XDD ENVIRONMENTAL

Do it Right, Do it once

Treatability Testing Webinar

Presented by

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Why Listen to XDD?

- Staff focused on remediation since early 1980's
- Involved in early development of most remediation technologies:
  - Soil vapor extraction (SVE)
  - Air (AS) and oxygen sparging / biosparging
  - In situ chemical oxidation (ISCO) and reduction (ISCR)
  - Aerobic and anaerobic bioremediation
  - Thermally enhanced remediation
  - Vapor intrusion mitigation
- Design and perform treatability testing for end-users, consultants, and contractors
- Wide range of capabilities and experience to solve difficult design problems

XDD Treatability Laboratory Services

- Chemical Oxidation
  - Catalyzed Hydrogen Peroxide
  - Activated Persulfate
  - Permanganate
  - Ozone
  - Solid Phase Oxidants
- Chemical Reduction
  - Zero Valent Iron (ZVI)
  - Bi-Metallic Particles (e.g., Ni-catalyzed ZVI)
  - Metal Sulfides
  - Mixed Reagents (e.g., EHC)
- Bioremediation: Biostimulation /Bioaugmentation
  - Aerobic
  - Anaerobic
- In Situ Stabilization / Solidification
  - VOCs - SVOCs
  - Metals
- Thermal Enhancements
  - SVE
  - Bioremediation
- Surfactant Enhanced Product Recovery / EcoVac
- Approved / Permitted to receive and test international soils
- Custom testing / research (e.g., SERDP metals immobilization during ISCO, PFAS)

XDD Treatability Laboratory Services

- In-House analytical capabilities
  - Dissolved Gases (methane, ethene, ethane)
  - Volatile Organic Compounds
  - Anions (chloride, bromide, sulfate, nitrate, nitrite)
  - Organic Acids (formate, lactate, acetate, proprionate)
  - Molecular Hydrogen by Reduction Gas Analysis

- XDD is not a certified analytical laboratory
  - Samples sent to a certified laboratory for analysis, if required (project specific)

Why Conduct Treatability Studies?

- Certainty of success / appropriate remedial design
  - Remedial events are expensive!
    - Treatability studies typically cost less than 1/10th of field applications
  - Select right site-specific technology
    - Determine failure mechanisms e.g., ISCO
      - Oxidant selection
      - Adverse reactions between oxidant and soil / groundwater
    - Determine field design parameters e.g., Bio
      - Need food (electron donor), nutrients, electron acceptor, correct bacteria?
      - Correct geochemistry?
    - Secondary effects (e.g., metals mobilization, unwanted by-products)
  - Determine correct amount of reagents applied in field
    - Cost savings
      - "over dosing" less likely
      - "under dosing" avoided, which can often result in apparent "failure" and subsequent mobilization events

"Testing is a Design Tool. Not R&D"

Case Study 1: Oxidant Stability Issue

- Catalyzed hydrogen peroxide (CHP) selected by USACE
- Treatment of chlorobenzenes in weathered bedrock and soil
- Bench tested CHP and persulfate to verify feasibility
  - CHP worked very well in bench testing....but short half-life
  - Activated persulfate worked well, and more stable...
  - Recognized advantages of persulfate system, but.....
- Required to conduct side by side pilot tests to prove:
  - Confirmed CHP failure (minimal effective ROI/instability)
  - Persulfate successful due to enhanced stability/contact
- Persulfate was applied successfully full-scale
- Saved $100,000’s on a failed application.

Northeast Superfund Site

Case Study 2: Navy Site

- Evaluated several oxidation and reduction technologies for treatment of carbon tetrachloride
- Technologies eliminated due to failure mechanisms
  - Some formed by-products/recalcitrant to further reduction (e.g., chloroform)
- Determined right approach and dosage – alkaline activated persulfate
- Applied successfully at pilot and full-scale

State of the Practice vs. State of the Art

Complex Remediation Concepts are Being Packaged in Easy to Use Products
Still Need to Apply With Care

State of the Practice	← Short-Term Cost Pressures	State of the Art

- Initial low cost
- Limited or "rule of thumb" design
- Lower certainty of success
- Ultimately higher cost?

