Chemical-Biological Stabilization Technology for the Remediation of Hydrocarbon Contaminated Soil and Oily Wastes

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INTRODUCTION

• Majority of remediation projects → reduce TPH concentration
• Supposition: lower TPH concentration = less toxicity
• However, many weathered hydrocarbons have low toxicity:
  • In bioassays (earthworm and bacteria) toxicity is only observed at > ~2.5 – 3.0 % TPH (25,000 – 30,000 mg/kg)
• None-the-less, very weathered hydrocarbons can affect plant development at low concentrations (~0.25 % = 2,500 mg/kg):
  • Physical-chemical changes in soil:
    • Reduced Porosity, Field Capacity, Cation Exchange Capacity
    • Increased temperature
    • Formation of Water Repellency

100 days later
ALTERNATIVE STRATEGY: Chemical-Biological Stabilization

- Strategy: recover Phys-Chem properties which are affected by hydrocarbons
- Restores soil structure, pH, eliminates toxicity and leachates in the short term (approx. 3 – 6 months), \( \rightarrow \) reduces TPH concentration in the long term
- Applicable to soil contaminated with very weathered hydrocarbons
- Applicable to treatment to drilling cuttings
- Works with high TPH concentrations (5 – 11 % TPH = 50,000 – 110,000 ppm)
- TPHs are transformed into humic soil substances:
  - Reduces or eliminates residual toxicity, leachates
  - Reduces water repellency
  - Increases field capacity, allows for a vigorous vegetative growth
  - In the long term, TPH concentration is reduced (3 – 5 años)
SITE BACKGROUND

• Sulphur mine which used the Frasch process to extract S from salt domes

• Waste: acid tailings, acid drainage, hydrocarbons and benonite based drilling fluids

• Acid drainage with hydrocarbons and bentonite was deposited into a large holding dam (320 Ha ≈ 800 acres)

• Neutralized with MgO, hydrocarbon problem persists ~5 – 7 % TPH (50,000 – 70,000 ppm)

• Very clayey texture (bentonite)
METHODOLOGY

• Extraction of 150 m³ of contaminated material from sediment “beach”

• Application of the Chemical-Biological Stabilization procedure:
  • 4 % (dry weight) calcium hydroxide, mix and wait 2-3 days
  • 4 % (dry weight) organic amendment (sugar cane cachasse), mix
  • After pH stabilization, seeding with humidicola grass (B. humidicola)

• Experiments carried out in a humid tropical climate (ave. temp. 27 °C, ave. annual precip. ~1,700 mm)
METHODOLOGY

- Monitoring and Evaluation
  - TPH (EPA 418.1)
  - Toxicity (Microtox)
  - Leachates (TCLP, TPH in extract by EPA 418.1)
- pH
- Field Capacity
- Water Repellency (MED-Molar Ethanol Droplet)
- Microbial respiration – 24 hr static method
- Root density

100 days later
PROCESSES INVOLVED

CONTAMINATED SOIL, DRILLING CUTTINGS, WASTE PITS

Chemical Stabilisation
Partial encapsulation and improvement in soil structure

Absorption
Reduction in mobility and toxicity

Microbial Mineralization
Destruction of easily biodegradable hydrocarbons

Microbial Humification
Transformation of hydrocarbons into soil organic matter (humus)

Phytoremediation
Further mineralization/humification
improvements in soil structure, moisture management and nutrition

REMEDIED, FERTILE SOIL
Apt for use in agriculture, forestry, livestock raising
INDUSTRIAL SCALE UP PROJECT
Texistepec Mining Unit
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Chemical Stabilization
INDUSTRIAL SCALE UP PROJECT

Chemical Stabilization
INDUSTRIAL SCALE UP PROJECT

CEISA Industrial Plant
Pile Design to Improve Drainage
INDUSTRIAL SCALE UP PROJECT
Biological Treatment – Application of Organic Amendment
INDUSTRIAL SCALE UP PROJECT
Biological Treatment – Application of Organic Amendment
INDUSTRIAL SCALE UP PROJECT

CEISA Plant
INTEGRAL SCALE UP PROJECT

Incorporation of Organic Amendment
INDUSTRIAL SCALE UP PROJECT

Classroom in the Field – Real-life Applications
INDUSTRIAL SCALE UP PROJECT
Planting Layout  Nov 2007
INDUSTRIAL SCALE UP PROJECT

Planting Layout
INDUSTRIAL SCALE UP PROJECT

Core samples
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Core samples
INDUSTRIAL SCALE UP PROJECT

Leachate collection
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Leachate collection
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Monitoring of Conditions March 2008

start of dry season
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Monitoring of Conditions May 2008

dry season nearly over
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CEISA Plant

