



University  
of Glasgow



**REMTECH EXPO**  
21-25 SEPTEMBER 2020  
*digital edition*

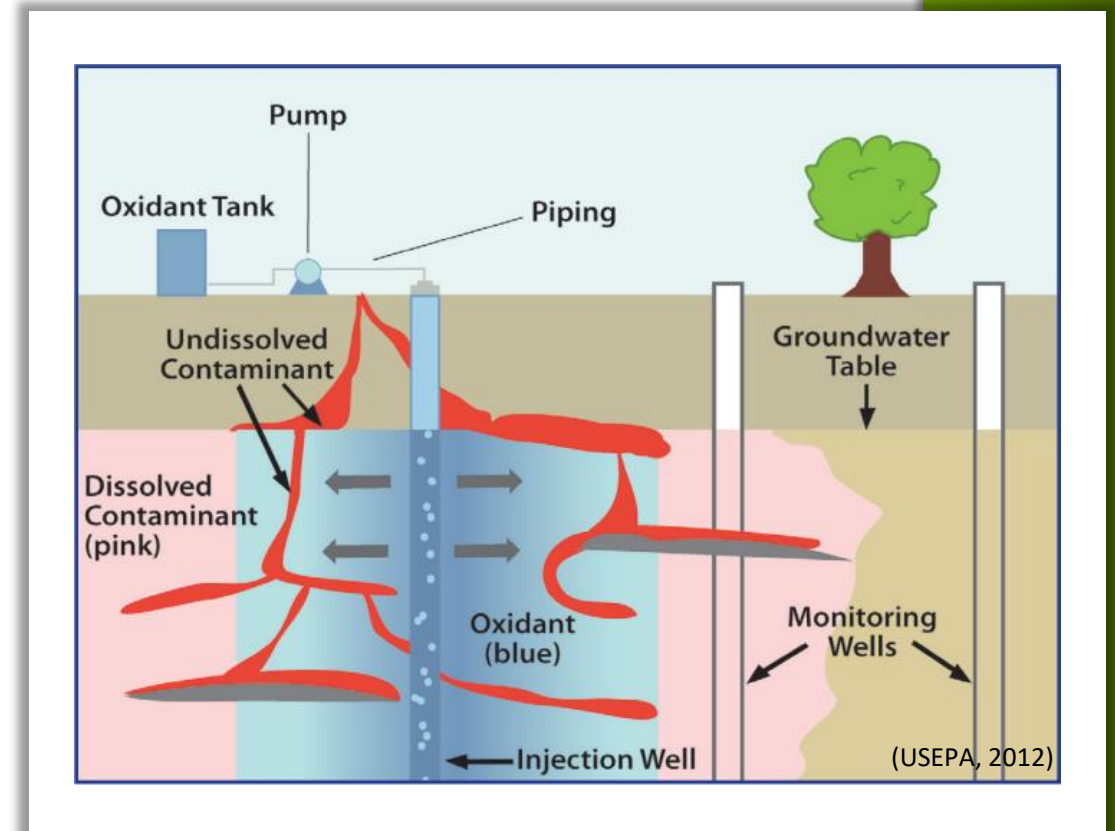
Use of respirometry for chemical oxidising agent activator type and concentration selection for saturated hydrocarbon contaminated soils

Christina Makri

Thomas Aspray

# What is ISCO?

- In situ chemical oxidation (ISCO) is an advanced remediation technique for hydrocarbon contaminated soil in the saturated zone.
- Examples of oxidising agents
  - Hydrogen peroxide
  - Ozone
  - Permanganate
  - Percarbonate
  - Persulfate
- Combined with one or more activator
- Selection based on contaminant degradation
  - E.g. Total Petroleum Hydrocarbon (TPH)
  - Destructive sampling
  - Impacted by sample heterogeneity (1-10 g samples)
  - Non-real time data
  - Cost



# Persulfate for chemical oxidation

---

- Efficient and stable in the subsurface
- Generation of radical species ( $\text{SO}_4^{\bullet-}$ ,  $\text{HO}^\bullet$ , and  $\text{O}_2^{\bullet-}$ )
- Activation methods
  - UV light
  - Heat
  - Activated carbon
  - Alkaline conditions
  - Transition metals (mainly  $\text{Fe}^{2+}$ )
- Activation by natural soil components
  - Metals
  - Organic matter components (e.g. phenols and quinones)

# Aim of project

---

Assess the suitability of using an automated respirometer for chemical oxidising agent treatability testing in saturated hydrocarbon contaminated soils.

# Samples and characterisation

- ERS yard soil and clean general builder's sand
- Sieved and homogenised soil
- Diesel - hexane spiking in batches



Matrix	pH <sub>H2O</sub>	Moisture content (%)	Organic matter (%)	Concentration (mg/kg)		
				Fe (total)	Fe (3+)*	TPH (total)
Soil	9.3	23.4	0.1	50 000	< 0.4	~ 4 000
Sand	9.6	n/d	n/d	n/d	n/d	~ 4 000

n/d – not determined; \*based on leachate prep; TPH – total petroleum hydrocarbon

# Oxidation experiments

---

- Oxidising agents
  - Sodium persulfate (SPS) ( $\geq 98\%$ , Acros Organics)
- Iron ( $\text{Fe}^{2+}$ ) activation
  - Iron (II) sulphate (Fisher Scientific)
- Alkaline activation
  - Sodium hydroxide (Acros Organics)

# Experimental design

---

- Polypropylene tubs
- 50 g soil or sand
- Moisture adjustment
- Control samples – soil/sand + water
- 2.0 g of SPS
- Activator
  - Iron – Fe:SPS (1:100, 1:10, 1:1)
  - Alkaline – pH > 10.5
- 4-6 treatments/control replicates
- Temperature control



# Respirometry

- Respicond automated respirometer
- Measurement of CO<sub>2</sub> production

HO<sup>•</sup> + SO<sub>4</sub><sup>•-</sup> + organics → Reaction intermediates + CO<sub>2</sub> + H<sub>2</sub>O + SO<sub>4</sub><sup>2-</sup>

- KOH traps with electrodes measuring change in conductance
- CO<sub>2</sub> production recorded at one-hour intervals
- Real-time observation of reaction kinetics
- Capacity for 96 samples
- Sensors not damaged by high moisture conditions





# Mineralisation of organics by persulfate

---

Hidden Data

# Iron activation assessment

---

Hidden Data

# Alkaline activation assessment

---

Hidden Data

# Kinetics of persulfate iron activation

---

Hidden Data

# Conclusions

---

- CO<sub>2</sub> mineralisation of organics can support chemical oxidation treatability testing
- Use of automated respirometer for chemical oxidation can support:
  - Matrix-specific assessment
  - Selection of activator type and concentration
- Potential to study kinetics of chemical oxidation reactions and mineralisation of organics

Thank you!

Christina Makri



[cmakri248@gmail.com](mailto:cmakri248@gmail.com)



[www.linkedin.com/in/christinamakri](http://www.linkedin.com/in/christinamakri)