- Potentially initial higher cost
- Appropriate testing and design
- Higher certainty of success
- Ultimately lower cost?

You Needed This:

But What You Got Was....

Feasibility and Treatability Studies

- "State of the Practice" is often skipping remedial design steps
  - Technical evaluation
    - Need expertise in design and implementation
  - Treatability evaluations (as applicable)
    - Confirm dosing ranges
    - Identify interferences
  - Field scale pilot testing (as applicable)

Not "Research"
These are Design Tools

Steps are Critical for Accurate Cost and Performance Assessment

Common State of the Practice

- **Remedial design using dosing spreadsheets**?
  - Usually a minimum dosing/application recommended
  - Good start…provides "Cost-Effective" starting point
- **Must account for sensitive design parameters (not typically in RI)**:
  - TOD, SOD, etc.
  - COD, BOD, abiotic reactions, etc. (interferences)
  - Interferences/scavengers, distribution, etc.
- **Very site-specific**
  - Additional evaluation often recommended by the vendors
  - ….and often ignored….

	A	B	C	D	E
1	OXIDANT/REAGENT VOLUME CALCULATIONS - This sheet takes the soil / groundwater volumes and contaminant mass estimat				
2	Site:	<Enter Site Name>			
3	Revision Date:	<Enter Data>			
4					
5					
6	Area 1				Eff. Pore Vol. (Gal) (from 'Site Info" Tab) =
7					Soil Mass (LBs) (from 'Site Info" Tab) =
8					
9	Peroxide (CHP) Injection Volume Estimates - Requirement for Contai				
10	Contaminant Demand (LBs H_2O_2) (from "Ox_Mass" Tab)				
11	Stock Peroxide Solution Calculations:				27% Stock Soln.
12	Peroxide Mass (LBs H_2O_2)				14,158
13	Peroxide Stock Soln. Volume (Gal)				1,542
14	Dilution Water Required to Yield Field Strength (Gal)				Dilutic
15					27% Stock Soln.
16					4.84
17					7,465
18	Total Diluted Peroxide Volume (Gal) (total volumes differ slightly due to minor rounding error)				9,007
19	Injection Pore Volumes Req'd to Emplace Oxidant Mass For Contaminant Demand [1]				0.15
20	Citric Acid, Monohydrate (LBs $C_6H_8O_7{*}H_2O$) Molar Concentration (mM)>>>			100	1,580
21	Straight Pore Volume Dosing Calculation - Assumes Full Pore Volume at Desired Field Concent				
22					27% Stock Soln.
23	Total Peroxide Volume (Gal) to Dose Desired Pore Volume (copied from Row 13 above)				1,542
24	Total Dilution Water Volume (Gal) to Dose Desired Pore Volume				28,754
25	Total Injection Volume (Gal) at Desired Field Concentration =				30,296
26	Injection Pore Volumes Req'd to Emplace Oxidant Mass For Contaminant Demand				0.5
27	Required Oxidant Concentration to Emplace Oxidant Mass For Contaminant Demand				1.51%
28	Citric Acid, Monohydrate (LBs $C_6H_8O_7{*}H_2O$) Molar Concentration (mM)>>>			100	5,314

