

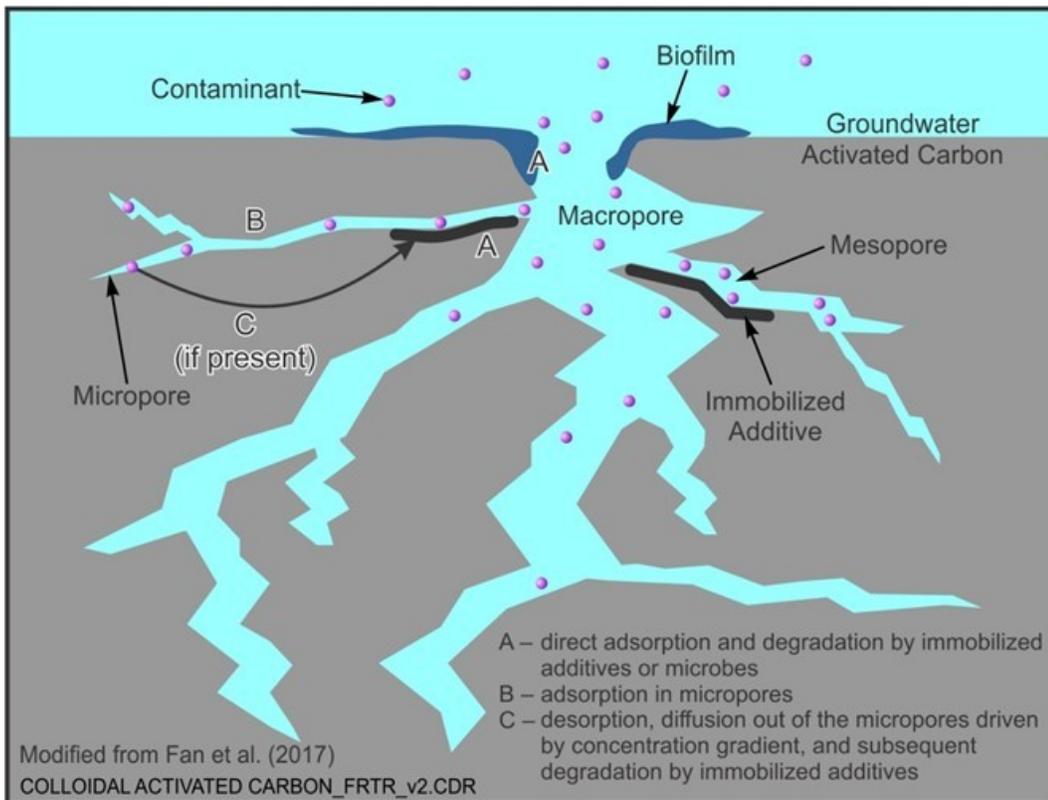
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# In Situ Activated Carbon

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## Schematic



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## In Situ Activated Carbon

# Introduction

Activated carbon (AC) consists of various forms of small-sized carbon particles in aqueous suspension, which can flow into aquifer flux zones. After delivery to the subsurface, AC particles attach strongly to the aquifer matrix, where they can act as passive adsorbents for chemicals of concern (COCs). Due to the small size of the particles, the kinetics of adsorption onto AC are much faster than can be achieved with granular activated carbon (GAC) for above-ground treatment applications, resulting in higher removal efficiencies. The primary function of AC is to adsorb and immobilize COCs to prevent further horizontal and vertical migration in groundwater within the treatment area, thereby mitigating long-term mass flux to downgradient receptors or facilitating natural attenuation within the distal portions of the plume. By flowing AC into the flux zones of an aquifer, COC mass flux due to groundwater advection moving through the treatment area, as well as longer-term COC matrix diffusion mass flux from lower permeability soil units, is adsorbed onto the AC surface and removed from the dissolved phase. AC also has been combined with other amendments such as zero valent iron, calcium peroxide, nutrients, and bacteria strains to facilitate secondary reactions to eliminate COCs.

