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Review of Amendment Delivery and Distribution Methods, and Relevance to Potential In Situ Source Area Treatment at the Hanford Site

September 2019

KA Muller
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Summary

The U.S. Department of Energy's Hanford Site in southeastern Washington State is a complex of multiple facilities where historical release events in the Central Plateau area have resulted in subsurface contamination of the vadose zone, a perched-water zone, and underlying aquifer. Although some contaminants have already migrated through the vadose zone into the groundwater, contaminants remaining in the unsaturated zone are a potential long-term risk as a source for further groundwater contamination. Moreover, a perched-water zone located in the 200-DV-1 Operable Unit at Hanford creates further remediation difficulties. Remediation options are limited for contaminants located in the vadose and perched-water zones within the Central Plateau due to considerable depth, co-located contaminants, and complexities associated with physical and biogeochemical heterogeneities. Existing comprehensive reviews (e.g., DOE/RL-2017-58 2019; Saslow et al. 2018) discuss potential remedial technologies relevant to Hanford Site conditions (e.g., deep vadose zone and perched water) and provide treatment technology recommendations. Many of the recommended in situ remediation technologies rely on introduction of amendments into the subsurface to achieve remedial goals. However, there are currently few review or guidance documents that provide a comprehensive look at mechanisms and considerations related to amendment delivery and distribution.

This document summarizes amendment types, delivery techniques, subsurface access methods, and the applicability of delivery methods and amendments for specific subsurface target zones, including in the context of Hanford Central Plateau applications. Guidance on the appropriateness of a remedial technology for a specific site and contaminant is not included within this document. Rather, this document is intended to be used when considering remediation technologies and the associated amendments. An overview of amendment types (i.e., liquid, gas, and solids) and access/distribution methods used in subsurface remediation is provided, along with discussion of the maturity level (low, medium, or high), advantages, and limitations that relate to the potential effectiveness of each approach in the context of site-specific factors (subsurface geology, geochemistry, contaminant properties, etc.). There are many Hanford Site-specific factors that influence the suitability and appropriateness of amendment delivery strategies. Excluding amendment delivery approaches that are unsuitable for the Hanford context, each approach was assessed for applicability to the following target zones: unsaturated high permeability, unsaturated low permeability, perched water, saturated high permeability, and saturated low permeability zones. This compilation and discussion related to amendment delivery mechanisms provides a useful resource for evaluating remedial alternatives for source area contamination in the Hanford Central Plateau.

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Acronyms and Abbreviations

AC	activated carbon
ASME	American Society of Mechanical Engineers
bgs	below ground surface
CFR	Code of Federal Regulations
DNAPL	dense non-aqueous phase liquid
DOE	U.S. Department of Energy
DP	Direct Push
EK	electrokinetics
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
EZVI	emulsified zero-valent iron
GAC	granulated activated carbon
ISCO	in situ chemical oxidation
LNAPL	light non-aqueous phase liquid
NAPL	non-aqueous phase liquid
NQAP	Nuclear Quality Assurance Program
nZVI	nano-scale zero-valent iron
PCE	tetrachloroethylene
PNNL	Pacific Northwest National Laboratory
PPT	pressure pulsing technology
PRB	permeable reactive barrier
ROI	radius of influence
STF	shear-thinning fluids
TCE	trichloroethylene
VOC	volatile organic compound
ZVI	zero-valent iron

