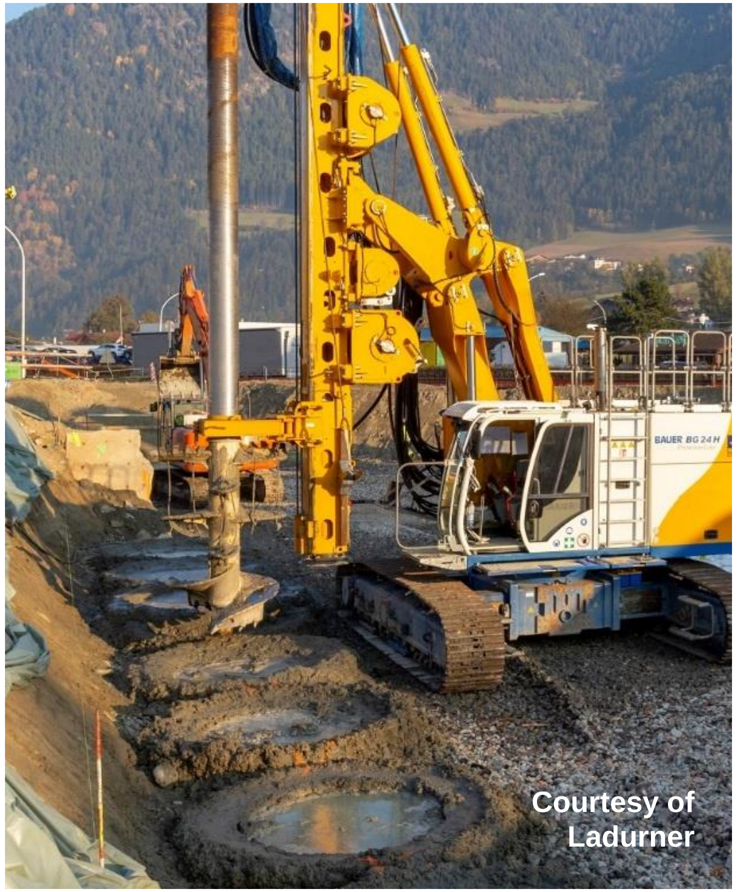
New Remediation Technology Formed by Combining Two Well Established Remediation Technologies: In Situ Stabilization (ISS) and In Situ Chemical Oxidation (ISCO)

