The Evolution of Two Remediation Technologies: Combined In Situ Stabilization (ISS) and In Situ Chemical Oxidation (ISCO)

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Presentation Outline

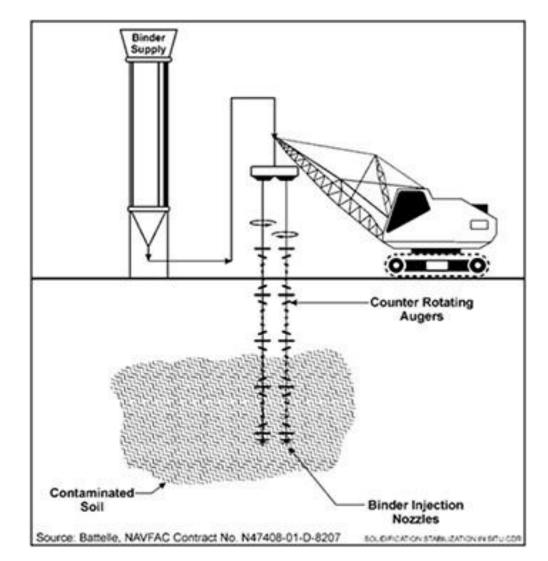
- Technology Overview
 - -ISS
 - ISCO
 - $-\operatorname{Combined}$ ISCO / ISS
- Why Combine ISCO/ISS
 - Synergies
- Case Studies





In Situ Solidification and Stabilization

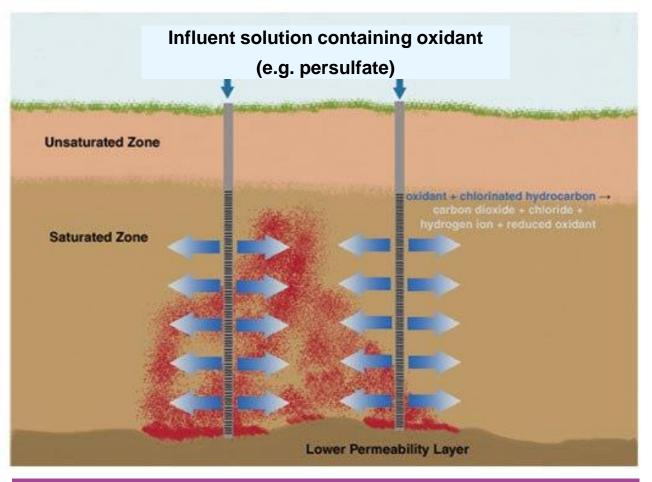
- Use of soil mixing to blend binding agent(s) with contaminated soils:
 - Portland Cement
 - Blast Furnace Slag
- Common objectives:
 - Reduced hydraulic conductivity
 - Increased Unconfined Compressive Strength (UCS)
 - Lower contaminant flux and leachate concentrations





In Situ Chemical Oxidation

- What it is:
 - Oxidants are reagents that <u>accept/take</u> electrons from, or oxidize, contaminants of concern \rightarrow CO₂
 - Typically applied via injection or soil mixing
- Objectives:
 - Contaminant destruction / mass reduction
 - Reduced concentrations in soil, groundwater, leachate and vapors



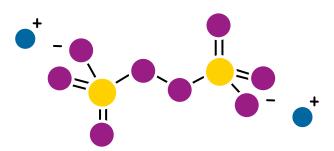
Examples (persulfate reactions): Benzene: $15 S_2 O_8^{-2} + C_6 H_6 + 12 H_2 O \rightarrow 6 CO_2 + 30 HSO_4^{-1}$ PCE: $2 S_2 O_8^{-2} + C_2 CI_4 + 4 H_2 O \rightarrow 2 CO_2 + 4 CI^- + 4 H^+ + 4 HSO_4^{-1}$

Klozur[®] Persulfate

- Sodium and potassium persulfate are strong versatile oxidants commonly used in environmental remediation applications
- At a pH above 10.5, persulfate will be activated and form both oxidative and reductive radicals
- Common ISS binders create alkaline conditions → activates persulfate
- Oxidative and reductive pathways → applicable for treatment of very broad range of contaminants

