At a Glance

- An emerging remedial technology combining adsorption by activated carbon (AC) and degradation by reactive amendments.
- Several commercial products of various AC particle size and different amendments.
- Synergy between adsorption and degradation for treating chlorinated solvents and petroleum hydrocarbons.
- Applied to treat plumes but also residual source in low-permeability zones.
- Primarily uses direct push injection, including high-pressure in low-permeability zones for granular AC- and powdered AC-based products and low pressure for colloidal AC-based products in high-permeability zones. Injection well has also been used for delivering colloidal AC-based products.
- Requires adequate characterization (i.e., a high-resolution conceptual site model (CSM)) for effective remedial design.
- Adsorption to AC results in rapid concentration reduction in aqueous phase after injection.
- Rebound may occur due to greater contaminant influx than the rate of adsorption and degradation, poor site characterization, or lack of effective distribution.
- Performance assessment may be subject to bias if AC is present in monitoring wells. Other lines of evidence are important.
- Field evidence of degradation is limited but promising. However, persistence and contribution of degradation need further validation.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Office of Superfund Remediation and Technology Innovation, concerns an emerging remedial technology that applies a combination of activated carbon (AC) and chemical and/or biological amendments for in situ remediation of soil and groundwater contaminated by organic contaminants, primarily petroleum hydrocarbons and chlorinated solvents. The technology typically is designed to carry out two contaminant removal processes: adsorption by AC and destruction by chemical and/or biological amendments.

With the development of several commercially available AC-based products, this remedial technology has been applied with increasing frequency at contaminated sites across the country, including numerous leaking underground storage tank (LUST) and dry cleaner sites (Simon 2015). It also has been recently applied at several Superfund sites, and federal facility sites that are not on the National Priorities List.

This fact sheet provides information to practitioners and regulators for a better understanding of the science and current practice of AC-based remedial technologies for in situ applications. The uncertainties associated with the applications and performance of the technology also are discussed.

What is AC-based technology?

- AC-based technology applies a composite or mixture of AC and chemical and/or biological amendments that commonly are used in a range of in situ treatment technologies.
- Presently, five commercial AC-based products have been applied for in situ subsurface remediation in the U.S.: BOS-100® & 200® (RPI), COGAC® (Remington Technologies), and PlumeStop® (Regenesis) are the four most commonly used commercial products. CAT-100® from RPI is the most recent product, developed based on BOS-100®. One research group in Germany also developed a product called Carbo-Iron®. Detailed properties and compositions of these products are shown in Exhibit 1.
- The AC components of these products typically are acquired from specialized AC manufacturers. These types of AC have desired adsorption properties for chlorinated solvents and petroleum hydrocarbons. Different products also have different AC particle sizes, which determine the suitable injection approach and the applicable range of geological settings.
How are contaminants treated by AC-based technology?

- AC-based technology involves two contaminant removal processes: adsorption and degradation. AC is responsible for adsorption and reactive amendments are responsible for degradation.
- AC is composed of randomly oriented graphite stacks. The random orientation results in a highly porous matrix having a wide range of pore sizes. Adsorption of typical groundwater organic contaminants (e.g., benzene, trichloroethylene) primarily occurs in micropores (<2 nm in diameter). Large pores, mesopores and macropores, mainly serve as transport conduits for contaminants to reach adsorption sites via intraparticle diffusion (Bansal and Goyal 2005).
- Under typical subsurface temperatures, physical adsorption is the dominant adsorption mechanism, which is a reversible process governed by the van Der Waals force (Karanfil and Kilduff 1999). Contaminant desorption can occur when equilibrium conditions (e.g., pH, plume composition) change, but AC applications in sediment remediation showed that the desorption rate from AC is much slower than that from indigenous sediment materials (Sun and Ghosh 2008).
- Chemical or biological amendments determine the contaminant groups treated and degradation pathways supported. BOS-100® treats chlorinated solvents via zero-valent iron (ZVI)-mediated abiotic dechlorination; BOS-200® treats petroleum hydrocarbons by bioaugmentation. COGAC® treats either group by chemical oxidation and likely subsequent biostimulation; and PlumeStop® treats either group by biostimulation or bioaugmentation depending on the specific amendments applied (Exhibit 1).
- Solid amendments (e.g., ZVI) or bacteria often have much larger size than micropores, the major adsorption sites of AC (Exhibit 2). Therefore, sorbed contaminants must be desorbed and diffuse out of micropores to be degraded. This process is driven by the concentration gradient between sorption sites and bulk liquid phase (Spetel Jr et al. 1989; Tseng et al. 2011).
- Contaminant removal is controlled by the dynamic equilibrium between contaminant influx, adsorption and degradation. This has been suggested to occur in biological activated carbon reactors for wastewater treatment, where the relative contribution of adsorption and biodegradation to contaminant removal varies at different operational stages (Voice et al. 1992; Zhao et al. 1999). Contaminants stay within the treatment zone when combined rates of adsorption and degradation exceed the incoming mass flux.