Remtech Conference, 2024

Stacey Telesz, Evonik
Josephine Molin, Evonik
Brant Smith, Evonik

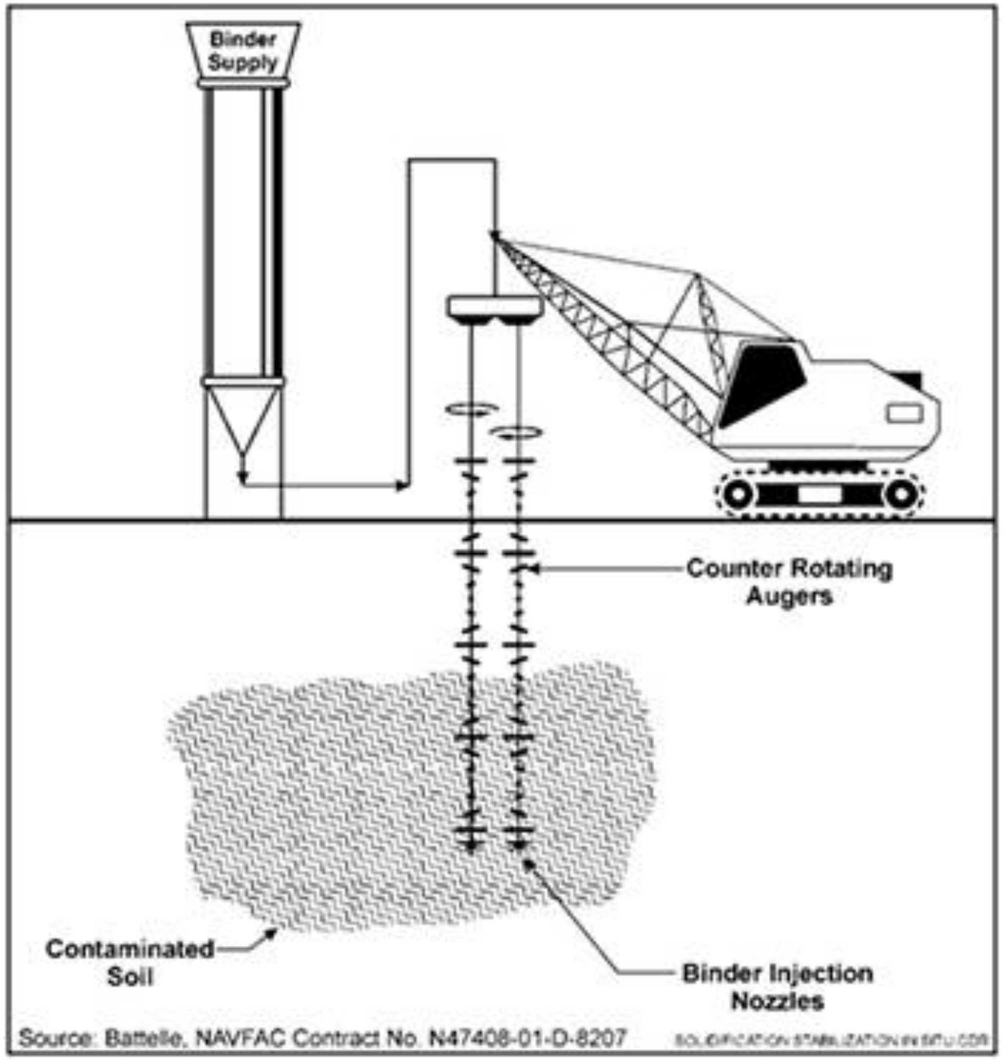
Presentation Outline

- Technology Overview
  - ISS
  - ISCO
  - Combined ISCO/ISS
- Why Combine ISCO/ISS
  - Benefits & Synergies
  - Common Remedial Goals
- Implementation Methods
- Case Studies



In Situ Stabilization (ISS)

- Used for immobilizing contamination in place and reducing mass flux
- Soil mixing is used to blend the binding agent(s) with contaminated soils:
  - Portland Cement
  - Blast Furnace Slag
- Common Objectives:
  - Stabilization:
    - Chemical processes that reduces leachability
  - Solidification:
    - Decreasing of hydraulic conductivity and effective porosity
    - Increasing compressive strength



Evonik
Leading Beyond Chemistry

Common Objectives of ISS

- Reduced Hydraulic Conductivity
  - 2-3 orders of magnitude below native soils
  - Typically, less than 1 x 10^{-6} cm/sec
- Increase Unconfined Compressive Strength (UCS)
  - "Workable" ~20-60 psi
  - Hardened
    - ISS often targets 50 psi
- Lower contaminant flux and leachate concentrations

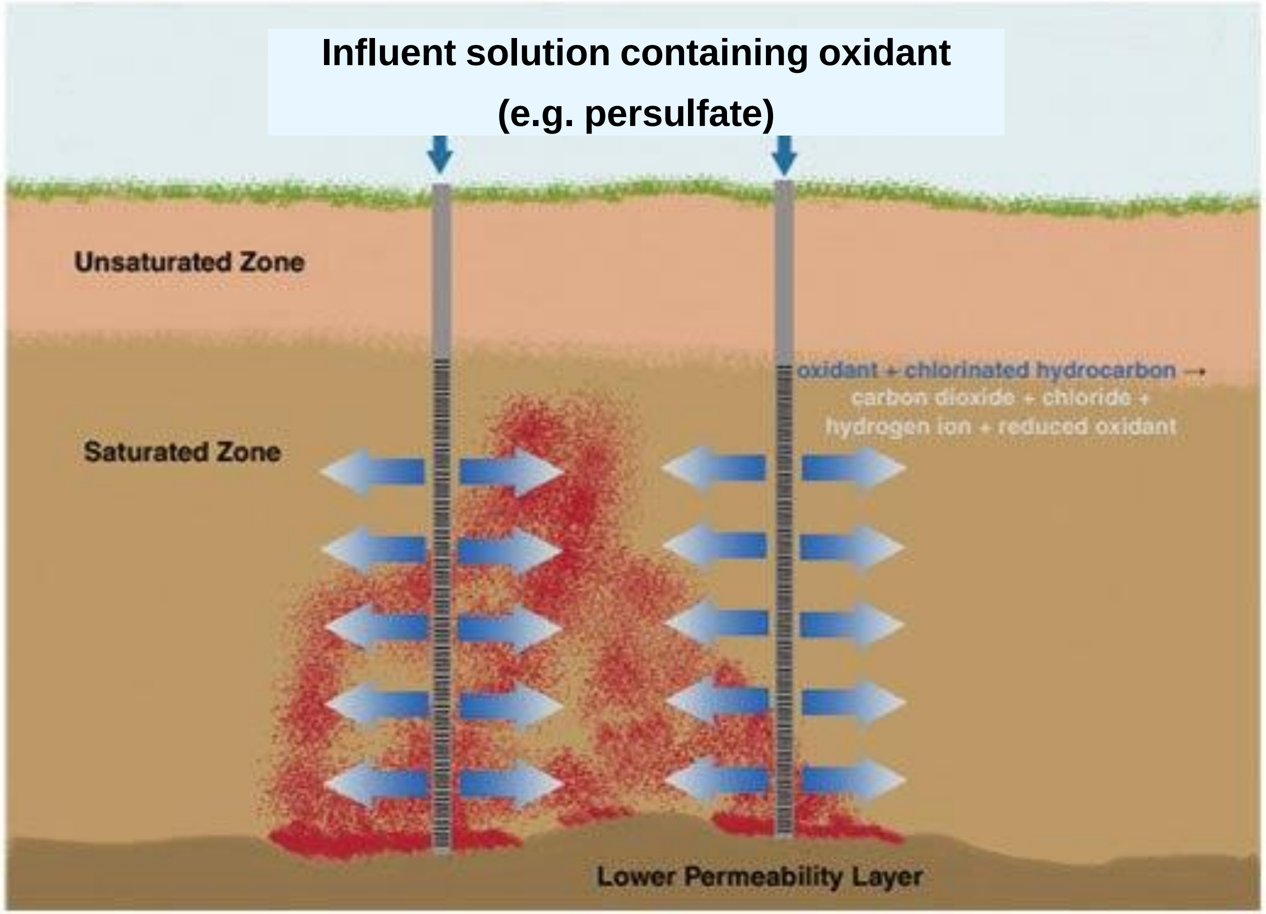
General Relationship between Soil Consistency and Unconfined Compressive Strength