Case Study 3: Oxygen Release Compound Mass Loading

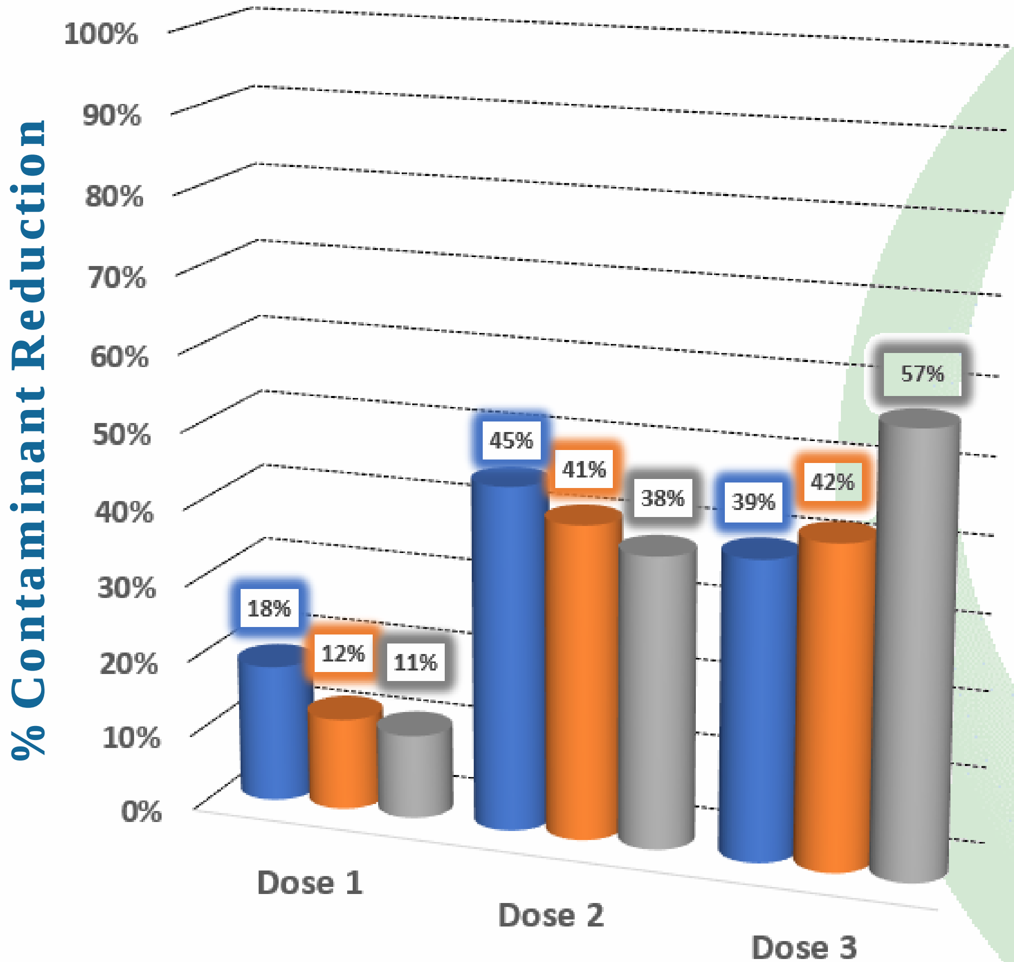
- Superfund site:
  - Multiple source/plume with chlorinated solvents and petroleum hydrocarbons

- Comparison of oxygen release products for petroleum plume
  - Evaluated three oxygen release compounds plus controls
  - Requested dosing recommendations from each product vendor to hit goals
  - Tested three products at the highest recommended dosage of any product*

* Some of above vendors recommended treatability testing to validate dosage assumptions

Case Study 3: Oxygen Release Compound Performance

Vendor Design Estimates (objective >90% Reduction with Single Dose)



All Products Failed, Even After 3 Applications at the Maximum Dose Recommendation

A Little More About the Details

Typical Treatability Test Set-up

- Controls
  - Bio: killed biological control
  - ISCO: no oxidant (site media only)
- Duplicate or triplicate reactors
- Test design groundwater to soil ratio to approximate field conditions (low pore volumes of reagents added)

- Testing of multiple technologies
  - Screening tests for emerging contaminants e.g., 1,4 dioxane or PFC's
  - Various oxidants to determine potential failure mechanisms e.g., CHP stability
- Non-target demand requirements
  - Test range in oxidant / oxygen concentrations likely for field application

Bench Scale Testing: Duration, Media Requirements, Waste Handling, Costs

- Test Duration
  - ISCO: 2 days to 8 weeks
  - Bio: 2 to 6 months
- Media Requirements
  - Soil: 2 to 30 pounds
  - Groundwater: 1 to 20 liters
  - From area of interest ☺