### Exhibit 1: Properties of six AC-based products that have been used for in situ applications

<table>
<thead>
<tr>
<th>Product</th>
<th>Property</th>
<th>Target Contaminant</th>
<th>Degradation Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOS-100®</td>
<td>Granular AC (GAC) impregnated by ZVI</td>
<td>Chlorinated solvents</td>
<td>Abiotic reductive dechlorination</td>
</tr>
<tr>
<td>BOS-200®</td>
<td>Powder AC (PAC) mixed with nutrients, electron acceptors, and facultative bacteria mix</td>
<td>Petroleum Hydrocarbons</td>
<td>Aerobic and anaerobic bioaugmentation</td>
</tr>
<tr>
<td>CAT-100®</td>
<td>BOS-100® and reductive dechlorination bacterial strains</td>
<td>Chlorinated solvents</td>
<td>Abiotic and biotic reductive dechlorination</td>
</tr>
<tr>
<td>COGAC®</td>
<td>GAC or PAC mixed with calcium peroxide, and sodium persulfate</td>
<td>Chlorinated solvents or petroleum hydrocarbons</td>
<td>Chemical oxidation, aerobic and anaerobic biostimulation</td>
</tr>
<tr>
<td>PlumeStop®</td>
<td>Colloidal AC suspension with an organic stabilizer, co-applied with hydrogen or oxygen release compounds, and/or corresponding bacterial strains</td>
<td>Chlorinated solvents or petroleum hydrocarbons</td>
<td>Enhanced biotic reductive dechlorination for chlorinated solvents and aerobic biodegradation for petroleum hydrocarbons</td>
</tr>
<tr>
<td>Carbo-Iron®</td>
<td>Colloidal AC impregnated with ZVI</td>
<td>Chlorinated solvents</td>
<td>Abiotic reductive dechlorination</td>
</tr>
</tbody>
</table>
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Exhibit 2. (Left) Conceptual structure and (Right) transmission electron micrograph (TEM) of Carbo-Iron® (Adopted from Mackenzie et al. 2016)

What are the potential benefits of using AC-based remedial technology?

- Adsorption can significantly retard contaminant migration and decrease dissolved phase concentrations. Retaining contaminants in the AC matrix allows longer residence time for contaminants to be degraded by reactive amendments. The coupling of adsorption and degradation reduces the potential for contaminant rebound that frequently is encountered with conventional treatment technologies (e.g., pump and treat (P&T) or in situ chemical oxidation (ISCO)).

- AC impregnated with nano zerovalent iron (nZVI) is shown to have more persistent reactivity than suspended nZVI particles (Choi et al. 2009). It was suggested that AC may protect nZVI from undesired side reactions with dissolved oxygen and water, which often outcompete contaminant degradation for nZVI because of their greater abundance.

