Latest Findings in In-situ Remediation of Hydrocarbon Impacted Soils using Hydrogen Peroxide

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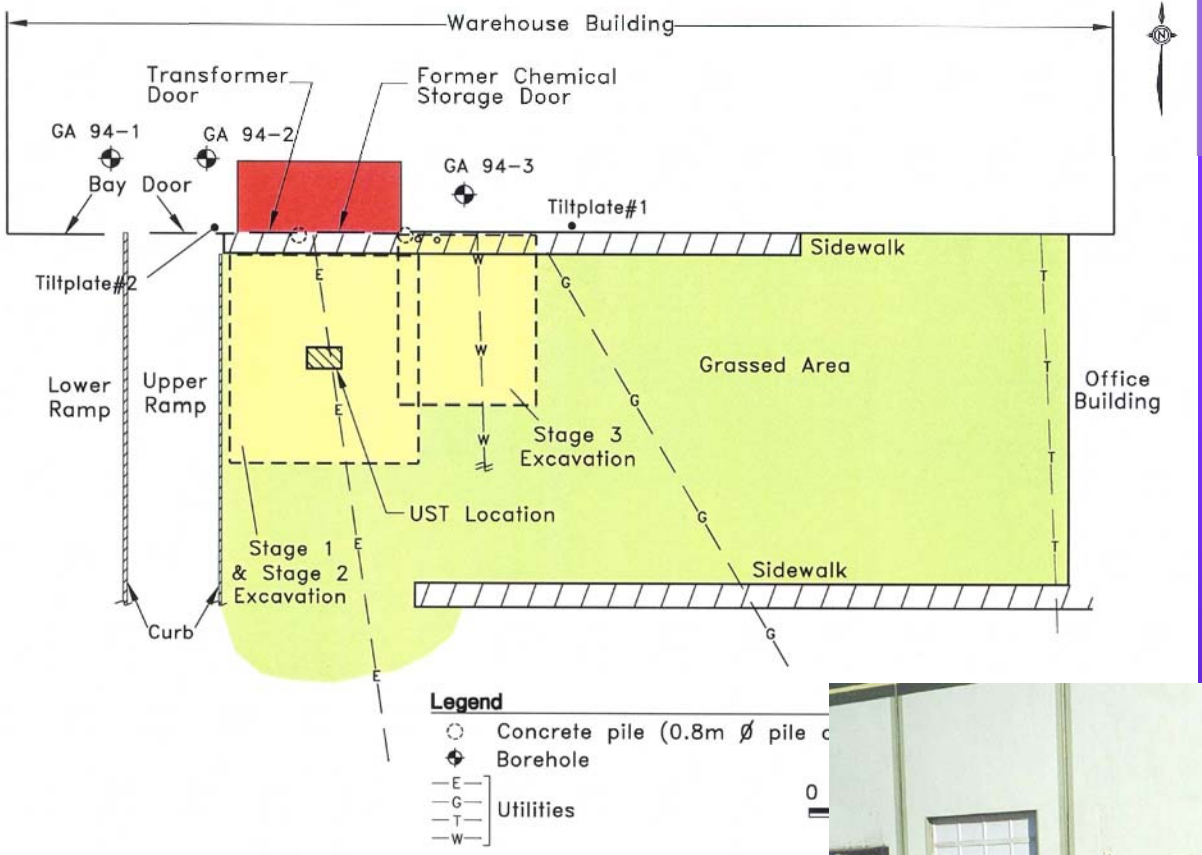
Background

- Hydrogen peroxide (H_2O_2) a strong oxidant is used to cleanup residual contaminants adjacent to structures with restricted access (Mahmoud et al. 2000)
- $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\cdot$
- $OH\cdot + C_xH_y \rightarrow H_2O + CO_2 + \text{heat}$
- $H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2$
- $OH\cdot + Fe^{2+} \rightarrow OH^- + Fe^{3+}$
- $HO_2\cdot + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+}$
- $H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot$

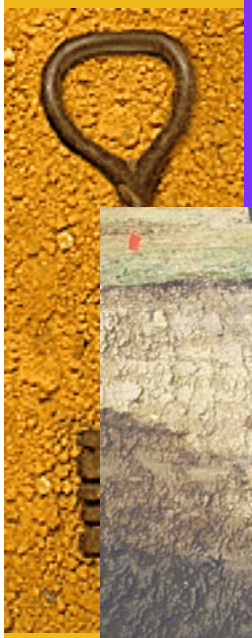
Site Front Elevation

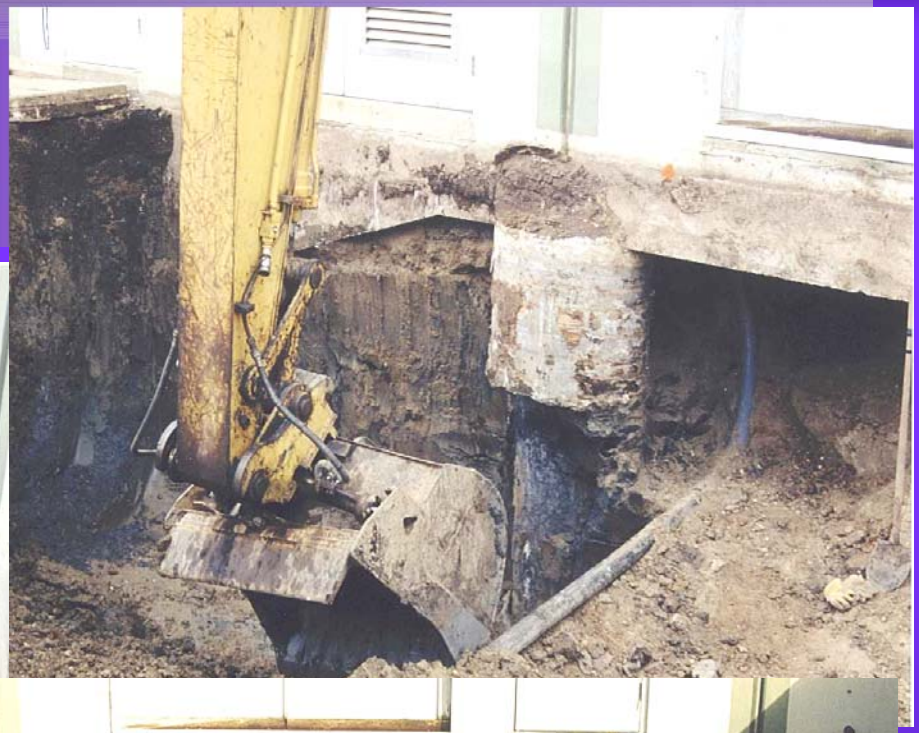
Chemical Storage Room



2 tiltplates installed for monitoring ground movements during injections

Restricted Access





Restricted Access

Two H_2O_2 Applications

- Initial concentration pre-determined based on contaminant concentrations and type of contaminant
- Typical concentrations: 10 - 25%
  - First ⇒ 16% concentration
  - Second ⇒ 20% concentration