Consistency	Unconfined Compressive Strength (UCS) Ranges			
	psi		kPa (KN/m^2)	
	Low	High	Low	High
Very soft	0	3	0	24
Soft	3	7	24	48
Medium	7	14	48	96
Stiff	14	28	96	192
Very Stiff	28	56	192	383
Hard	>56		>383	

Typical target range for "workable" soils ~20-60 psi

In Situ Chemical Oxidation (ISCO)

- Applying Oxidants typically by injection or soil mixing
  - Oxidants accept/take electrons from contaminants of concern, breaking them down to CO_2
- Common Objectives:
  - Contaminant destruction and mass reduction
  - Reduced concentrations in soil, groundwater, leachate and vapors

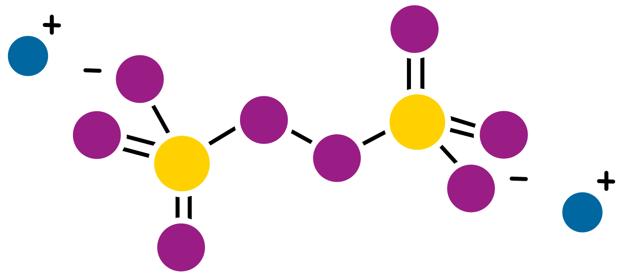


Examples (persulfate reactions):

Benzene: $15\ S_2O_8^{-2} + C_6H_6 + 12\ H_2O \rightarrow 6\ CO_2 + 30\ HSO_4^{-1}$

PCE: $2\ S_2O_8^{-2} + C_2Cl_4 + 4\ H_2O \rightarrow 2\ CO_2 + 4\ Cl^{-} + 4\ H^{+} + 4\ HSO_4^{-1}$

Klozur® Persulfate



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

Alkaline activated persulfate:

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

Oxidant	Standard Reduction Potential (V)
Hydroxyl Radical ($OH\cdot$)	2.59
Sulfate Radical ($SO_4\cdot^{-}$)	2.43
Ozone	2.07
Persulfate Anion	2.01
Hydrogen Peroxide	1.78
Permanganate	1.68
Superoxide ($O_2\cdot^{-}$)	-0.33
ZVI	-0.45

Notes: 1. Siegrist et al. (2011), 2. CRC (76th Edition)

Klozur® Persulfate Degradation Pathways / Contaminants Treated

Oxidative | **Either** | **Reductive**

Oxidative

- Petroleum Hydrocarbons
- Gasworks Residuals
- BTEX
- PAHs
- Oxygenates
- 1,4-Dioxane

Either

- PCE, TCE, DCE and VC
- Chlorobenzenes
- Phenols
- Select Pesticides
- Select Fluorinated Compounds
- PCBs
- Select Energetics

Reductive

- Carbon Tetrachloride
- 1,1,1-Trichloroethane
- Dichloroethanes
- Select Pesticides
- Select Energetics

Activation Methods: Alkaline, Hydrogen Peroxide, and Heat

Activation Method: Iron Chelate

Single Technology Limitations

- **ISCO:**
  - Multiple applications may be needed for heavily contaminated sites → cost prohibitive
  - Contaminants that sorb strongly to the soil with low partitioning in water (high K_{oc}) more challenging to treat, sometimes requiring multiple applications
- **ISS:**
  - More mobile contaminants (low K_{oc}) are more difficult to stabilize → requires higher dose binder
  - Addition of binders can cause soils to swell (increase in volume), which then requires treatment or disposal → significant cost factor
  - Contamination is left in place maintains environmental liability

Combining the Technologies ISCO/ISS

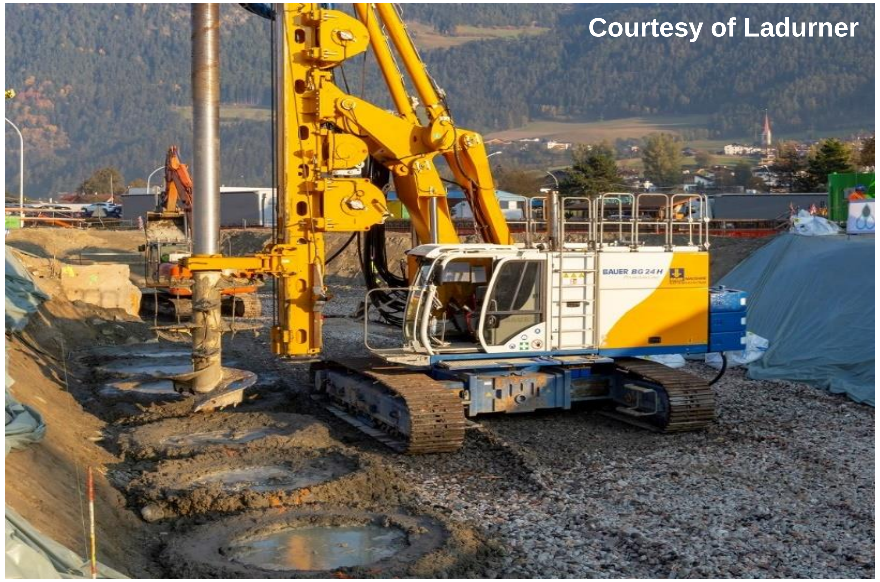
- In 2016, Vipul Srivastava et al published a study concluding that combining ISCO and ISS provided a more complete and cost-effective treatment for heavily impacted sites

