-frame.
- Low levels of persulfate were observed downgradient from the PRB, however the pH was unchanged at both downgradient locations. This indicated that the alkaline conditions generated to activate the persulfate within the PRB transect were not sustained downgradient of the PRB.
- Despite the loss of alkaline conditions, the contaminants of concern were reduced by over 80 percent at the monitoring location 10 ft down gradient and by over 60 percent

Event	Klozur Persulfate (g/L)	pH	Contaminant Concentrations (µg/L)					Reduction VOCs (%)
			DCA	DCE	1,4-Dioxane	VOCs*		
MW-1 (3 ft downgradient of PRB transect)								
Baseline	NA	6.9	21	40	30	115		
3 month	7.2	12	0.2	ND	ND	0.2	99.8%	
6 month	NA	NA	0.2	ND	ND	0.2	99.8%	
8 month	14.2	12	NA	NA	NA	NA	NA	
MW-2 (10 ft downgradient of PRB transect)								
Baseline	NA	7.2	44	72	55	184		
3 month	3	6	10	11	ND	26	86%	
6 month	NA	NA	16	ND	16	34	82%	
8 month	2.5	6.8	NA	NA	NA	NA	NA	
MW-3 (25 ft downgradient of PRB transect)								
Baseline	NA	7.2	89	270	200	610		
3 month	NA	NA	46	82	69	216	65%	
6 month	NA	NA	63	30	110	230	62%	
8 month	8	6.5	NA	NA	NA	NA	NA	