# Other Technology Names

Activated Carbon-Based Technology for In Situ Remediation  
In Situ Remediation by Activated Carbon-Based Amendments  
Carbon-Based Injectate

## Description

AC amendments consist of various proprietary formulations that are manufactured and patented by several vendors. Each AC amendment mixture contains a specific form and particle size of carbon and may also incorporate biological or chemical amendments capable of degrading target COCs. Amendments typically used for in situ treatment (e.g., biodegradation, oxidation/reduction) also can be introduced separately following the initial delivery of the AC.

AC amendments typically are used to mitigate COC mass flux and plume expansion, especially targeting more transmissive groundwater units where plume migration is a concern. Potential applications include treatment of source areas and/or downgradient portions of the plume, as well as to provide a [permeable reactive barrier](#) to prevent COC migration to protect sensitive receptors and to mitigate further plume expansion.

In situ treatment using AC amendments typically involves a two-step process - adsorption and subsequent degradation. Adsorption by the AC is designed to provide rapid initial removal of COCs from the aqueous phase. Degradation of the COCs can be implemented by the delivery of typical in situ biological or chemical treatment amendments, which are either directly incorporated into the AC amendment mixture or delivered separately in a treatment train approach. Applying these additional treatment amendments may serve to regenerate the AC surface area and create a dynamic equilibrium between contaminant influx, adsorption, and degradation to allow for continued adsorption of COC mass flux in groundwater. AC has the potential to improve the effectiveness of in situ treatment technologies involving direct amendment delivery to the subsurface. For example, AC provides a substrate and surface area for microbial growth and contact with the COCs to facilitate biodegradation (similar to GAC and powdered activated carbon applications for various wastewater biological treatment technologies).

Adsorption onto the surface of the AC is attributed to its highly porous internal structure. The pores inside the AC can be divided into macropore (>50

nanometer or nm), mesopore (between 2 and 50 nm) and micropore (<2 nm). The micropores serve as adsorption sites for COCs such as trichloroethylene (TCE) and benzene due to their similar dimensions (Fan et al., 2017). Physical adsorption is the dominant mechanism under typical subsurface conditions. It is a reversible process governed by weak Van der Waal forces and adsorption and desorption are always in dynamic equilibrium. However, chemisorption, which results from a chemical reaction between the compounds and the surface of the adsorbate, also may occur and can form a much stronger bond between the COCs and the AC. The properties of the AC, such as its microporosity and surface acidity, determine the saturation adsorption capacity for a specific COC. The intrinsic properties of AC amendments may differ due to different AC sources. Additionally, adsorption capacities may differ due to various site-specific environmental factors and processes that can change the physiochemical properties of the AC after emplacement.

The degradation processes involved with reactive AC amendments are the same processes that are utilized by other technologies including [chemical reduction](#), [chemical oxidation](#), and [reductive dechlorination](#). Manufacturer's proprietary and often patented formulations include the addition of electron acceptors/donors, microorganisms, oxidants, or reductants to the AC to target a specific degradation pathway. Theoretically, COCs are immobilized inside the pores within the AC, where they can then contact the reactive material and be degraded.

AC amendments are emplaced using methods that are commonly used to emplace other types of amendments. Direct push injection is a commonly used delivery method, but vertical wells also can be used. AC may be delivered in situ using a grid pattern in source zones to immobilize COCs, or it may be injected in a transect pattern perpendicular to the width of a plume as a migration control barrier to mitigate contaminant flux from groundwater advection. The adsorption capacity longevity of the AC typically is longer than for other types of treatment amendments, but will be dependent upon rates of COC mass flux, presence of co-contaminants, and groundwater geochemistry.