- Adsorption may enrich chemicals (including both contaminants and nutrients) over time to facilitate formation of active biofilm and biodegradation (Voice et al. 1992). The combined effects may significantly reduce the time frame to reach remedial objectives.

- For high concentration of chlorinated VOCs, adsorption onto AC decreases the initial high aqueous contaminant concentration that inhibits biological dechlorination and shortens the lag phase for biodegradation (Aktas et al. 2012).

How is AC-based remedial technology implemented in field?

- Grid injection that targets a well-defined contaminated area commonly is used if the footprint of treatment areas is relatively small, such as some LUST sites or localized hotspots.

- For plume, barrier applications commonly are used. AC-based amendments typically are emplaced in transects to form a series of permeable reactive zones that are perpendicular to the direction of plumes. An external water supply typically is needed to mix and dilute amendments in these barrier wall configurations.

- High-pressure injection (typically 300 to 1000 psi), (i.e., hydraulic fracturing), is used for emplacing Granular AC (GAC)- or Powder AC (PAC)-based amendments due to the need to open up the formation for emplacement of the large particles. As fracturing is more effective in low-permeability formations, GAC or PAC-based amendments typically are injected in tight formations, such as clays and silts (Winner and Fox 2016).

- Less frequently, soil mixing or trenching has also been used for emplacement of GAC or PAC-based amendments provided suitable hydrogeological conditions. For example, BOS-100, a GAC-based product, was emplaced by deep soil mixing in a sandy aquifer during a pilot test at the Vandenberg Air Force Base, after high-pressure injection showed poor amendment distribution (ITRC 2011).

- Colloidal AC-based amendments are emplaced by low-pressure injection (e.g., 30–50 psi) using direct push or permanent injection wells without creating artificial fractures. As a result, the amendment primarily is applied to more permeable formations such as sands and gravels. However, even a low-permeability aquifer may contain permeable (flux) zones that permit application of colloidal AC-based amendment.
How is AC-based amendment distributed in the subsurface?

- For GAC- and PAC-based amendments, high-pressure injection typically produces thin seams or lenses of AC in seemingly random directions. In tight geologies, fractures typically have higher permeability than surrounding formations. This difference may allow contaminant desorption and diffusion from the low-permeability formations into the fractures. The conceptual model is shown on the left in Exhibit 3. Tight injection spacing in both horizontal and vertical directions is recommended to obtain sufficient coverage as it is difficult to control the formation and growth of fractures (Murdoch, 1995). Some recent improvements have been made to better control the direction and development of fractures (i.e., direct push jet injection), but these approaches have not been applied to injecting AC-based amendments.

- For colloidal AC, the particles infiltrate into the permeable zone or formation upon low-pressure injection and eventually deposit onto the surface of soil grains due to surface-surface interactions. The presence of an organic polymer improves the colloidal stability and transport in the subsurface. Therefore, the distribution of amendments in flux zones is expected to be more uniform than induced fracturing of AC-based amendments of larger particle size (Exhibit 3, on right).

![Exhibit 3. Different conceptual distribution patterns between GAC- or PAC-based amendment (left) and colloidal AC-based amendment (right). Dark regions represent the forms of amendment distribution and arrows represent the directions of contaminant flux entering the AC zone. (Adapted from Fan et al. 2017).](image)

What are the key factors to consider during remedial design?

- Design of AC-based remedies primarily focuses on defining optimal injection locations and loadings, which are affected by the treatment approach and objective (e.g., area treatment to reduce mass flux or barrier application to intercept plume). The key to effective remedial design of AC-based technology (or any in situ remedial technology), is to conduct adequate site characterization to create a sufficiently detailed CSM.

- Subsurface geology and contaminant mass distribution are the two major aspects to characterize during remedial design investigation (Winner and Fox 2016). Subsurface hydrogeology can be characterized by grain size distribution analysis, clear water injection, or hydraulic profiling (Birnstingl et al. 2014). Contaminant distribution can be qualitatively determined by various in situ rapid screening tools, such as the membrane interface probe (MIP) (Winner and Fox 2016; EPA 2016); laser induced fluorescence (LIF) technique for non-aqueous phase liquid (NAPL); or a photo ionization detector (PID) for soil screening on-site. Selected samples can be subject to more rigorous laboratory analysis if needed.