* VOCs listed. Not including acetone

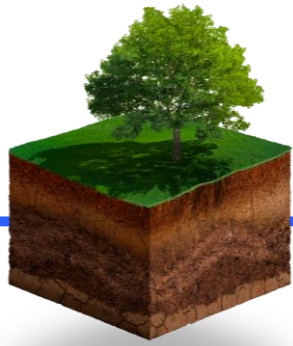
ND: Non-detect, NA: Not analysed

Combining ISCO and Bio

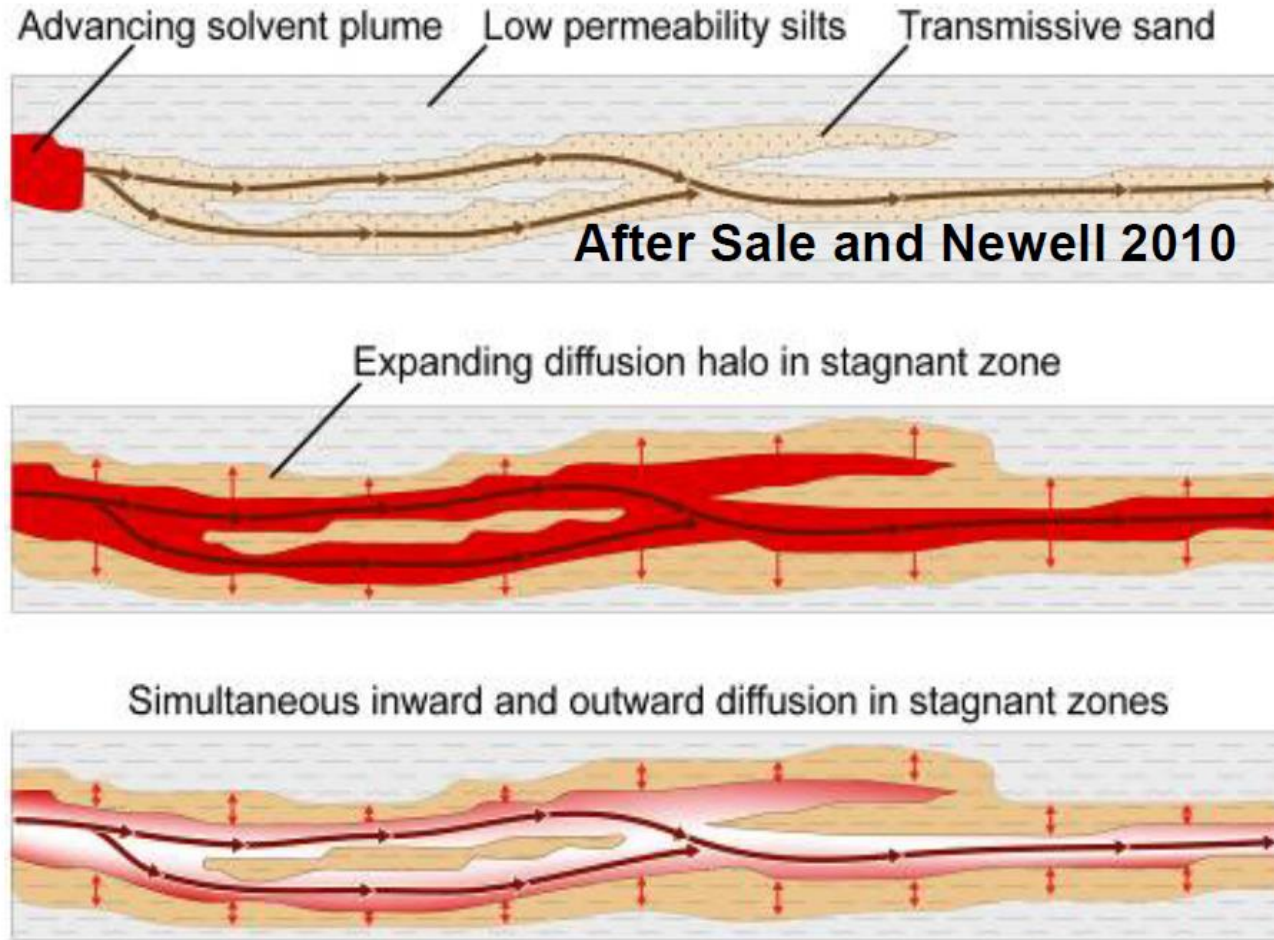


The Back Diffusion Issue



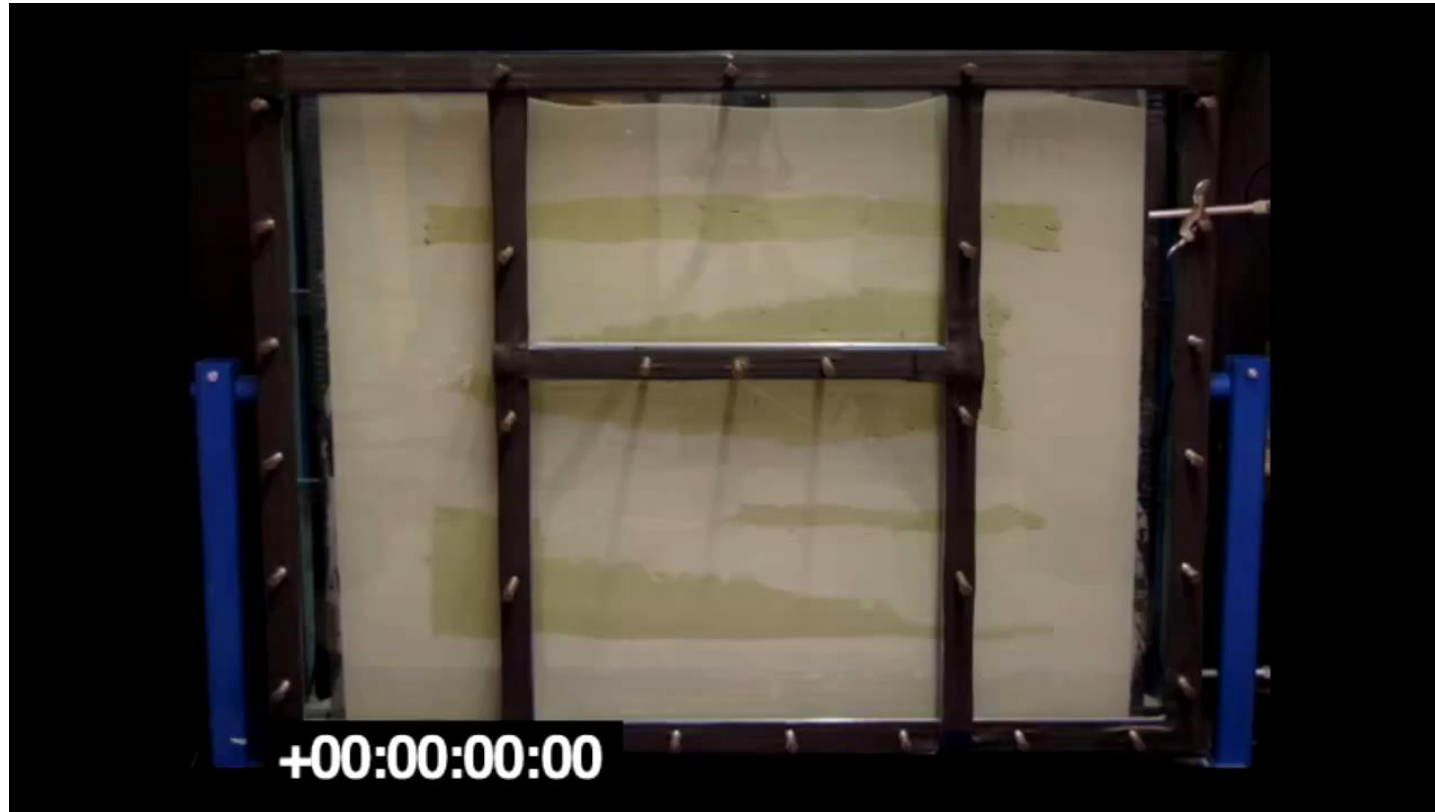