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

  - ISCO treated the more soluble (mobile) fraction of the contamination that is preferentially treated via oxidation

  - ISS stabilized the remaining heavier contaminant fractions

Soil mixing using excavator with dual axis mixing attachment

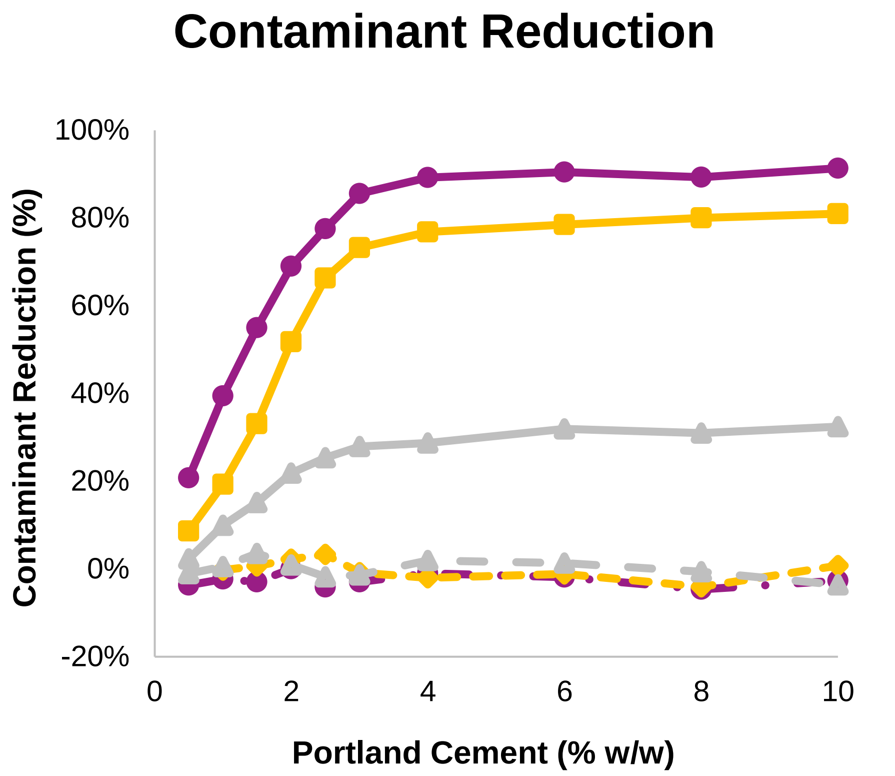


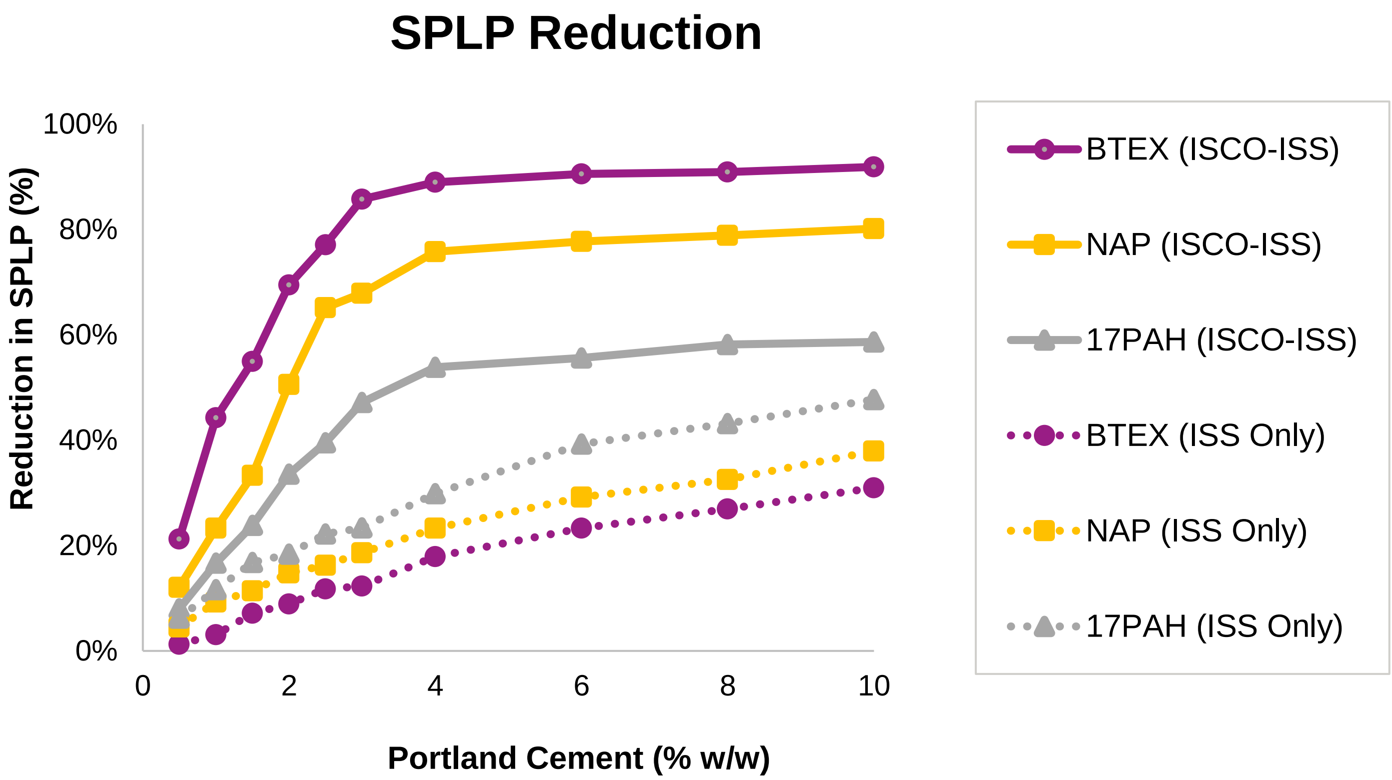
Soil mixing using large diameter augers

EVONIK
