Solutions for Complex Sites: Combining In Situ Stabilization/Solidification & In Situ Chemical Oxidation

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SMART Remediation
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PeroxyChem

Solutions for Complex Sites: Combining In Situ Stabilization/Solidification & In Situ Chemical Oxidation

Presented by Jean Paré, P. Eng.

March 2019

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Presentation Agenda

- ✓ **Technology overview**
  - In Situ Solidification-Stabilization
  - In Situ Chemical Oxidation
- ✓ **Combined Remedy**
  - Synergies and Benefits
- ✓ **Reagent Blend**
  - Match to site specific remedial goals
- ✓ **Strategies and Applications**
- ✓ **Summary**

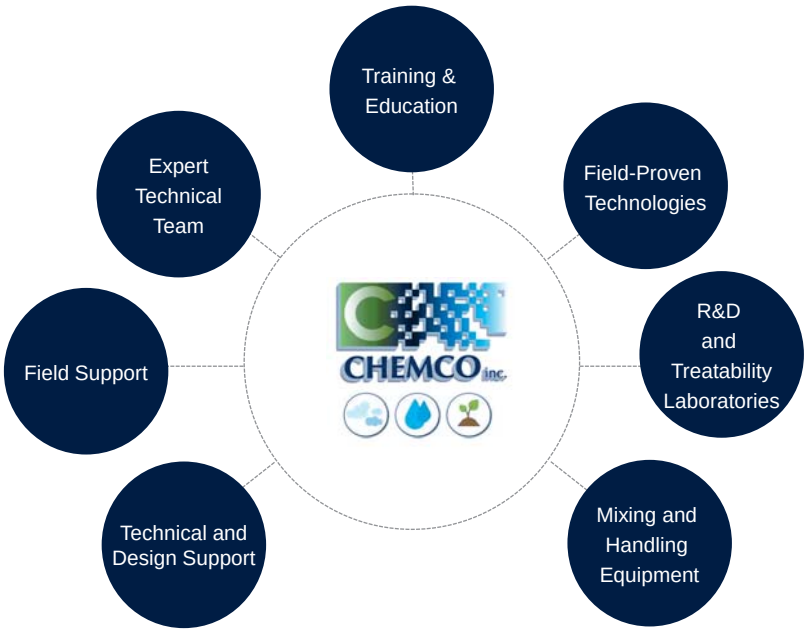
About us

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 soil Washing
- Enhanced Bioremediation
- Permeable Reactive Barrier Amendments
- Metals Stabilization



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ADVANCED OXIDATION TECHNOLOGY (AOT) *Since 2005*

PeroxyChem *Since 2005*

CARBONE CANADA *Since 2014*

BIOCONSERVACION *Since 2014*

CARUS® *Since 2014*

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EOS Remediation, LLC *Since 2016*

ChemBio Formulation *Since 2017*

IVEY-SOL® Surfactant Technology *Since 2017*

SiREM *Since 2017*

Höganäs *Since 2018*

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Technologies In Situ – Key Drivers

- ✓ Temps alloué versus coûts
- ✓ Accessibilité des contaminants (infrastructures souterrainnes, services publics, édifices, routes, etc.)
- ✓ Contribution à la développement durable (site de disposition ou traitement éloigné, mise en décharge sans traitement, production d'énergie)
- ✓ Polissage pour atteindre des critères fondés sur les risques
- ✓ Amélioration du taux d'élimination des contaminants par rapport à l'atténuation naturelle

- ✓ Polishing steps to achieve Risk Based Criteria
- ✓ Improvement in contaminant removal rate versus natural attenuation

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
- ✓ Enhanced Bioremediation
- ✓ Risk Analysis
- ✓ Stabilization /Solidification
- ✓ Soil Washing
- ✓ Phytoremediation
- ✓ Reactive Barriers
- ✓ Thermal degradation/desorption
- ✓ Activated Carbon Sorption Technology

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

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

- 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 apply with 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

