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Combined In Situ Chemical Oxidation and Stabilization/Solidification for Full-Scale Remediation of a Coal Tar Source Area

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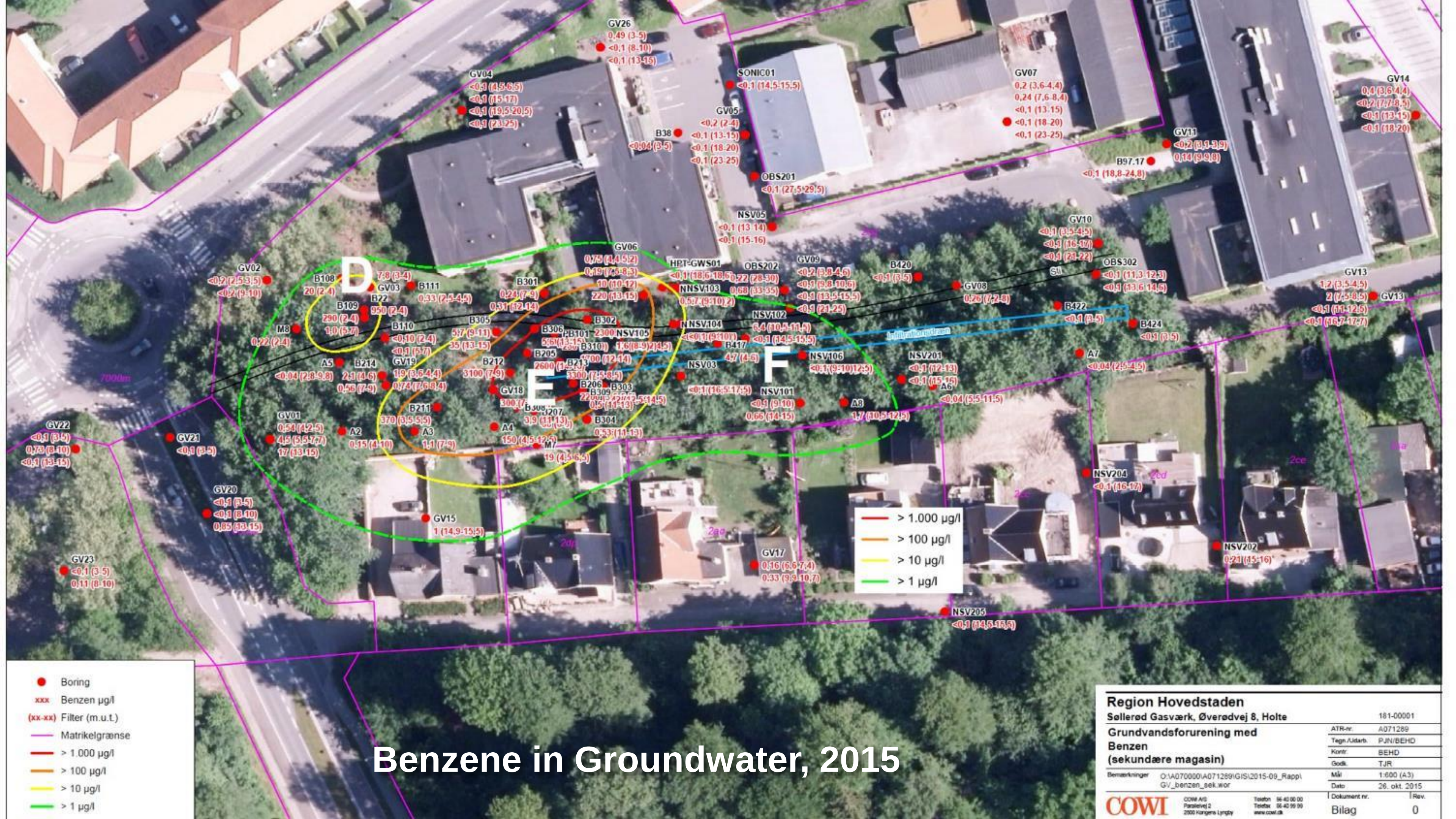
Søllerød Gaswærk Site, 1954



Benzene in Groundwater, 2015

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

- 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.

