

# Geosyntec D

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# WEBINAR

Wednesday, October 30th
11 AM and 2 PM EDT

Fundamentals of Combining In Situ Solidification and Stabilization (ISS) with ISCO

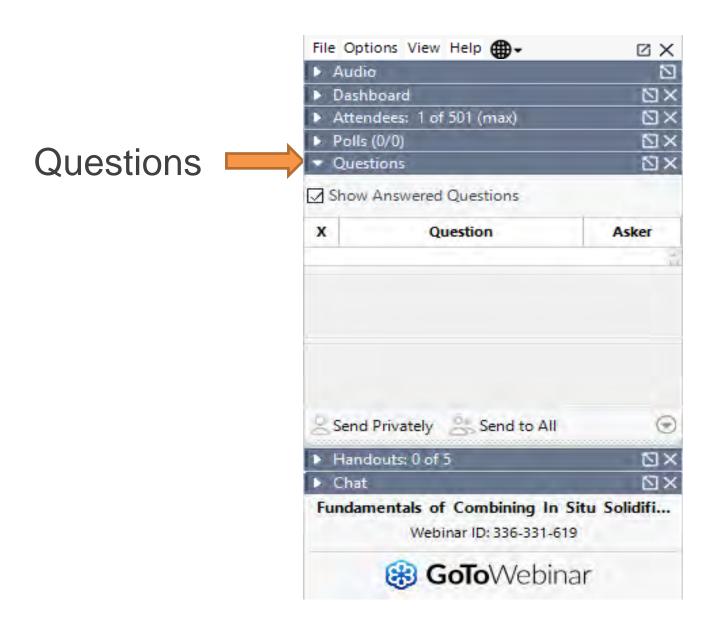
Dr. Brant Smith of PeroxyChem and Chris Robb of Geosyntec will present the fundamentals of combining in situ solidification and stabilization with in situ chemical oxidation.



Brant Smith, PhD, PE PeroxyChem Technical Applications Manager

Chris Robb, PE Geosyntec Principal Engineer

## Welcome!



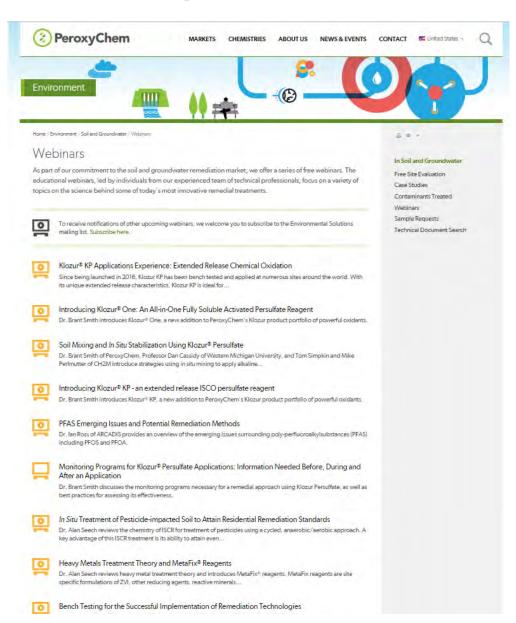
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#### **Enhanced Reductive Dechlorination**

- ELS® Microemulsion
- ELS® Concentrate

#### **Metals Remediation**

• MetaFix® Reagents





## **Previous Soil Mixing Webinar**



- Overview of soil mixing
- Bench testing
  - ISCO-ISS

- Case Study
  - Site now closed

#### January 2017 Speakers

- Tom Simpkin, Ph.D, P.E.
  - Remediation Technology Leader and Senior Technologist for CH2M-Denver
  - Ph.D. University of Wisconsin-Madison
  - Over 30 years of experience
- . Dan Cassidy, Ph.D., P.E.
  - Associate Professor at Western Michigan University
  - Over 400 Bench Scale Treatability Studies
  - 37 peer-reviewed publications
- Mike Perlmutter, P.E.
  - Senior Technologist CH2M Atlanta
  - M.S. University of Texas-Austin
  - Over 20 years experience



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Brant Smith, PhD, PE PeroxyChem Technical Applications Manager

Chris Robb, PE Geosyntec Principal Engineer

#### Introduction

# Geosyntec consultants

Chris Robb, 23 years experience; 17+ with ISS technologies

- B.S. Civil Professional Engineer (WI, FL)
- Remediation design and construction "Develop Constructible Designs"
- In situ stabilization/solidification (ISS)
  - Engineer of record, remedial action coordination, constructability review, and senior technical expertise for over 500,000 cubic yards of ISS/DSM implementations across more than 20 project sites in US, Europe and Australia
  - Led design and implementation of first successful ISCO/ISS application in Denmark
  - ISS Experience on CVOC, MGP, CERCLA, SAS, Sediment, and CCR Sites
- Significant Contributions to the Practice:
  - Featured Presenter/Instructor: Theme Day 1 Soil Mixing as A Remediation Method, Winter Meeting 2019, ATV Jord of Grundvand, Vejle, DK
  - Principal Investigator/Author: Corrective Action Technology Profile: Practical Feasibility of In Situ Stabilization/Solidification as a Source Control for Coal Combustion Residuals, EPRI Report 3002008475, December 2016
  - Contributing Author: Development of Performance Specifications for Solidification/Stabilization,
     Interstate Technology & Regulatory Council (ITRC), July 2011
  - Inventor: United States Patent No. US 9,909,277 B2, "IN SITU WASTE REMEDIATION METHODS AND SYSTEMS" March 6, 2018





#### **Outline**



- Technology overview
  - ISS
  - ISCO-ISS
- Benefits of a combined Remedy
- Case study
- Lessons learned
- Summary

## ISS as a "Stand Alone" Treatment Technology



#### **TREATMENT**

- Mixing of contaminated materials with cementitious/pozzolanic reagents:
  - Reduces contaminant migration via Advection, Hydrodynamic Dispersion and Diffusion

