Can a Pilot Demonstration be too Small?

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Case Study of a Small Pilot

- A Pilot demonstration was requested to validate the effectiveness of a technology on chlorinated compounds in impacted soils at a site where dry cleaning businesses have operated for over 20 years.

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Pilot Objectives

- Demonstrate the viability of the technology to reduce the tetrachloroethene (PCE) concentrations within the pilot area to the below regulatory limits.

- Determine information to optimize the treatment of the entire site.

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Approach / Activities

Cool-Ox® was selected for the pilot demonstration based upon successes treating dry cleaner sites.

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Selection

- A highly contaminated area adjacent to the former Dry Cleaner's building was targeted.
- A small area was selected (5 x 6 x 5 ft. bgs.) to save money.

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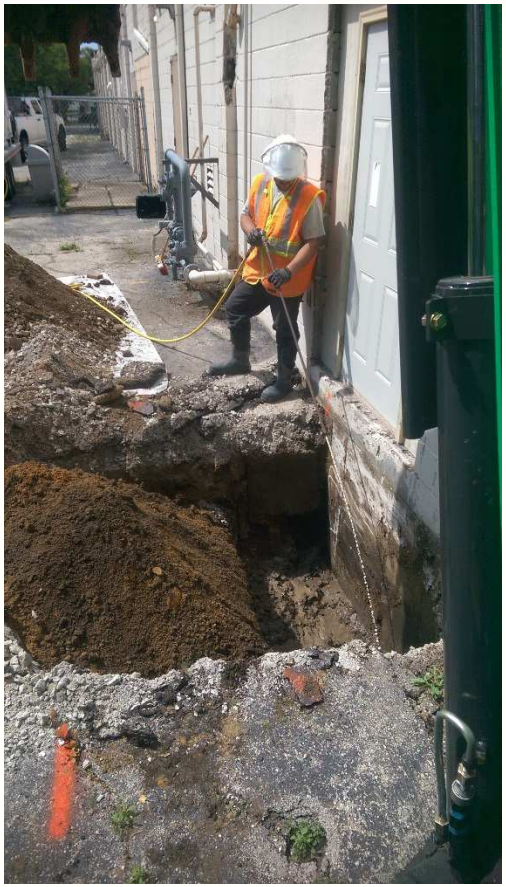
Application



- Dosage-ten (10) gallons per cubic yard
- Application technique – soil blending

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Observations

- Very active reactions were observed with the evolution of significant quantities of carbon dioxide gas indicating presence of perc.
- No heavy foams were observed indicating no Stoddard solvent present.

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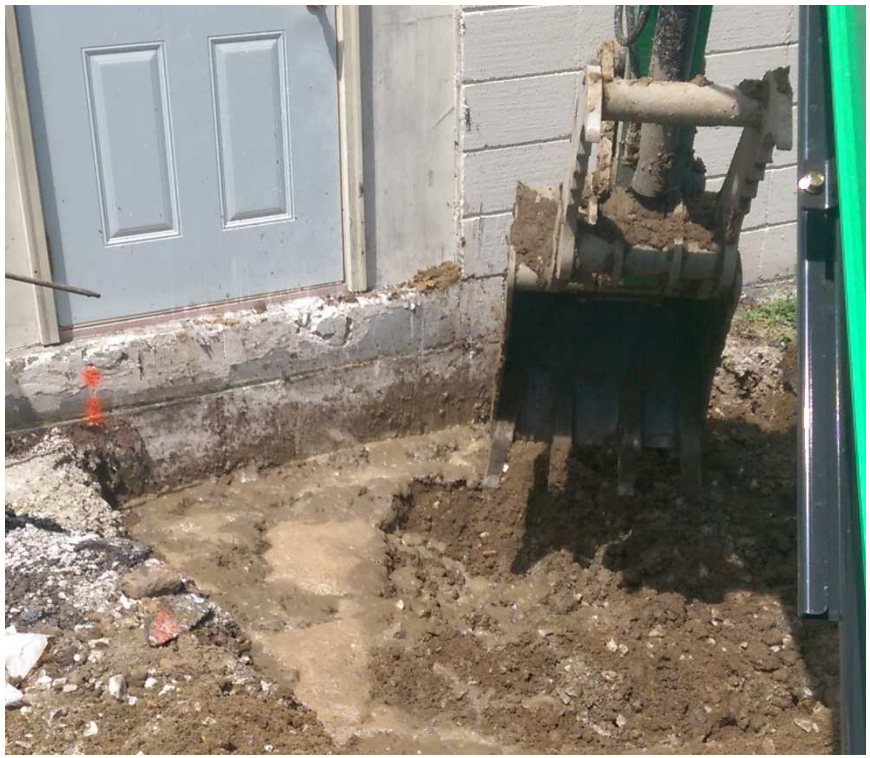
Reactions