Alkaline activated persulfate:

 $S_2O_8^{-2} + pH > 10.5 \rightarrow SO_4^{-1} + OH + O_2^{-1}$



Oxidant	Standard Reduction Potential (V)
Hydroxyl radical (OH.)	2.59
Sulfate radical (SO ₄ . ⁻)	2.43
Ozone	2.07
Persulfate anion	2.01
Hydrogen Peroxide	1.78
Permanganate	1.68
Superoxide (O ₂ . ⁻)	-0.33
ZVI	-0.45
Notes: 1. Siegrist et al. (2011), 2. CRC (76 th Edition)	

Klozur[®] Persulfate Degradation Pathways / Contaminants Treated

Oxidative	Either	Reductive	
	PCE, TCE, DCE and VC		
Petroleum Hydrocarbons	Chlorohonzonoo	Carbon Tetrachloride	
Gasworks Residuals	Chlorobenzenes	1,1,1-Trichloroethane	
BTEX	Phenols	Dichloroethanes	
DILX	Select Pesticides		
PAHs	Salaat Eluarinated Compounds	Select Pesticides	
Oxygenates	Select Fluorinated Compounds	Select Energetics	
1 A Dievene	PCBs	_	
1,4-Dioxane	Select Energetics		
Activation I	Methods: Alkaline, Hydrogen Peroxide, and	d Heat	
Activation Method: Iron	n Chelate		



- ISCO:
 - Multiple applications may be needed for heavily contaminated sites \rightarrow cost prohibitive
 - Contaminants that sorb strongly to the soil (low partitioning in water / Koc value) more challenging to treat, sometimes requiring multiple applications

- ISS:
 - Contamination is left in place maintaining environmental liability
 - Addition of binders can cause soils to swell (increase in volume), which then requires treatment or disposal



Combining the Technologies ISCO/ISS

ISCO (sodium persulfate) and ISS reagents applied together in single application:

- Treatment of more soluble (mobile) fraction of the contamination preferentially treated via oxidation
- Remaining heavier contaminant fractions stabilized





Soil mixing using excavator with mixing attachment

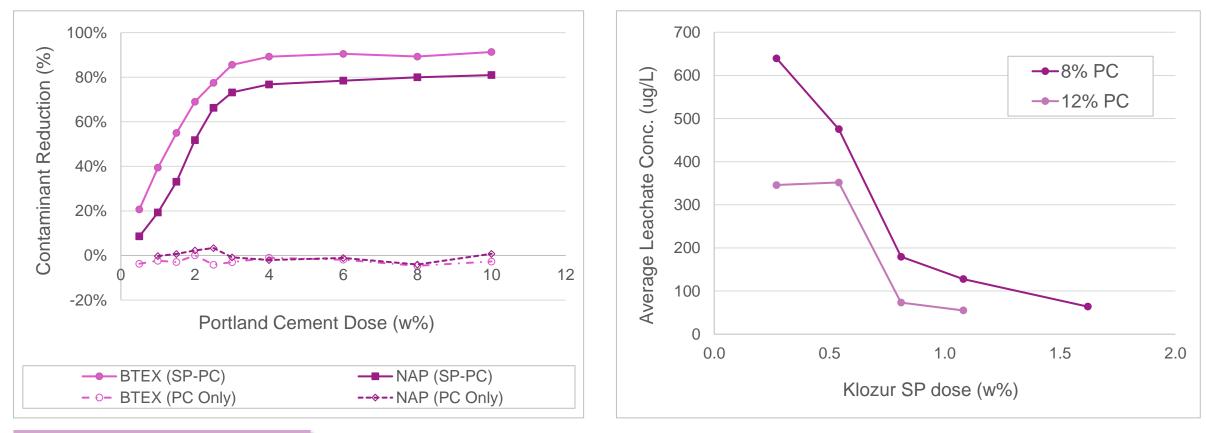
Soil mixing using large diameter augers



Synergistic benefits with combined approach

Common ISS reagents create alkaline conditions \rightarrow Low-cost activator for persulfate