Monitoring should be performed during (process monitoring) and after (performance monitoring) application of the AC amendment mixture. Oftentimes, a baseline set of data is collected prior to introducing the AC amendment mixture, to which post-application performance monitoring data may be compared. Process monitoring performed during application may consist of on-site field measurements and visual observations. Groundwater levels may be measured to provide an indication of distribution of amendments and potential for surfacing to occur during application. Changes in

groundwater quality parameters including oxidation reduction potential (ORP), pH, and conductivity can provide additional information regarding amendment distribution and visual observations also may be measured to evaluate the presence of AC.

Performance monitoring is conducted to evaluate the long-term effectiveness of the remedy, identify the need for additional application of amendments, assess progress toward achieving remedial goals and remedial action objectives, and determine if rebound is occurring. Performance monitoring should be conducted in monitoring wells and not in injection wells since data from injection wells may be biased due to the introduction of high concentrations of amendments. In general, it should consist of measuring concentrations of COCs along with groundwater quality parameters and water levels. Soil sampling also can be performed to evaluate long-term distribution and persistence of amendments.

## Development Status and Availability

The following checklist provides a summary of the development and implementation status of colloidal AC technology:

- At the laboratory/bench scale and shows promise
- In pilot studies
- At full scale
- To remediate an entire site (source and plume)
- To remediate a source only
- As part of a technology train
- As the final remedy at multiple sites
- To successfully attain cleanup goals in multiple sites

AC amendments are available through the following vendors:

- Commercially available nationwide
- Commercially available through limited vendors because of licensing or specialized equipment
- Research organizations and academia

# Applicability

**Contaminant Class Applicability Rating for In Situ Activated Carbon**

(Rating codes: ● Demonstrated Effectiveness, ◐ Limited Effectiveness, ○ No Demonstrated Effectiveness,  
 ♦ Level of Effectiveness dependent upon specific contaminant and its application/design, I/D Insufficient Data)

Nonhalogenated VOC	Halogenated VOC	Nonhalogenated SVOC	Halogenated SVOC	Fuels	Inorganics	Radionuclides	Munitions	Emerging Contaminants
●	●	I/D	I/D	●	I/D	I/D	I/D	♦

With proper placement and appropriate sizing, AC technology has been demonstrated to be effective in addressing a range of dissolved-phase COCs in groundwater and possibly treat source areas containing residual non-aqueous phase liquid (NAPL). However, these AC amendments may not be as effective in source areas containing a large volume of NAPL due to the mass of amendments that would be required to degrade the adsorbed COCs and adequately regenerate the long-term adsorption capacity, which could be cost prohibitive and potentially result in adverse impacts to the aquifer (e.g., reduced hydraulic conductivity). The same treatment limitations that apply to the various in situ amendment injection technologies would also apply to the ability to adequately degrade the adsorbed COCs and regenerate the AC adsorption capacity.

AC amendments have been shown to be effective at adsorbing and immobilizing non-halogenated and halogenated volatile organic compounds (VOCs) from groundwater. They have also effectively removed petroleum-related semivolatiles organic compounds (SVOCs) such as naphthalene and are being field tested to treat per- and polyfluoroalkyl substances (PFAS). At least one application to date has successfully demonstrated that PFAS compounds can be treated using in situ AC (McGreggor, 2018) and other applications and demonstrations are ongoing.

With proper placement, appropriate sizing, and appropriate site conditions, AC amendments can be applied to contain COC migration in groundwater within the source area and downgradient portions of the plume. Because of the longevity of AC amendment mixtures (i.e., not physically depleted like other treatment amendments), these amendments can provide an effective method of immobilizing continuing rebound that could occur due to COC back diffusion from lower permeability soil units over prolonged periods of time at a very slow rate. When combined with appropriate treatment amendments, COC degradation also can be achieved. Application can be particularly effective if the treatment areas are relatively small, such as in a localized source area or to protect a specific downgradient receptor; whereas [permeable reactive barrier](#) (PRB) or [groundwater pump and treat](#) or recirculation approaches may provide more cost-effective methods of migration control for larger plume dimensions. The specific configuration used should be based on additional factors including remedial action objectives, site lithology, subsurface infrastructure, and treatment depth.