EVOLUTION - ISS and ISCO

- **ISCO**
  - Benefits of some ISS
- **ISS**
  - Benefits of Klozur persulfate
- **Combined Remedy**
  - ISCO combined with ISS

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**

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** Klozur SP
2. **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**

ISCO Benefits – Alkaline activation

ISS reagents

- Portland cement (~65% CaO)
- Calcium hydroxide [$Ca(OH)_2$]
- Calcium oxide (CaO)
- Fly Ash (Class C & F)
- Blast furnace slag
- Lime kiln dust
- Cement kiln dust
- Pozzolans
- Bentonite

Common ISS reagents can activate Klozur SP

Activated Klozur persulfate reagents

- Klozur Sodium Persulfate (oxidant)
- Klozur Potassium Persulfate (oxidant)

- Alkaline activation*. One (or more) of the following:
  - 25% NaOH (typical for injections)
  - Calcium hydroxide [$Ca(OH)_2$]
  - Calcium oxide (CaO)

- Heat activation
  - CaO upon hydration releases heat

* PeroxyChem LLC ("PeroxyChem") is the owner of U.S. Patents No: 7,576,254 and its foreign equivalents. The purchase of PeroxyChem's Klozur® persulfate includes with it, the grant of a limited license under the foregoing patent at no additional cost to the buyer.

Case Study 1 - Turtle Bayou

- **ISCO and ISS are already being combined at several sites**
  - 2008 Turtle Bayou (URS-AECOM)
    - COCs: BTEX, cVOCs and PAHs
    - Klozur SP, hydrated lime, and Portland cement
      - 760,000 lbs Klozur SP
    - Met remedial goals
      - ISCO: 84% to 97% treatment
      - ISS: Stabilized soils

Lesson Learned : Chemical compatibility with reagents, and benefits of alkaline activated persulfate

Wiley and Block, (2010) D-021, "Chemical Oxidation Using Sodium Persulfate at a Superfund Site in Texas," Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA

ISCO Benefits from ISS Soil Strength

- ISCO applied with soil mixing and no ISS reagents may not have desirable post application soil characteristics
  - Low levels of ISS reagents can enhanced post application soil characteristics
    - Site specific (approximately 0.5 to 1.5% Portland cement)

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 20-50 psi

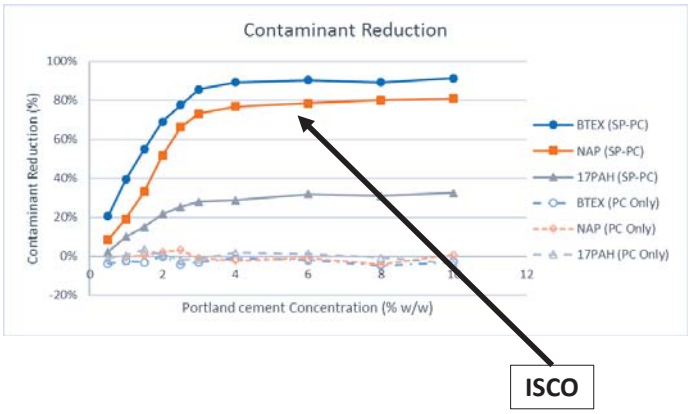
Case Study 2 - Combining ISS and ISCO

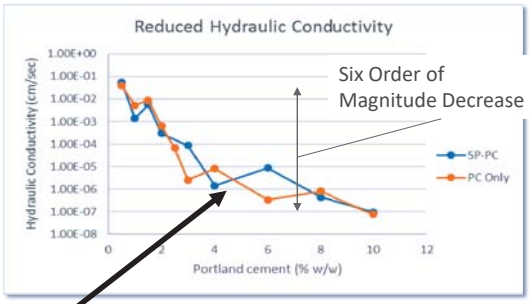
Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

