Soil washing with a surfactant solution: Pilot test at a gas station (Laval, Québec, Canada)

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[CdT = [Cd2+] = 10nmol

Centre - Eau Terre Environnement

By:



Context

• Gasoline is persistent in soils and groundwater

 Most conventional in situ remediation technologies cannot or struggle to reach environmental standards for groundwater and soil quality



In situ technologies limitations

- <u>Slurping</u>: At residual saturation, gasoline is immobile and unrecoverable (in the saturated zone).
- <u>Chemical oxidation</u>: Gasoline adsorbed or trapped into pore spaces resists to oxidation.
- Soil washing:
 - Generates huge volume of washing solutions that have to be treated or disposed of
 - Ingredients costs make this technology non economical if not recycled



Research project

Coupling slurping and chemical oxidation with soil washing to reach environmental standards



Technology train progress



Micelle

Oil phase

Surfactant solution theory

- Surfactant solution = surfactant + cosolvent + water
- Surfactant: amphiphilic molecule: 2 different polarity parts, 1 hydrophilic and 1 lipophilic
- Aqueous phase • Formation of micelles

Monomer-

- Two main recovery mechanisms:
 - Solubilization: Active matter (surfactant + cosolvent) partitions preferentially into the aqueous phase
 - Mobilization: Active matter partitions preferentially into the oil phase (oil volume is increased and mobilized via an oil bank)



Preliminary Steps (Prior to Pilot Test) → Phase Diagrams

Identify promising surfactant/cosolvent solutions by titration (Cloud point technique)
Phase diagram for different Active Matter/Water/Gasoline systems





Preliminary Steps (Prior to Pilot Test) → Sand Columns Experiment

• Select optimal surfactant/alcool solution \rightarrow Sand columns experiment





Field Context

- Gas station location: Laval, Québec (5km north of Montréal)
- Two spill/leak episodes (1962 and 2005) from pipes and underground storage tank (UST)
- Estimated plume area: 2500 m²
- Geology: Silty sand with limestone boulders underlain by a fractured limestone bedrock.
- Water table at 7,0 m depth
- Slurping was made over a period of 12 months







Pilot Test – Cell specifications

- 7-point hexagonal pattern (Central injection + 6 extraction wells)
- Cell area: 45 m²
- Targeted depth interval: 7-8 m depth
- Cell volume: 45 m³
- Total porosity: 20%
- Cell PV: 8,7 m³
- Injection/extraction flow rate ratio = ½ (Feflow – Numerical modelisation)
- Injection Extraction wells mean distance: 4,26 m
- 4 observation wells inside and 11 outside cell





Injected Solution Pathway

1. Solution 1 m³ tote tank

- 2. Diaphragm Pump
- 3. Gate Valve + Flowmeter
- 4. Injection Well
- 5. Aquifer
- 6. Extraction well
- 7. Bladder Pump
- 8. Effluent 1 m³ tote tank
- 9. Open-top Container
- 10.Effluent treatment and disposal





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Pilot Test – Costs of chemicals

- 300 kg of pure surfactant at 10,80\$/kg = 3 240 \$
- 300 kg of cosolvent at 3,70\$/kg = 1 110 \$
- 180 kg of salt (NaCI) at 0,55\$/kg = 100 \$
- 5 kg of polymer at 11,90\$/kg = 60\$

Total cost of chemicals = 4510 \$ (45 m³ of contaminated soil) Unit cost \approx 100 \$/m³ of contaminated soil



Field Test – Injection Steps

- 1. Reach steady state
 - Injection/pumping of water
 - Water level monitoring until steady state (stabilized)
- 5 m³ (0,57 PV) of salted water bank (Pre flush)
- 3. 4 m³ (0,46 PV) of micellar solution (Washing)
- 4. 4 m³ (0,46 PV) of micellar polymer solution (Washing + sweep)
- 5. 10 m³ (1,15 PV) polymer solution (Rinse)



PV calculus based on total porosity of 20%



Field Test – Water Sampling

Objectives

- Establish initial conditions in the cell
- Follow the injected fluids in the cell
- Measure recovered gasoline from the cell

Sampling locations

- Extraction wells
- Injection well
- Observation wells
- Effluent reservoir
- Injection reservoir