H_2O_2 Treatment Apparatus

Drums of 50% concentration H_2O_2

H_2O_2 Injection

Assessing required concentration

Laboratory Program

- Impact of hydrogen peroxide on heave of soil
- Investigate major process variables in use of hydrogen peroxide for remediation
  - Influence of iron catalyst
  - Use of surfactant
  - Multiple applications of hydrogen peroxide
- Study the distribution of hydrogen peroxide in soil upon injection
- Impact of hydrogen peroxide injection hydraulic conductivity

Test Conditions

- Major contaminant - diesel
- Heave Study
  - Sandy soil (with 0.55 % organic content)
  - concentrations of 0, 2000, and 5000 mg/kg
  - H_2O_2 concentrations of 5%, 10%, 15%, 25% and 30% by volume
- Other Experiments
  - Three soil types
    - Sandy silt (UC soil; 63.9% sand, 26.1% silt and 7.9% clay, 0.4% orgs., 1.9% iron content
    - Silty clay (SH soil; 44% sand, 23.2% silt and 31.4% clay, 1.87% orgs., 1.55% iron content)
    - Ottawa sand (as control)
  - concentrations of 0, 500, 1000, 5000 & 10,000 mg/kg
  - H_2O_2 concentrations of 5%, 10% and 20% by volume

Characteristics of Diesel

No. 2 diesel: C9 –C20, 160 °C and 360 °C

Major physical properties

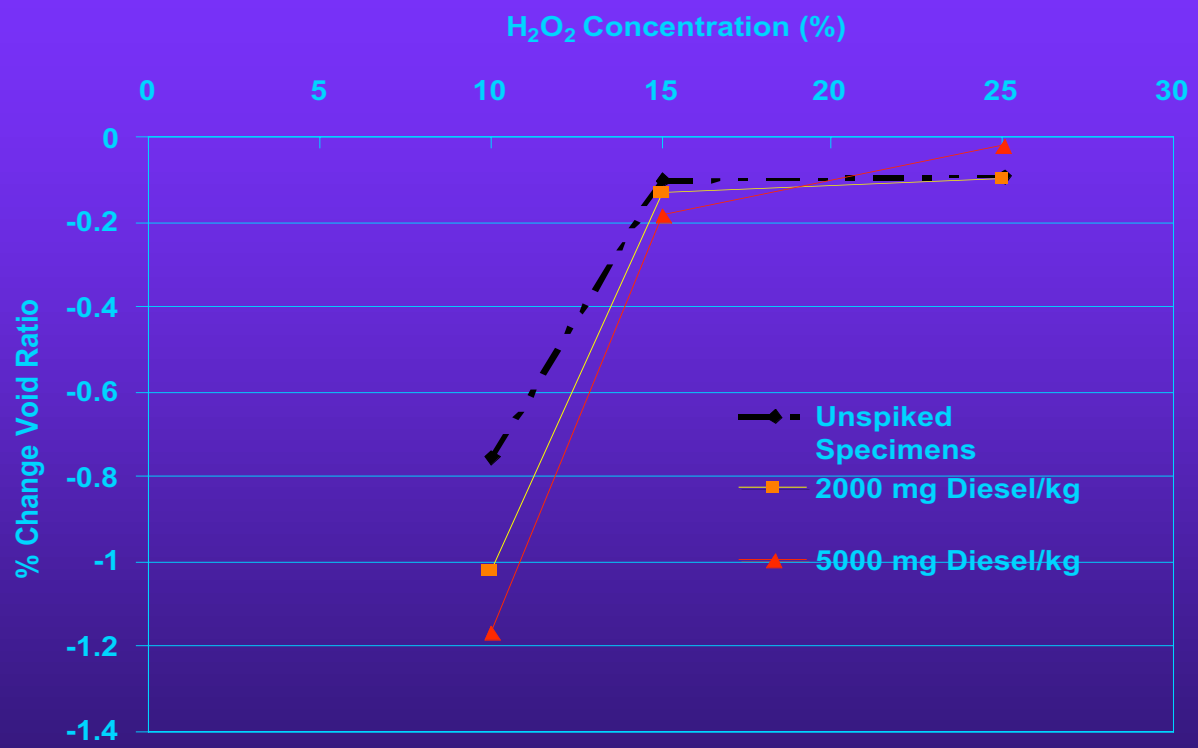
Index	*Specifications*
Density (g/cm^3)	0.82 – 0.87
Viscosity (cSt)	1.3 – 4.1
Solubility (mg/L)	2.3 – 8.3 (Distilled Water) 2.8 – 39.1 (Fresh water)
Volatility (%)	57 (5 day evaporation @22 C)

Major chemical compounds

Compounds	*Percent by weight*
Alkanes (normal, branched & cycloalkanes)	70 - 80
Aromatics	20 - 30

