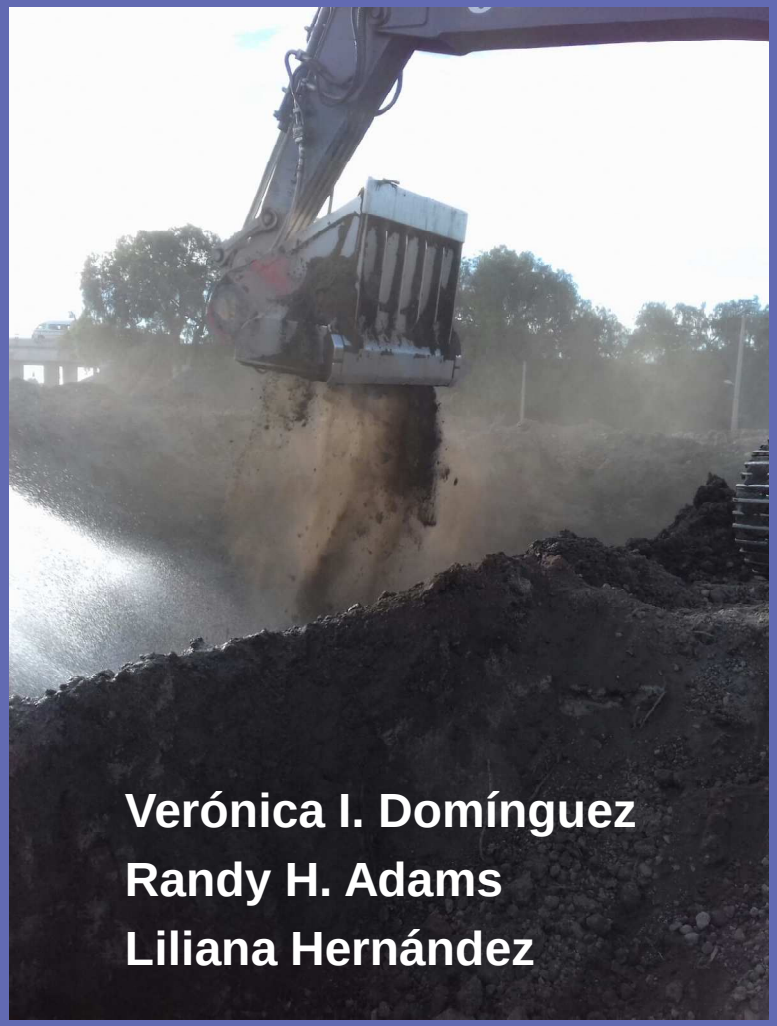
Rapid Remediation of Bunker C Fuel Oil Contaminated Soil by Chemical Oxidation and use of Surfactants and Solvents Formulation