#### **STABILIZATION**

- ➤ Chemical reaction between reagents and contaminated materials designed to reduce the leachability of targeted contaminants by:
  - Binding free liquids
  - Immobilizing targeted contaminants
  - Reducing solubility of the contaminated material

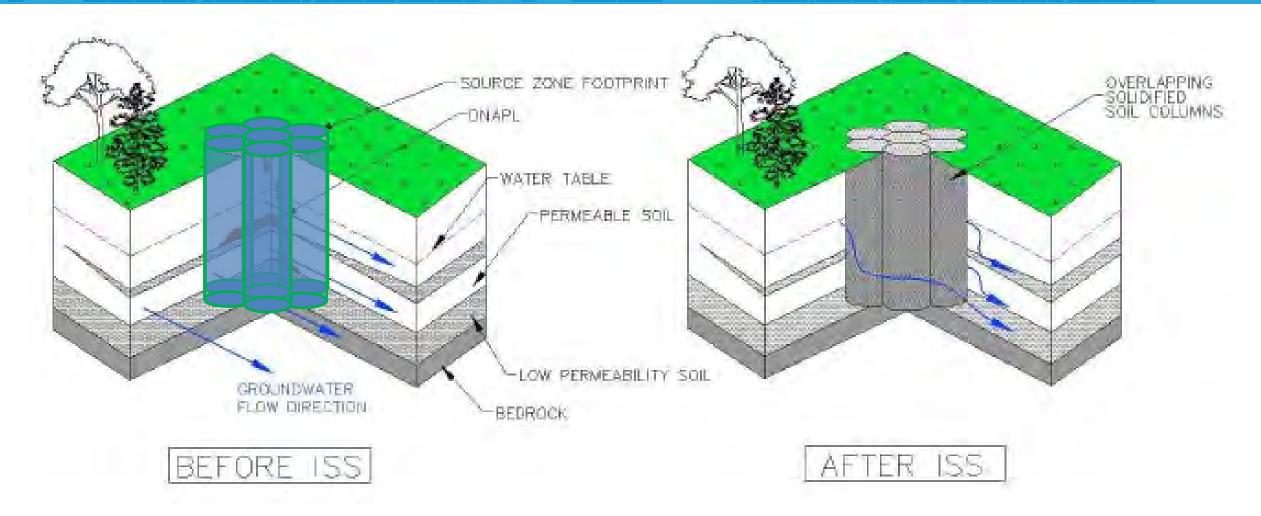
#### **SOLIDIFICATION**

- Contaminated materials are encapsulated (physically trapped) to form a solid material that restricts contaminant migration by:
  - Reduction of permeability and effective porosity
  - Increasing compressive strength and media durability

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#### In Situ Stabilization/Solidification (ISS) Conceptual Model





Source: Development of Performance Specifications for Solidification/Stabilization, Interstate Technology & Regulatory Council (ITRC), July 2011

## ISS as a Treatment Technology

# Geosyntec consultants









# Why In Situ Chemical Oxidation (ISCO) + In Situ Stabilization / Solidification (ISS)?

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- ✓ Treats all waste on-site.
- ✓ Rapid implementation.
- ✓ In U.S.A., ISS typically is applied alone. ISS is a mature technology used at hundreds of sites.
- ✓ At Søllerød, proximity of downgradient municipal supply well prompted need for destructive treatment (ISCO) as well as ISS.
- ✓ Published laboratory studies show promise for ISCO + / ISS.



Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

In situ solidification and in situ chemical oxidation combined in a single application to reduce contaminant mass and leachability in soil

Vipul J. Srivastava<sup>a</sup>, Jeffrey Michael Hudson<sup>b</sup>, Daniel P. Cassidy<sup>b,\*</sup>

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<sup>b</sup> Department of Geosciences, Western Michigan University, Kalamazoo, MI 49006, USA

28 May 2016

# ISCO and ISS: Complementary Technologies

#### Where can ISCO aide ISS?

- > Contaminants are not destroyed or removed
- ➤ Effectiveness for some contaminants (e.g., HVOCs) may require additional design measures
- ➤ Uncertainty in long term behavior / protection of sensitive receptors

#### Where can ISS aide ISCO?

- ➤ Contact and distribution of ISCO using LDA techniques
- > Alleviate soft ground after treatment
- > Residual contaminants rendered immobile

## COMBINED ISS/ISCO TECHNOLOGY CONCEPTS Geosyntec consultants

#### Combining technologies to capitalize on attributes

- LDA Mixing Key Attributes
  - Overcomes heterogeneities
  - Complete mixing/contact
  - Overcomes contact/distribution challenge
- ISCO Key Attributes
  - In situ technology that results in contaminant destruction
  - Chemistry is proven contaminants such as gasworks residuals and chlorinated solvents can be oxidized/reduced, etc.
- Combined ISS/ISCO Concept
  - Contaminant sequestration/destruction followed by solidification/stabilization
  - Useful when contamination destruction and greater leaching reduction is needed
  - Commingled plume applications
  - Overcomes soft ground challenges
  - ISS components can be used to heat / activate reactants (e.g., persulfate activated by cement heat of hydration and high pH)



#### **Drum Mixer Based ISCO-ISS**



ISCO-ISS
Indiana
Courtesy of
SME and Lang
Tool



## **Remedial Goals and** Reagent Ranges



ISCO and ISS reagent doses can be varied to achieve a variety of remedial goals **Solidification** Remedial Goals **Destruction ISCO-ISS ISCO** ISS **ISCO** Reagents **ISS** Reagents



## Reagents



- Binder plus Klozur<sup>®</sup> SP (sodium persulfate).
  - ISS with ISCO
    - 3-8% Portland cement
    - 0.5-2% Klozur SP
  - ISCO with ISS
    - 1-6% Portland cement
    - 1-5% Klozur SP
- Common ISS binder reagents can also create alkaline activated conditions for persulfate
- Typically less binder material is needed to achieve ISS goals when combined with sodium persulfate
  - Reduced handling and disposal of excess soils

#### Common ISS reagents

- Portland cement (~65% CaO)
- Calcium hydroxide [Ca(OH)<sub>2</sub>]
- Calcium oxide (CaO)
- Fly Ash (Class C & F)
- Blast furnace slag
- Lime kiln dust
- Cement kiln dust
- Pozzolans
- Bentonite

<sup>\*</sup> PeroxyChem LLC ("PeroxyChem") is the owner of U.S. Patents No: 7,576,254, US App 62/890,098 and their 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.