Back Diffusion Visualization



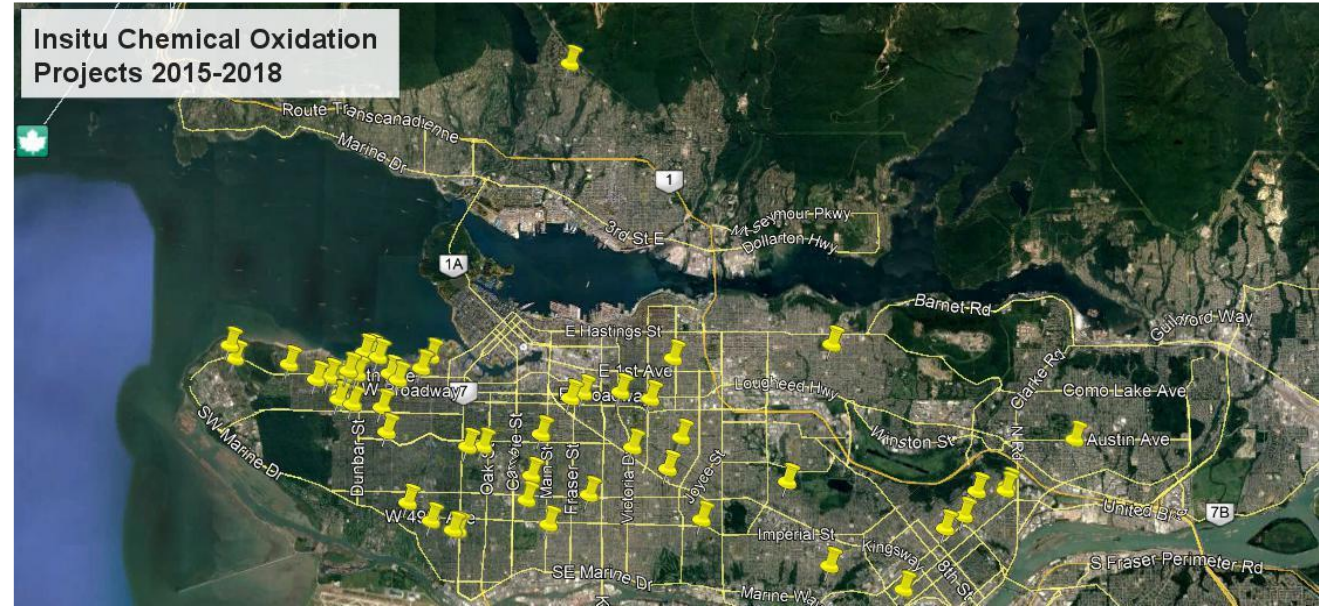


Back Diffusion Visualisation



Source – Colorado State University

In Situ Chemical Oxidation and Bioremediation in the Complex Geologies of the Lower Mainland of British Columbia