Verónica I. Domínguez
Randy H. Adams
Liliana Hernández

Mariloli Vargas
Rubén Viornery

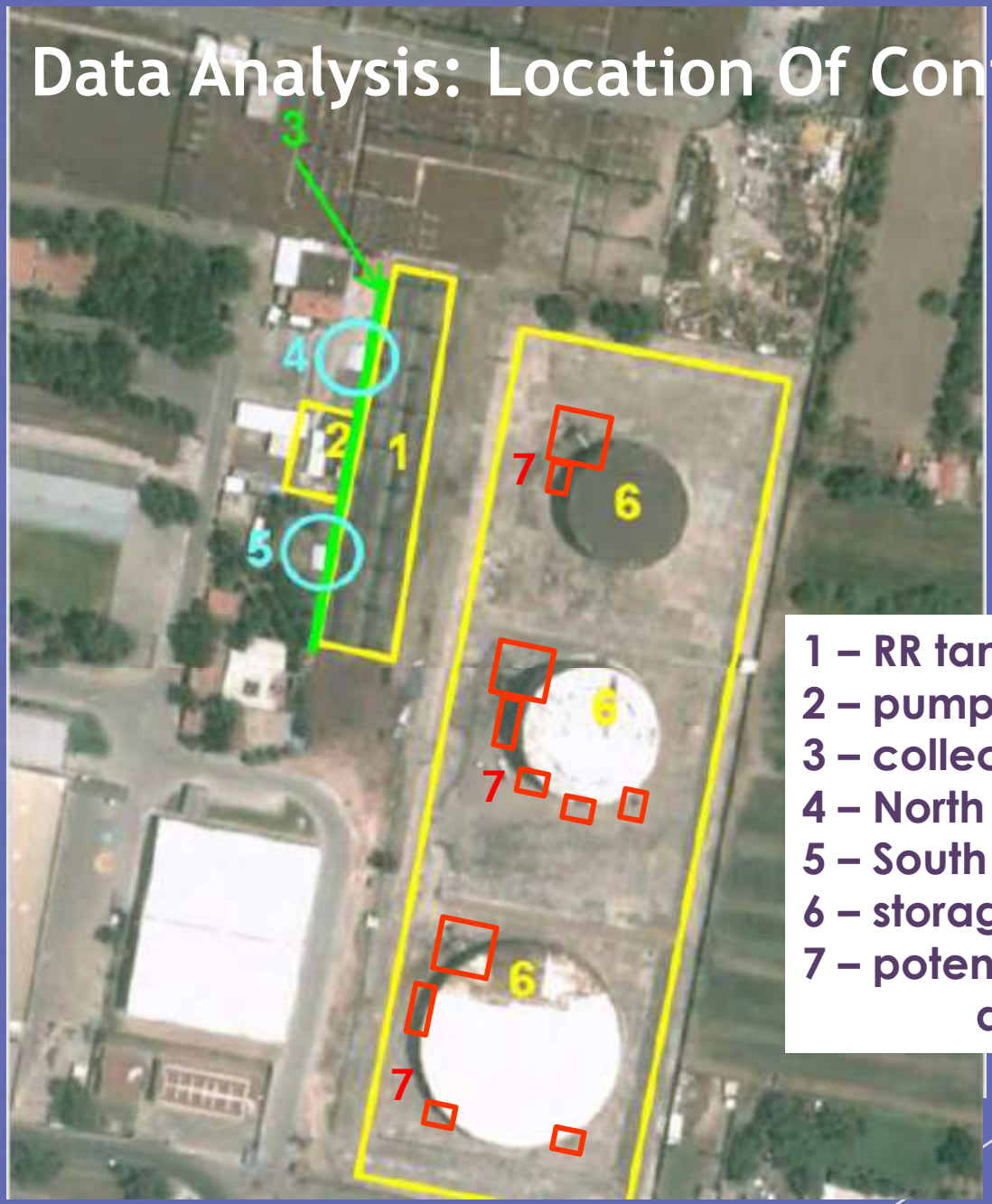
Problem Situation

- Demographic Growth → requirement for more electricity
- Extension of the actual plant → approx. double capacity
- But, it is necessary to remediate soil before construction of Plant II

- Plant I begins operation in 1963
- Used Bunker C fuel oil for thermo-electric generators
- Inadequate historical practices: storage, transport