Leading Beyond Chemistry

Synergistic benefits with combined approach

Contaminant destruction can result in lower leachate concentration compared to ISS Only





2:1 Ratio of PC:SP

>37,000 mg/Kg MGP Residuals

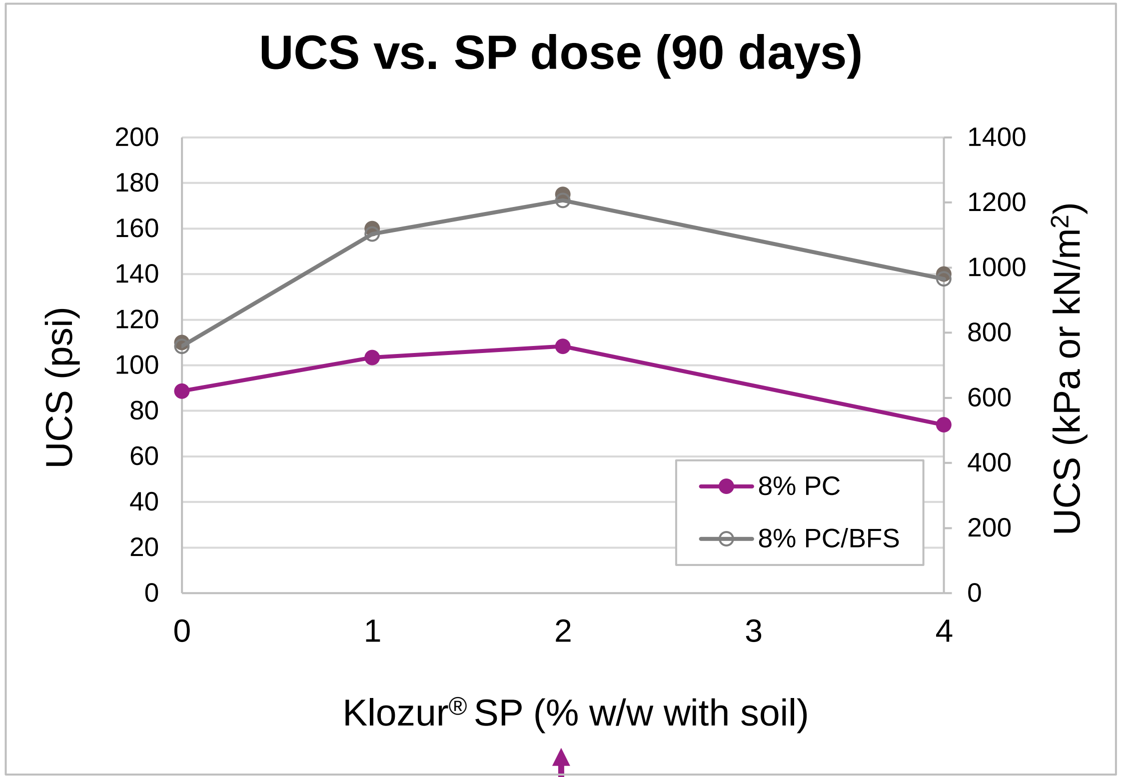
Reference: Srivastava, V.J., Hudson, J.M., and Cassidy, D.P., (2016b) "Achieving Synergy between Chemical Oxidation and Stabilization in a Contaminated Soil," Chemosphere, 154, 590-598