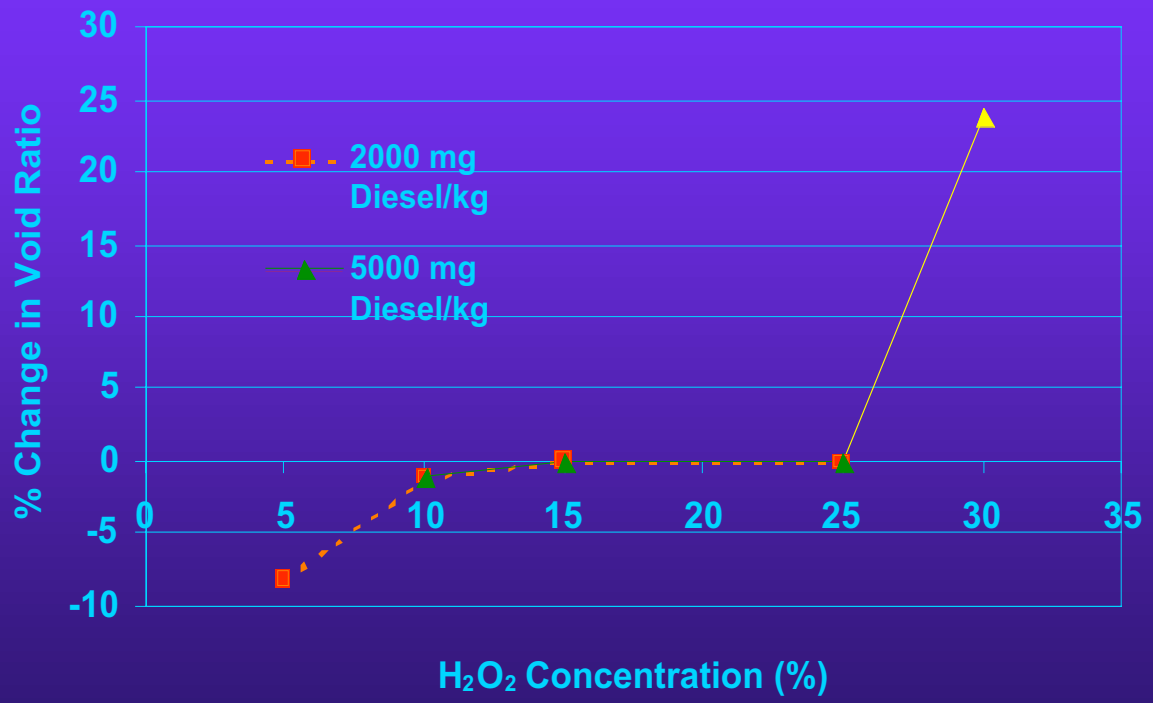
Results – heave of soil

- Initial volumetric change in specimens



Results – heave of soil

- Long term volumetric change in specimens

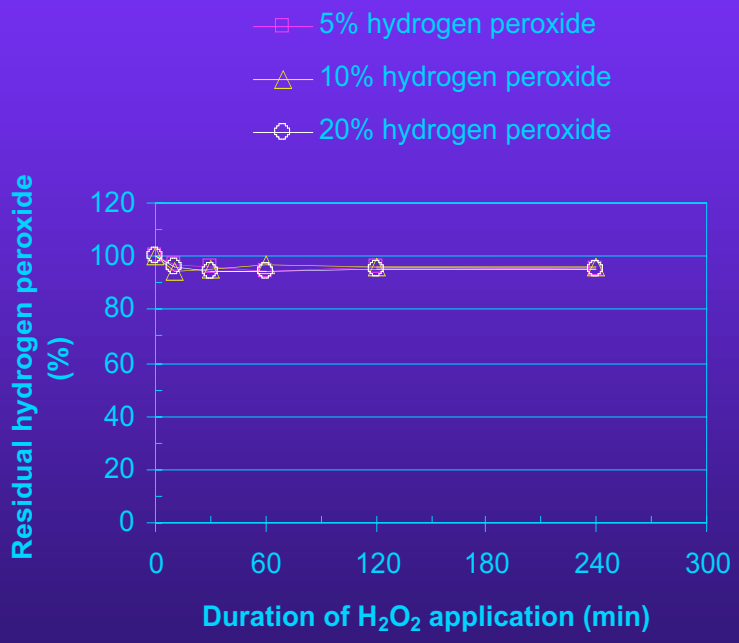


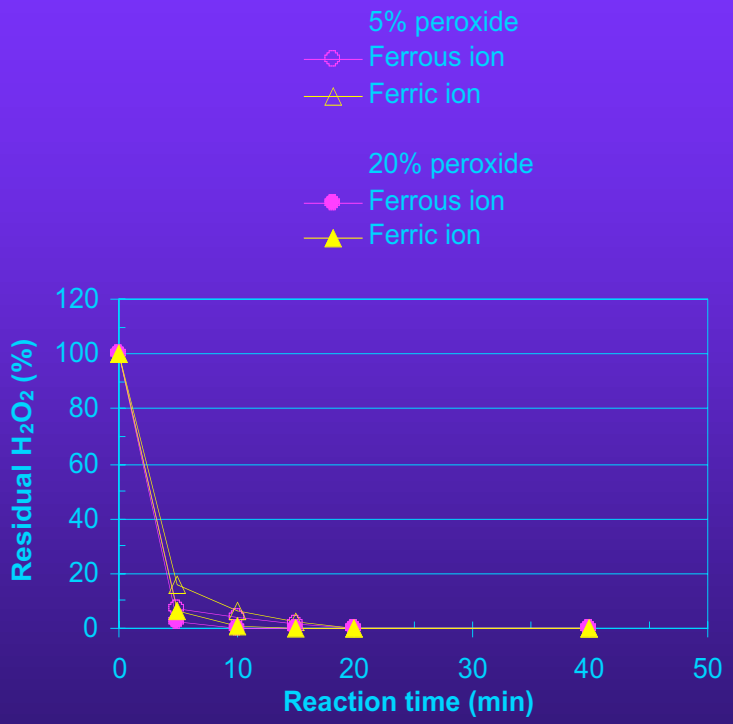
Results - Major process variables

- H_2O_2 consumption
- Soil buffering capacity and pH effect on DROs degradation
- Iron catalysts and mineral iron oxides
- Gas quantification/qualification
- Enhancement of diesel degradation

H_2O_2 consumption during remediation of Ottawa sand

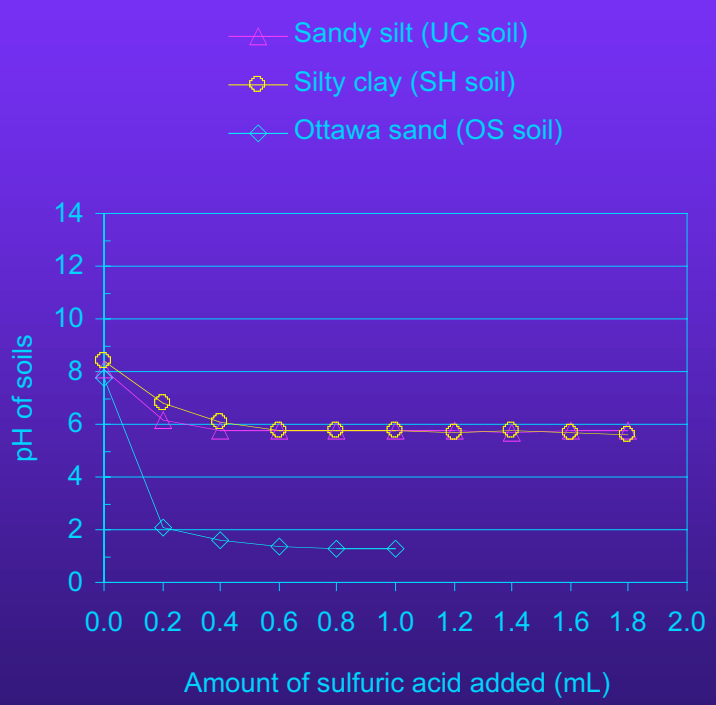
- No iron added
- Iron added (720 mg/L)

