Experience with Carbon Emplacement for Remediation of Petroleum

September 15, 2015

Department for Environmental Protection
Environmental & Public Protection Cabinet

To Protect and Enhance Kentucky’s Environment
Kentucky PSTEAF (Fund) Basics

- Fund (Motor fuel tax pays for remediation)
- Spending $20 million annually
- Contractors hired by the tank owner/operator
- State directs work by fixed price directive
- Non-fixed cost items are priced by bid.
- Present # of sites in remediation = 780
Kentucky Geology Basics

- Low permeability clay and silty-clay soils
- Karst regions (Fractures holding contamination).

In situ remediation by conventional methods such as soil vapor extraction or biodegradation are often ineffective at low permeability media sites due to poor accessibility to the contaminants and severe mass transfer limitations (Siegrist et al., 1999). Consistent with KY’s experience!
Core mechanism activated carbon is adsorption

- Intermolecular attractions in the smallest pores of the carbon particle result in adsorption forces that
  - Cause precipitation of adsorbates from solutions
  - Cause condensation of adsorbate gases

Molecules are then held in place on the interior surfaces of activated carbon

Picture courtesy of Calgon Carbon
5 grams of carbon has an adsorptive, internal surface area equivalent to the surface of a professional football field - including the end zones! (5348 m²)

Picture courtesy of Calgon Carbon
A moment on molecular structure

- Million-fold range in pore sizes in an AC granule
  - From visible cracks/crevices down to molecular scale pores (macro, meso, and micro pores)
  - Edges are 17 to 20-fold more active in binding.

- Only the smallest 5-fold range of pores adsorb
  - Some pores transport and some adsorb

Memory Device: Highways and parking lots

Picture courtesy of Calgon Carbon hand drawing by R. Franklin 1950-51.
Carbon Pores: The working edge

- **Transport pores** are greater than 5 molecular diameters to visible cracks and crevices. Transport pores are too large to adsorb and act simply as diffusion paths to transport the adsorbate to the adsorption sites.
  - Macropores (> 50 nm diameter)
  - Mesopores (2-50 nm diameter)

- **Adsorption pores** are the smallest pores within the particle, consisting of gaps between the graphite plates of about 1 to 5 molecular diameters in size. 40% of the carbon particle/granule volume
  - Micropores (< 2 nm diameter)

- **Three groups** according to the **pore size** in the **IUPAC** system (International Union of Pure and Applied Chemistry):
  Macro and mesopores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics while micropores are the pakinglots.
General, limited point about carbon types

Activated carbon

- **Granular**
  - Large internal surface area and small pores
  - 1. Total surface area 500 and 2000 m²/g
  - 2. Micropore surface area 175 to 650 m²/g
  - 3. Micropore volumes 0.15 to 0.70 cm³/g

- **Powered**
  - Small internal surface area and large pores

Iodine values from 450 to 1100 mg/g are typical and is used as a measure of micropores (0 to 20Å ≈ 2.0nm)
Mechanisms by which carbon assists in the remediation

- **Adsorption**
  - Carbon mechanism: generally
    - Reduction of contamination concentrations in aqueous and gaseous phase
      - Contact is required for adsorption

- **High pressure emplacement:**
  - Formation of pathways allowing “freed” contamination to move to the injectate (Murdoch & Slack, 2002; See also Murdoch & Chen, 1997).
  - Filling of existing pathways such as old infrastructure, plant root hollows, clay fractures, etc.
    - Assume areas of “local avoidance”, that is, you sometime miss some contamination (Murdoch, 1995).
Installation: Fracture Emplacement

- “Many in situ cleanup technologies require the use of amendments, such as chemical oxidants, reductants, or biologically stimulating agents and microbes. These amendments depend upon direct contact to treat or stabilize contaminants of concern. In soil with low effective porosity, the amendments will often follow subtle preferential pathways that avoid contact with much of the contaminant volume. Fracturing can establish a network of preferential pathways within the contaminated soils that allows treatment of areas that were not directly accessible before.”