Contents

Tables

1.0 Introduction

The U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State is a complex of multiple facilities that were built as part of the Manhattan project for plutonium production and separation operations, with reactor operations continuing through the subsequent Cold War and ending in 1987. Historical waste disposal practices included discharge of waste streams to surface structures (e.g., cribs, trenches). Additionally, operations and waste handling resulted in chemical spills and leaks into the soil. In certain areas of the Hanford Site, these historical events have resulted in contamination in the vadose (unsaturated) zone of the subsurface, with significant quantities of contaminants remaining in the vadose zone. Although some contaminants have already migrated through the vadose zone into the aquifer, contaminants remaining in the vadose zone are a potential long-term risk as a source of further groundwater contamination. Moreover, a perched-water zone located in the 200-DV-1 Operable Unit at Hanford is a source for water table aquifer contamination. Remediation options are limited for contaminants located in the vadose and perched-water zones within the Central Plateau due to the considerable depth involved, co-located contaminants, and complexities associated with physical and biogeochemical heterogeneities. A comprehensive review of potential vadose zone remedial technologies relevant to Hanford Site conditions was recently completed (DOE/RL-2017-58 2019) providing recommendations for treatability testing and identifying associated data gaps. Many potentially relevant in situ remediation technologies rely on introduction of amendments into the subsurface to achieve remedial goals. Because the ability to successfully deliver and distribute amendments to the subsurface is a key factor in the success of a remedy, this document provides an in-depth review of potential approaches for amendment delivery and identifies approaches relevant to Hanford conditions.

1.1 Intended Use of Document

This document focuses on amendment delivery techniques, subsurface access methods, and the applicability of delivery methods and amendments for specific subsurface target zones at the Hanford Site. This document does not provide guidance on selecting a remedial technology for a specific site and contaminant(s); other resources provide remediation technology information and evaluations. Rather, the information here is intended as a resource for feasibility studies and remedial alternative assessments to provide insight into how amendments can be delivered for in situ remediation technologies.

A document such as the recent *Technology Evaluation and Treatability Studies Assessment for the Hanford Central Plateau Deep Vadose Zone* (DOE/RL-2017-58 2019), which provides a comprehensive evaluation of remediation technologies applicable to the vadose zone, can be used, in conjunction with this document, to identify a set of potential remedial alternatives for a feasibility study. Once appropriate candidate technologies and amendments are identified, this amendment delivery mechanisms document provides insight into how amendments can be delivered, emplaced, and/or distributed to a specific subsurface target zone. For example, if a candidate technology, such as particulate-phase chemical sequestration, is identified as a promising technology for uranium treatment in a perched-water zone, then the solid amendment information in Section 2.0 and the Section 3.0 information on appropriate access methods to deliver solids, will be useful for understanding how to deliver the particulate-phase amendment. Section 4.0 then puts amendment delivery in the context of the Hanford perched-water zone.

1.2 Brief Description of Hanford Site Conditions

Much of the liquid waste discharged into the Hanford vadose zone occurred in the Central Plateau, a 190 km² (75 mi²) area that includes approximately 800 waste sites. The contaminants of potential concern for the Hanford Site generally include carbon tetrachloride, carbon-14, cyanide, hexavalent chromium, iodine-129, nitrate, strontium-90, technetium-99, trichloroethene, tritium, and uranium, though each operable unit has its own specific contaminants of concern. The climate at the Hanford Site is semi-arid, meaning that natural recharge and soil moisture are relatively low. Hanford geology is described in DOE/RL-2017-58 and references cited therein, but is also briefly outlined here. The Hanford Central Plateau vadose zone is thick, extending to a depth of more than 76 m (250 ft). Major lithologic units in the subsurface include the Hanford Unit (a permeable sandy/sandy gravel material), the Cold Creek Unit (which includes fine grained and cementitious material), and the Ringold E Unit (sandy material). Heterogeneities within the larger stratigraphic units are also known to exist, for instance in the B-Complex Area of the Central Plateau (Serne et al. 2010), but can be difficult to characterize owing to the large scale of the subsurface and disparities of scale between measurements and subsurface features. A perched-water zone is present at about 69 m (225 ft) below ground surface beneath the B-Complex Area and extends to approximately 5 m (15 ft) above the water table at its lowest point. Groundwater at the Hanford Site generally flows toward the Columbia River, which is the primary exposure route for contaminants to reach human and ecological receptors.