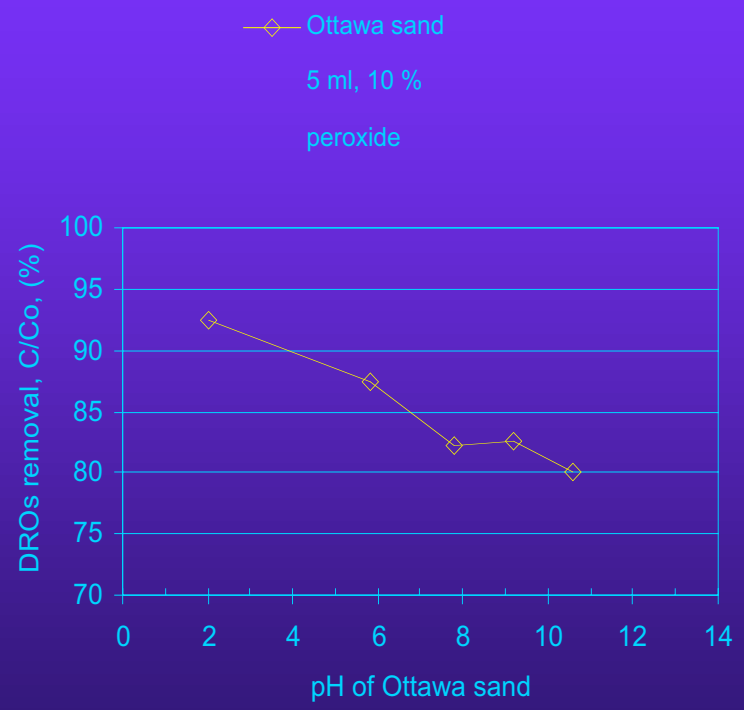




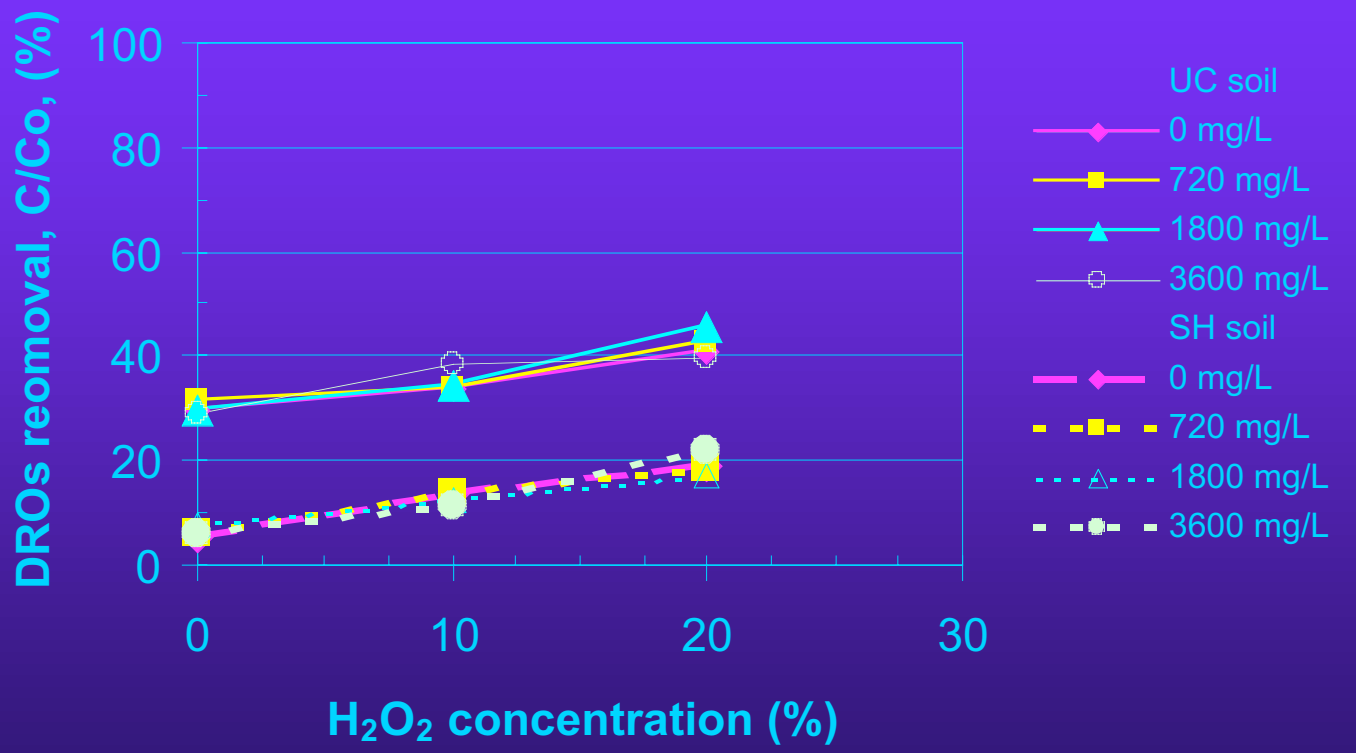
Low soil pH – Beneficial but difficult to attain