- Waste Handling
  - Disposal in accordance with licensed waste facility
  - Small Quantity Generator status
- Costs
  - $2,000 to $50,000 or greater (function of scope and sample numbers)

Case Study 4: Ex Situ Advanced Oxidation

- Landfill leachate and groundwater extraction system (50-100 gpm)
- 1,4-dioxane up to 322 µg/L (has attenuated over time)
- Water currently treated using powdered activated carbon/sand filtration
- Advanced Oxidation Process (AOP) being evaluated to address 1,4-dioxane that is not treated by PAC / filtration
- Objective to treat 1,4-dioxane to regulatory standard while maintaining by-products within regulatory standard
  - Complication: Bromide up to 1,300 µg/L

AOP Process

- Reaction between H_2O_2 and O_3 produces hydroxyl free radical (•OH) – proven effective on 1,4-dioxane
- Bromate (BrO_3^-) is a common disinfection by-product
  - Formed during common water treatment process (e.g., chlorination, direct ozonation, AOP, etc.)
  - Naturally occurring bromide ions (Br^-) in the raw ground water/surface water source is the pre-curser to bromate formation
  - MCL for bromate is 10 μg/L in drinking water

1,4-Dioxane Destruction Results

Test Scenario	Impact on 1,4-Dioxane			Impact on Bromate		
High Spike, 240 µg/L 1,4-dioxane O_3 Dose = 5, 10, 13, 20 mg/L H_2O_2:O_3 Molar Ratio = 1.0 (all scenarios) 7 injection nozzles except the 20 mg/L ozone dose which used 9 nozzles.	O_3 (mg/L)	H_2O_2 (mg/L)	Final 1,4-dioxane (µg/L)	O_3 (mg/L)	H_2O_2 (mg/L)	Final Bromate (µg/L)
	5	3.6	48	5	3.6	64
	10	7.1	6.6	10	7.1	190
	13	9.2	1	13	9.2	290
	20	14.2	1	20	14.2	430
	Result: 1,4-dioxane destruction is more effective as ozone dose is increased.			Result: Bromate conc. increased significantly as ozone dose increased.		

Conclusions: Hydrogen peroxide/ozone molar ratio requires optimization to reduce bromate formation. Also, likely to require more nozzle injection points to reduce bromate while achieving desired 1,4-dioxane destruction (7 to 9 nozzles used in Round 1, increased to 20 to 30 in Round 2).

Case Study 5: Thermal Enhancement

Question was: Is thermal enhancement beneficial / cost effective?

Site History (CHA)

- Manufacturing operations: approximately 1910 to 1997
- 1994/1995: RI/FS
- 2004: All operations cease, buildings razed
- Low permeability layer that varies in thickness and depth across the Site
- VOC and SVOC impacts
- Aggressive remediation schedule

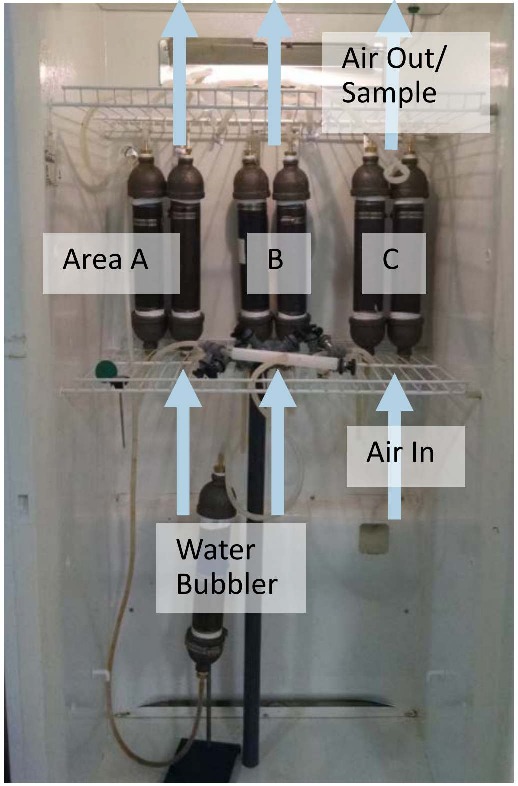
Overview: Questions to Address

- What temperature is needed for site remediation using thermally enhanced soil vapor extraction?
  - Flow-through column experiments
  - Three soils: Test Areas A, B, and C
  - Three temperatures: 35 °C, 50 °C, 70 °C