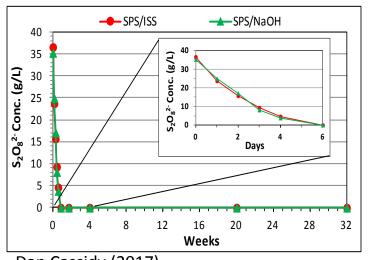
## ISCO Perspective (w/ISS)



- Remedial Goal:
  - Destruction

- Application:
  - Soil mixing
- Soils need some post application strength
  - Clays

- Strategies
  - Reagents combined in single application



Dan Cassidy (2017)

- Reagents applied in sequence
  - 1. ISCO technologies
  - 2. ISCO/ISS or ISS only







- Reduced hydraulic conductivity
  - 2-3 orders of magnitude below native soils
  - 1 x 10<sup>-6</sup> cm/sec

- Unconfined Compressive Strength (UCS)
  - "Workable" ~20-60 psi
  - Hardened

 Lower contaminant flux and leachate concentrations

General Relationship between Soil Consistency and Unconfined Compressive Strength								
Consistency	Unconfined Compressive Strength (UCS) Ranges							
	р	si	kPa (KN/m²)					
	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



#### 1) Contaminant Destruction: **Lower Leachate Concentrations**



NAP (PC Only)

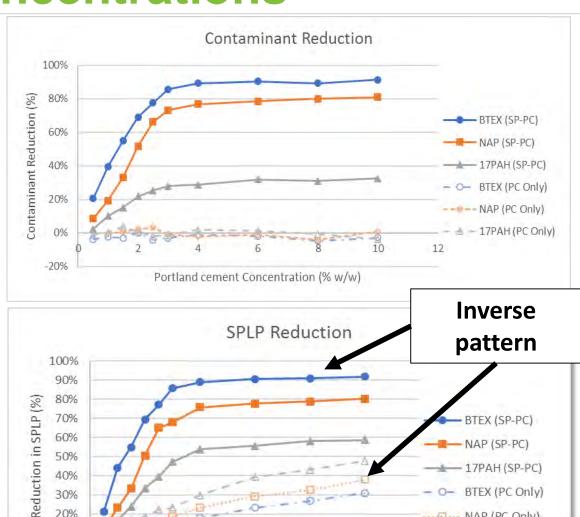
- ≜ − 17PAH (PC Only)

10

12

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

- Highly contaminated soils (MGP) rešidúals)
  - >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 alkaline persulfate activation
- ISCO:
  - Persulfate underdosed for complete treatment of
  - Preferential treatment of soluble contaminants

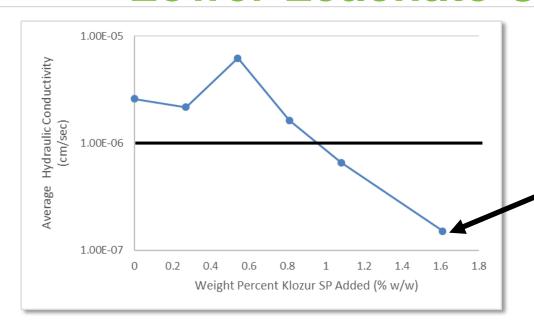


Portland cement (% w/w)

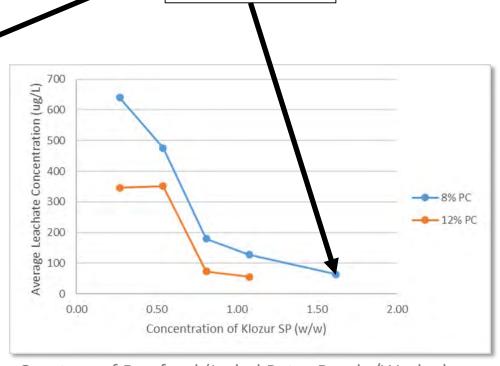


# 2) Lower Hydraulic Conductivity: Lower Leachate Concentrations





Theory: Organic matter can impede cementitious process. Oxidizing organic matter can help the cementitious process.



1.6% Klozur

SP

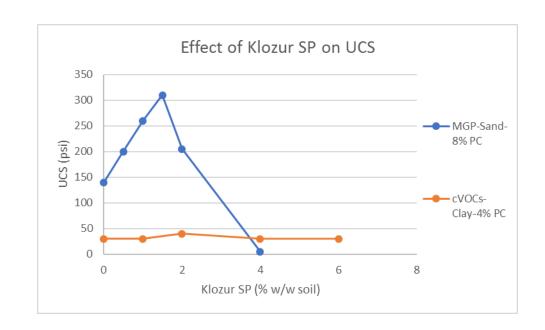
Courtesy of Brasfond (Isabel Peter Rando/Worley) Geosolutions (Tony Moran/Entact)

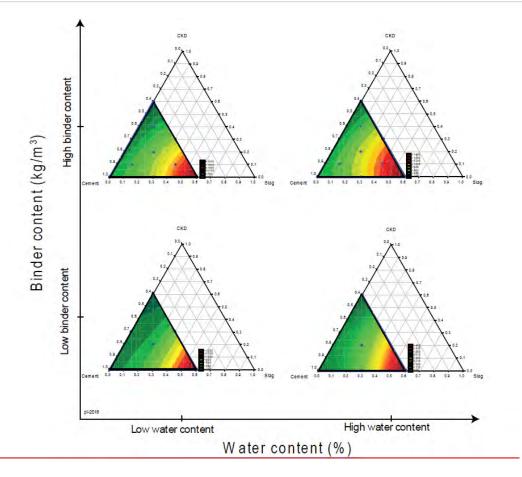


#### 3) Greater UCS/Control over UCS



- Klozur SP can impact UCS
  - Potential break point
- Final UCS is a function of more than one variable