First rainy season July 2008 (fenced)
INDUSTRIAL SCALE UP PROJECT

CEISA Plant
Sexual Reproduction (seeds) of pasture and sedge *Cyperus* sp. July 2008
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CEISA Plant
INDUSTRIAL SCALE UP PROJECT

CEISA Plant

After Removal of Weeds and cropping  Oct 2008
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CEISA Plant

After Second Rainy Season  Feb 2010
INDUSTRIAL SCALE UP PROJECT

CEISA Plant

After Second Rainy Season  Feb 2010
SOIL FERTILITY RECOVERY

- Microtox toxicity in soil below background (< 10 TU)

- TPH in TCLP leachates \( \sim 1 \text{ mg/L} \) and safe for human consumption

- Increase in Field Capacity by 36 % and to a high level (34 % Humidity)

- Soil water repellency was reduced exponentially (1 yr) maintaining moisture above critical levels (even during the driest parts of the year).

- Good root density similar to “reference” area.

- Earthworms toxicity is nul = reference area
SOIL RESPIRATION

1) Sandy coastal soils pasture/coconut – Tabasco, Mex.
2) Vertisol with pasture – Tabasco, Mexico
3) Alluvial soil with pasture – Tabasco, Mexico
4) Alluvial soil with sugar cane/cacao – Tabasco, Mex.
5) Remediated bentonitic mud – Veracruz, Mexico
6) Floodable pasture – Veracruz, Mexico
7) Savannah with pasture – Chiapas, Mex. (degraded)
8) Savannahs with pasture – Venezuela
9) Savannahs with native vegetation – Venezuela
10) Savannahs and dry forests – Costa Rica
11) Savannah forest mosaic – Venezuela
12) Gallery forest – Venezuela
13) Gallery forests – Costa Rica
SOIL RESPIRATION

• indicator of the overall activity and robustness of the microorganisms in the soil
• good respiration rates, same range as:
  • rich alluvial soils under cultivation
  • good savannah soils with pasture
  • gallery forests
• Transformation into soil-like material apt for cultivation, livestock raising or conservation.
COSTS and BENEFITS

Advantages:

Uses locally available materials, machinery, labour, and know-how

• Machinery, fuel and operator needs are generally less than 2 weeks
• Costs are 1/3 to 1/2 less than land farm or wind row bioremediation
• Logistically simple
• Reduces soil leachates to safe levels
• Completely eliminates toxicity
• Recovers soil structure and fertility
• Can be used to treat drilling cuttings, converting it to useable soil
• Can be used to treat soil with TPH concentrations > 10%
• Can be used to treat soils contaminated with viscous, very weathered hydrocarbons and old, historic spills
### COSTS and BENEFITS

**Costs:**

Unit cost analysis for bioremediation vs. chemical-biological stabilisation of hydrocarbon contaminated sediments

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<thead>
<tr>
<th></th>
<th>Unit cost (per m³)</th>
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<tbody>
<tr>
<td></td>
<td>%</td>
<td>Euros*</td>
<td>US Dollars*</td>
<td>Mexican pesos</td>
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<tr>
<td><strong>Concept</strong></td>
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<tr>
<td></td>
<td><strong>Bioremediation (land farm)</strong></td>
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<tr>
<td>Materials</td>
<td>68</td>
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<tr>
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<tr>
<td>Labor</td>
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<td>1,97</td>
<td>2,76</td>
<td>36,57</td>
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<tr>
<td><strong>Total</strong></td>
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<td><strong>€ 12,96</strong></td>
<td><strong>$ 18,13 USD</strong></td>
<td><strong>$ 240,24 M.N.</strong></td>
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<tr>
<td><strong>Chemical-Biological Stabilisation</strong></td>
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<td>Materials</td>
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<tr>
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<td>Labor</td>
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<td>1,00</td>
<td>1,40</td>
<td>18,54</td>
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<tr>
<td><strong>Total</strong></td>
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<td><strong>€ 7,29</strong></td>
<td><strong>$ 10,20 USD</strong></td>
<td><strong>$ 135,11 M.N.</strong></td>
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CONCLUSIONES

• Este método se enfoca primariamente en restaurar propiedades del suelo
  • elimina la toxicidad
  • reduce el TPH en lechadas a niveles aceptables
  • restaura la capacidad de retención de humedad (capacidad del campo)
  • reduce la repelencia de agua del suelo a niveles aceptables
  • proporciona un microambiente favorable para el desarrollo de las raíces
  • aumenta la respiración microbiana a niveles sanos

• Sencillo de implementar utilizando materiales, maquinaria y conocimiento comúnmente disponibles en áreas tropicales
  • No requiere mezcla constante (como en bioremediación de tierra)
  • Puede utilizarse en cortes de perforación
  • Puede utilizarse en suelos con altas concentraciones de hidrocarburos desgastados