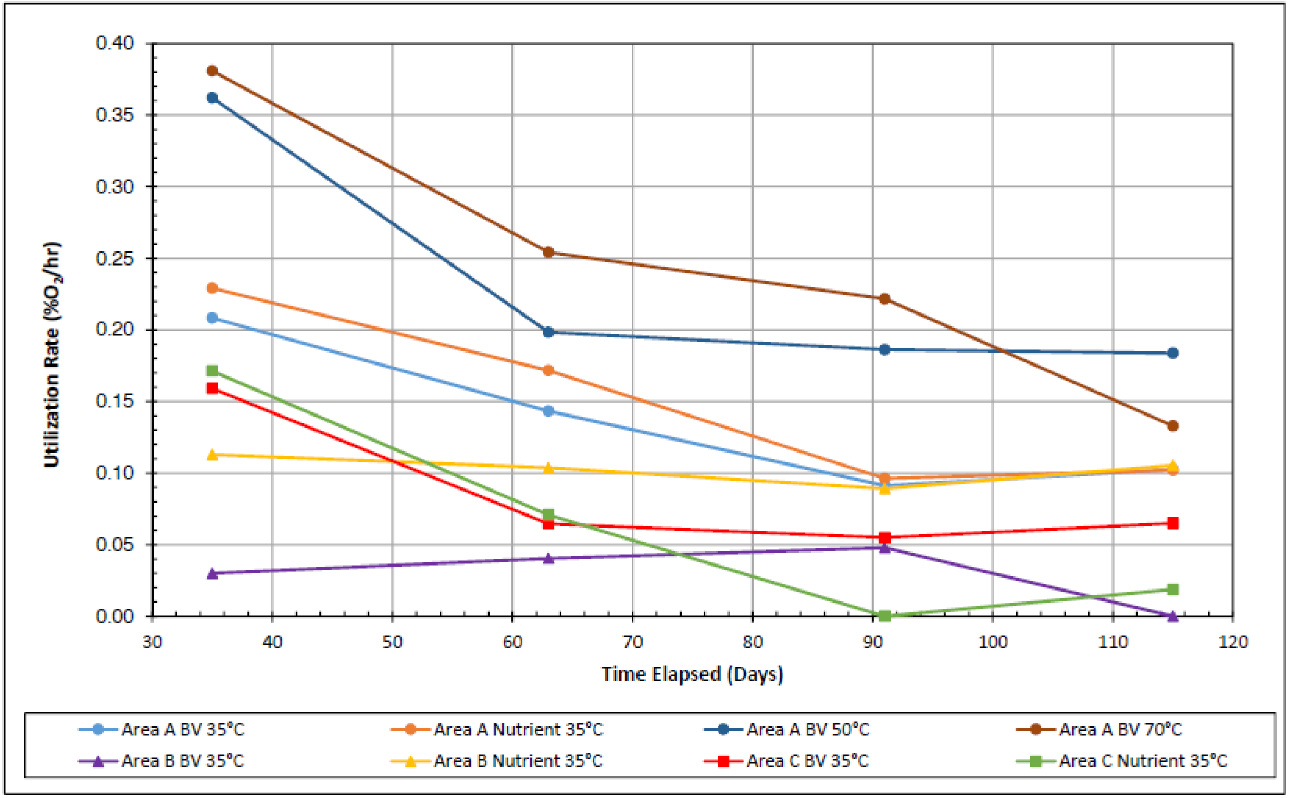
- To what extent does bioventing assist in site remediation?
  - Flow-through column experiments
  - Transition several columns to bioventing phase through decreasing flow rates and measuring oxygen utilization with time
  - Add nutrients to half of the conditions to determine if needed