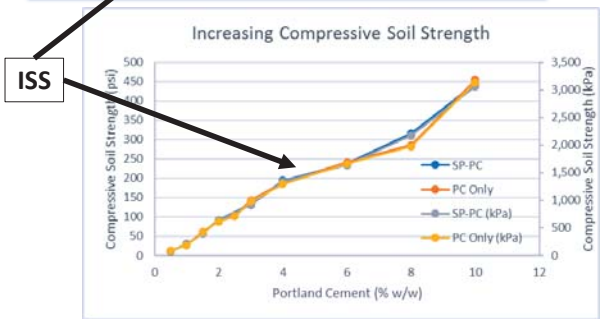
- Highly contaminated soils
  - >36,900 mg/Kg TPH
  - ~6,800 mg/Kg BTEX
  - ~13,400 mg/Kg Naphthalene (Nap)
  - ~16,900 mg/Kg 17 PAHs (not including Nap)
- Klozur SP: Portland Cement (PC) ratio (1:2 w/w)
  - **CaO in PC facilitates persulfate activation**
- ISCO:
  - Persulfate underdosed for complete treatment of TPH
  - Preferential treatment of soluble contaminants

Combining ISS and ISCO

Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

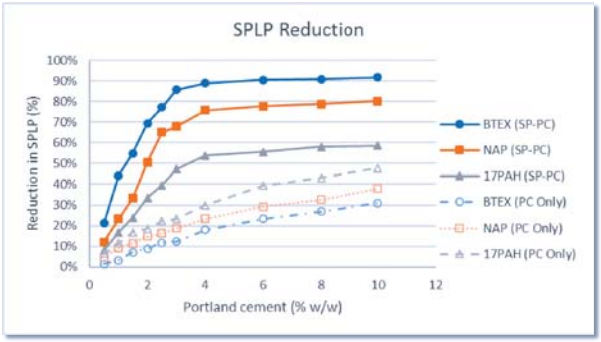






ISS Benefits: Leachate Concentrations

- **Contaminant leachate reduction**
  - Greater reduction in leachate concentrations with Klozur SP and Portland cement than Portland cement only
  - ISCO preferentially reduced more soluble contaminants
  - Portland cement alone only preferentially reduced leachate concentrations of larger, less soluble compounds

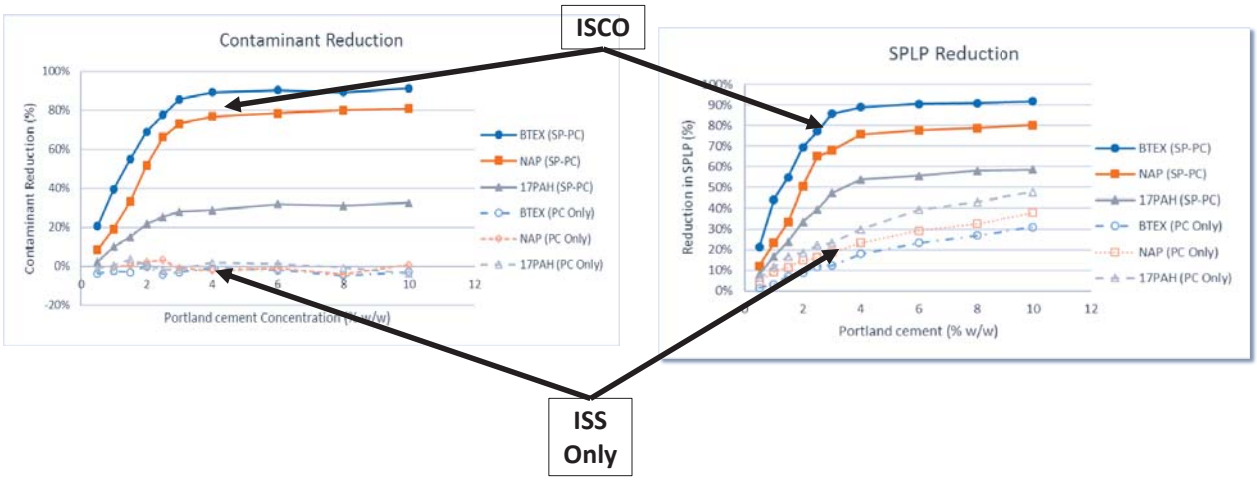


SPLP (synthetic precipitation leaching procedure)

Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

EVOLUTION - Combining ISS and ISCO

Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

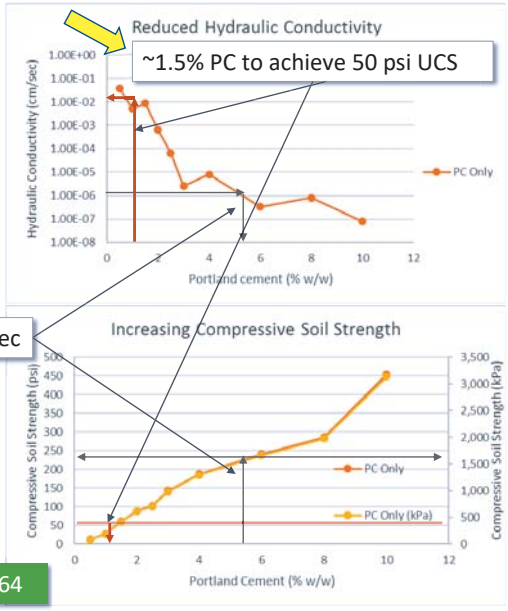


ISS Benefits: Control of Soil Characteristics

- **ISS is typically used to achieve multiple remedial goals. For example:**
  - Hydraulic conductivity (common < 10^{-6} cm/sec)
  - Compressive soil strength (common 20-50 psi)
- **Using ISS reagents alone may be difficult to achieve both hydraulic conductivity and compressive soil strength goals**

~5.5% PC to achieve <10^{-6} cm/sec

- **ISS with ISCO**
  - ISS and persulfate dosage rates can be varied to better achieve both hydraulic conductivity and compressive soil strength goals



Srivastava et al (2016), J. Environ Chem. Engineering, 4, 2857-2864

Optimizing Ratio of Reagents

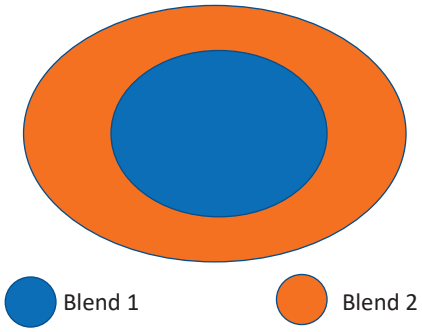
- **ISCO and ISS reagents can be combined for their mutual benefit**
- **The ratio of reagents can adjusted to achieve site specific remedial goals**

Case Study 3 - Application Strategy

Different reagent blends can be used at the same site

Example:

- Highly contaminated center
  - Stabilize: ISS, or ISS (with ISCO)
  - Treat and stabilize: ISCO with ISS
- Less contaminated outer ring:
  - ISS is balanced with ISCO to maximize reduction in hydraulic conductivity to create a hydraulic barrier