Location: 150 in Vancouver, BC from 2015 to 2021

Lead Consultant: Ventus

Technical Support: Chemco

Contaminants:

Petroleum Hydrocarbons

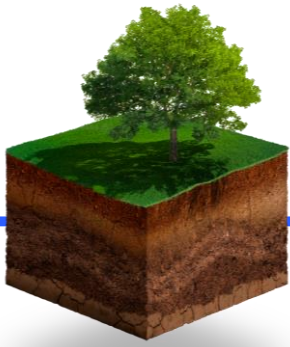
Oxidant:

Klozur® CR

Strategy:

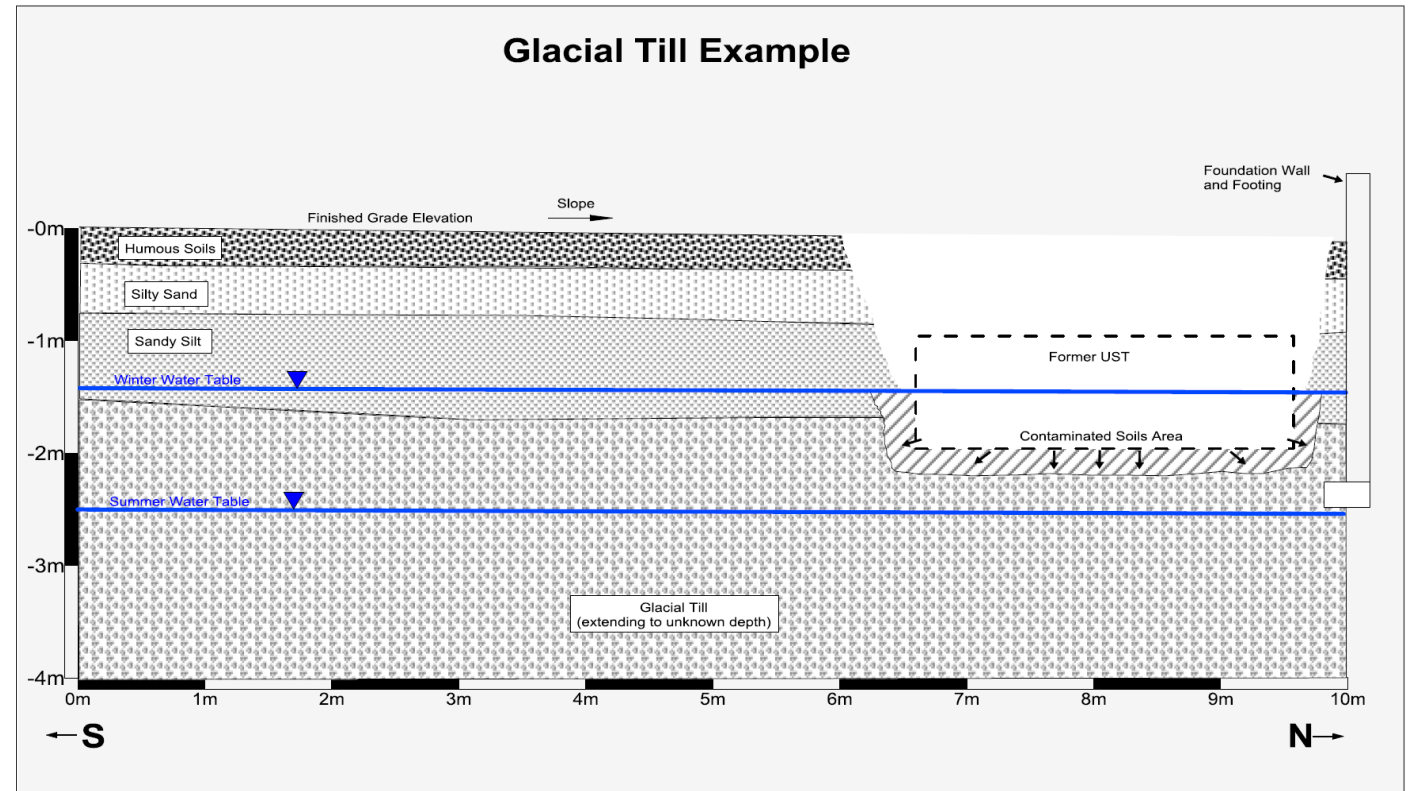
In Situ Applications of Klozur CR

- Soil mixing
- Filled via boreholes
- Excavation backfill amendment