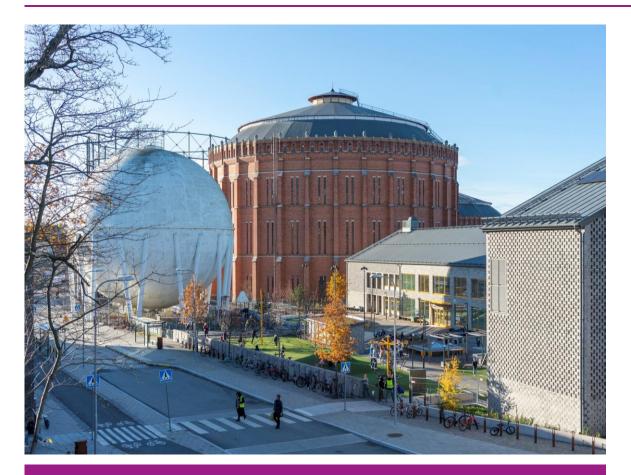
Adding persulfate to ISS reduces binder loading to reach leach targets → Less soil bulking





Srivastava et al (2016)

Former MGP Site – Stockholm, Sweden



This project is a collaboration between multiple parties, incl City of Stockholm, PEAB, Golder, Elander Miljöteknik, RGS, Sheeba, Arkil, Evonik, Geomind

City of Stockholm Technical Project Contacts: Sofia Billersjö: sofia.billersjo@stockholm.se Helen Österberg helen.osterberg@extern.stockholm.se

- Klozur Persulfates are being employed to remediate a former MGP site in Stockholm
 Using Injection and ISCO/ISS
- The old MGP area is being redeveloped into a residential area
- Soil and groundwater impacted by coal tar residue, incl. Polycyclic Aromatic Hydrocarbons (PAHs)
- Goal with soil and groundwater remediation is to limit vapor intrusion to new residential buildings
- Bench and pilot testing in 2017-2020
- Full-scale implementation started March 2021



Aerial View of Stockholm Royal Seaport

- Part of one of Europe's most extensive urban development areas
- A total of 12,000 new homes and 35,000 new workplaces are planned for greater Royal Seaport Area:
 - 1500 new apartments planned at the former MGP area
- This is one of the city's designated sustainability profile areas:
 - Treating soil in place was the chosen sustainable remedial approach