## Cost

Cost drivers for in situ AC technology include the type and quantity of amendments required, and the injection or emplacement methods needed. As with all in situ technologies, application costs vary according to site conditions and contaminants. Major cost drivers include:

### Upfront Costs

- Detailed characterization supporting development of a high-resolution CSM at the scale of injection or emplacement, and throughout the design treatment zone is crucial for effective treatment in low permeability and highly heterogeneous sites.
- The nature and amount of residual COC mass, which influences the type and amount of both the AC amendment mixture and any complementary treatment

amendments required.

- Treatment objective, which can include residual source remediation and/or plume control.
- Size and depth of treatment area also impact the amount of both the AC amendment mixture and any complementary treatment amendments required, as well as the number and depth of treatment and monitoring points.
- Aquifer type and permeability, which can affect the delivery or emplacement method.
- Bench-scale treatability studies or small-scale field treatability testing is often needed prior to site-scale application.

### **Operation and Maintenance Costs**

- Longevity of amendments. AC may become saturated, requiring regeneration by additional amendment injections or the delivery of additional AC amendment mixture. Depending on the amount of residual COC mass and rate of long-term matrix diffusion rebound, reactive additives,
- Monitoring requirements. The number of locations and frequency of monitoring impact the cost. Results of the monitoring may identify the need for additional application of amendments.
- Performance criteria. Performance criteria can impact the frequency that the treatment zone must be replenished with additional amendments to ensure maintaining the required concentration reduction over the long term.

The list above highlights those cost dependencies specific to AC amendments and does not consider the dependencies that are general to most in situ remediation technologies. Click [here](#) for a general discussion on costing which includes definitions and repetitive costs for remediation technologies. A project-specific cost estimate can be obtained using an integrated cost-estimating application such as RACER® or consulting with a subject matter expert.

## **Duration**

Remediation using AC amendments is a long-term technology requiring several years to implement. Although an immediate reduction of COCs in groundwater is usually realized within days due to rapid adsorption of dissolved-phase COCs within the treatment area, a much longer time is required to degrade the adsorbed COCs. The potential longevity of the AC amendments in the aquifer is advantageous to counter slow and persistent COC rebound from lower

permeability soil units (from diffusion, desorption, and dissolution), and is one of the major benefits of this technology (EPA, 2018).

A factor that may affect the long-term effectiveness of the technology is competitive adsorption. It occurs when the strongly adsorbed compounds displace weakly adsorbed compounds as the AC adsorption capacity is used up, resulting in release of the latter. For example, adsorbed benzene may be displaced by xylene in a petroleum hydrocarbon plume, and cis-dichloroethene or vinyl chloride may be displaced by TCE in a chlorinated solvent plume. Performance assessment data should be collected and evaluated to determine such long-term effects.

Application of AC amendment mixtures and complementary treatment amendments have achieved concentrations of COCs much lower than baseline values one or more years after treatment was performed. Although this technology shows promise to effectively treat a variety of COCs, there is a lack of monitoring data to assess long-term performance due to either recent implementation or lack of long-term performance monitoring data at many sites. Some reported cases have identified later rebound of COC groundwater concentrations above regulatory levels after sites have been closed. Thus, the long-term effectiveness and other potential impacts from any continuing matrix diffusion mass flux or desorption of COCs from the AC need to be evaluated as data become available and additional research is performed.

## Implementability Considerations

The following are key considerations associated with implementing the AC technology:

- Since the use of AC amendments provides the most benefits when used to quickly mitigate COC migration and continued source area mass flux to groundwater, especially if sensitive receptors may be threatened, applications typically target moderate to higher permeability lithology. Since COC migration within less permeable and heterogeneous lithology is relatively slow, the potential benefits of using AC amendments versus direct amendment injections or other source area treatment technologies may not offset a potentially higher incremental cost. Because of the limited distribution capabilities for AC amendments, a cost/benefit comparison of AC amendment applications versus other potential source treatment or COC migration control technologies should be performed.