1.3 Remediation Technologies and Amendment Delivery Considerations

A multitude of remediation technologies have been developed for in situ treatment of subsurface contamination (e.g., CLU-IN 2019; DOE/RL-2017-58 2019; FRTR 2019; etc.). The specific technology selected for an in situ remedy depends on a number of factors, including the nature of the contamination, the subsurface zone in which the contamination is located (e.g., vadose zone or aquifer), and the estimated effectiveness of the technology. At a high level, technologies can be categorized by general response action: treatment (in situ or ex situ contaminant destruction/transformation), containment (e.g., immobilization, encapsulation), or removal (with an implied volume reduction). Remediation technology types are based on a variety of mechanisms, including thermal, chemical, biological, and physical treatment processes, and can be grouped into process options based on technologies with similar functionality. The general response actions, technology types/process options, or technology variants (i.e., with a specific mode of application) can be considered when assembling remedial alternatives for comparison and eventual selection of one as a site remedy.

While the underlying mechanisms of a remediation technology may show promise at the laboratory scale, issues related to subsurface delivery and distribution are typically responsible for limited effectiveness when implemented in the field (e.g., Kitanidis and McCarty 2012). Ineffective contact between amendments and contaminants is often cited as the primary factor when remedial objectives are not met. Subsurface heterogeneities (e.g., lower-permeability zones, areas of permeability contrasts, fractured media, etc.) can create inaccessible areas due to preferential flow paths and/or flow bypass areas that limit the ability to deliver amendments to targeted areas. Incomplete treatment of less accessible geologic regions is often responsible for a "rebound" in contaminant concentrations during a post-cleanup time period (Thomson et al. 2008). The objective of amendment delivery is to provide enough mass over a sufficient subsurface volume with an adequate residence time to meet the needs of the remedial approach (e.g., volumetric treatment, a permeable reactive barrier, etc.). The specific nature of the amendment, the targeted subsurface zone, and the mode of treatment action will constrain the approaches for subsurface access and amendment delivery. The complexity of the multiple interwoven considerations for achieving delivery and distribution of an amendment into the subsurface is illustrated with the questions in Table 1. The success of delivery will impact remediation effectiveness and implementation needs (e.g., a small radius of influence [ROI] could require more injection points), which, in turn, defines the feasibility and cost of the technology.

Table 1. Amendment Delivery Considerations.

Relevant Questions	Potential Responses
What is the mode of action of the remediation technology to achieve treatment?	Immobilize, destroy, or remove
How can the subsurface be accessed?	Wells/injection points, trenches, augering, surface infiltration, or formation fracturing
How is the amendment emplaced in the subsurface, or what is the driving force for emplacement?	Advection from pressure/vacuum, advection from gravity, diffusion/concentration gradients, direct placement, electrical field, thermal or density gradients, or the use of specific operational strategies
What is the nature of the amendment, and is it applied as a pure product or mixed with a carrier fluid?	Amendment phase (aqueous, non-aqueous phase liquid [NAPL], gas, solid), ionic nature, surface properties (composition, functional groups, charge, etc.), size, solubility, volatility, diffusivity, viscosity, redox sensitivity, pH sensitivity, partitioning behavior, sorption behavior, reactivity, and concentration
What is the nature of the targeted subsurface zone?	Permeability, heterogeneity, moisture content, pH buffer capacity, organic matter/mineral composition, and hydraulic flow conditions
How far/widespread is it possible to distribute the amendment? How much mass can be delivered (i.e., what is the amendment longevity/capacity)? How fast does the amendment react? What residence time is needed for treatment?	These are the fundamental questions that will drive success of amendment delivery. Answers to these will depend on the specifics of the amendment, subsurface characteristics, and remediation technology.

1.4 Scope of Review

This work consists of a literature review to provide a broad survey of methods used to deliver and distribute amendments for in situ remediation, including discussion of amendment types, subsurface access methods, and amendment emplacement approaches. Potential target zones in the subsurface are defined and discussed relative to the challenges associated with amendment delivery in each zone. The applicability of delivery mechanisms to specific subsurface zones is assessed, with a focus on source area treatment applications for the Hanford Site Central Plateau.