Case Study - Treatment of EPH C10-19 Contaminated Soils

- 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 Klozur[®] CR can be mixed and poured directly into an open excavation.



Case Study - Treatment of EPH C10-19 Contaminated Soils

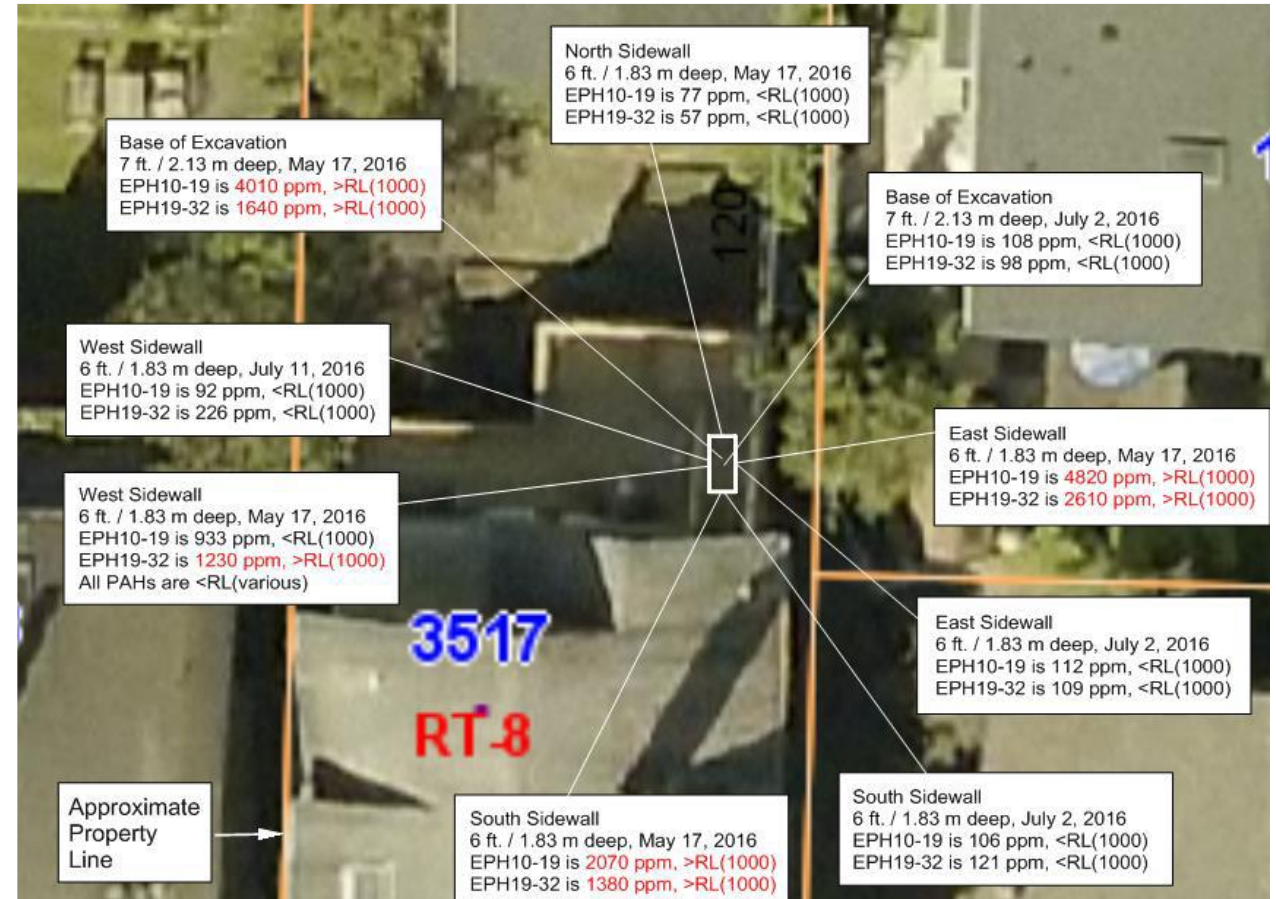
- Thick slurries of Klozur[®] CR applied:
 - Into tightly spaced boreholes
 - Base of excavation of former USTs
 - Via Jetting