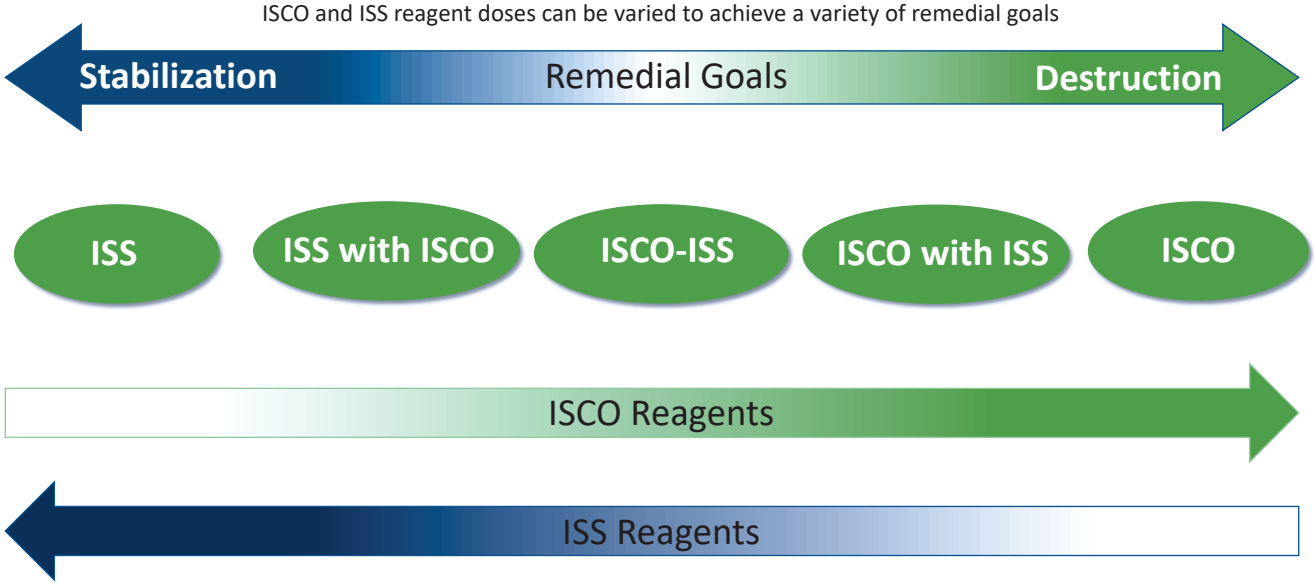
Can be used as alternative to sheet piling

Salinity Parameters Aquifer Impact (Persulfate Alkaline Activation with Hydrated Lime)

Parameters (All unit in mg/l other than for SAR – no unit)	Blank	Alkaline (Hydrated Lime) Activated Sodium Persulfate	Alkaline (Hydrated Lime) Activated Potassium Persulfate	Alkaline (Hydrated Lime) Activated Ammonium Persulfate
SAR	4.1	82	0.37	0.47
Calcium	96	770	1300	850
Magnesium	11	5.8	4.6	91
Sodium	160	8400	48	54
Potassium	7.8	15	9000	42
Sulfate	410	19 000	13 000	4300

ISS-ISCO Reagent Ranges

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



Summary

- **Blends of ISCO and ISS using soil mixing can be a powerful combined remedy**
  - Degrades the contaminant
  - Reduces contaminant flux
  - Controls post-application geotechnical characteristics of a site
- **Has been found to be lower cost alternative**
  - Less Excess soil displaced, less mixing/handling
  - Combined remedy in a single application
- **Technology synergies:**
  1. Shared alkaline sources
  2. Contaminant degradation by ISCO can reduce leachate (SPLP) concentrations
  3. ISCO can oxidize organics interfering with the cementitious process resulting in lower hydraulic conductivities if dosed appropriately
  4. Control over post soil mixing application soil characteristics

Acknowledgements & Ressources

- ✓ Peroxychem
- ✓ Journal articles from Vipul Srivastava and Dan Cassidy/Western Michigan University
  - Cassidy et al, (2015) J. Hazard Mater. 297, 347-355
  - Srivastava et al, (2016) Chemosphere, 154, 590-598
  - Srivastava et al, (2016), J. Environ Chem. Engineering, 4, 2857-2864
- ✓ Conference presentations
  - Wiley and Block, (2010) D-021, "Chemical Oxidation Using Sodium Persulfate at a Superfund Site in Texas," Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA
  - Klemmer et al, (2017) "Combining In Situ Chemical Oxidation and In Situ Solidification for Coal Tar – Synergy or Conflict?" 19th Railroad Environmental Conference, Champaign, IL
  - Cassidy and Srivastava, (2018) "Dose-Response Curves Comapre the Effectiveness of Combined Cement-Persulfate Treatment with Standalone ISS and ISCO in Ten Different Soils," Eleventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Palm Springs, CA
  - Cassidy and Srivastava, (2018) "Long-Term Anaerobic Bioremediation of Petroleum Contaminants by Iron- and Sulfate-Reducing Bacteria following Combined Cement-Persulfate Treatment," Eleventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Palm Springs, CA

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