1.5 Nature of Available Literature

Approaches for amendment delivery are generally discussed in disparate literature sources that focus on a specific technology or are held as professional knowledge based on experience. There is currently only one review/guidance document (NAVFAC 2013) that provides a reasonably broad look at a number of mechanisms and considerations related to amendment delivery and distribution. This Naval Facilities Engineering Command report focuses on best practices for injection of in situ chemical oxidation, in situ chemical reduction, and enhanced in situ bioremediation amendments. A few other guidance documents provide information more narrowly focused on specific technologies (e.g., in situ chemical oxidation (ISCO) guidance), amendment types (e.g., aqueous solutions or edible oil), or distribution enhancement methods (e.g., circulation wells). Yet other literature provides information on a specific amendment delivery approach as part of technology development or case studies. Relevant literature, including these focused guidance documents and review articles are listed in Table B.1 in Appendix B.

2.0 Amendment Types

Types of amendments are described in this section. Amendments are organized based on the physical state, and then subcategorized based on additional factors such as reactivity and partitioning. Approaches and example applications are described for the different amendment types.

In addition to the nature of an amendment in terms of physical properties (phase, size, viscosity, etc.), the nature of the amendment reactivity and corresponding mode of treatment action is important to identify. Reactive and non-reactive amendment classification is described below and presented in Table 2. Non-reactive amendments generally provide treatment by encapsulating contaminants (to immobilize and prevent release/exposure), by enhancing contaminant mobility (e.g., decreasing sorption on soil, increasing solubility, etc.) for capture by extractive technologies, or by facilitating mass transfer from one phase to another for capture by extractive technologies. Reactive amendments act to change the biogeochemical environment (e.g., redox or pH conditions) and facilitate or decrease contaminant mobility, to facilitate immobilization (acting as an adsorbent), or to stimulate reactions (biotic or abiotic) for degradation.

Table 2. Amendment Types.

Non-Reactive		
Process	Treatment	Example Amendments
Immobilization/ Stabilization	Encapsulation	Grout, molten wax
	Soil Desiccation	Dry air/N_2
Transfer & Removal	Air Sparing	Air
	Soil Flushing	Water
Enhanced Mobility	Surfactant Flooding	Surfactants
Reactive		
Process	Treatment	Example Amendments
Biogeochemical	Alter subsurface environment	Acidic/basic solutions, alkalinity, sodium dithionite, ammonia gas
Chemical Degradation	Chemical oxidation	Ozone, permanganate, hydrogen peroxide
Biological Degradation	Biostimulation Biosparging Bioventing	Oxygen, lactic acid, emulsified vegetable oil, microbes, nutrients
Decrease Contaminant Mobility	Sorption	Activated carbon, hydroxyapatite, ferric iron oxide nanoparticles

Overlap between reactive and non-reactive amendments can exist. For example, soil flushing with a surfactant has a primary treatment mode of extraction, but the surfactant "reacts" with the contamination to enhance mobility. Another example is biosparging, which is primarily designed to stimulate biologically mediated contaminant transformation, but can also transfer contaminant to the gas phase for removal.

For reactive amendments, potential issues with distribution, reaction, and longevity are described below:

1. Effective Amendment Distribution. Effective amendment distribution to a suitable extent in field applications is challenging because of the nature of the subsurface porous media and the reactive amendments. For example, because ammonia is highly soluble in the soil moisture, the ROI (distribution) for injection of gaseous ammonia into the vadose zone is a function of moisture content,

injected ammonia concentration, soil permeability, pressure driving force, and duration of injection. The ammonia front will advance slower than an inert gas because it readily partitions into the aqueous phase of the soil moisture.