Over 500 liquid samples taken



Field Test – Water Sampling

Effluent reservoir

 Homogenize the effluent in the reservoir prior to sampling





Field Test – Water Sampling

Observation wells

 Low flow sampling: Peristaltic pump via a flexible Viton[®] tubing connected to a ¼" Teflon [®] tubing





Effective porosity estimation → from salted water bank breakthrough curve



Electric Conductivity of Water in Well PO-125 as a function of injected volume

Radius from injector well to well PO-125: 1,23 m



Effective porosity estimation → from micellar solution bank breakthrough curve

Relative concentration C/C_{max} in Well PO-125 as a function of injected volume



Increase of effective PV (4,2% \rightarrow 8,8%) partly caused by solubilization/mobilization of absorbed gasoline in porous media by micellar solution



Effective porosity of silty sand

Usually estimated at: 20%^{*}

*Payne et al. 2008

- From tracer tests: less than $10\% (2\% 10\%)^*$
- Present Case: 4,2% to 8,8%

Injected solutions PV adjustment

- 1. 5 m³ Pre flush: 0,57 PV \rightarrow 2,74 PV (θ_{eff} = 4,2%)
- 2. 4 m³ Micellar solution: 0,46 PV \rightarrow 1,04 PV (θ_{eff} = 8,8%)
- 3. 4 m³ Micellar Polymer solution: 0,46 PV \rightarrow 1,04 PV (θ_{eff} = 8,8%)
- 4. 10 m³ Polymer solution: 1,15 \rightarrow 2,61 PV (θ_{eff} = 8,8%)



Gasoline vs Surfactant breakthrough curves in well PO-125



Relative concentration C/C_{max} in Well PO-125 as a function of injected volume

Gasoline bank arrives before surfactant solution bank = Mobilization (as an oil bank)

Gasoline concentrations follow surfactant concentrations = Solubilization



Gasoline recovery in effluent



Total recovered gasoline mass: 5,9 kg (7,5 L) Remediation impact on gasoline concentrations in soil: 67 mg/kg removal



Surfactant recovery in effluent



Total recovered surfactant mass: 204,1 kg (72% of initial injected mass) 28% of initial injected mass (81 kg) in the cell



Surfactant concentrations in water after Pilot Test

- Mean surfactant % per well (in cell): 0,0185%
- Estimation of equivalent surfactant mass for the whole cell: 0,0185% x 43,5 m³ x 8,8% x 1155 kg/m³ = 81,8 kg

 $%_{surfactant}$ x V_{cell} x θ_{eff} x $\rho_{surfactant}$

Surfactant Balance

Recovered in effluent:	204,1 kg
Inside the cell:	81,8 kg
Total:	285,9 kg
Real mass injected:	284,9 kg

No washing solution went out of the cell! (Injection/Extraction flow rate ratio with Feflow modelisation was correct)



Gasoline concentrations in wells of the cell

Well #	Before Test (mg/L)	After Test (mg/L)	↑Or ↓ In concentrations	Surfactant % after test (% m/V)
PO-new	3,02	0,729	\downarrow	< 0,01
PO-111	1,64	0,69	\downarrow	< 0,01
PO-124	2,46	3,17	\uparrow	0,02
PO-125	0,76	3,29	\uparrow	0,03
PO-128	7,60	17,11	\uparrow	0,03
PO-129	9,03	27,80	\uparrow	0,02
PO-130	4,04	9,83	\uparrow	< 0,01

Gasoline available in solution for following chemical oxidation!



Conclusion

- Laboratory tests are necessary prior to soil washing (eg: phase diagrams and sand columns)
- Ingredients costs for soil washing: 100\$/m³ of contaminated soil (Lower cost for a larger project)
- Effective porosity must be determined via tracer test prior to washing solution injection.
- Effective porosity will increase during soil washing and is related to initial oil saturation
- Gasoline is recovered by two mechanisms: Mobilization and Solubilization
- Impact of washing solution remediation:
 - Direct: Decreases gasoline mass in soils
 - Indirect: Helps chemical oxidation by bringing adsorbed / trapped gasoline into solution to be oxidized

Thank you!

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Questions?

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