BC Case Study - Treatment of EPH C10-19 Contaminated Soils

- In 8 to 9 weeks EPH (C10-C19) soil concentrations decreased:
 - Excavation base: 4010 ppm to 108 ppm
 - Sidewall: 4820 ppm to 112 ppm
- Dig and dump remediation would have required destruction of the deck (worth \$18,000 CAD), making ISCO the safest easiest and cheapest approach to remediation. Remediation Cost was about \$10,000.



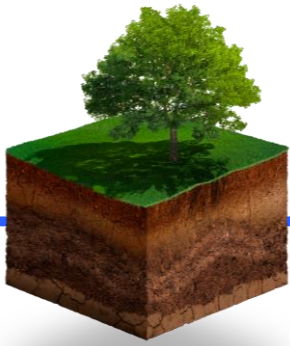
Case Study - Treatment of EPH C10-19 Contaminated Soils

- Over 180 Locations treated with Klozur® CR from 2015 to 2022
- 148 of the sites have been successfully closed
- Klozur® CR used:
 - In conjunction with excavation of the worst of the material
 - Treat more lightly contaminated soils



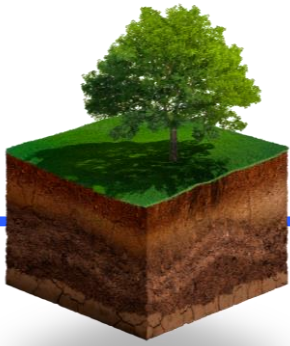
Conclusions

Do's and Don'ts



Do's

- ✓ Understand your site and your contaminant
- ✓ Perform bench-scale treatability studies to test one or more amendments using site-specific soils and groundwater **BEFORE** getting to the field
- ✓ Source zone treatment possible **In Situ Soil mixing**
- ✓ **Reactive Oxidative PRB now possible**
- ✓ Great for **GW contamination**
- ✓ Aqueous Solution Injection or Direct Push / Fracking emplacement for slurry
- ✓ **Open excavation = opportunity**
- ✓ **Post injection monitoring** is performed to evaluate the long-term effectiveness of the remedy, identify the need for additional application of amendments, assess progress toward achieving remedial goals and remedial action objectives, and determine if rebound is occurring



Don'ts

- ✓ 10 000 mg/kg and above / 10 000 ppb in GW = questions yourself
- ✓ Have proper Health and Safety plan in place
- ✓ Be aware of the amendment reactivity with on site material
- ✓ Check the material BEFORE accepting delivery
- ✓ Fast groundwater flow velocity might limit the effectiveness of soluble amendments due to dilution / amendment movement
- ✓ Long term & extended release treatment amendments (years rather than months) must be favored to deal with back diffusion for the contaminant



*Thank you for your attention !!
Questions ?!?*



**Ottawa EnviroWorkshops
November 2022**

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