2. Reaction Kinetics. Reaction kinetics are a key consideration for achieving amendment distribution. For example, consider injection of an aqueous lactate solution into an aquifer via a well to stimulate contaminant enhanced in situ biodegradation. Because the lactate is dissolved in water, it is easily transported with the injected water through the aquifer. However, lactate is also readily consumed by bacteria, leading to near-well bacterial consumption of the lactate and a decreased flux of lactate with distance from the well. Simultaneously, bacterial growth can foul the injection well, decreasing the injection flow rate into the aquifer (for a given injection pressure).
3. Longevity. The volume, concentration, and frequency of delivery with respect to the reactivity and kinetics of the amendment will determine longevity, and ultimately, the effectiveness of treatment. For example, consider the injection of zero-valent iron nanoparticles for the in situ treatment of trichloroethene in groundwater. Although the small particle size reduces the filtration effects of flow through the porous media and achieves a larger ROI, the smaller particle size has less mass, which limits the reaction longevity.

2.1 Liquids

Liquids span a range of materials, including amendments dissolved in water, neat oils, non-Newtonian fluids, and foams. In some applications, the liquid is the amendment, but the liquid can also be used as a carrier for delivering dissolved or entrained amendments.

2.1.1 Aqueous Solutions

Aqueous amendments are routinely used at field sites to support remedial technologies. Aqueous solutions can be introduced into the subsurface as: 1) amendments (e.g., chemical reductants) for altering subsurface conditions to reduce and immobilize contaminants; 2) subsurface remediation activity support by altering conditions to enhance remediation (e.g., use of acids or bases for pH control); or 3) direct amendments to provide the chemicals necessary to drive a reaction (e.g., substrate addition to support bioremediation). For example, aqueous solutions are widely used (e.g., hydrogen peroxide, permanganate, or persulfate) with ISCO. Although ISCO is limited to a narrow range of contaminants, available information on-site specific factors (e.g., hydrogeology, lithology, groundwater composition, soil parameters, etc.) can be used in a priori calculations/models to determine the likelihood of success and an appropriate remedial design for use of aqueous solutions for treatment (ITRC 2005).

A variety of subsurface access methods can be used to deliver liquids, such as injection wells, direct push injections, infiltration galleries, in-well recirculation systems, and hydraulic or pneumatic fracturing with injection. The number of wells, well configuration, and injection rates can be designed to accommodate the required amendment mass loading for site-specific treatment of either a source zone or a contaminant plume (NAVFAC 2013). When aqueous amendments are injected into the subsurface, typically distribution is enhanced using hydraulic control methods, where a set of injection and extraction wells impose flow conditions designed to optimize distribution (ITRC 2005; Thomson et al. 2008).

The delivery of liquid amendments is most effective in fully saturated porous media with limited heterogeneity. Heterogeneity will decrease the effectiveness of this delivery approach. Even under fully saturated conditions, delivery of aqueous amendments is dictated by groundwater flow patterns (lateral and vertical) and may not successfully penetrate targeted areas due to bulk stagnant zones, dead-end pores, regions of reduced permeability due to immobilized materials (e.g., biofilm coatings or previously injected emulsions), or due to heterogeneities (e.g., the presence of clay lenses). Rather, flow will follow the path of least resistance through the aquifer (i.e., high-permeability zones, previously drilled wells or injection sites, fracture networks, etc.) (e.g., Pac et al. 2019). Heterogeneity of aquifer materials leads to a wide distribution of flow paths, with the majority of flow occurring via advection through higher-permeability zones and only limited, diffusive exchange occurring with lower-permeability regions (e.g., Suthersan et al. 2009).

Using aqueous solutions to deliver amendments often requires a balance between providing sufficient amendment-contaminant contact time, while obtaining the required ROI. In aquifers with a high groundwater flow rate, aqueous amendments may only be able to provide short-term treatment. Because soluble amendments are transported with groundwater flow, amended water may flow in and through the targeted zone without providing long-term treatment. In this case, multiple injections or active hydraulic control are required to extend the contact time between the amendment and the contaminants (ITRC 2005).