- Forcing a decrease in soil pH
- Impact of soil pH on DRO removal

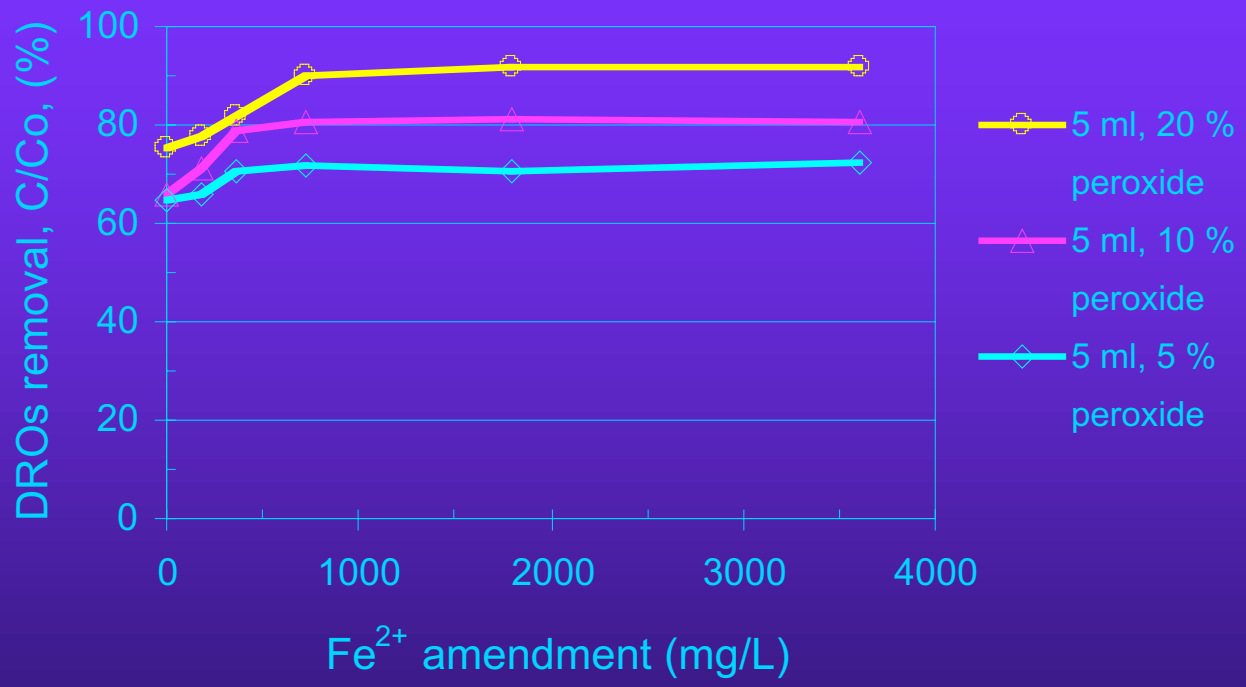




Impact of External Iron Addition to UC and SH soils

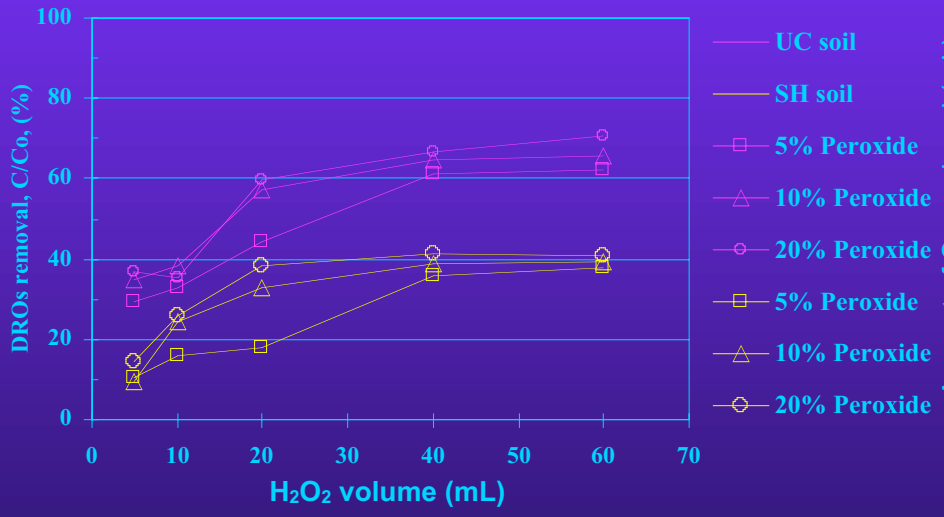


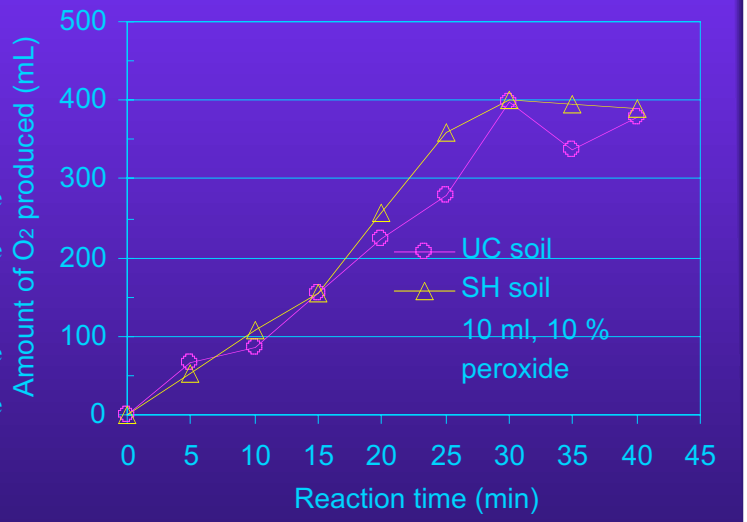
Impact of External Iron Addition to Ottawa Sand



Degradation Efficiency and Gas Production

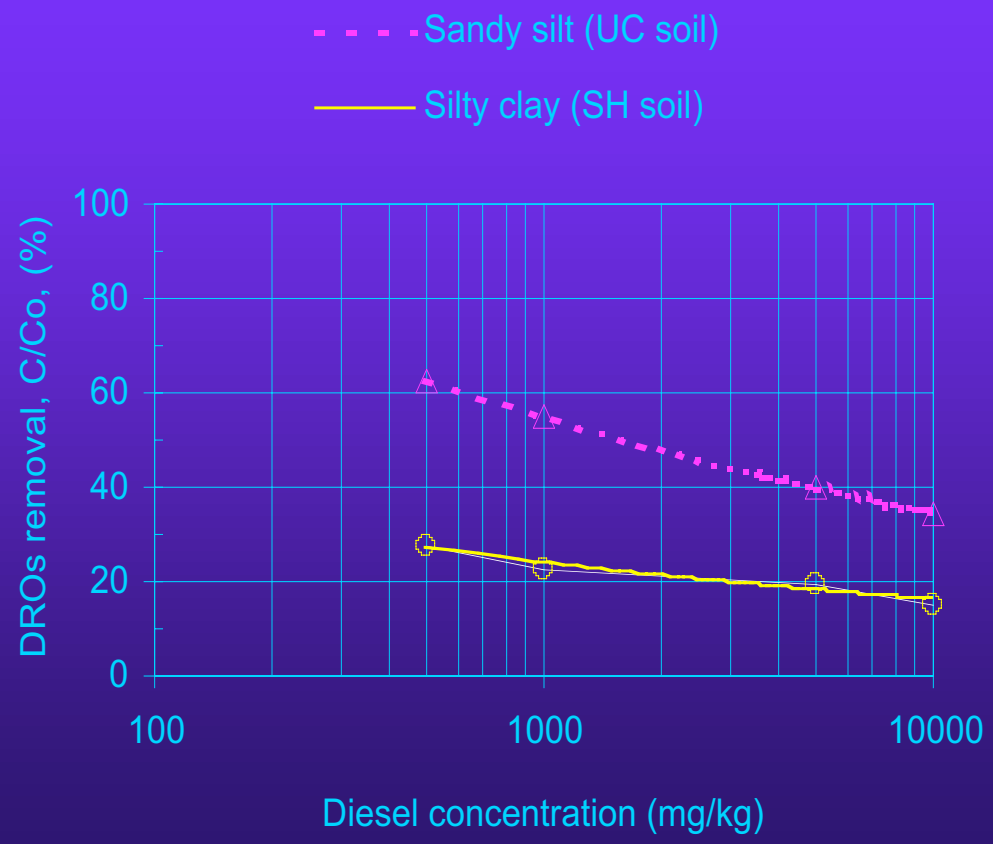
- Diesel Degradation Efficiency
- Oxygen generation – indication of scavenging of H_2O_2





