Rapid Thermally Enhanced Degradation of Methylene Chloride at a Spill Site in the UK

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Background

- Methylene Chloride (Dichloromethane) was accidentally released from an underground pipe, directly into groundwater (approximately 15,000kg)

- Unusual Project
  - Recent spill, not a planned legacy project
  - Emergency response
  - Speed - time of the essence: carried out design/installation in parallel
  - Third party land impacted/remediated
  - Site fully operational and treatment zone in high activity area
ERM has integrated the SuRF framework with key stages in project delivery

Stage A - Setting the remediation specification and strategy

Stage B - Setting the remediation technical approach

- Community & stakeholder engagement
- Sustainable Procurement
Site Characterization

HRSC has lower carbon footprint than traditional SI

DNAPL observed during investigation
Remedial Options Appraisal: MCA Results

- Steam enhanced vacuum extraction selected on the basis of:
  - Challenge of water management
  - Large mass spilt into ground (11,000 litres)
  - Rapid remediation required
  - Relatively stringent remedial goals
  - Low boiling point of DCM
Sustainable Remedial Design

- Electrical boiler converted to run on gas (increased energy efficiency)
- Process equipment to reduce GAC use
- Optimize steam heating – via a thermal model
- Operational approach included heat re-use (up-gradient injection first)
- Thermal processes. Originally expected volatilization would be key mechanism (DCM BP 40°C, but evaluated abiotic or biotic processes)
System Installation: *Steam Boiler*
System Installation: Vapour/Liquid Processing

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System Installation: *Carbon Treatment*
System Installation: *Pipework*

Vapor extraction well head

Steam injection well head
Groundwater Sampling – DCM Results (Baseline)

Some migration since HRSC, but majority of mass remained onsite

Jan/Feb 2014 (Baseline)
Remedial Strategy

![Diagram of Remedial Strategy]

- **Steam Injection Well**
- **Extraction Well**
- **Thermocouple String**

TMP – 1.7, 3.0, 5.0 varies
System Operation: *Thermocouple Data Example*

Heating optimization – track temperatures, reduce energy consumption
Expected Mass Recovery Mechanisms (2)

Note: Temperature data taken from the top three thermocouples in wells R1-R20
Actual Mass Recovery (August 2014)

- Vapour Phase Recovery
- Hydrous Pyrolysis Oxidation
- Liquid Phase Recovery

Mass recovered (kg) vs Date

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Groundwater Sampling – DCM Results (August 2014)

Data indicates >90% DCM reduction achieved (16 weeks operational time)
Chloride Distribution (August 2014)

Zone of limited heating
DCM Degradation Mechanisms

- Reaction Chemistry:
  - Aerobic thermophillic biodegradation:
    - $\text{CH}_2\text{Cl}_2 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{HCl}$
  - Thermal hydrolysis:
    - $\text{CH}_2\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{HCHO} + 2\text{Cl}^- + \text{H}_2\text{O}$

- Biological degradation initially suspected:
  - Large sulfate reduction pre-thermal
  - Significant CO$_2$ removal during heating
DCM Degradation Mechanisms (2)

- But post thermal microbial population decreased
- Chloride may also be derived from abiotic mechanisms (hydrolysis) and a single round of CSIA confirmed abiotic degradation has occurred – but only one sample event
- Ultimately, hard to resolve exact mechanism, but significant reductions observed and remainder of treatment zone heated to lower temperatures to complete the project
DCM Concentration Results (*October 2014*)

- >95% DCM reduction achieved
- Low temperature mechanisms enabled 5 week project duration reduction
- Regulatory approval obtained. No further action required and prosecution avoided
Conclusions

- Despite energy consumption, thermal techniques directed at source reduction offer a lower carbon footprint, especially when sustainable design and operational approaches are applied.

- Carbon Footprint Reduction
  - Accurate source zone delineation
  - Multi-Criteria Analysis
  - Gas powered heating process
  - Process engineering innovation
  - Optimized heat control and delivery
  - Low temperature mechanisms observed
Questions?