Aquifers with low hydraulic conductivity also are problematic, with a hydraulic conductivity value of less than 1.5 m per day (5 ft per day) typically being more challenging because of the slow injection rates required to avoid fracturing the formation (Divine et al. 2018). Furthermore, shallow injections (e.g., less than 3 m (10 ft) below ground surface [bgs]) into a low-permeability aquifer can be difficult, creating high backpressures, which can cause “surfacing” or “daylighting” of the injected fluids. Surfacing occurs if the aquifer cannot support the injection rate or volume (In Situ Remediation Reagents Injection Working Group 2009).

Depending on the nature of the aqueous amendment, injection/recovery well or formation fouling can be a significant issue. Biofouling most commonly occurs with enhanced bioremediation, where nutrient additions or geochemical changes can lead to stimulation of microbial activity. Fouling from mineral precipitation can also occur when changes in groundwater chemistry result in decreased mineral solubility. For example, Thomson et al. (2008) found that unintended precipitation of manganese oxides during delivery of permanganate caused a reduction in hydraulic conductivity of the formation, hindering subsequent injections. Reaction pathways that produce gases can cause gas lock within the aquifer, where gas bubbles block or constrict flow pathways (NAVFAC 2013). Furthermore, if a light NAPL (LNAPL) is present, there is an increased risk for the NAPL to “smear” into the unsaturated zone, if injections cause water table fluctuations (EPA 1996).

In the vadose zone, injected water or aqueous solutions are highly influenced by gravity, wettability, and soil permeability, with water flowing through the most permeable pathways. Increasing the water content of the vadose zone with injection of aqueous solutions can unintentionally enhance transport of pollutants towards the groundwater (Zhong et al. 2010; Zhong et al. 2009).

2.1.2 Non-Aqueous Phase Liquids

A NAPL can be used as an amendment for site restoration efforts by either sequestering organic contaminants and/or, in the case of neat edible oils, acting as the amendment itself (Riha et al. 2009). Injection of pure NAPL into the saturated subsurface can be completed using injection wells or direct push methods, but distribution away from the injection site is typically very limited. For neat oil injections, 40 to 90% of the pore space near the injection site can be occupied with oil, with the only way to deliver NAPL further from the injection point being to continue to inject additional oil (Borden 2006). NAPL injections can supply significant quantities of amendment, but at the expense of large permeability loss, especially in fine-grained sediments (Coulibaly and Borden 2004). Permeability reduction becomes problematic because groundwater will flow around this zone, limiting direct contact with the amendment.

Neat soybean oil has been introduced into the lower portion of the vadose zone (right above the water table) via gravity feed for the purpose of sequestering and enhancing degradation of chlorinated solvents at a Savannah River Site (Riha et al. 2012) and another DOE site in Mound, Ohio (DOE 2014). At these sites, the injected oil accumulated as a thin layer on the water table, effectively creating a reactive barrier between vadose zone contaminants and groundwater (Riha et al. 2009; Riha et al. 2012). The neat oil injections were designed to create an approximately 10 m (33 ft) diameter zone of influence within the silty sand using wells screened above the water table. The original remedial design involved using an extraction well to lower the water table in hopes of enhancing lateral oil movement, but low flow rates, likely due to oil-clogged pores, prevented the water table from being successfully lowered (Riha et al. 2009).

2.1.3 Emulsions

Emulsions are regularly used for environmental cleanup efforts, most commonly to provide an electron donor in support of bioremediation via emulsified vegetable oils (EVOs). However, emulsions can also be used for mobility control, contaminant stabilization, and as a vehicle to deliver reactive amendments. The Environmental Security Technology Certification Program (ESTCP) document "Protocol for Enhanced In Situ Bioremediation Using Emulsified Edible Oil" provides guidance on the use of emulsified oils (Borden 2006).