Lab: TSVE/Bioventing

35 °C Incubator



Oxygen Utilization During Bioventing



Notes:
$\%O_2$/hr = percent oxygen per hour; BV = bioventing; °C = degrees Celsius

Primary Treatability Observations

- Higher impacted soils were very tight / silts
  - Supported additional site permeability variation testing, and 3-D modeling in SVE design
- The majority of the treatment occurred during the bioventing phase
  - There was high oxygen utilization in the impacted columns and growth in the biological population
  - Oxygen utilization decreased with time due to dwindling contaminant source (electron donor)
- Nutrient addition had limited additional benefit
- Increased temperature accelerated contaminant reductions
  - Contaminant transformation rates not significantly greater for 50 °C and 70 °C columns

System Operation

- Over initial 8 months of operation mass of VOCs and SVOCs decreased by 58% and 73%, respectively
  - Calculated from 2007 and 2017 samples

	VOC (lb)	SVOC (lb)	Total (lb)
2007	39,500	2,100	41,600
2017	16,600	550	17,150
% Reduction	58%	73%	59%

- Approximately 86% of the mass reduction occurred via biodegradation (21,080 lb.)
  - Validated through oxygen utilization / COD measurements
- After 12 months operation evaluation of site closure ongoing
  - 90% of system shutdown approved by regulatory agency

Case Study 6: Enhanced Bioremediation, ME

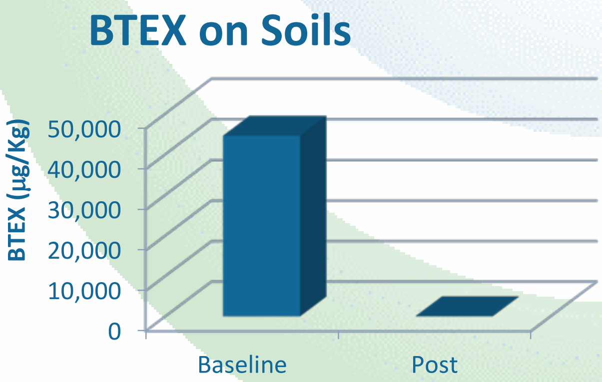
Chlorinated Solvents in Fractured Rock

- Laboratory treatability study determined:
  - Limited food / electron donor
  - Limited nutrients
  - No appropriate bacteria
  - pH not ideal
- Adverse site conditions
  - Fractured bedrock
  - Ensure metals mobilization would not be an issue
  - Prior to treatment hot spot area required pump and treat
- Full-scale applied using pull-push approach adding treatability determined reagents and dosage
  - two applications over 12 month period
- Remedy successful: the pump and treat system evaluation permitted shutdown

Case Study 7: In Situ New York, NY

Petroleum Hydrocarbons Treatment with ISCO

- **One shot deal**
- **Treatability Study**
  - Tested multiple oxidants
  - Alkaline activated persulfate selected
  - Oxidant loading determined
- **Logistical Issues**
  - Tight schedule: complete in 2 weeks, before building slab construction
  - Chemical compatibility with construction materials
  - Space limitations
  - Working around construction activities
  - Maintain traffic accessibility
- **Six days of chemical injection**
  - Design based on bench testing results
- **Site closed by NYSDEC**
  - 92 to 95 % groundwater concentration reduction
  - > 99 % reduction of BTEX, DRO + GRO on soils



Case Study 8: Ex Situ Process

Iron and TOC/COD Removal

- Large Industrial Site/Capped with P&T System
- High iron and TOC/COD
- Performed treatability and field support for optimization of various pretreatment processes
  - Pre-GAC treatment included:
    - Coagulation/flocculation and settling
    - pH adjustment
    - TOC/COD removal via modified zeolite/selectivity analysis
- Pretreatment steps save client $56k/year

Questions?

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