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

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ISCO / ISS Bench Test Approach

- **Reagents/Additives:**
  - ISCO using base-activated persulfate (BAP) [2, 3, 4%]
  - ISS using CEM III/B (slag cement) [8 to 10%]
  - CEM I 42,5 N - SR5 (similar to Portland Type V marine cement)

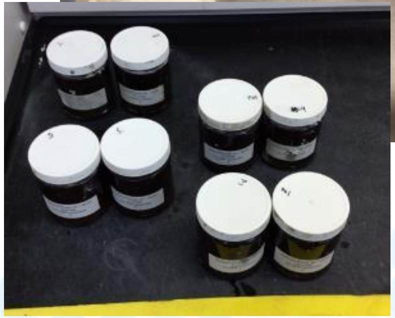
- **Performance Targets:**
  - Oxidation and **reduction in leaching** of dissolved phase coal tar constituents (i.e., BTEX, sVOCs, and phenolic compounds);
  - Acceptable values of slurry density, viscosity, and pH (API RP13B-2);
  - Average **hydraulic conductivity (K_h)** < $1x10^{-6}$ cm/s with no more than 10% of the samples > $1x10^{-5}$ cm/s
  - **Unconfined compressive strength (UCS)** > 0.15 MPa at 28-day

Bench Test Phase 1A – ISCO Optimization

Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

- E2+E3 (67:33) spiked with neat benzene to target a concentration of 10 mg/kg (dry weight basis)
- 350 g/L persulfate solution
- 2%, 3%, and 4% by dry weight BAP
- Amended with 10 M NaOH to target a pH of 11.5

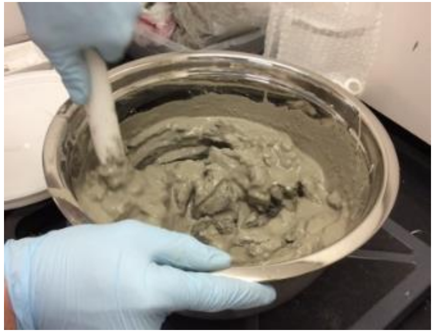


Bench Test Phase 1B – ISS Optimization

Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

Phase 1B – ISS Optimization



- Spike with neat benzene to target a concentration of 10 mg/kg
- ISS Mix Designs
  - 8% CEM III/B (dry weight)
  - 10% CEM III/B (dry weight)
  - 8% CEM I 42,5 N – SR5 (dry weight)
  - 1:1 W:C
- UCS (ASTM D1633)
- Hydraulic Conductivity (ASTM D5084)
- Leach Testing (USEPA LEAF 1315)