- “Environmental fracturing technologies are techniques that enhance or create openings in bedrock or soil with low effective porosity, such as clay….”

- “Injection is usually done in more permeable soils or in rock formations where the decision is made that the existing fracture network is adequate for reaching remedial goals.” Injection is not fracture emplacement.

USEPA CLU-IN, https://clu-in.org/techfocus/default.focus/sec/Environmental_Fracturing/cat/Overview/ (Sep. 2015)
Installation considerations

- Gravity Feed: advection and dispersion

- Pressure Injection below fracture pressure: The amendment must be on a molecular scale smaller than soil pore throat size.

- Pressure Injection above fracture pressure makes new openings and follows regions of less resistance
A bit about fracture emplacement

- Emplacement every 5 to 7.5 ft (~10-25 cm (Christiansen, 2010))
- Ideal ratio is 3 ft horizontal for every 1 ft vertical
- Practical ratio is 1/1
- Pressures ≈100 to 400 psig
- Daylighting occurs
  - Degree is site specific
    - Could be 20% on sites with previous drilling and infrastructure paths
    - ≈ 3 to 5% daylight around the rod
  - Soil conditions

Top right picture: Murdoch & Slack, 2002.
Installation into the smear zone areas slightly above, within and below the water table.
Must identify the mass of contamination

- Site characterized sufficient to make a reasonable estimate of contamination mass.
- Reasonably certain you’ve located a significant % of the mass.
Site Characterization is Key
Installation of a treatment field

- 407 injection points
- 5ft centers (Tight Grid)
- 40,800 pounds carbon injectate
- 13 ft injection interval length (Typical interval for KY sites has been 9±4ft)
- Push about every 2 ft of vertical interval targeted
Clay’s Ferry Truck Stop
Shallow Rock Benzene Plume
Significant Benzene Plume
Informed selection of boreholes and pilot test

Total estimated areas of influence* of BOS 200 injections in May 2013 pilot study are shown here.

Bedrock injection locations included BR-3, BR-4, and BR-5.

Highlighted lines are surface geophysics transect lines (electrical resistivity) used to select bedrock borehole/injection locations.

*“Influence” includes water level changes in nearby wells and daylighting of BOS 200.
Estimated areas of injectate influence

**Total estimated areas of influence** of BOS 200 injections in April 2014 are shown here.

Bedrock injection locations included BR-2, BR-4, BR-6, BR-9, BR-10, and BR-11.

*“Influence” includes water level changes in nearby wells and daylighting of BOS 200.*
Post emplacement monitoring

Graph showing the benzene concentration over time from 2009 to 2015, with key points indicating September 2012 benzene concentration and post-pilot test injection concentration. The GW3 benzene SL is 0.31 mg/L.
The high efficiency of **activated carbon to quickly adsorb and sequester** PCBs from aquatic sediments has previously been demonstrated. Co-localizing PCB-degrading microbes onto the surfaces of activated carbon in the form of biofilms and utilizing it as a microbial inoculum delivery system provides a number of benefits.

- First, the **sequestering capacity of activated carbon further lowers aqueous concentration** of PCBs that have leached from sediment.
- Second, by providing a large population of PCB-degrading **microbes directly adjacent** to sequestered PCBs, the **degradation capacity and ability of the adherent microbial populations are augmented**. These close spatial relationships are required for microbes to utilize PCB as an electron acceptor and enable subsequent degradation.
- Third, since microbes are embedded within an **adherent biofilm**, they can be applied to aquatic environments and maintained in high numbers without being washed away in the fluvial system. The application of the enriched sludge biofilm system is an alternative approach, where the biofilm has already formed on the organic backbone of the sludge comparable to the activated carbon particles.