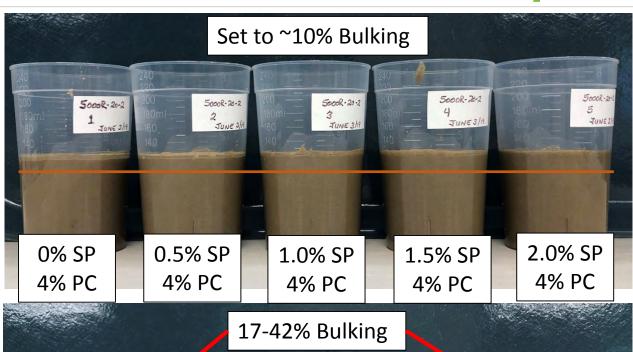


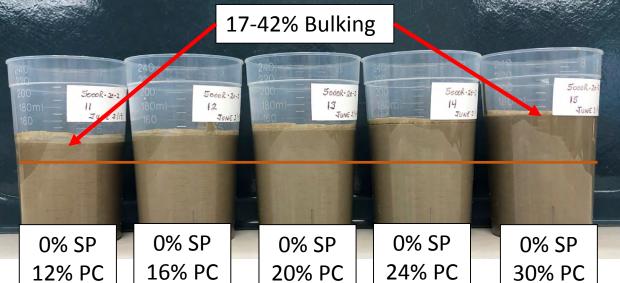


Courtesy of Per Lindh, Vintermode 2019, Temadag om Soil Mixing som afvaergemetode



## 4) Less Binder: Less Displaced Soils





 Minimizing binder and water needed

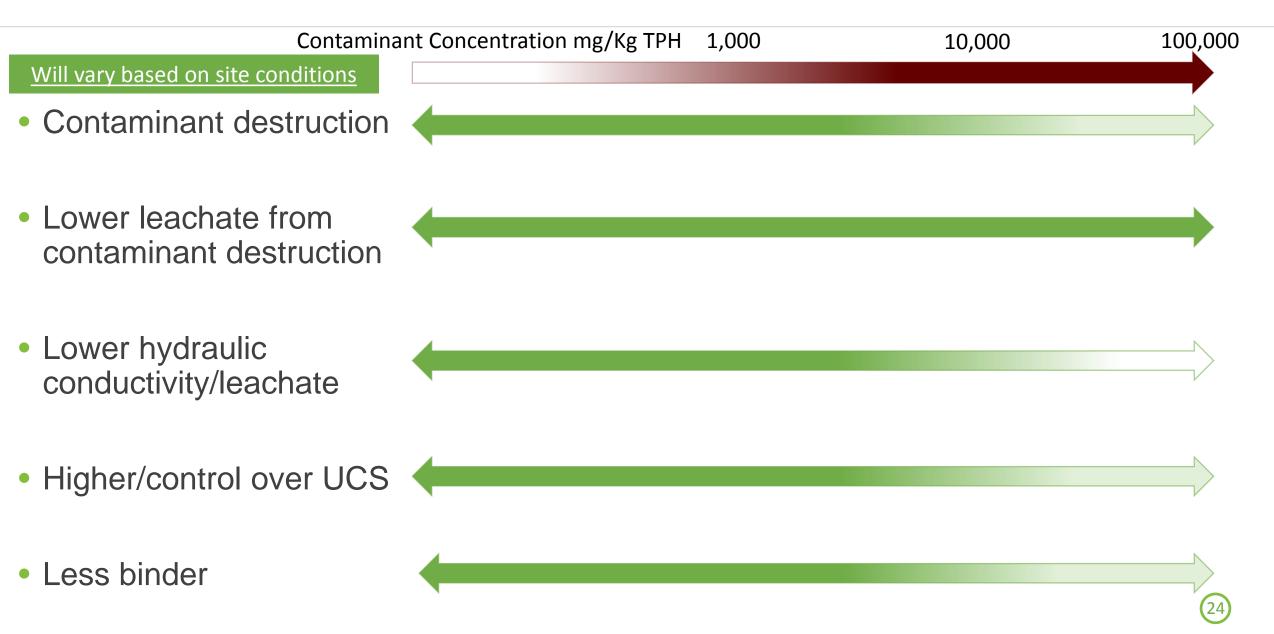
- Minimizes soil bulking
- Lower carbon footprint

 Less material handled and disposed of results in cost savings



#### **Benefits: When and Where**





#### CASE STUDY: SØLLERØD GASVÆRK SITE

Holte,
Capital Region of
Denmark

October 30, 2019

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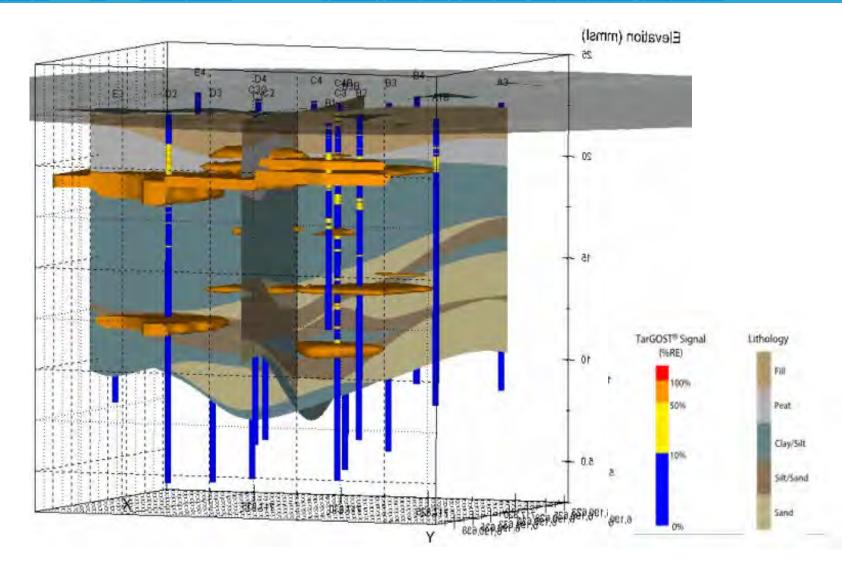