Project site



Residential Development Completed along the Channel





Aerial view from 2013

Current view

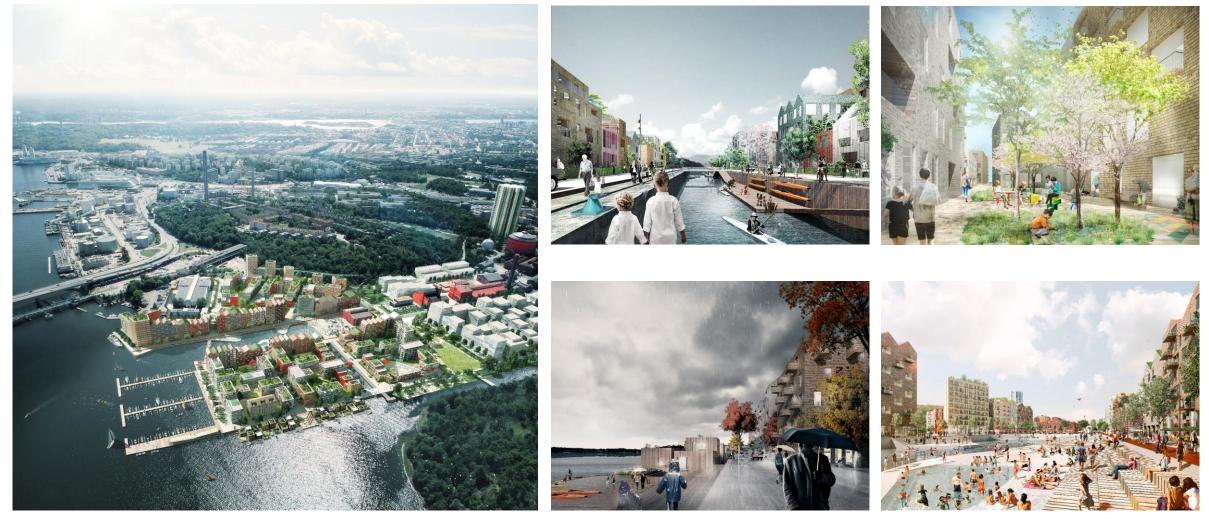


ISCO/ISS Remediation Area – area next to former tar factory





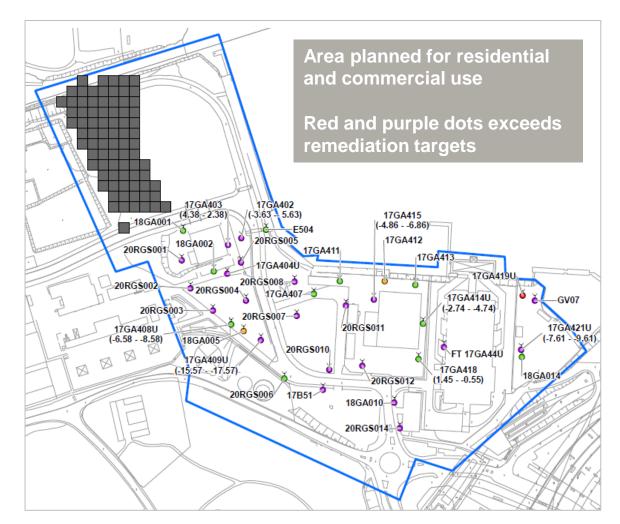
And this is what is planned.. 1500 new apartments being built in the area.



Pictured: An early-stage visionary illustration of the final Stockholm Royal Seaport district.

Before construction can begin the soil needs to be treated

- Soil and Groundwater impacted by MGP residual contamination including Polycyclic Aromatic Hydrocarbons (PAHs)
- PAHs present in two subsurface units:
 - Clay unit down to ~7 m below ground surface
 - Volume: 50,000 m³
 - More permeable "Moraine" layer (sand, gravels, and rock) beneath the clay
 - Volume 70,000 m³





Site Specific Remedial Targets developed to prevent vapor intrusion

Clay unit remediation goal:

• <250 mg/kg PAH-16

Groundwater remediation goals:

- Naphthalene <6200 ug/L
- Fluoranthene <12 ug/L
- Benzene <300 ug/L

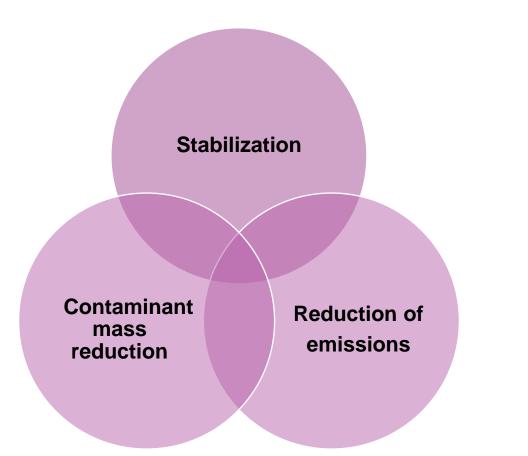
16 Priority PAH (PAH-16) by molecular weight (low, medium, and high)

PAH-L	PAH-M	PAH-H
naftalen	fluoren	benso(a)antracen
acenaften	fenantren	krysen
acenaftylen	antracen	benso(b)fluoranten
	fluoranten	benso(k)fluoranten
	pyren	benso(a)pyren
		dibens(ah)antracen
		benso(ghi)perylen
		indeno(123cd)pyren



Remediation Approach

- After several years of bench and pilot field scale testing, Klozur SP selected to treat both the clay and moraine layer units:
 - Clay unit treated with ISCO/ISS to both degrade and solidify contaminants in a soil mixing strategy (~50,000 m³).
 - Underlying moraine layer treated via injection of Klozur SP solution (~70,000 m³).