*Quote from Birthe Kjellerup, 2013*
Bacteria cells on the surface of activated carbon

Figure 10. The image shows DF1 biofilm formed on the surface of an activated carbon particle. The bacteria were labeled with the DNA specific stain SybrGreen that only targets DNA (i.e., bacterial cell material) and not the background such as activated carbon and/or media components. This method was not included in the original proposal, since it was developed in the meantime, but showed to be very valuable.
Indications of biological activity

1. Nitrates drop almost immediately

2. Sulfates drop over time (≈20% of wells may not drop)

3. Reduction potential is generally negative.

4. Dissolved oxygen generally decreases

Note: Reduction potential does not characterize the capacity to acquire electrons and be reduced. It is a measure of intensity.
Outcomes

To date fifty-seven (57) UST sites in Kentucky have utilized carbon injection. Of those remedial actions, twenty-nine (29) have received a No Further Action (NFA) from the Commonwealth. NFA has been requested on three (3) sites. Twenty sites are in monitoring associated with 2014-15 injections. The remaining five (5) sites fall into a number of categories. One (1) site was a pilot studies not intended to result in NFA. In addition, three (2) sites were insufficiently characterized and, therefore, carbon injection was premature. On one (1) site the contractor has not provided monitoring data. One site exceeds goal immediately adjacent to the UST pit. To date carbon injection has been successful on greater than 85% of all sites in Kentucky on which it has been employed as measured upon completion of the post injection monitoring period.
Costs

- The cost per site having received NFA has averaged $116,400.00 (± $31,970.00) with an average of 15,550 (±8,298) pounds of carbon installed. The cost per injection point is bimodal averaging $865.00 (±$1833.00). The average number of horizontal injection points per site is 441(±115) and the average number of vertical injection points is 5 (±2). The time to remedial goal achieved is typically 1 year. Late updated in Feb. 2015.

- Modeling of the cost data indicates that the number of injection points and the shots per point are largely controlling of overall remedy costs associate with carbon. Injectate cost is less significant.
  - Point: cheaper injectate will not be as important in controlling costs as will more efficient application techniques.
Companies whose reports contributed to this presentation.

Thanks to Lawrence C. Murdoch, Clemson University for a helpful discussion of injection.
Abstract 2/2015

• **Full Abstract:** Kentucky’s Experience with Carbon Injections for the Remediation of Petroleum Releases from Underground Storage Tanks

A clear understanding of the mechanisms by which carbon injectate acts to assist in the remediation of petroleum releases is indispensable for successful installation of this remedial measure. However, these mechanisms are often misunderstood. While the core mechanism is sorption of petroleum to the carbon, the approach to installation in various media alters the functionality and influences efficacy. Pre-treatment or follow-on treatments and/or co-injectates also influence results. In addition, a recent study shows bench test studies may not be helpful in understanding proper installation. As a proving ground for remedial technologies, Kentucky offers a broad array of geological settings, including unconsolidated materials ranging from interbedded clays to sands and complex bedrock environments from karst to fractured sandstones and shales. In these varied settings, carbon injectate has been successful in achieving remedial goals.

• To date thirty-four (39) UST sites in Kentucky have utilized carbon injection. Of those remedial actions, twenty-seven (27) have received a No Further Action (NFA) from the Commonwealth. The remaining seven (7) sites fall into a number of categories. Two (2) sites were pilot studies not intended to result in NFA. In addition, three (3) sites were insufficiently characterized and, therefore, carbon injection was premature. Thirteen (13) additional sites are scheduled for injection. To date carbon injection has been successful on greater than 80% of all sites in Kentucky on which it has been employed.

• The cost per site having received NFA has averaged $116,400.00 (± $31,970.00) with an average of 15,550 (±8,298) pounds of carbon installed. The cost per injection point is bimodal averaging $865.00 (±$1833.00). The average number of horizontal injection points per site is 441 (±115) and the average number of vertical injection points is 5 (±2). The time to remedial goal achieved is typically 1 year.
Expectations associated with microbial biodegradation

- AC provides a substrate for indigenous microbes or supplies
- A treatment field constitutes a new “ecosystem” additional “territory”
- New ecosystems like new gardens have to be nurtured (assertion)
- AC can function in-situ for decades