Emulsion transport and retention is dictated by bulk emulsion properties, including viscosity, density, and emulsion stability. Also important are the droplet properties, including droplet concentration, surface charge, zeta potential, size distribution, and interfacial characteristics. The release rates (and extent) of active ingredients from emulsions are also affected by emulsion droplet properties. Stabilized oil droplets created through emulsification will ideally result in uniform droplets of a size that achieve good mobility through porous media while still retaining droplets on the soil particles to achieve treatment. Micro- and nano-EVOs show superior transport properties over emulsions with larger droplet sizes. One benefit of using emulsions is the retention of oil droplets along the flow path. However, this process can lead to aquifer clogging when retention is too high, illustrating the inherent tradeoff between concentration and ROI.

Active ingredients have successfully been encapsulated within emulsions, allowing for improved amendment delivery and distribution without compromising reactivity. For example, reactive iron particles (Berge and Ramsburg 2009; Quinn et al. 2004; Quinn et al. 2005) and alkalinity releasing particles (i.e., $CaCO_3$ and MgO) (Muller 2016) have been encapsulated within oil-in-water emulsions. The particles held within the emulsions were able to provide long-term treatment as amendments slowly released from the emulsion oil droplets retained in the porous media. To support bioremediation, soluble substrates and nutrients have also been incorporated into emulsion mixtures of edible oils (Borden 2006). The oil of the emulsions can also absorb contaminants (mainly organic pollutants such as benzene), thus retarding pollutant mobility and increasing contact time for bioremediation to occur (Lee et al. 2019).

Emulsions can be pressure injected via wells or direct push methods. Multi-well recirculation systems where water is flushed through the treatment zone behind an injected emulsion can improve distribution. However, viscosity contrasts between the emulsion and flushing fluid may affect distribution (Borden 2006). Injection wells have also been used to create EVO permeable reactive barriers (PRBs). For example, an EVO bio-barrier was created in a shallow groundwater aquifer comprised of low soil organic fraction sandy loam for containment and migration control of a benzene and petroleum-hydrocarbon plume (Lee et al. 2019). Beyond creating EVO barriers, the viscous nature of emulsions can also improve sweeping efficiency into low-permeability layers and through contrasts in permeability (e.g., Jung et al. 2006, Silva et al. 2012). Oil droplets of the emulsion become trapped in the pore throats, forcing flow to bypass through different paths (Cobos et al. 2009; Guillen et al. 2012), which can lead to more successful distribution into lower-permeability zones.

Emulsion concentration becomes important for delivery of remedial amendments because of the tradeoff between mobility and amendment dosing (i.e., higher oil contents will lower the ROI, but allow for more amendment to be housed within the emulsion). Studies have shown that it is possible for highly concentrated emulsions (up to 23 wt.%) to transport well in one-dimensional columns of sandy porous media while depositing droplet mass for subsequent amendment release (Muller et al. 2018).

Successful field-scale emulsion applications have predominantly been for the delivery of biodegradable substrates (i.e., electron donor) throughout the subsurface (Borden 2006; Borden 2007: Riha et al. 2012; Watson et al. 2013) or as a bio-barrier (Hunter 2001; Lee et al. 2019). Emulsified vegetable oil (EOS® 598 product, EOS Remediation, LLC.) was injected at the 100-D Area at the Hanford Site to stimulate bioremediation (Truex et al., 2009). Although there was a moderate reduction in aquifer permeability due to the introduction of immiscible oil, the injection resulted in an emulsion ROI of about 8 m (25 ft), and supported microbial activity and the reduction of targeted species over the 10-month monitoring period. At the DOE Savannah River Site, AquaBupHTM, an EVO amended with pH buffer, was injected by gravity feed followed with a water flush to enhance distribution away from the injection point (Riha et al. 2012). At another DOE site (Mound, Ohio, Site OU-1), emulsified oil blended with nutrients was injected under low pressure through temporary screened wells below the water table to create a targeted 6.1 m (20 ft) diameter reactive zone (DOE 2014). A 17 wt. nano-scale zero-valent iron (nZVI) EVO emulsion was delivered to the groundwater via pressure pulsing technology and hydraulic and pneumatic fracturing to treat a trichloroethylene (TCE) source zone at NASA's Launch Complex 34 (Quinn et al. 2004; Quinn et al. 2005). Soil concentrations of TCE and TCE groundwater concentrations were significant reduced (57 to 100%) at four of six soil sampling locations via application of the nZVI EVO. Direct push, pneumatic injection, and pressure pulsing technology showed promise for EVO delivery, whereas hydraulic fracturing with injection was deemed unsuccessful.