### Søllerød Gasværk Background

# Geosyntec consultants

- Free phase tar (up to 15 m deep)
- Alternating geology
- Non-coherent pollution distribution



#### Laboratory Study Objectives



 Assess in situ solidification/stabilization (ISS) with in situ chemical oxidation (ISCO) for treating source area coal tar contamination in soils at the former Søllerød Gasværk Site in Holte, Denmark

#### Performance Targets:

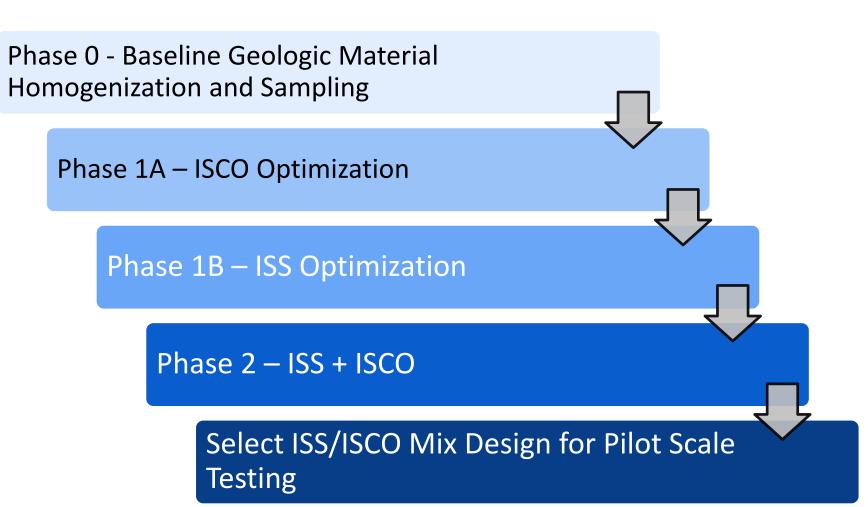
- Oxidation and reduction in leaching of dissolved phase coal tar constituents (i.e., BTEX, sVOCs, and phenolic compounds),
- Acceptable values of fresh slurry density, viscosity, and pH (API RP13B-2);
- Average hydraulic conductivity  $< 1 \times 10^{-6}$  cm/s with no more than 10% of the samples  $> 1 \times 10^{-5}$  cm/s with the least quantity of additional reagents
- Unconfined compressive strength > 0.15 MPa at 28-day curing engineers | scientists | innovators

#### Design of Laboratory Study



#### Study:

- ✓ Phase 0 Soil Compositing and Geotechnical Index Testing
- ✓ Phase 1A assess ISCO reactant dosage (base activated sodium persulfate) performance
- ✓ Phase 1B assess ISS reagent dosage (CEM III/B and CEM I 42,5 N – SR5)
- ✓ Phase 2 assess combined ISS/ISCO



## **Laboratory Study Results**



	Unit	Phase /10/	ISCO	ISS	ISS+ISCO - One step	ISS + ISCO- Two step	Target value
Geotechnical test							
Geotechnical structure (soil strenght)	MPa	Phase 1B; Table 2-2, 3- 5	NA	3.8	0.59	2.92	0,15 Mpa (> 24 psi)
Average hydraulic conductivity	cm/s	Phase 1B; Table 2- 2(ISS); Table 3-5 (Step 1 and step 2?)	NA	1.9 x 10 <sup>-5</sup> *	2.7 x 10 <sup>-7</sup>	1.8 x 10 <sup>-8</sup>	< 1x10 -6 cm/s w ith no more than 10% of the samples > 1x10 -5 cm/s w ith the least amount of additional reagents
Swell of geologic materials	%	Phase 2; Table 2-1, 3-1	NA	14-22	23-31	24-33	Not defined
Mass destruction	estruction						
Benzene	%	Phase 1A; Table 1-2; Phase 2; Table 3-2	99	NA	100	100	Not defined
Phenol			100	NA	83	83	
TPH			26	NA	39	37	
Naphthalene			-19	NA	58	77	
Leach reduction	each reduction						
Benzene	%	Phase 2 - Annex M	NA	>99	>99	>99	>75
Phenol			NA	>99	>99	>98	
TPH			NA	NA	NA	NA	
Naphtalene			NA	93	80-98	80-84	

#### Notes:

<sup>\* -</sup> Hydaulic conductivity samples may have been influenced by channeling due to a difference in the mold diameter and test cell diameter.

# Transition of Laboratory Results to Pilot Scale

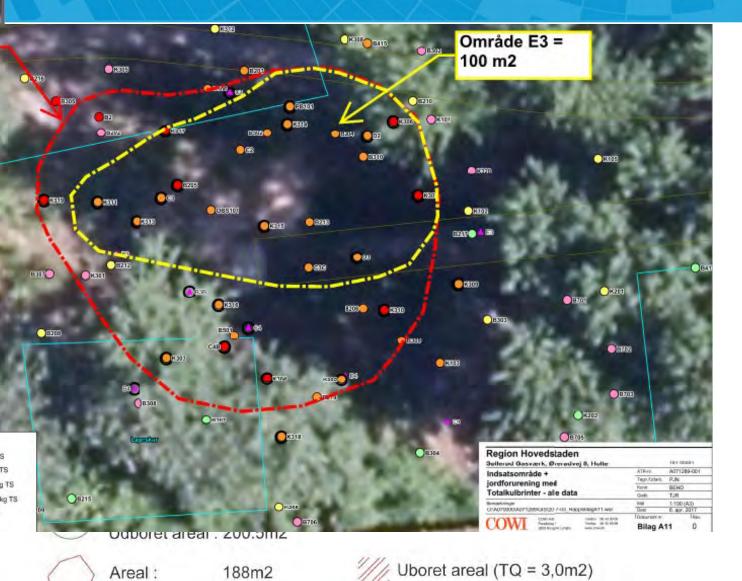
Geosyntec consultants

- Pilot Test Challenges
  - First-time use in Denmark (learning)
  - Process scale up from bench to field
  - Residential neighborhood, spatial constraints above ground, proximity to houses
  - Challenging Geology: 3m to 5m peat –
     stability concerns, highly plastic clay,
     confined aquifer, tight site logistics
  - Verification of treatment performance
  - Handling and mixing of potentially
     corrosive materials engineers | scientists | innovators