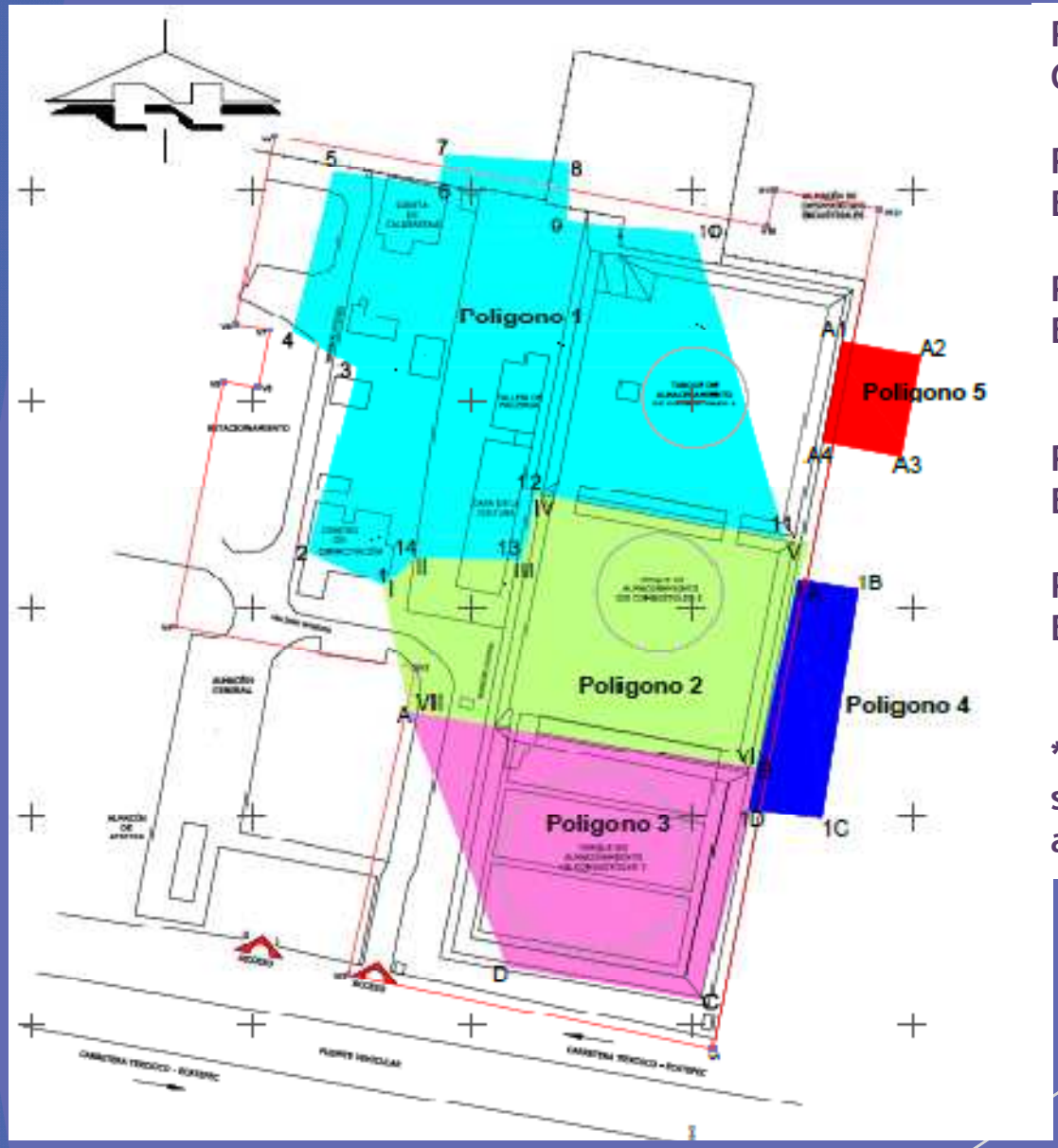
- Site characterization according to Mexican norm NOM-138-SEMARNAT/SSA1-2012
- Risk-based determination of clean-up criteria:
  - 9,625 mg/kg Heavy Oil Fraction
  - 7,044 mg/kg Medium Fraction

Data Analysis: Location Of Contaminated Soil



1 – RR tanker-car discharge area
2 – pump house
3 – collector channel
4 – North recollection pit
5 – South recollection pit
6 – storage tanks
7 – potentially problematic areas near tanks

Proposal – Official Resolution



Polygon 1 Phase 1 29,208 m^3, up to 7m
Chem. Oxidation + Bioremediation*

Polygon 2 Phase 2 12,928 m^3, up to 3m
Bioremediation

Polygon 3 Phase 3 5,147 m^3, up to 1m
Bioremediation

Polygon 4 Phase 3 658 m^3, up to 3m
Bioremediation/soil replacement

Polygon 5 Phase 3 264 m^3, up to 6m
Bioremediation/soil replacement

*Use of proprietary formula of surfactants/solvents and organic amendment to stimulate remediation

Note: the remediation method and cleanup goal were pre-estabilshed in Official Resolution

Optimization Tests (Lab)

Results of hydrocarbon analyses made on different treatments

Treatment	Initial TPH (ppm)	Final TPH	% reduction	Reduction ppm
Peroxide 1% + Fenton	30000	11584	61	184165
Peroxide 0.84%	30000	16191	46	138093
***Peroxide 1.3%**	**30000**	**11271**	**62**	**187287**
Peroxide 1.7%	30000	12078	60	179221
Peroxide 2.3%	15000	12656	59	177525
Peroxide 2.51%	30000	9910	67	20896
Peroxide 0.84%+ Formulation 2L/m^3	15000	12341	18	2659
Formulation 4L/m^3	15000	7606	49	7394
Formulation 6 L/m^3	15000	7675	49	7325
Formulation 1 L/m^3	**15000**	**8144**	**46**	**6856**
Formulation 2 L/m^3	15000	6643	56	8357
Peroxide 2.7%	30000	10128	71	24872
***Peroxide 1.3%+ Formulation 1 L/m^3**	**30000**	**10288**	**67**	**20712**