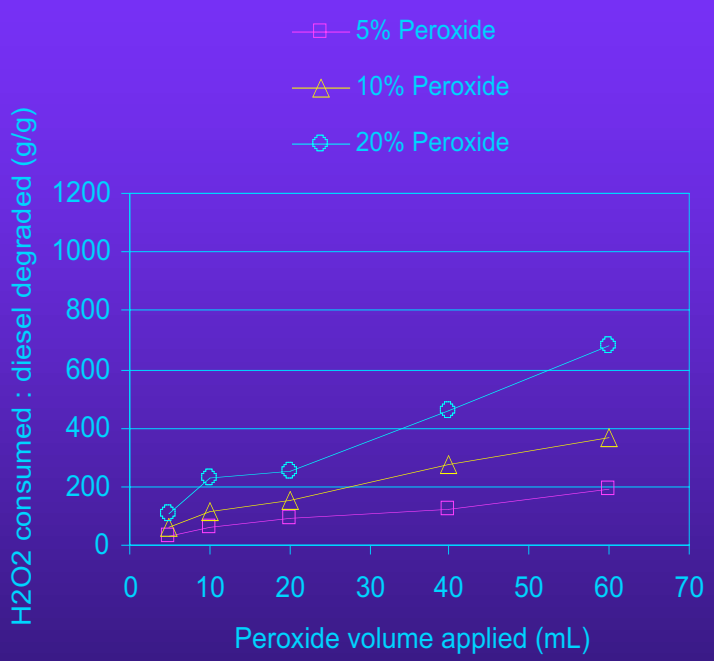
Effect on Diesel Concentration on DRO removal