### Conceptual Full-Scale Layout of ISS Columns

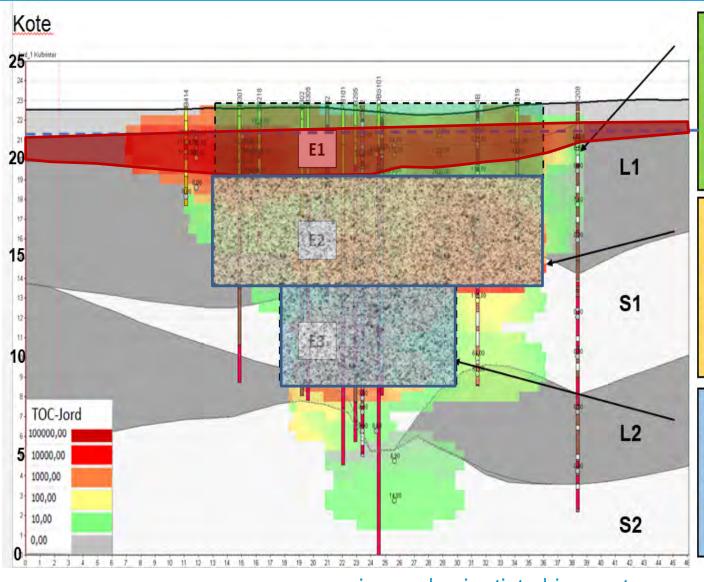




Design	
Slag Cement (CEM II/B)	8 % dw
Persulfate	3 % dw
Auger diameter	2 m
Auger Mixing area	$3.14 \text{ m}^2$
Total target treatment area	188 m <sup>2</sup>
Number of columns	75
Area of all columns	235.5 m <sup>2</sup>
Column overlap	35 m <sup>2</sup>
Overlap %	17.5

#### REMEDIAL ACTION AREAS

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Område E.1:

Areal: 185 m2

Dybde: 0 - 2/5 m u.t.

Volumen: ca. 700 m3

Geologi: Fyld/tørv/silt

Hydrogeologi: Mættet fra ca. 2 m u.t.

Område E.2:

Areal: 185 m2

Dybde: 2/5-8/10 m u.t.

Volumen: ca. 1150 m3

Geologi: Ler og silt med sandstriber

Hydrogeologi: Mættet

Område E.3:

Areal: 100 m2

Dybde: 10-12/15 m u.t.

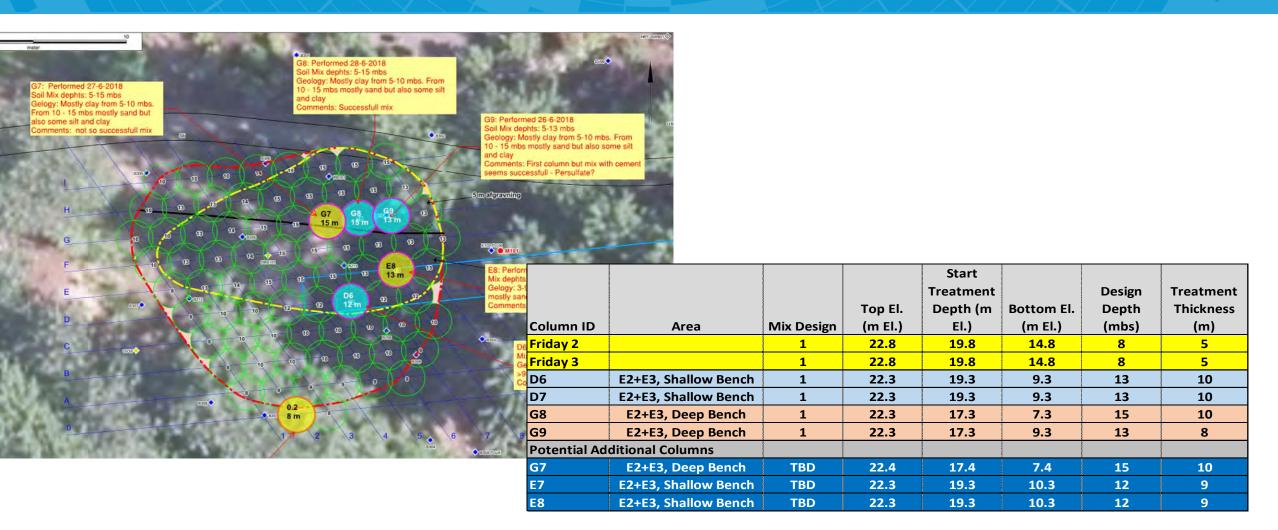
Volumen: ca. 400 m3

Geologi: Sand med silt-/lerindslag

Hydrogeologi: Mættet, spændt

#### Design of Pilot Scale Study





#### Pilot Test Findings & Lessons for Full-Scale



- • $K_h$ . All QA/QC samples met criterion of  $\leq 1 \times 10^{-6}$  cm/sec.
- •UCS. 8 of 13 samples exceeded 0.35 MPa and 10 of 13 samples exceeded minimum criteria of 0.15 Mpa. (3 samples failed initially but cured later in time)
- UCS improved by optimizing blade rotation / mixing energy, sealing leaks, reducing slurry water content
- Contaminant destruction reduction in benzene concentrations ranged from 6x to 133x.