- For GAC- and PAC-based amendments, it is important to profile the vertical distribution of contaminant mass as it determines the vertical injection interval and injection loading at each interval, especially when the remedy is designed to treat a residual source area with heterogeneous lithology. At a former manufacturing site in Denver, the initial injection of BOS-100® near the source area did not achieve performance objectives. Further high-resolution site characterization...
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revealed highly heterogeneous contaminant distribution in the vertical direction. Subsequent injection loading and approach were adjusted to the contaminant distribution pattern, which significantly improved the remedy performance (Noland et al. 2012; Harp 2014).

- For colloidal AC-based amendments, it is important to locate the high-permeability zones and estimate the mass flux across those zones to determine where to apply the amendments, and how much is needed.
- Contaminants associated with soil (e.g., sorbed) and residual NAPL phase represent the majority of the contaminant mass stored in low-permeability zones, and can serve as a long-term source for groundwater contamination. The calculation of contaminant loading needs to consider the rates of back diffusion of source material or the total mass of contamination.
- Laboratory-measured adsorption capacity often serves as a benchmark value to calculate amendment loading. However, the actual adsorption capacity varies with contaminant concentration and can be further complicated by competitive adsorption and potential growth of biofilm.
- Vendors often are willing to actively participate in the remedial investigation and design phases to ensure successful implementation and desired performance of their products. Spreadsheets are available from the vendors to calculate the loading rates of amendments based on estimated contaminant mass (or mass flux), adsorption capacity, remedial objectives, and the designed lifetime of the remedy. However, the calculation is largely empirical due to various uncertainties caused by subsurface heterogeneity. Based on discussion with the vendors, a safety factor of 5 to 20 is recommended for estimating amendment loading.

How does the AC-based remedial technology perform in the field?

- The four commercial AC-based products combined have accumulated more than 1500 applications in North America and Europe as of 2015 (Simon 2015). To date, this technology has been used or selected at four NPL sites and one RCRA corrective action site.
- Field data generally show rapid decrease of aqueous contaminant concentration after emplacement of the amendments when initial contaminant concentration is high. The decrease is more gradual when initial contaminant concentration is low (e.g., <100 ppb). Temporary rebound shortly after injection is common, and may occur when equilibrium is reestablished after enhanced contaminant desorption from aquifer solids, or when plume is temporarily displaced by injection of amendments in large volumes.
- Regenesis evaluated the performance of PlumeStop® applied at 24 sites between 2014 and 2016 by pooling contaminant concentrations from 34 monitoring wells (Davis 2016). Regenesis found more than 65% of wells achieved >95% reduction within 1–3 months after injection. The initial rapid response is most likely due to rapid adsorption process.
- Rebound of contamination has been observed at some sites that applied AC-based amendments. The same study by Regenesis (Davis 2016) found that 15% of the wells examined showed some rebound over an average of 6-month time frame but the rebound is generally <10% of pre-treatment concentrations. Early applications of PAC-based products at LUST sites in Colorado also identified frequent rebound (Fox 2015). Possible reasons cited for rebound include underestimation of contaminant mass due to poor site characterization (Fox 2015); insufficient amendment distribution due to large injection spacing or poor implementation (Fox 2015); or contaminant mass influx exceeding the combination of adsorption and degradation (Mackenzie et al. 2016).
- AC frequently is observed in monitoring wells post injection. Given amendment distribution is likely not uniform, especially when high-pressure injection is used, caution needs to be taken when using impacted monitoring wells for performance evaluation. Concentrations measured in those wells may not accurately represent the aquifer concentrations. In addition, impacted wells also typically should not be used for attainment monitoring because post remediation conditions may not be reached (EPA 2013; EPA 2014)1. Other lines of evidence are recommended for confirming the treatment performance achieved in the treatment zone.
- Several measures have been taken to improve confidence in performance assessment using monitoring wells. Examples include preventing or