- 10 ml of 10% H_2O_2 used

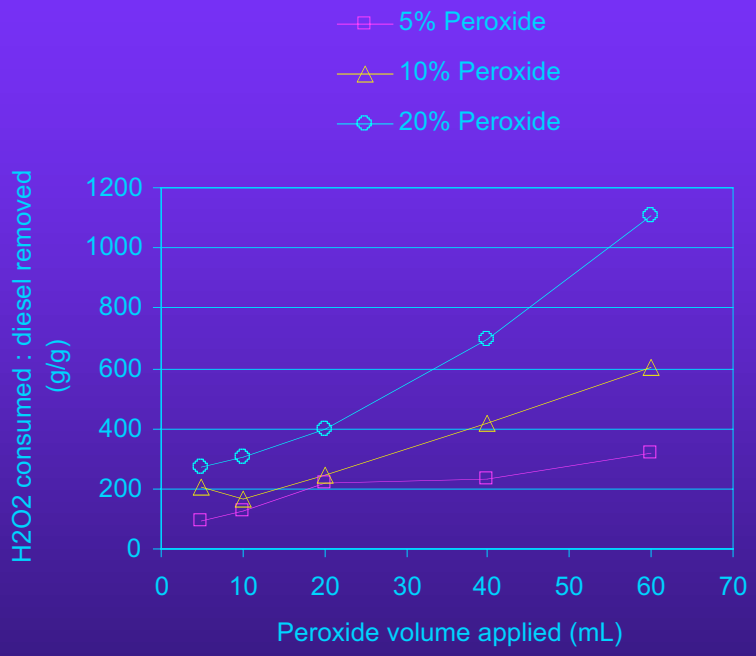


Degradation efficiency – ratio of H_2O_2 consumed to diesel degraded

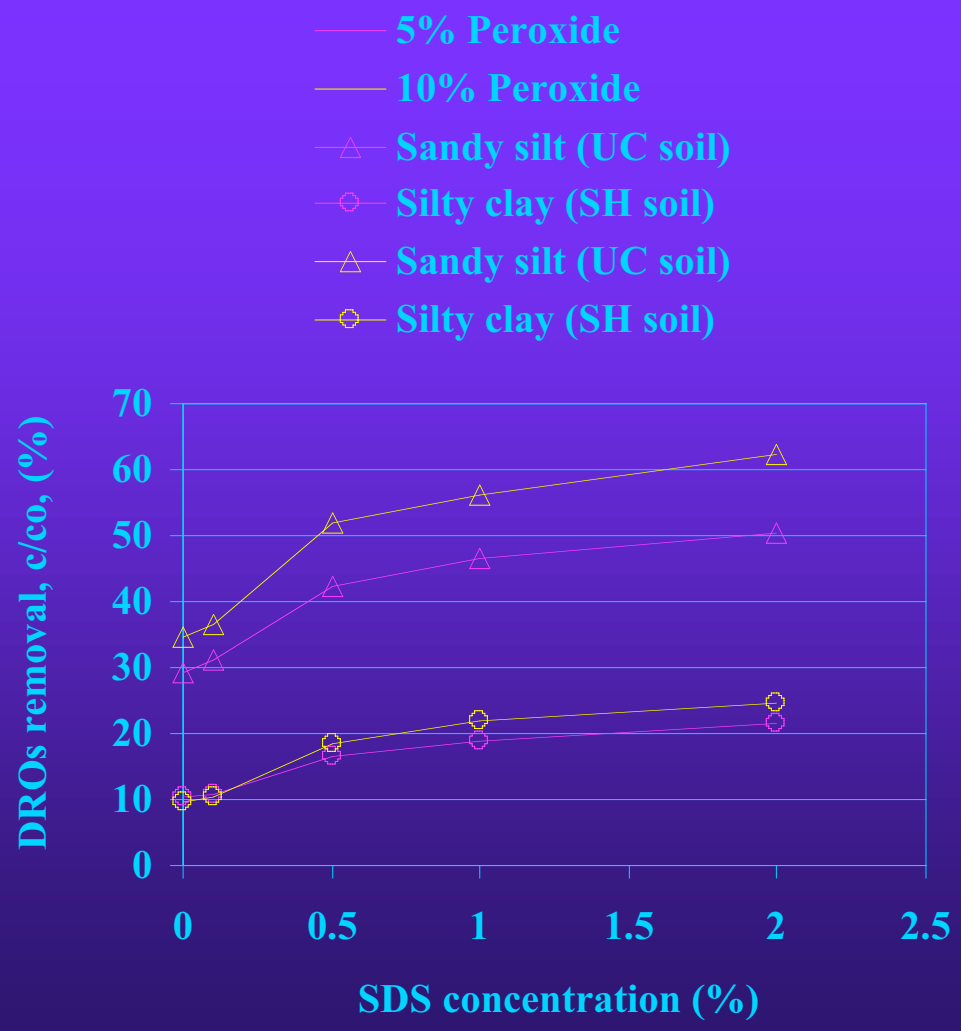
- Sandy silt



- Silty clay

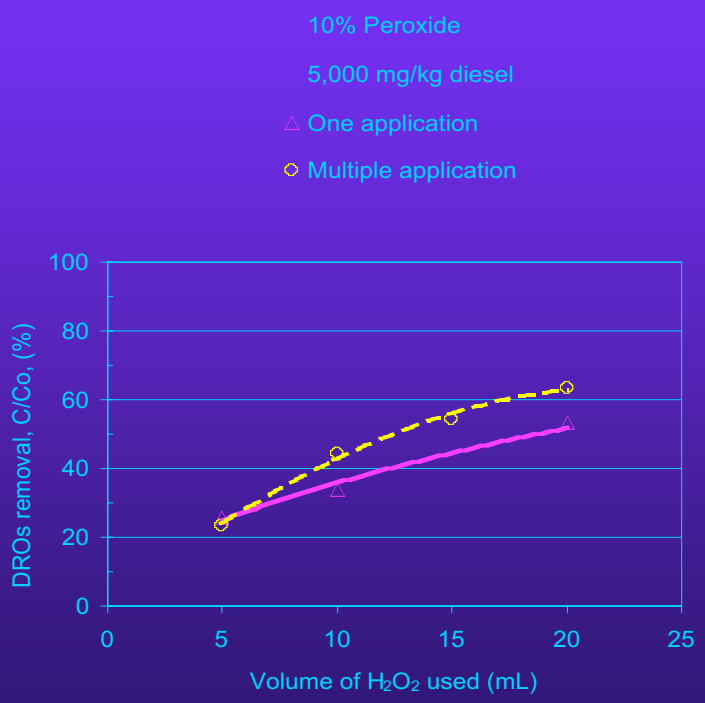


Surfactant Enhanced Diesel Degradation

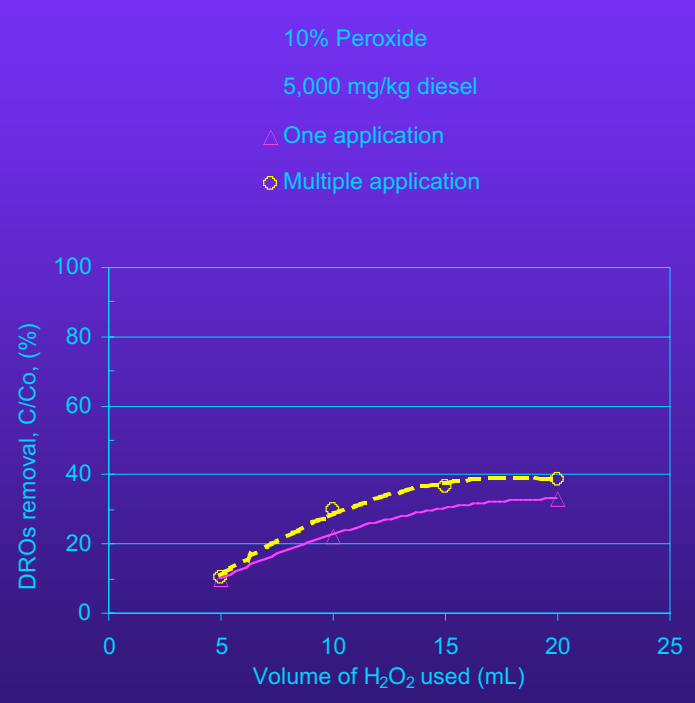


Impact of Multiple Applications

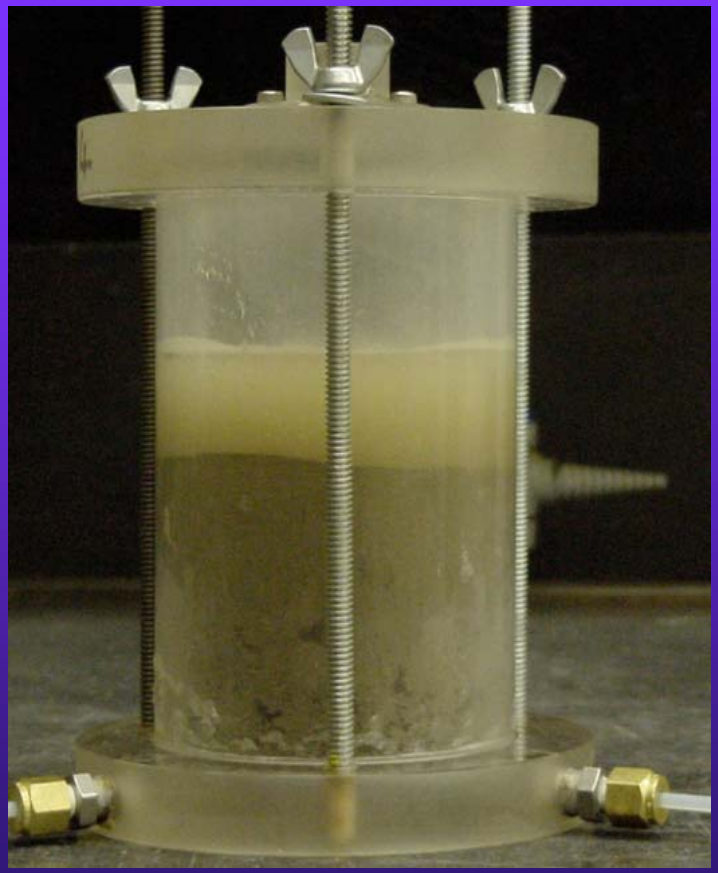
- Sandy silt

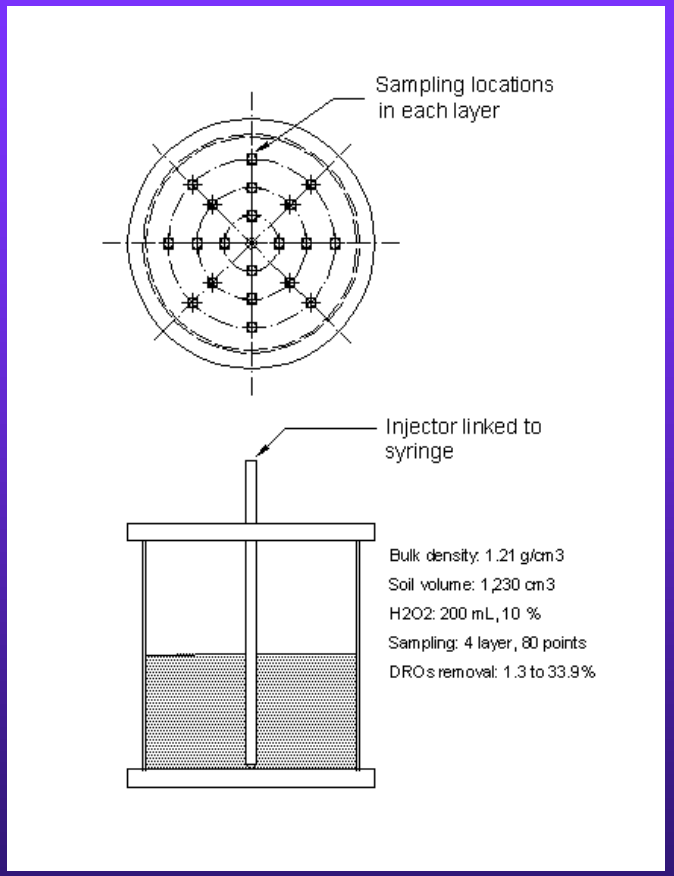


- Silty clay

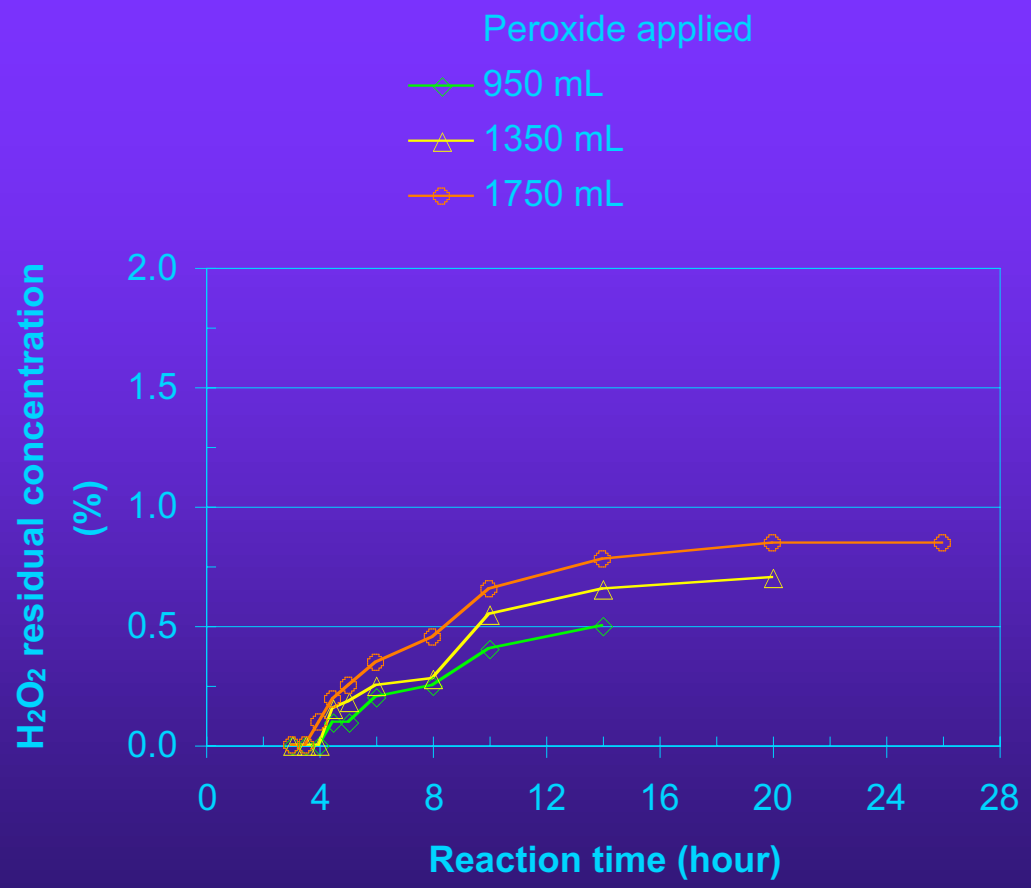


H_2O_2 Infiltration & Injection

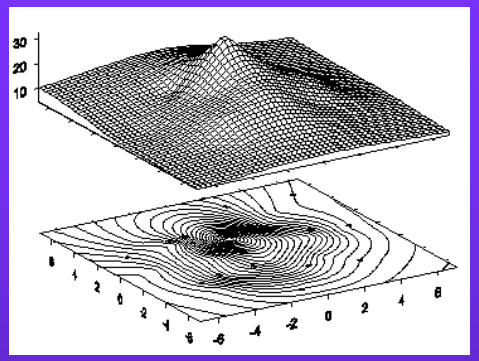


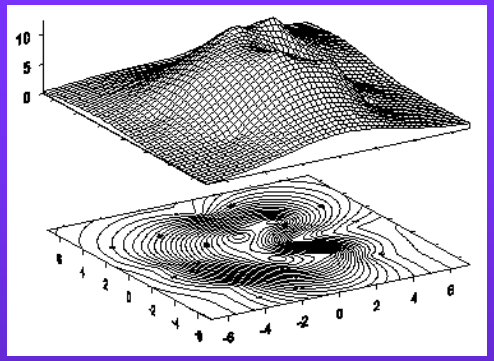


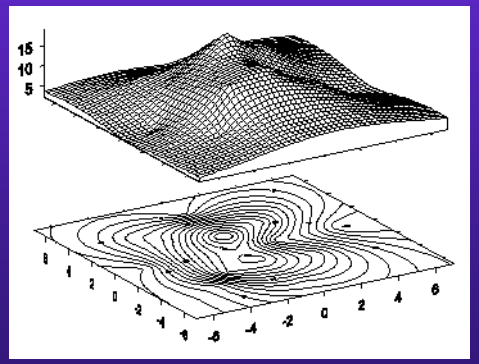
Breakthrough Curve

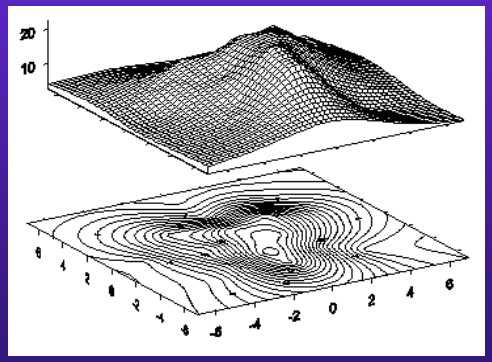


Injection Test Results









Injection Test Results

- Two major concerns
  - Uneven distribution of H_2O_2 and remediation
  - H_2O_2 making its way to the top along the injector due to “refusal”

Hydraulic Conductivity Results

- Hydraulic conductivity of H_2O_2 is 30 times lower than that of water
- Reason – gas generation and increased resistance due to gas pressure
- Surface application not very effective due to reaction at the surface

Conclusions

- Soil volume changes encountered
- Heave
  - Below a 15% H_2O_2 concentration, treated soil experience immediate settlement
  - Settlement decreases as H_2O_2 concentration increases
  - Above 10% H_2O_2 concentration immediate settlement is followed by rebound
  - At 30% H_2O_2 concentration and high diesel content significant volume increase (heave) takes place

Conclusions

- Process variables
  - Presence of iron necessary
  - Concentration and volume of H_2O_2 are both important process variables
  - High concentration of H_2O_2 had higher degradation, at a lower efficiency
  - Soil pH, if it can be lowered, would increase degradation
  - Optimum dosage for remediation: 8 mL of 5% H_2O_2 (or 4 mL of 10% H_2O_2) per gram of 5000 mg/kg diesel contaminated soil

Conclusions

- SDS improves the treatment efficiency when SDS concentration > than CMC
- Multiple application somewhat increased degradation efficiency

- Injection and Infiltration Tests
  - Uneven distribution of H_2O_2 during injection
  - Refusal due to reaction and gas production may be concern
  - Hydraulic conductivity lowered by gas production

Acknowledgements

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