EVONIK Leading Beyond Chemistry

Synergies: Improved Unconfined Compressive Strength

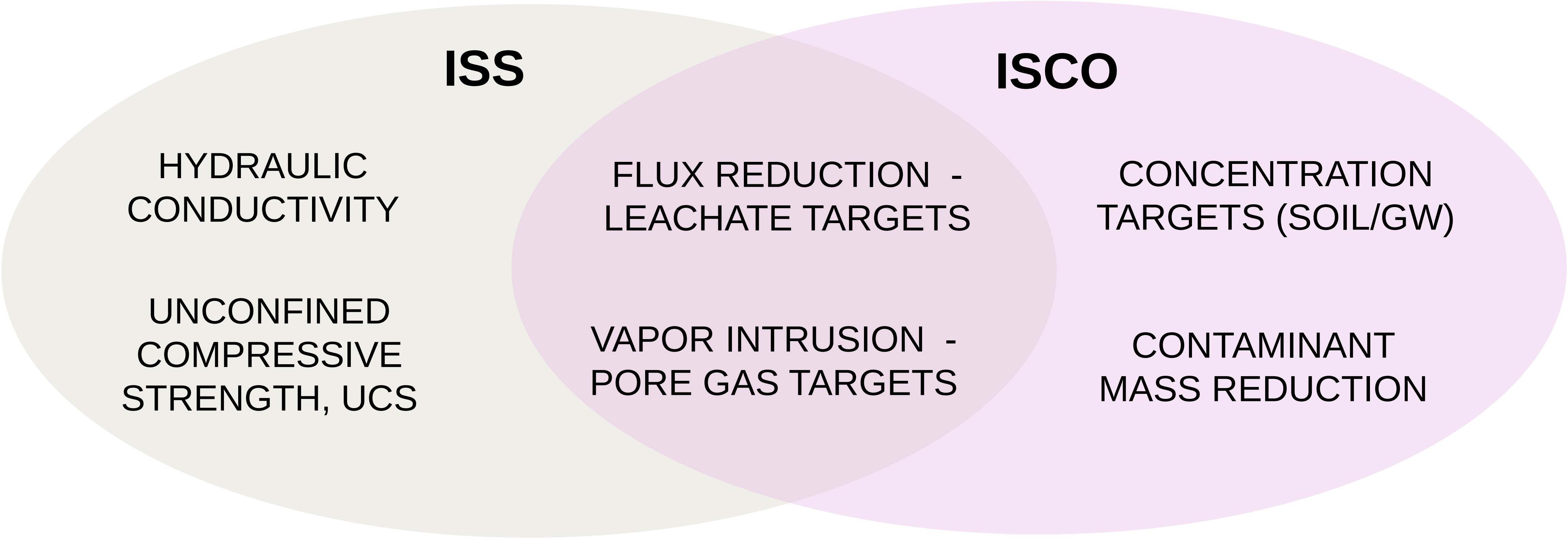
- Adding a small amount of persulfate (1-2%) can improve UCS to a certain point
  - Resulting in adding less binder to achieve remedial goals
  - Which would lead to less soil bulking → Cost savings

Klozur® SP (% w/w soil)	8% PC		8% PC/BFS	
	Day 90 UCS (psi)	% of ISS only	Day 90 UCS (psi)	% of ISS only
0	90	100%	110	100%
1	105	117%	160	145%
2	110	122%	175	159%



Bench Testing can help determine the sweet spot for optimum dosing

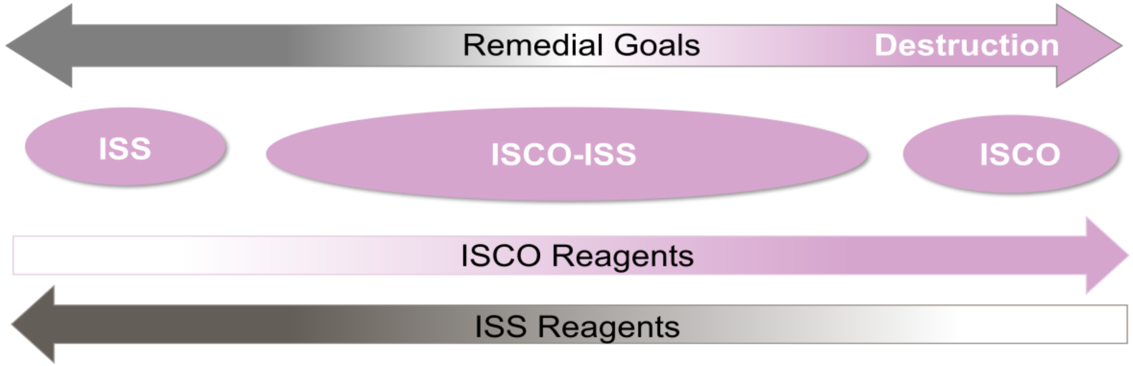
Common Remedial Goals



ISCO Can Help

Benefits of Combined Approach

- ISCO and ISS reagent doses can be varied to achieve a variety of remedial goals
- Benefits of adding ISS to ISCO soil mixing applications:
  - Improved soil stability allowing for site activities and redevelopment soon after the application.
  - Low-cost alkaline activators for Klozur® persulfate.
- Benefits of adding ISCO to ISS applications:
  - Small additions of ISCO reagents can lower the amount of ISS reagents needed to reach UCS and hydraulic conductivity targets, resulting in less soil bulking and disposal costs.
  - Lower long-term risk due to contaminant mass reduction.
  - Faster plume reduction due to reduced flux.