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Results

- Based on the sampling results, it appeared that insufficient or no destruction of contaminants was observed? Why?

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Causes

- No samples were taken immediately after the application.
- Time elapsed, allowed contaminate intrusion from surrounding soils.
- Thus, it appeared that no destruction of contaminants occurred.
- But, how do we know….

Remember the foam!

Let’s learn from another expert.

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ISCO Chemistry

The Conventional Understanding of ISCO Chemistry:

Oxidation of PCE*:

$$4H_2O_2 = 4H_2O + 4O^{+2}$$

$$4O^{+2} + C_2Cl_4 = 2CO_2 + 4Cl^-$$

Brown cautions that SOD may "rob" O^{+2}

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SOD

If SOD acts as an O+2 sink, then:

- Little or no PCE reduction should have occurred
  - (but we saw substantial reduction!)
- Site's SOD data suggest that ~200 applications will be needed to "break even"
- Therefore, the site's empirical data suggest that SOD is not acting as a "sink", and thus is not relevant.
- What does this mean?
- Maybe the conventional theory is flawed…

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ISCO Chemistry

An alternative explanation of ISCO Chemistry:

Bimolecular nucleophilic substitution (S_n2) of chloride ion:

$$2H_2O_2 = 4OH^-$$

$$4OH^- + C_2Cl_4 = C_2(OH)_4 + 4Cl^-$$

$$2CO_2 + 4\ CL^-$$

The OH^- displaces Cl^-, and thus SOD is irrelevant

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S_n2 Theory

The S_n2 Theory is supported by Site's data:

- Substantial PCE reduction occurred

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The Chemistry

(Produce Hydrogen Peroxide In-Situ)

$$CaO_2 + H_20 \rightarrow Ca^{+2} + OH^{-1} + H_2O_2 + O_2$$

(Chelates Activate Intrinsic Catalysts – Produces Radicals)

$$H_2O_2 + Fe^{+2} \rightarrow OH^{-1} + [OH]^{\bullet} + Fe^{+3}$$

$$H_2O_2 + Fe^{+3} \rightarrow OH^{-1} + [OOH]^{\bullet} + Fe^{+2}$$

(Radicals React with Contaminants – Oxidation By-products)

$$[OH]^{\bullet} \,\&\, [OOH]^{\bullet} + C_x \rightarrow C_x(OH)_y + CO_2$$

(Biodegradable By-products Used by Microbes)

$$C_x(OH)_y + O_2 \rightarrow CO_2$$ Totally Green

(Reductive Dechlorination)

$$_nC_2(Cl)_x + (OH)^- \rightarrow {}_nCO_2 + (Cl)^-$$

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Lessons Learned

- Had a larger area (say 10 x 10 feet) been treated, samples could have been collected from the center of the treatment area where reductions would have been apparent.

- Our understanding of conventional ISCO chemistry was revised where halogenated compounds are present.

- SOD is irrelevant when employing abiotic reductive dechlorination.

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Thank you

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