- Empirical data for application of AC amendments, especially for sustained treatment of cVOCs, currently are limited; hence, there is a need for high-quality, field-scale demonstration and validation projects in a variety of hydrogeological regimes.
- It can be challenging to achieve adequate distribution of AC amendments and complementary treatment amendments in heterogeneous, low permeability, and fractured bedrock aquifers. The CSM should be well defined. The horizontal and vertical distribution of COCs and locations of high and low permeability zones must be known to properly estimate the total immobilized residual COC mass within the treatment zone pore structure and to select the appropriate interval(s) to apply the amendment.
- Low pressure injection often is effective in moderate to high permeability soils; however, greater pressures may be needed to distribute the AC amendments and any complementary treatment amendments into lower permeability formations. Controlled hydraulic or pneumatic fracturing may be necessary to distribute amendments in lower permeability soils or bedrock. As with all in situ technologies that rely on the application of amendments, the ability to adequately distribute sufficient amendment volume to degrade the total COC residual mass and achieve necessary subsurface redox conditions for complete degradation can be difficult to predict and generally is not homogeneous. Some AC amendments rely on the use of higher injection pressures for distribution, which can cause uncontrolled fracturing within the subsurface.
- Alternative technologies should be considered in source areas when a large volume of NAPL is present, because the NAPL mass will quickly overwhelm the adsorption capacity of the AC and treatment capacity of any complementary amendments.
- In the event that the added treatment amendments become depleted and degradation of the adsorbed COC mass no longer occurs to allow for regeneration of the AC adsorption capacity, continued mass flux loading from groundwater flow can eventually lead to breakthrough and desorption of COCs, resulting in the rebound of COC concentrations in groundwater and possible downgradient migration. Consequently, complementary treatment amendment injections must continue until such time that there is a level of confidence that any continued long-term COC groundwater mass flux (including from matrix diffusion) will not result in saturation of the AC adsorption capacity and resulting breakthrough.
- The use of AC amendments could have the added benefit of providing long-term removal of continuing slow COC mass flux from matrix diffusion. Consequently, the potential matrix diffusion rate of COCs from lower permeability soil units must also be considered when determining the amount

of AC amendment that should be applied, since an appreciable percentage of residual COC mass often resides in the lower permeability soil units (EPA, 2018).

- Competitive adsorption may occur. Hence, the application should be designed to include a safety factor to ensure adequate adsorption of the target COCs is achieved.
- Surfacing of reagents and groundwater can occur during application. The frequency and severity of surfacing may be minimized by reducing water flowrate, injecting at lower pressures, and using a recirculation approach where groundwater is extracted downgradient, amended with the AC amendment mixture, and then injected into upgradient points or wells.
- Concentrations of COCs in groundwater generally decrease rapidly after emplacement of AC amendments. However, long-term monitoring (several years) is required after emplacement to ensure later rebound and breakthrough does not occur, and that COCs either remain adsorbed to the AC or are degraded by a secondary mechanism such as reductive dechlorination or chemical reduction.
- Monitoring wells may be exposed to AC, even if AC is not directly injected into those wells. As a result, groundwater samples collected from those wells may not accurately represent the true concentrations of COCs in groundwater.
- Because of the longevity of AC within the subsurface, it is not known if potable wells can be installed within application areas post-treatment because of the potential for future maintenance issues associated with the drawing of suspended particulates into the system. A permanent groundwater use restriction may need to be implemented for AC amendment application areas.
- Because AC amendment is a developing technology, the long-term effectiveness and sustainability of AC amendments are unknown.
- Hydraulic clogging and bypass, particularly in low permeability and heterogeneous sites, can occur.