Optimization Tests (Lab)

Treatment	% Reduction
1.3% H_2O_2 + 1 L/m^3 Formulation	73
1.3% H_2O_2 + 2 L/m^3 Formulation	73
1.3% H_2O_2 (Sandy Fluvisol)	74
1.3% H_2O_2 + 1 L/m^3 Formulation Soil from site	63

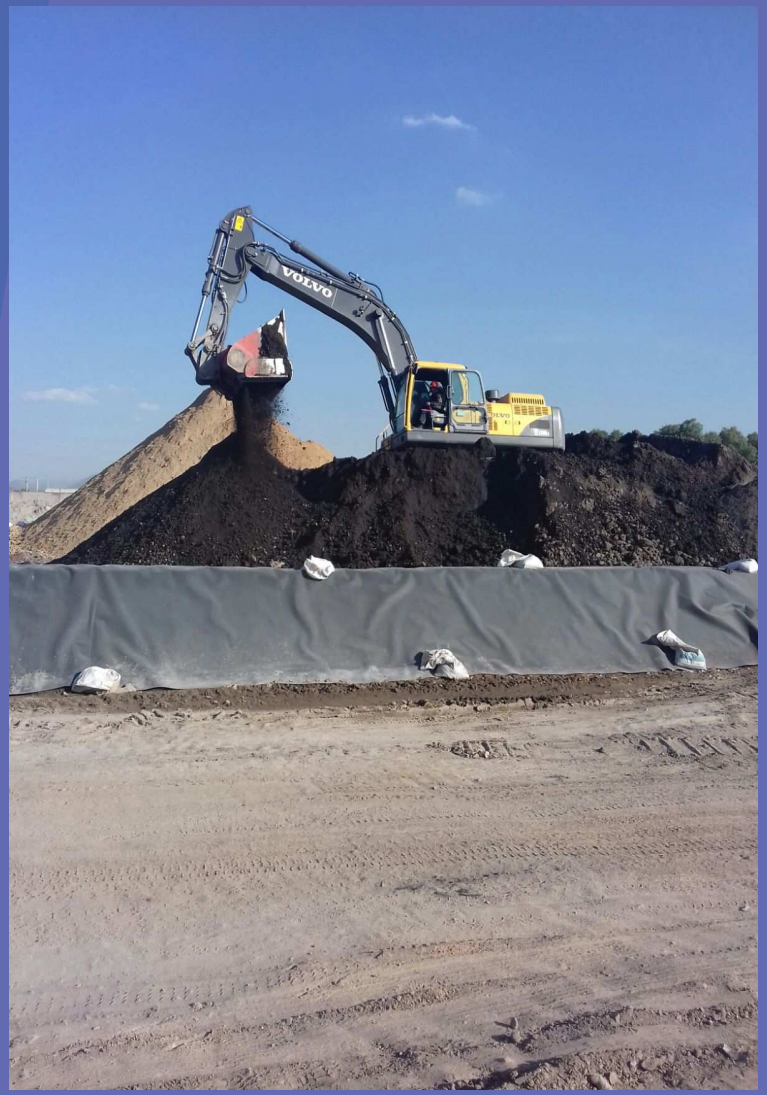
Remediation Process

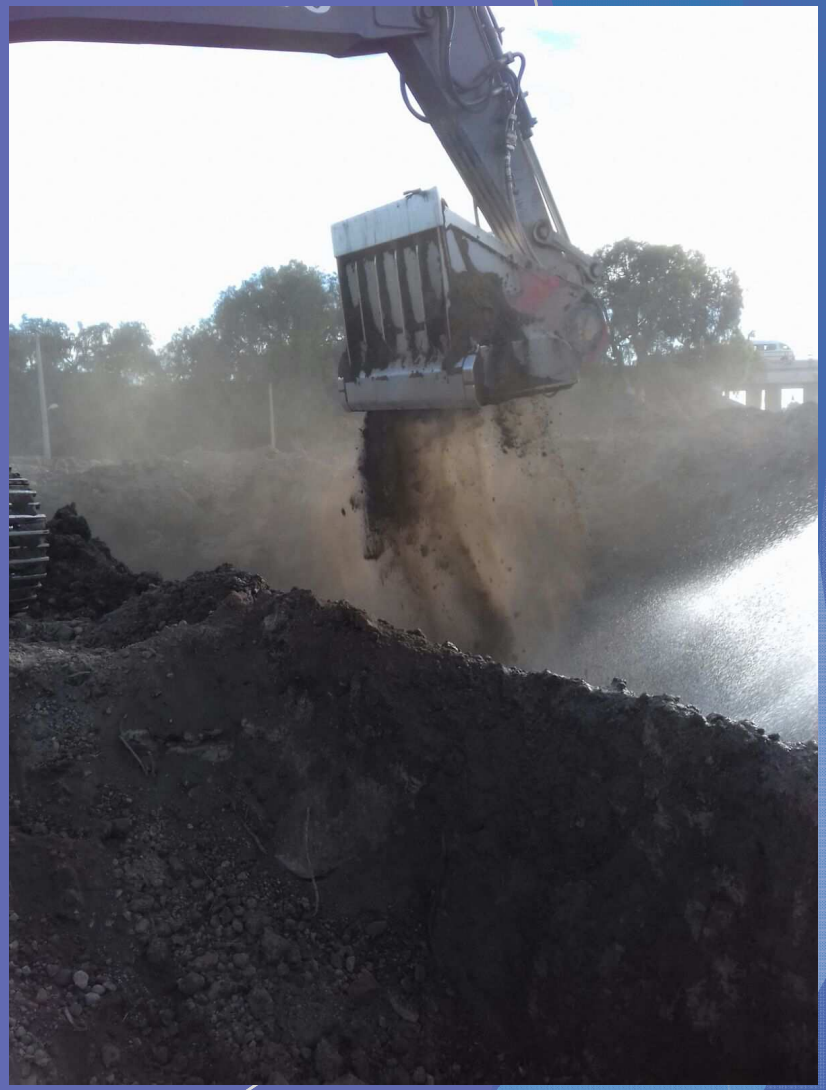
Treatment with specialized machinery

- Instead of excavators, ALLU crusher
  →(specialized to crush and mix)
- Application of H_2O_2 in treatment piles by spraying during mixing with ALLU crusher
- Application of bioremediation stimulator formula by spraying and mixing with ALLU crusher
- Reduction in treatment time for chemical and biorem. phases
- Soil sampling in center of piles in recently mixed soil
- In-house monitoring with PetroFlag, calibrated using site soil and hydrocarbons