## Full-Scale Implementation

#### Final Recommendations



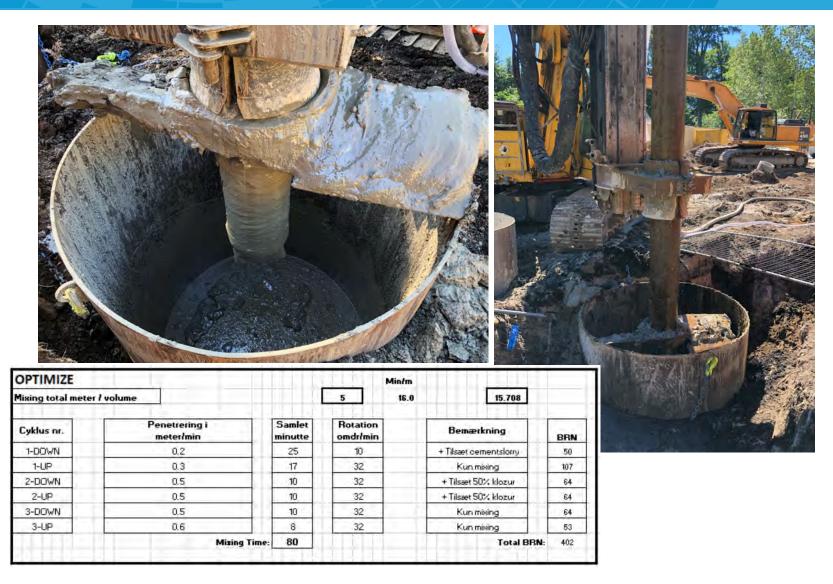
- Recommendation to proceed to full scale ISS/ISCO treatment of area E:
  - Strength results were indicative of the long term durability of the ISS/ISCO treatment and preventing long term soft ground conditions
  - Samples that did not exhibit adequate strength were located in the upper portions of the columns and correlated with high moisture content (> 35%)
  - Hydraulic conductivity reductions translated from laboratory to pilot scale implementation
  - Optimize LDA operations

### 2-m Diameter Mixing Auger, Column Casing

# Geosyntec consultants

#### Geology/Stability Solution:

- Excavated peat in 2m
   DIA steel casing to 3 to
   5 mbs
- ISS through each casing
- 3 mixing passes –
   established optimum
   blade rotation number
   to mix plastic clay
- Cleaned augers after first mixing pass to remove accumulated clay



## Full-Scale ISCO/ISS By the Numbers

- Treatment Area 188 m<sup>2</sup>
- Treatment Volume ~ 1,865 m<sup>3</sup>
- 75 columns, 17% overlap
- Rate 100 m<sup>3</sup>/day (10 m<sup>3</sup>/hr)
- Cement 15 tons/day
- Water 32 m³/day
- Persulfate 6.5 tons / day
- Mixing cycles 3 cycles; 300 m³/day





#### Results of Full-Scale ISCO/ISS



- Hydraulic Conductivity (K goal: 1 X 10<sup>-6</sup> cm/s)
  - Average:  $3.1 \times 10^{-7} \text{ cm/s}$  (Lab:  $2.7 \times 10^{-7} \text{ cm/s}$ )
  - Range:  $2.6 \times 10^{-9} \text{ cm/s} 1.5 \times 10^{-6} \text{ cm/s}$
  - $-92\% < 1 \times 10^{-6} \text{ cm/s} (1 \text{ of } 14 > 1 \times 10^{-6} \text{ cm/s})$
- UCS (Min: 0.15 MPa; 90% ≥ 0.35 MPa)
  - 36 samples; 22 ≥ 0.35 MPa; 29 ≥ 0.15 MPa
  - Direct correlation between the UCS and the water content average moisture content of 32 % - 6 samples < 0.15 Mpa</li>
  - 3 samples < 0.05 MPa. Average moisture content of 36 %.</li>
  - Follow up CPT and 365 day UCS tests performed

#### Results of Full-Scale ISCO/ISS



Category	Units	Benzene	Total hydrocarbons	Naphthalene	Phenols
Treatment Area	m³	1,865	1,865	1,865	1,865
Treatment Area (assuming 2 tonnes/m³)	Tonnes	3,730	3,730	3,730	3,730
Contamination Mass Before ISCO/ISS	Kg	50-100	2000-3000	400-600	Approx. 10 kg
Concentration after ISCO/ISS	mg/kg	0	321	23	0.04
Contamination Mass after ISS/ISCO	Kg	0	1,200	85	0.1
Pollution reduction after ISS/ISCO	%	Approx. 100%	40 - 60%	80 -85%	Approx. 99%

- Degradation measured in laboratory tests:
  - Benzene = 100%
  - Phenols = 83%
  - Total hydrocarbons = 39%
  - Naphthalene = 58%
- Improved degradation in full-scale tests

#### Some Lessons Learned





- Field verify strength development
   multiple lines of evidence
- Best day 36 m<sup>3</sup>/hr (113 m<sup>3</sup>)
- Many days 0 m<sup>3</sup>
- Corrosivity of persulfate stock solution requires special handling
- Control of water content is critical

   additional cement was added to
   some columns
- Mixing energy delivered to soils is critical – contractor experience

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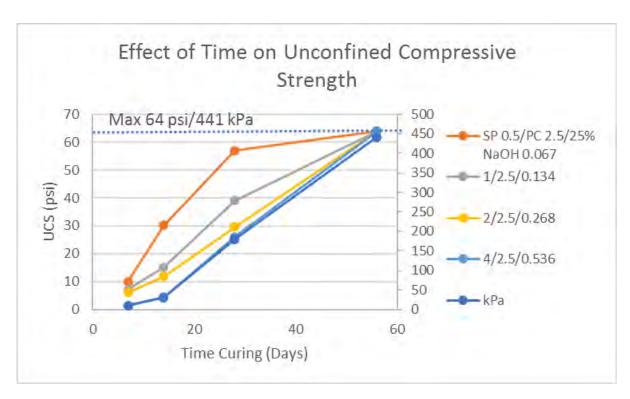