## Resources

### **Air Force. Final Operable Unit A - Site WP008 Little Mountain Test Facility Interim Remedial Action Completion Report, Hill Air Force Base, Utah (2019)**

This report presents a case study using the COGAC® amendment mixture to treat petroleum amendment mixtures at a sandy/silty aquifer.

### **[Air Force. Final Second Five Year Review Report Lowry Air Force Base, Colorado \(October 2013\)](#)**

This Five Year Review report presents a case study using the BOS 100® amendment mixture to treat chlorinated solvents at alluvium and bedrock water-bearing units.

**Battelle and Naval Facilities Engineering Command (NAVFAC). [Best Practices for Injection and Distribution of Amendments \(2013\) \(PDF\)](#)**

(81 pp, 2.62 MB)

This guidance document presents the "best practices" through the evaluation of past applications for introducing liquid- and solid-phase amendments into aquifers and improve the likelihood that these amendments are adequately distributed for technologies including in situ chemical reduction, enhanced reductive dechlorination, and in situ chemical reduction.

**EPA. [Remedial Technology Fact Sheet – Activated Carbon- Based Technology for In Situ Remediation \(2018\) \(PDF\)](#)** (9 pp, 915 KB)

This fact sheet provides an overview of the technology including principles, application considerations, field performance and monitoring, and long-term effectiveness, with links to additional resources.

**Davis. [PlumeStop® Liquid Activated Carbon Technology Multi-Site Performance Review. West Virginia Brownfields Conference, Charleston, West Virginia \(2016\) \(PDF\)](#)** (58 pp, 5.23 MB)

This presentation reviews the performance (concentration reduction, rebound, etc.) of AC amendments at multiple sites between 2014 and 2016.

**Fan, Gilbert, and Fox. [Current State of In Situ Subsurface Remediation by Activated Carbon-based Amendments. Journal of Environmental Management \(2017\)](#)**

This journal article presents a review of the AC-based remedial technology for in situ subsurface remediation focusing on both the scientific and practical aspects.

**Fox. [Petroleum Remediation Using In-Situ Activated Carbon \(A Review of Results\). National Tanks Conference and Expo, Phoenix, Arizona \(September 2015\) \(PDF\)](#)** (39 pp, 5.87 MB)

This presentation provides a review of the AC-based remedial technology for the remediation of petroleum hydrocarbons, with an emphasis on full-scale applications.

**Harp. [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 \(2014\) \(PDF\)](#)** (9 pp, 712 KB)

This paper presents a case study using AC amendments for the remediation of a TCE plume.

**Kjellerup, Naff, Edwards, Ghosh, Baker, and Sowers. [Effects of Activated Carbon on Reductive Dechlorination of PCBs by Organohalide Respiring Bacteria Indigenous to Sediments. Water Research \(2014\)](#)**

This journal article presents the results of a bench-scale microcosm study to determine how granular AC results in the reduction of aqueous concentration within PCB-contaminated sediment.

**McGreggor. In Situ Treatment of PFAS-Impacted Groundwater using Colloidal Activated Carbon. Remediation, The Journal of Environmental Cleanup Costs, Technologies, and Techniques (2018)**

This journal article describes the results of a study that applied colloidal AC at a site in Canada to treat PFAS compounds.

**Mackenzie, Bleyl, Kopinke, Doose, and Bruns. [Carbo-Iron as Improvement of the Nanoiron Technology: From Laboratory Design to the Field Test. Science of the Total Environment \(2016\)](#)**

This paper presents theory and testing of AC amendments for the treatment of chlorinated solvents. Discussion of bench-scale testing and field-scale applications are provided.

**Navy. [PlumeStop® Demonstration Study Report, Naval Industrial Reserve Ordnance Plant \(NIROP\) Fridley, Minnesota \(2017\). \(PDF\)](#) (831 pp, 42.5 MB)**

This report presents a case study using the PlumeStop®, HRC, and BDI products to treat chlorinated solvents at a sandy aquifer.

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