- For most areas remediation was achieved in 2 – 4 weeks

Application of Reagents and Mixing with Specialized Equipment



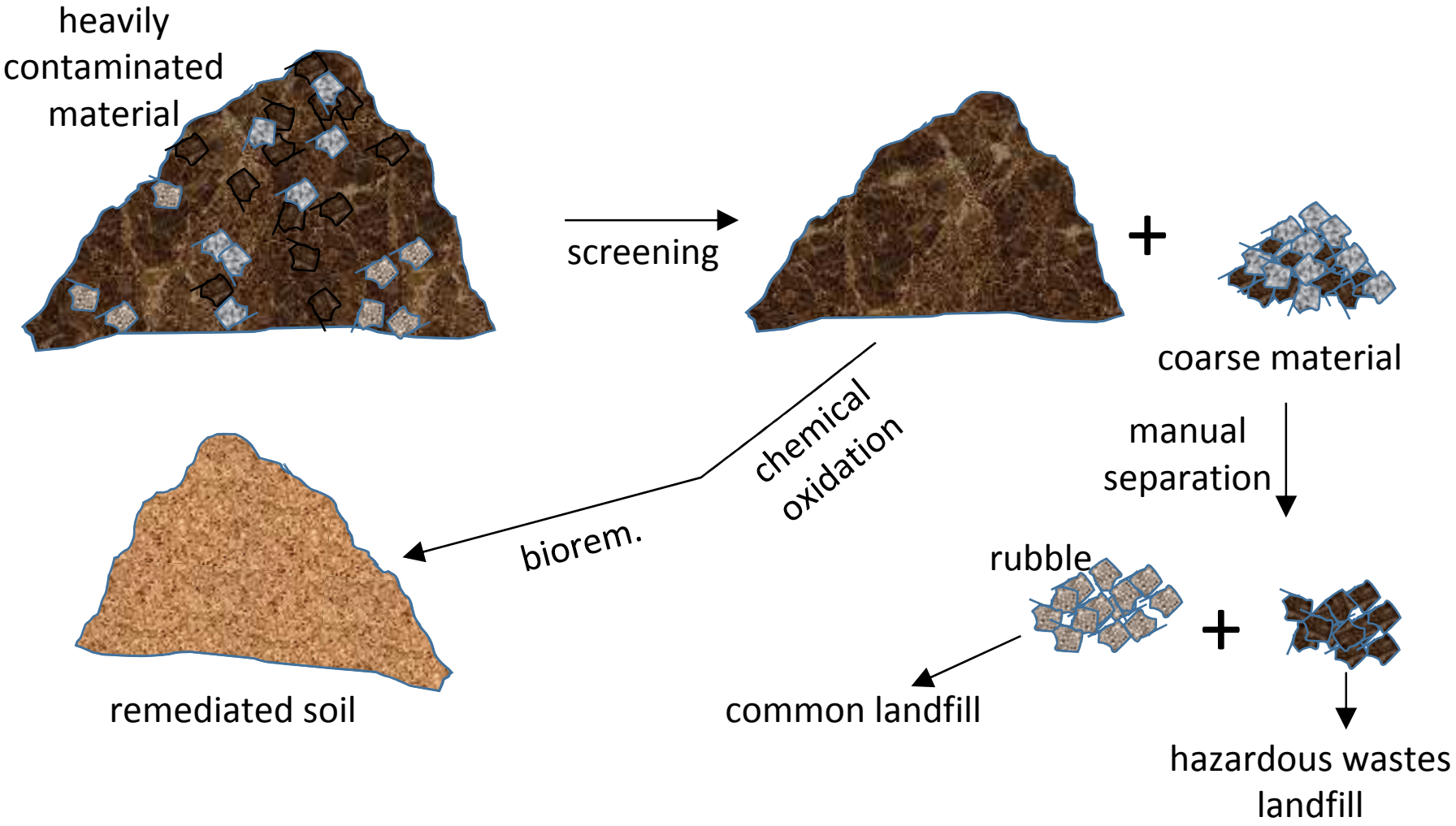


Treatment of Material with Large, Weathered HC Clumps

Some areas of site had concentrated HC clumps

- Treatment by screening to remove large clumps, rubble