## Lessons Learned: Set Up Time



- Set up time is longer
  - CaSO<sub>4</sub> slows set up time

 Blast furnace slag may have better performance

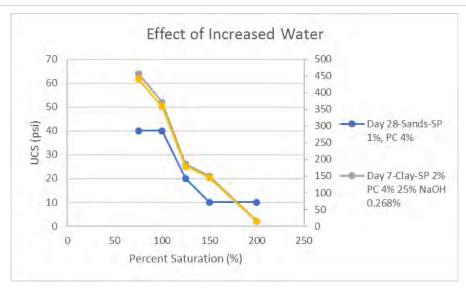


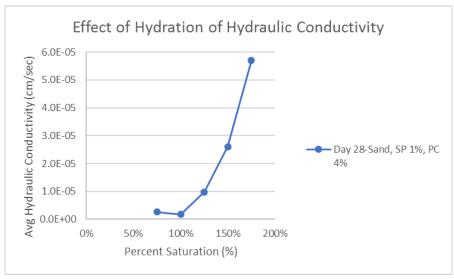


## **Lessons Learned: Hydration**



- Hydration impacts
  - UCS
  - Hydraulic conductivity
- Hydration
  - Present in subsurface
  - Used to dissolve reagents
  - Used to lubricate subsurface







## Lessons Learned: Chemical Compatibility

 Neutral pH persulfate can be very corrosive to carbon steel

Persulfate generates acid as it decomposes







### Best Practices: Compatible Materials



Chemically compatible equipment needs to be used for all wetted equipment parts or parts that may come in contact with the reagents

- Compatible with persulfate:
  - 304 and 316 stainless steel, PVC, CPVC, polyethylene, Plexiglas®, glass, FRP (fiber reinforced plastic, e.g. Derakane©), Fiberglass specifically vinyl ester resin, Polyester
  - Elastomers:
    - Long term duration: Teflon or PTFE, PVDF, or Gylon<sup>®</sup>
    - Short term duration: EPDM
    - Safety gear: butyl rubber, neoprene
- Corrosion rates increase at higher persulfate concentrations

Note: The pH of persulfate solutions can decrease over time and can become acidic

Table 4: Results for Alkaline Activated Klozur Persulfate Solutions, 20 wt% and 40 g / L at Room Temperature After 1 Month Exposure Time

mpy – milli-inches per year; √ - compatible material, Θ - non-compatible material

Material	20 wt% concentration	40 g / L	Comments	
Stainless steels (304L, 316L)	<b>✓</b>	1	< 1 mpy. No noticeable corrosion over 1 month	
Copper Brass	✓	<b>√</b>	Negligible general corrosion (< 2 mpy). Black film formation observed.	
Carbon steel	¥	✓	Negligible general corrosion (< 2 mpy). Isolated rust spots observed	



#### **Best Practices**



- Combine and coordinate chemistries with applications method
  - Design with understanding of contractor abilities and requirements
  - Amount of hydration
    - Dry reagents
    - Aqueous phase dissolved reagents
  - Bench test materials to be used in field



**Courtesy of Cascade** 



#### **Best Practices: Bench Tests**



- Variables
  - Binder (test actual materials)
    - Portland cement
      - Type I or Type II
    - Blast furnace slag
  - Klozur SP
  - Water content
    - Multiple test conditions
  - Soil type

- Contact time
  - Contaminants: 14 days
    - Modified SPLP
  - UCS: 28 day and 56 to 80 days
  - Hydraulic conductivity (with final UCS)
- Experimental Design
  - Multiple test conditions
  - Contaminants: all
  - UCS and hydraulic conductivity
    - Based on contaminants treated

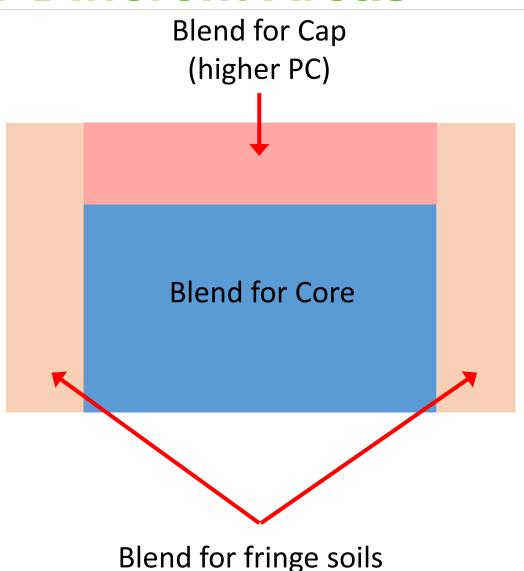




### Different Blends for Different Areas

Several projects have developed custom approaches for different areas, favoring goals such as:

- Higher UCS in the cap
- More treatment in the core
- Lower permeability/leachate in the fringe soils





## **Summary**



- Chemically compatible materials should be used
  - Decontamination procedure
- Coordination between contractor, labs, design engineer and chemical vendors

- Bench scale tests
  - Water content needs to be considered along with reagents
  - Curing time is expected to take significantly longer than normal concrete



## Summary



- Two valid remedial technologies that can be combined
  - ISCO perspective (destructive remedial goal)
    - Control post soil mixing geotechnical characteristics
    - Can apply in sequence or combined
  - ISS perspective (solidification remedial goals)
    - Lower leachate concentrations
    - Lower hydraulic conductivity
    - More control over final geotechnical parameters (UCS)
    - Less binder
      - Less excess soils requiring handling and disposal
        - Cost savings
        - Fewer trucks in neighborhood
      - Smaller carbon footprint



### Questions??



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