1 "The attainment monitoring phase typically occurs after EPA makes a determination that the remediation monitoring phase is complete. When the attainment phase begins, data typically are collected to evaluate if the well has reached post remediation conditions (i.e., steady state conditions) where remediation activities, if employed, are no longer influencing the groundwater in the well." (EPA 2013)
minimizing well impact using geochemical parameters as early indicators for breakthrough of AC; installing new wells near the existing impacted wells to demonstrate that either amendment distribution is not localized or AC-free wells exhibit similar treatment effects as AC-impacted wells; and monitoring downgradient wells adjacent to the treatment zone to observe for decreasing contaminant trend (Winner and Fox, 2016). Removing AC from impacted wells prior to sampling could be another solution. It has been shown to be moderately successful for colloidal AC but not work for AC with large particle sizes, according to vendors and practitioners.

What is the evidence for degradation?

- Degradation is generally an indispensable component of contaminant removal processes by AC-based amendments. Without degradation, AC-based remedial technology may serve only to stabilize the contaminants, and contaminants may break through once adsorption capacity is exhausted or when desorption occurs. Throughout the development of the technology, the uncertainty regarding the importance and persistence of degradation has been a major hurdle for wide acceptance of the technology.

- Bench-scale tests have demonstrated the effectiveness of degradation processes involved in AC-based remedial products (Birnstingl et al. 2014). However, controlled laboratory results may not guarantee field effectiveness, especially for biodegradation that is more variable because of field heterogeneities.

- It is difficult to confirm contaminant degradation in the field. Both adsorption and degradation can result in decreasing contaminant concentrations without the appearance of daughter products, which may also be adsorbed by AC. Use of contaminant data from monitoring wells does not distinguish contaminant removal by adsorption from that by degradation.

- To date, field evidence of degradation has been limited and largely qualitative. For petroleum hydrocarbons, depletion of nitrate or sulfate, and production of volatile fatty acids, have been suggested as evidence of biodegradation.

- For chlorinated solvents, production of chloride has been used to indicate dechlorination, but this line of evidence only applies when background chloride concentration is low or contaminant concentration is very high (i.e., near the source area). In one pilot test of Carbo-Iron, significant elevation of ethene and ethane was used as evidence for abiotic reductive dechlorination (Mackenzie et al. 2016).

- More recently, environmental molecular diagnostic (EMD) tools have shown promise for assessing biodegradation of petroleum hydrocarbons and chlorinated solvents (ITRC 2013). The following recent data was provided to EPA by three vendors of AC-based products to demonstrate degradation:

  - At one chlorinated solvent site where PlumeStop® was injected with a hydrogen release compound (HRC®) and Dehalococcoides cultures, the combination significantly increased the abundance of degraders and functional genes in the aqueous phase after injection. The high abundance was sustained for over 500 days, even though the dissolved tetrachloroethene (PCE) remained below the detection limit. This pattern suggests that enhanced concentrations of microbial indicators resulted from enhanced microbial activity in the up-gradient AC barrier.

  - At one petroleum site where COGAC® was injected, groundwater samples were collected one year after injection. In these samples, the abundance of six anaerobic BTEX (benzene, toluene, ethylbenzene and xylenes) and PAH (polycyclic aromatic hydrocarbon) degraders was found to be 2 to 4 orders of magnitude higher in samples collected from wells within the injection influence zone than in samples collected from a well outside the injection influence zone.

  - At one petroleum site where BOS-200® was injected to form a permeable reactive zone, compound specific isotope analysis (CSIA) was conducted on samples collected from wells up- and downgradient of the PRB two years after injection. Compared to the upgradient well, the downgradient wells consistently show small but evident enrichment of C13 for several BTEX compounds, indicating occurrence of biodegradation of these compounds.