- Remediation of screened by chemical oxidation and bioremediation (with surfactant/solvent formula)
- Manual separation of clean rubble
- Very heavily contaminated material (>10% heavy oil) and hydrocarbon clumps sent to landfill

Separation of Heavily Contaminated Soil and HC Clumps



The Problem with Asphaltenes

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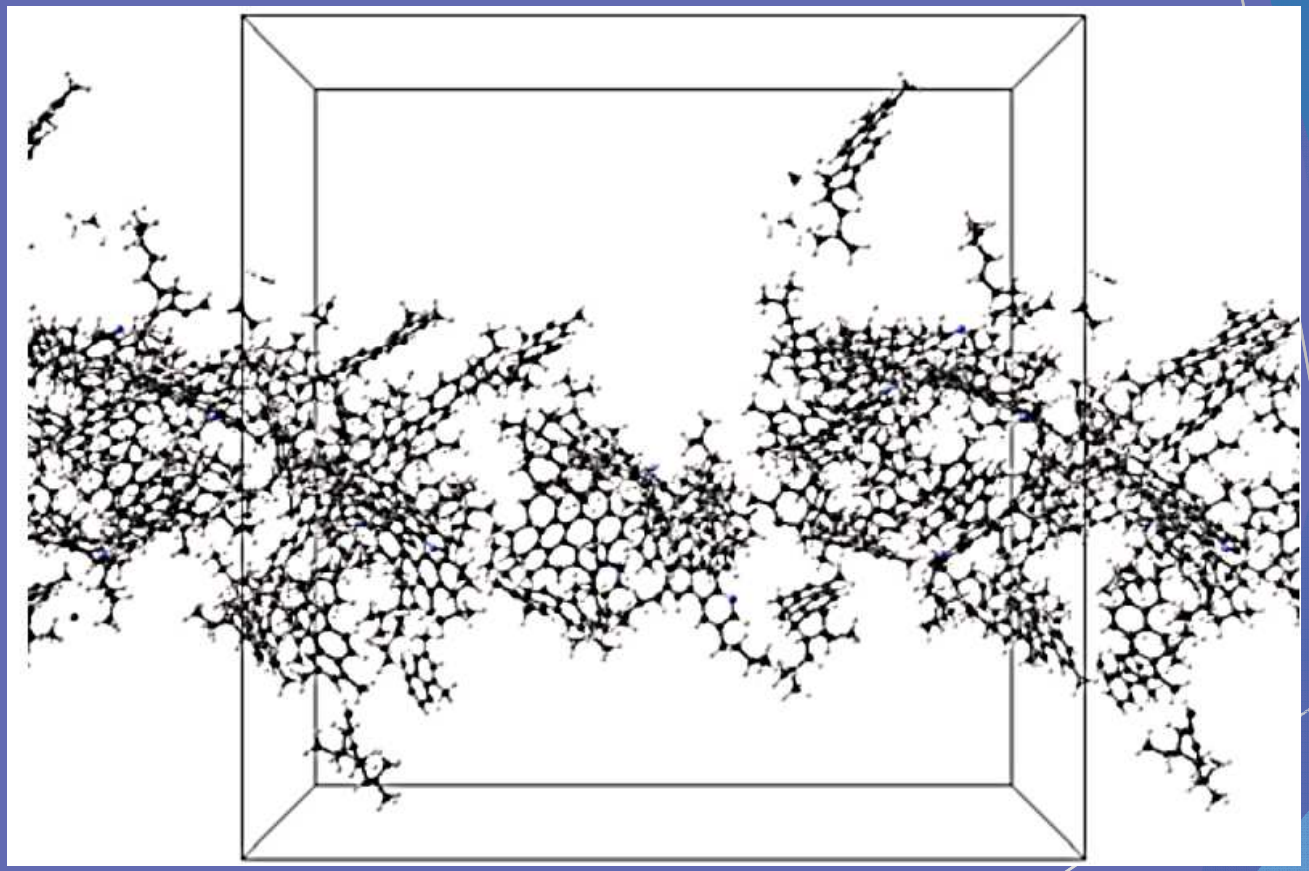