EVONIK
Leading Beyond Chemistry

What Data is Needed to Screen Sites

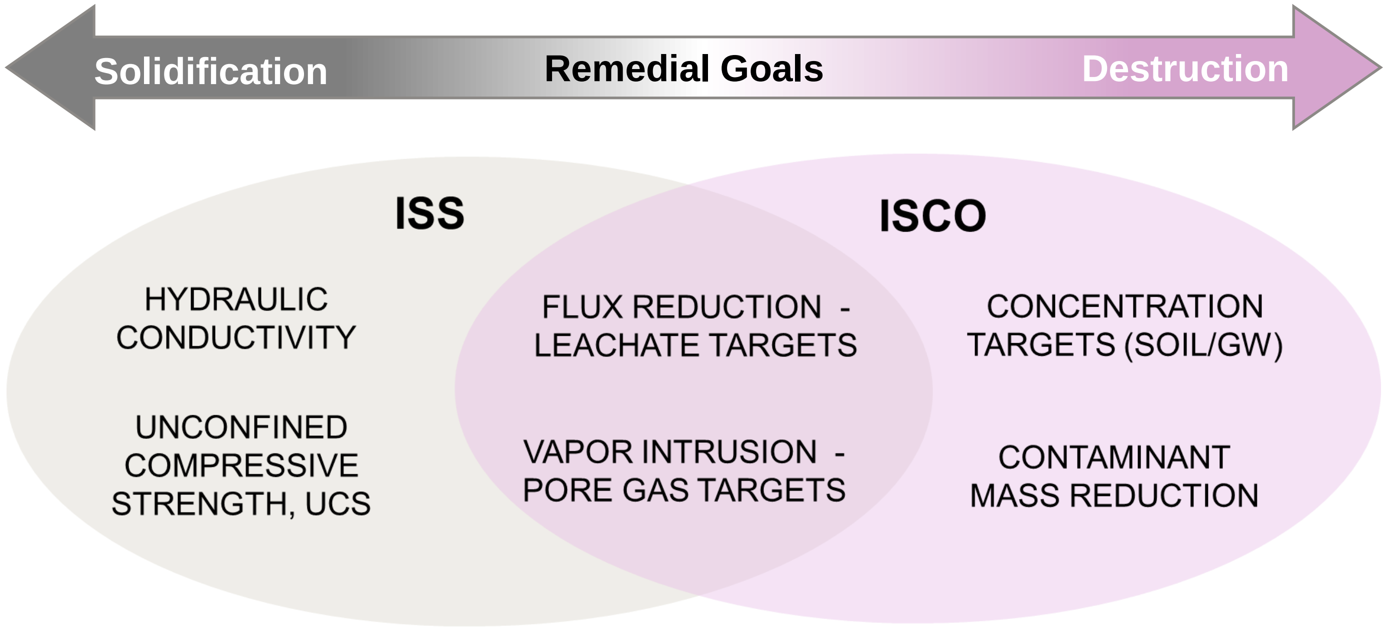
- Site Access
  - ISCO-ISS applied via soil mixing → need physical access
- Can soils be mixed?
  - Overburden soil / no boulders
- Can contaminants be treated?
  - Limits to ISCO (~10,000 mg/Kg)
- Remedial Goals
  - Can goals be achieved with ISCO-ISS
- Bench scale testing highly recommended to optimize dosages to meet project goals

Baseline Parameters
Contaminants (Soil & GW)
Soil Type
Moisture Content
Dry Bulk Density
Boulders (size)
Native UCS
Fraction Organic Carbon on Soil
Sodium/Potassium/Sulfate Ions
Soil Oxidant Demand (SOD)
Hydraulic Conductivity
Oxidation-Reduction Potential
pH
Dissolved Organic Carbon

Additional resource: Section 3 & 4, Interstate Technology & Regulatory Council (ITRC), 2011, "Development of Performance Specifications for Solidification/Stabilization"

Bench Study Scope Varied Based on Site-Specific Goals

- Bench studies are designed to confirm site goals and generate design parameters
- Scope varied based on site specific goals



Common Analysis

- Soil Oxidant Demand, SOD
- Base Buffering Capacity, BBC
- Soil stability, UCS
- Hydraulic Conductivity, K
- Soil Analysis
- Leach Testing
- Soil Volumetric Expansion

Soil Mixing Implementation Methods

Bucket Mixing

- Can reach up to 20 ft (6 m) below work pad (limit to length of excavator arm)
- Reagents applied dry at the surface → Best suited for depths up to 8 ft (2.5 m) for homogeneous mixing
- May need a rotary tool as a “polishing” step to improve blending

Adding dry reagents

Blending & addition of water

Wet mixing completed

Area after backfill

(Photo Documentation Courtesy of Trident)

EVONIK
Leading Beyond Chemistry

Rotary Mixing Attachments

- Various tools in the market (Lang Tool, Allu, Alpine, etc.) with varying penetration depths up to ~26 ft (8 m)
- Can apply in lifts to reach greater depths
- Reagents injected via mixing head – more homogeneous placement
- Hard soil may require pre-loosening with excavator

Lang Tool's Dual Axis Blender

Lang Tool's Deep Digger Blender

Allu Mixer Attachment

EVONIK
Leading Beyond Chemistry

Sufficient Moisture is important!

- Typically target approximately ~1.5x times full saturation
- Visually want the soil to look soupy with some standing water upon application
- Both Portland cement and Klozur® SP consume water as they react

Video courtesy of Lang Tool

Large Diameter Augers

Courtesy of Ladurner

- Typically used for depths greater than 30 ft (9 m)
- Can extend to depths of 60+ feet (20+ m) below the work pad
  - > 60 ft (> 20 m) is possible by specialized contractors
- Auger diameter may range from 3 to 11+ feet in diameter
  - Varied based on soil density, strength, depth, etc.
- Becoming increasingly cost-effective, especially for larger sites


Courtesy of Arkil


Courtesy of Geosyntec

ISCO-ISS Successfully Remediates Petroleum Contaminated Soils for Site Redevelopment

Location: Bolzano, Italy

Lead Consultant: Ladurner Bonifiche S.r.l.