- Applications of AC in other contaminant removal processes such as wastewater and sediment treatment have suggested that AC enhances biodegradation by promoting the formation of biofilms, which can be attributed to increasing nutrient retention, enhanced resistance to environmental shocks, and increased microbial diversity (Simpson 2008; Kjellerup et al. 2014).
What is the long-term effectiveness of AC-based remedial technology?

- The longevity of AC-based remedial technology is of particular interest because the long-term effectiveness to counter slow and persistent contaminant flux (from diffusion, desorption, and dissolution) is one of the major benefits claimed for this technology.
- Currently, there is lack of sufficient monitoring data to assess the long-term performance due to either recent implementation or the lack of long-term monitoring requirements at many small sites. Thus, the long-term effectiveness of this technology remains to be further evaluated when data become available.
- The relative contribution of contaminant adsorption versus degradation is a critical parameter for evaluating the long-term performance. As contaminant can eventually break through when adsorption capacity becomes exhausted, degradation is the main driver in maintaining the long-term effectiveness of the technology. This aspect remains to be further investigated.
- Competitive adsorption may affect long-term effectiveness. Competitive adsorption refers to a process where strongly sorbed compounds may displace weakly sorbed compounds, resulting in release of the latter. Competitive adsorption should be evaluated for treating comingled plumes or plumes where degradation intermediates are expected to form if degradation stalls or does not proceed to completion. For example, sorbed benzene may be displaced by xylene in a BTEX plume. For a chlorinated solvent plume, daughter products such as cis-dichloroethene (DCE) or vinyl chloride may be displaced by PCE or trichloroethene (TCE). This potential desorption behavior again highlights the importance of supporting degradation activity and including (bio)degradation assessment in a long-term monitoring plan.

Where and when should AC-based remedial technology be considered?

- AC-based remedial technology provides an effective approach to address persistent plumes emanating from low-permeability sources, desorption, or dissolution of residual NAPL phase. AC-based remedial technology could be considered when other remedial options at a site have demonstrated limited effectiveness. For example, applications of AC-based remediation at LUST sites in Colorado and Kentucky (primarily PAC-based amendments) mainly occurred at sites dominated by low-permeability formations, including fractured bedrock, where soil vapor extraction or bioremediation was not successful (Winner and Fox 2016).
- AC-based remedial technology can serve as a cost-saving alternative to active P&T to prevent plume migration. It may also complement an existing P&T system to contain a plume by reducing the rate or area for pumping. Several recent Superfund AC applications used AC only without adding reactive amendments for treating low-concentration chlorinated solvent plumes. The approach was selected to avoid potential generation of poorly sorbed daughter products or avoid secondary groundwater quality issues resulted from changes in subsurface redox conditions due to application of reactive amendments. At one site, the effectiveness of the adsorption mechanism alone is proposed to last sufficiently long to allow time for source treatment. However, long-term monitoring data are required to confirm long-term performance.
- While emplacement of AC-based amendments typically is not considered as a source treatment technology due to concerns of exhausting the adsorption capacity quickly, emplacements of AC in sources or around source areas as a barrier have been applied in the field. The goal is to significantly reduce contaminant mass flux out of the sources to reduce downgradient impacts. The technology can be coupled with source zone treatment technologies, such as in situ thermal treatment, or with excavation when not all contaminated material can be removed.
- In scenarios where fast groundwater flow velocity might limit the effectiveness of soluble amendments due to dilution, colloidal AC-based amendments may be considered since they more rapidly adsorb to aquifer materials and are more likely to remain in the target treatment area.

Where can I find more information?

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- Harp, T. 2014. Obtaining high-resolution data to demonstrate BOS 100 performance in a large TCE plume with extensive DNAPL present. The Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California.


- Noland, S., R. Boyle, and T. Harp. 2012. Innovative injection technique to treat DNAPL in granular and fine-grained matrices. The Eighth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California.


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