Bench Test Phase 2 – ISCO + ISS

Phase 0 - Baseline Geologic Material Homogenization and Sampling

Phase 1A – ISCO Optimization

Phase 1B – ISS Optimization

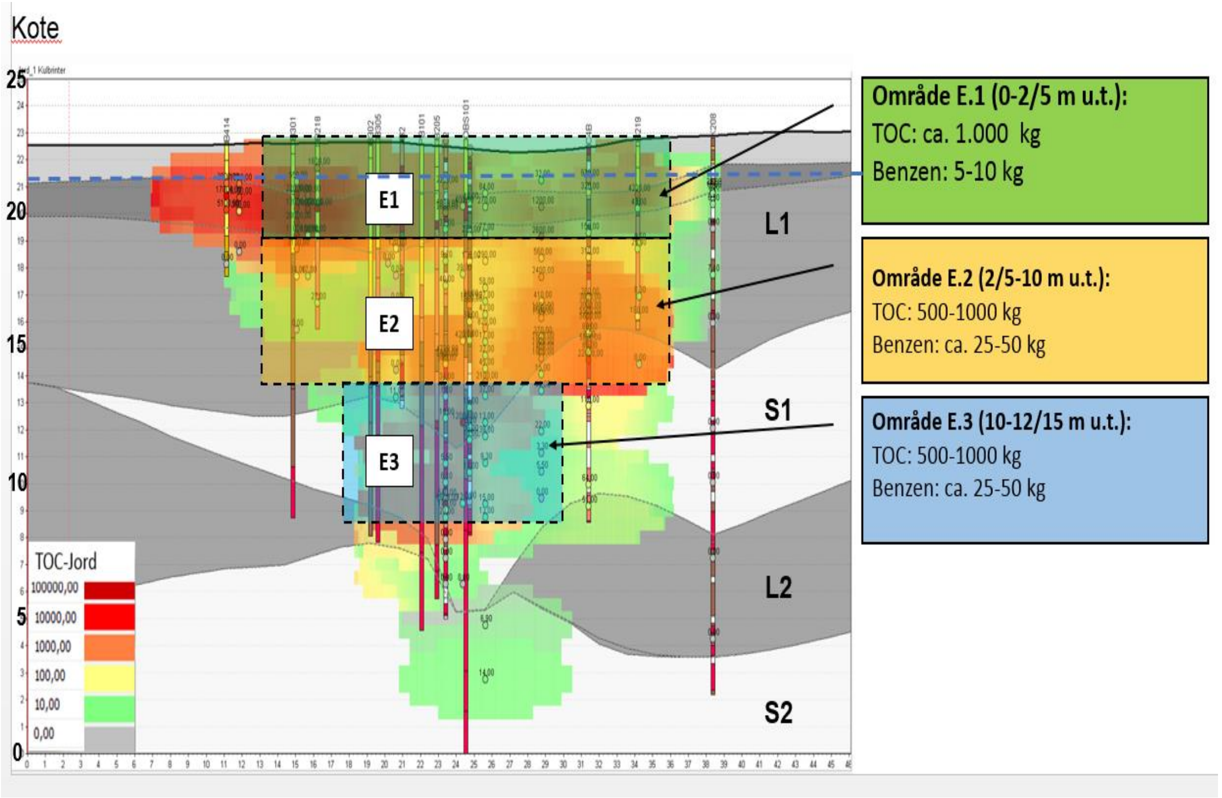
Phase 2 – ISCO + ISS

- spike with neat benzene to target a concentration of 10 mg/kg
- Optimal ISS+ISCO Combination:
  - 8% CEM III/B (dry weight)
  - 3% BAP (dry weight)
- **Two-Step** (Sequential ISCO – ISS)
  - NaOH base activation
  - 15-day reaction time
  - Followed by ISS
- **One-Step** (Simultaneous ISCO + ISS)
  - Cement hydration activation
  - ISCO/ISS treatment same day
- UCS, K, Leach Testing

Bench Test Results Summary

	Unit	ISCO	ISS	ISS+ISCO - One step	ISS + ISCO- Two step	Target value
Geotechnical test						
Unconfined compressive strength (UCS)	MPa	NA	3.8	0.59	2.92	0,15 Mpa (> 24 psi)
Average hydraulic conductivity	cm/s	NA	1.9×10^{-5} *	2.7×10^{-7}	1.8×10^{-8}	< 1x10 -6 cm/s with no more than 10% of the samples > 1x10 -5 cm/s with the least amount of additional reagents
Swell of geologic materials	%	NA	14-22	23-31	24-33	Not defined
Mass destruction	%					Not defined
Benzene		99	NA	100	100	
Phenol		100	NA	83	83	
TPH		26	NA	39	37	
Naphthalene		-19	NA	58	77	
Leach reduction	%					>75
Benzene		NA	>99	>99	>99	
Phenol		NA	>99	>99	>98	
TPH		NA	NA	NA	NA	
Naphthalene		NA	93	80-98	80-84	