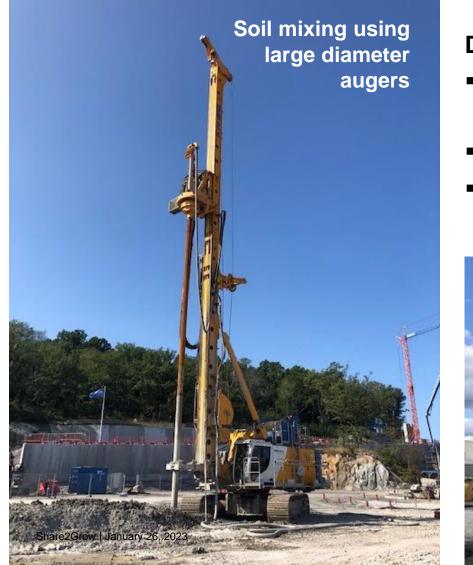


Why these Technologies used at Stockholm

- Klozur[®] Persulfate: Powerful oxidant capable to degrading full suite of contaminants found at site (MGP residuals and PAHs)
- Clay unit ISCO-ISS:
 - Soil mixing more effective for establishing contact between the reagents and contaminants in the low permeability soils
 - ISS increases clay compressive strength to allow for above ground construction of roads and buildings
- Moraine layer Injection of persulfate solution:
 - Injection strategy more effective in more permeable soils
 - Rocks prevents soil mixing



Full-Scale Installation of ISCO/ISS to Clay Unit



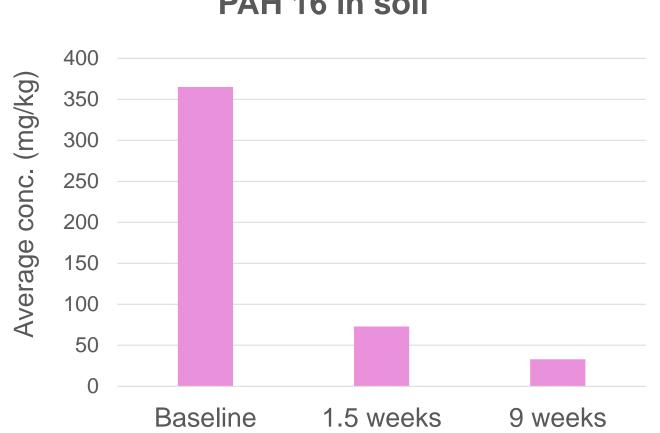
Dose applied:

- Cement: 4-8 wt%
 - Higher dosing for areas with roads.
- Klozur SP: 1.8 wt%
- Water: 4-7 wt%





Full-Scale Results – Contaminant Destruction – PAH 16



PAH 16 in soil

Reference: Uppföljning av föroreningshalter i pelare efter stabilisering och kemisk oxidation av lera (ISS-ISCO), Golder, Jan 2022

PAH 16 concentrations:

Baseline:

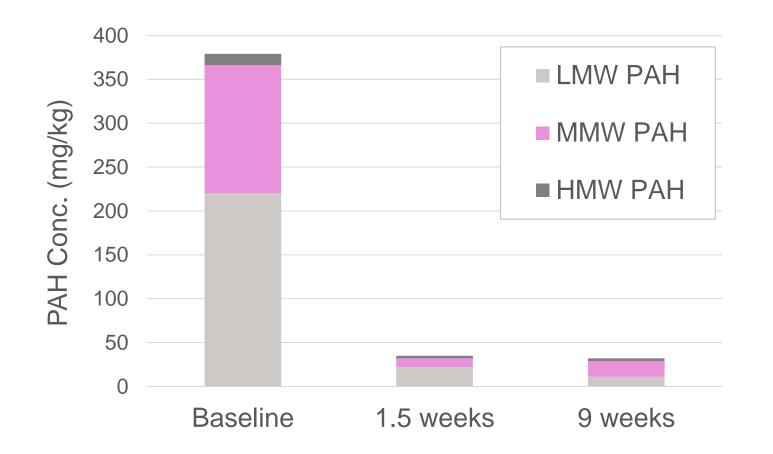
- Average: 365 mg/kg
- Range: 1-2700 mg/kg

9 weeks post treatment:

- Average: 33 mg/kg
- Range: 5-120 mg/kg
- All samples below remedial goal of 250 mg/kg



Full-Scale Results – Contaminant Destruction



Higher % reduction in lower molecular weight PAH fractions.