Contaminants: Petroleum Hydrocarbons

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

Treatment volume: 3,500 m^3, 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: 2.8×10^{-6} to 7.3×10^{-7} cm/sec

Less than 15% soil bulking

ISCO-ISS Applied using Large Diameter Augers in Bolzano, Italy

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,

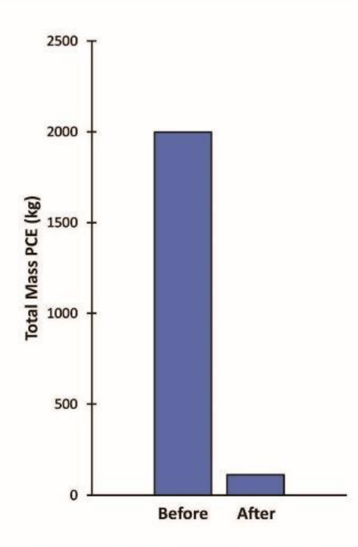
Reagent Dose (w/w soil):

- 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



Former MGP Site in Stockholm being Redeveloped into Residential Area

Client: City of Stockholm

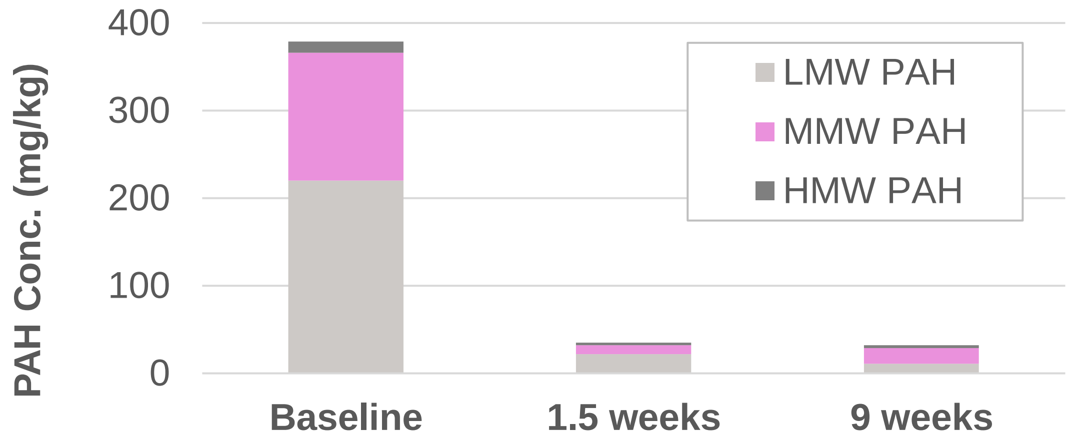
Contractor: PEAB / ARKIL

Treatment Volume: 50,000 m^3 clay layer

Remedial Goals: Prevent vapor intrusion to planned buildings via combination of stabilization and contaminant reduction

Reagent dose:
•1.8wt% Klozur® SP
•4-8 wt% Slag cement

Klozur® SP, cement and water applied using large diameter auger



- ~95% reduction in PAH-L
- ~90% reduction in PAH-M
- ~80% reduction in PAH-H
- Higher % reduction in lower molecular weight fractions.
- All samples below remedial goal of 250 mg/kg

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

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

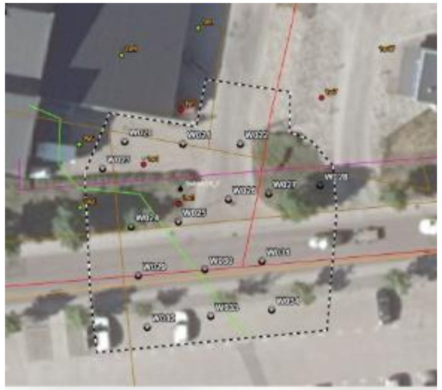
Soil Mixing Contractor: SMG

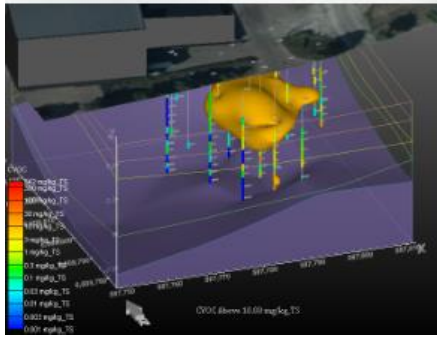
Goal: Reduce TCE mass by 50%

Treatment volume: 600 m^3 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%

Summary

- ISCO-ISS is combined remedy of two established technologies
  - Single application
    - Treat/degrade significant portions of contaminant mass
    - Residual is solidified in a monolith
  - Several synergistic benefits:
    - Higher UCS, lower leachate, lower hydraulic conductivity
    - Less soil bulking can decrease project costs
    - Site ready for redevelopment/access shortly after application

Bench studies can help optimize the dosages of ISCO and ISS reagents

Thank You!

Questions?

Stacey Telesz

Technical Sales Manager

Evonik

stacey.telesz@evonik.com

949.280.5765

Evonik Corporation

Soil & Groundwater Remediation

www.evonik.com/remediation

Leading Beyond Chemistry