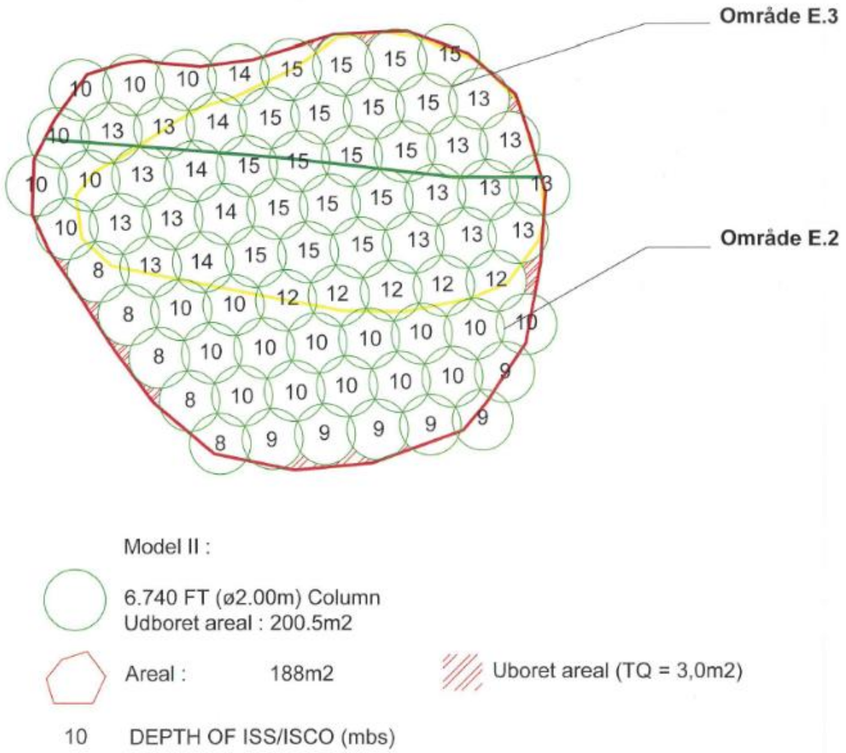
Target Treatment Zones – Cross Section Residual Tar in All Zones (~ 3 tonnes)



Transition From Bench to Pilot Scale

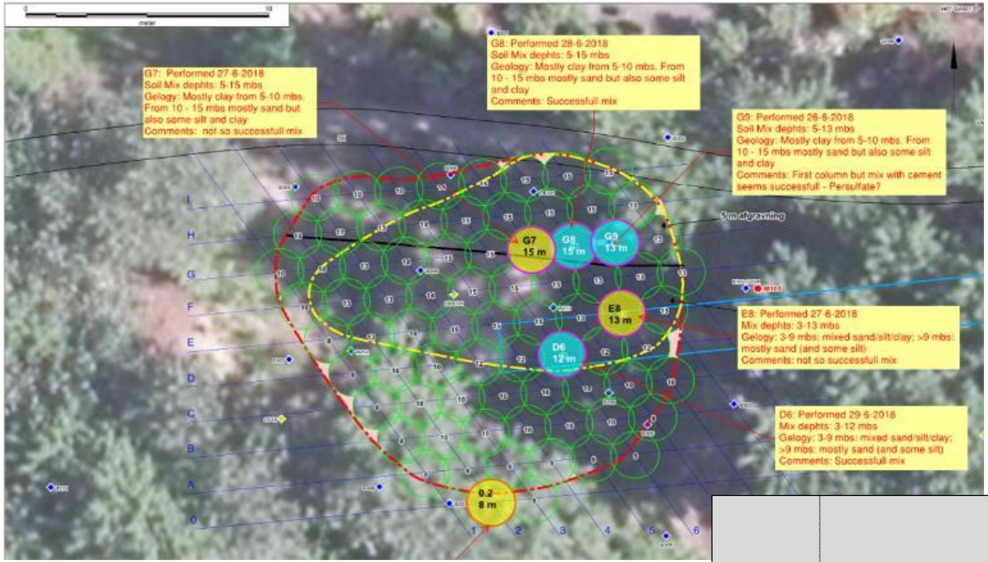
- **Pilot Test Challenges**
  - First-time use in Denmark (learning)
  - Process scale up from bench to field
  - Residential neighborhood, spatial constraints above ground, proximity to houses
  - Challenging Geology: 3m to 5m peat – stability concerns, highly plastic clay, confined aquifer, tight site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