Reduction in PAH conc. following 9 weeks:

- ~95% reduction in PAH-L
- ~90% reduction in PAH-M
- ~80% reduction in PAH-H



Reference: Uppföljning av föroreningshalter i pelare efter stabilisering och kemisk oxidation av lera (ISS-ISCO), Golder, Jan 2022

- Phases thus far have been a success:
 - ISCO-ISS portion was completed between March 2021 and April 2022 has achieved goals for less than proposed budget
 - Injection portion initiated in January 2022 and completed in February 2023:
 - Monitoring is currently ongoing
 - Preliminary results are very positive most cells met remedial targets after the first application round, only a few cells needed a second injection round
- More work to come:
 - New area using injection strategy has already started in 2023
 - New ISCO-ISS area is anticipated for 2024, although that area is still being characterized

Working with Evonik's Soil and Groundwater Group since 2017; City of Stockholm has successfully developed strategies that address the needs and concerns at their site.



ISCO-ISS Successfully Remediates PCE DNAPL at Former Dry Cleaner in Residential Neighborhood

Location: Former Kent Cleaners, Lansing, Michigan Lead Consultant: Hamp Mathews & Associates

Contractor: Lang Tool

Regulator: EGLE

Contaminants: PCE (up to >1,000 mg/kg)

Goal: Reduce vapor intrusion risk

Treatment volume: 12,354 cy soil,

Reagent Dose (w/w soil):

- Klozur SP: 1-2% (440K lbs)
- Portland Cement: 4% (1.6M lbs)

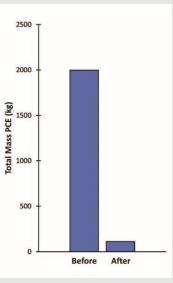




Results

- ➢ 94% reduction in PCE mass
- UCS of 25-50 psi (Day 60)
- Underlying GW conc. reduced by 90 to 99%

Saved client >\$2.5 Million compared to excavation estimate



ISCO-ISS Successfully Remediates Petroleum Contaminated Soils for Site Redevelopment

Location: Bolzano, Italy

Lead Consultant: Ladurner Bonifiche S.r.I.

Contaminants: Petroleum Hydrocarbons

Goals: Combination of contaminant reduction, soil stability targets, limit soil bulking

Treatment volume: 3,500 m³, from 3-8 m bgs

Dose (w/w soil):

- Klozur SP: 0.7-1%
- Portland Cement: 4-8%

Installation: 556 columns w. large diameter auger



ISCO Results & Goals:

- Benzene: 100% samples < 2 mg/Kg
- TPH (C4-C12): 100% samples <250 mg/Kg
- TPH (C13-C40): Over 50% samples <750 mg/Kg

ISS / Geotechnical Goals Achieved:

- UCS: 30 to 70 psi
- Permeability: 2.8 x 10⁻⁶ to 7.3 x 10⁻⁷ cm/sec

ISCO-ISS Successfully Remediates TCE Contaminated Soils Achieving Clean-Up Goals in One Week

Site: Former Industrial Site / Redevelopment

Location: Västerås, Sweden

Contaminants: TCE source area (up to >500 mg/kg)

Lead Consultant: Wescon

Soil Mixing Contractor: SMG

Goal: Reduce TCE mass by 50%

Treatment volume: 600 m³ soil

Reagent Dose (w/w soil):

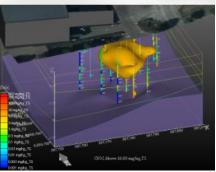
- Klozur SP: 0.8% (8 tons)
- Portland Cement: 7% (70 tons)



Results:

- Goals reached after 1 week and confirmed after 5 weeks
- The stability of the soil was improved
- Infrastructure was minimally affected





Significant cost savings (~70%) relative estimated excavation and disposal costs

	Baseline: CVOCs before treatment	Results: CVOCs 5 weeks post treatment	Reduction
Maximum conc (mg/kg)	542	16.5	97%
Average conc (mg/kg)	45	4.5	90%
Estimated CVOC mass (kg)	35-40	7-9	74 to 83%

Thank You! Questions?



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