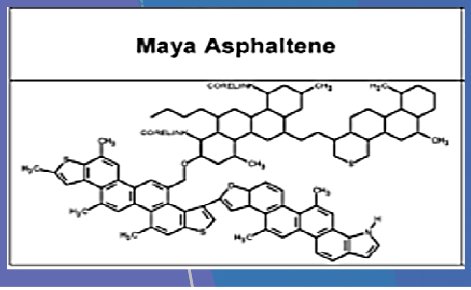
3-D Structure of Asphaltenes and Self-Agglutination

http://www.materialdesign.com

The Problem with Asphaltenes

Pipeline plugging due to asphaltenes
(London Centre for Nanotechnology www.london-nano.com)

The Problem with Asphaltenes



- Asphaltenes are not determined with standard gravimetric test (i.e. EPA1664A) using hexane as a solvent

- We ran alternative test using hexane and dichloromethylene as solvent:
  → differences of up to 2-3 fold

- Total asphaltenes content in HC in soil:
  6 - 19% in problem soil

- Total HC in soil (not including asphaltenes but only extractable with DCM): 7 – 12%

- Total HC in soil (including asphaltenes):
  8 – 13 % in problem soil!

Feasibility Studies of Problem Soil with Asphaltenes

Treatment	Initial TPH (ppm)	Final TPH	% reduction	reduction ppm
5% Peroxide + $FeSO_4$	78,560	14,465.8	81.58%	64,094.2
7% Peroxide + $FeSO_4$	81,112	14,339.0	82.23%	66,773
9% Peroxide + $FeSO_4$	79,120	13,818.0	82.53%	65,302
5% Peroxide + Form. 2L/m^3	73,005	11,094.60	84.80%	61,910.4
7% Peroxide + Form. 2L/m^3	74,215	13,485.0	81.82%	60,730
9% Peroxide + Form. 4L/m^3	73,000	11,292.7	84.53%	61,707.3

- Increase in peroxide, formulation, has diminishing returns
- Reductions of up to 84%
- But still not meeting cleanup level (9625 ppm)

Conclusions

Optimization using:
1) lab/field test for reactant ratios

2) Specialized equipment designed for mixing (ALLU)

3) Formulation of surfactants/ solvents/conditioners

- **Allows for rapid cleanup times (approx. 2 – 4 weeks)**
- **TPH reduction of 65 – 85% for Bunker C contaminated silty sand**
- **Longer but possible up to 70,000 ppm initial TPH concentration**
- **Complications with higher concentrations, especially in asphaltenes contaminated soil**

Thank you for your attention