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 m^2
Total target treatment area	188 m^2
Number of columns	75
Area of all columns	235.5 m^2
Column overlap	35 m^2
Overlap %	17.5

Pilot Test ISCO / ISS Columns



Objectives

- Test auger mixing approach
- Test persulfate and cement mixing
- Collection of QA / QC samples
- Attainment of UCS, K_h performance criteria

- 5 test columns in target treatment area
- 1 outside treatment area

Column ID	Area	Mix Design	Top El. (m El.)	Start Treatment Depth (m El.)	Bottom El. (m El.)	Design Depth (mbs)	Treatment Thickness (m)
Friday 2		1	22.8	19.8	14.8	8	5
Friday 3		1	22.8	19.8	14.8	8	5
D6	E2+E3, Shallow Bench	1	22.3	19.3	9.3	13	10
D7	E2+E3, Shallow Bench	1	22.3	19.3	9.3	13	10
G8	E2+E3, Deep Bench	1	22.3	17.3	7.3	15	10
G9	E2+E3, Deep Bench	1	22.3	17.3	9.3	13	8
Potential Additional Columns							
G7	E2+E3, Deep Bench	TBD	22.4	17.4	7.4	15	10
E7	E2+E3, Shallow Bench	TBD	22.3	19.3	10.3	12	9
E8	E2+E3, Shallow Bench	TBD	22.3	19.3	10.3	12	9

2-m Diameter Mixing Auger, Column Casing

- **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

OPTIMIZE — Min/m

Mixing total meter / volume	5	16.0	15.708

Cyklus nr.	Penetrering i meter/min	Samlet minutte	Rotation omdr/min	Bemærkning	BRN
1-DOWN	0.2	25	10	+ Tilsæt cementslorry	50
1-UP	0.3	17	32	Kun mixing	107
2-DOWN	0.5	10	32	+ Tilsæt 50% klozur	64
2-UP	0.5	10	32	+ Tilsæt 50% klozur	64
3-DOWN	0.5	10	32	Kun mixing	64
3-UP	0.6	8	32	Kun mixing	53
	Mixing Time:	80		Total BRN:	402

Tools Supporting Quality Control Assessment

“Trap Door” Sampler for Wet Grab Samples

Pocket Penetrometer for Field measurement of UCS

Construction Quality Assurance Sample Processing

- Verification of homogenous mixing
- Field measurement parameters: moisture content, pH, temperature
- Field Observations: unmixed clods, color/ consistency, free phase NAPL
- Screening and molding CQA samples
- Curing samples

Pilot Test Findings & Lessons for Full-Scale

- **K_h**. All QA/QC samples met criterion of ≤ 1 x 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

Full-Scale Design By the Numbers

- Treatment Area – 188 m^2
- 75 columns, 17% overlap
- Rate - 100 m^3/day (10 m^3/hr)
- Cement – 15 tons/day
- Water – 32 m^3/day
- Persulfate – 6.5 tons / day
- Mixing cycles – 3 cycles; 300 m^3/day

Some Lessons Learned

- 2.0 diameter auger successful with 100 ton rig
- Best day – 36 m^3/hr (113 m^3)
- Many days – 0 m^3
- Corrosivity of persulfate stock solution requires special handling
- High water content of clay matrix slowed rate of cement curing, but
- UCS achieved in field was faster than in lab QA/QC samples (field temp in August > lab)

Søllerød Post-Remediation

Questions

Further Information

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