Depending on the oil type and concentration, EVO can be slightly less dense than groundwater, impacting its subsurface delivery. Density effects were suspected at an injection site where EVO was introduced into a high-permeability gravel aquifer to supply electron donor for bioremediation of uranium at the DOE Oak Ridge Integrated Field Research Challenge site (Watson et al. 2003). At this site, EVO traveled through the aquifer 2 to 5 times faster than the non-reactive tracer bromide. The enhanced transport was hypothesized to be a size-related effect, with the 1 μm EVO droplets being preferentially transported through faster velocity pores and bypassing the smaller pores. Since the majority of the injected EVO was deposited along the contaminant travel path, it still proved to be a long-term, degradable electron donor source.

2.1.4 Foams

Surfactant foams have been widely applied for enhanced petroleum recovery operations and remediation of petroleum-contaminated soils, as reviewed by Karthick et al. (2019). Foams can provide an increased sweeping efficiency, particularly through heterogeneous media, used to decrease formation permeability for diversion of groundwater flow around a source zone, or to deliver remedial amendments.

In the field, use of foams as a selective permeability reduction agent has been demonstrated. For example, pre-generated surfactant foams were used to confine a chlorinated solvent source zone and reduce dissolved contaminant release to the surrounding aquifer (Portois et al. 2018).

In the laboratory, foams have been used to deliver amendments (e.g., calcium polysulfide, sodium phosphate, carboxyl-modified polystyrene latex microspheres as a surrogate for nanoparticles) (Zhong et al. 2009; Zhong et al. 2011; Shen et al. 2011) to unsaturated sediments more successfully than aqueous solutions. Liquid amendments are supplied to the unsaturated zone during transport via a process where foam bubbles break and release the encapsulated liquid amendments. Amendments then sorb to the sediment while the gas flows through the soil pores. Gravity has less influence on foam transport than liquids, allowing for enhanced delivery both laterally and to low-permeability regions, an improved uniform sweeping efficiency, and decreased contaminant mobilization at the fluid front (Zhong et al. 2010; Zhong et al. 2009; Zhong et al. 2011).

One-dimensional column experiments completed by Zhong et al. (2009) suggest that foams can be used to create reactive barriers in the vadose zone that could intercept percolating contaminated water. Because foam responds to pressure gradients, as opposed to gravity, as is the case with liquids, foam delivery in the unsaturated zone is more successful than injections of liquids. The authors note that amendment delivery via foams can be controlled by foam flow rate, foam quality, and the concentration of amendment in the foam. Two-dimensional aquifer cells further demonstrated the ability of foams to distribute amendments laterally and through heterogeneous vadose zone sediments (Zhong et al. 2011). Laboratory testing also suggests the ROI in unsaturated one-dimensional columns and two-dimensional aquifer cells containing permeability contrasts could be improved by first injecting a biodegradable foam because it created a foam water network that allowed for more uniform delivery of an oxidant solution (Bouzid et al. 2018).

Although foam transport shows promise in smaller scale column experiments, attempts to inject foam into 20-25 ft long columns resulted in high pressure (>100 psi) and provided limited reagent delivery (i.e., the phosphate amendment was transported less than 1 meter) (Szecsody et al. 2009). Such high injection pressures, and the resulting limited ROI, may be problematic when scaling up for a field application. Furthermore, caution is warranted for foam use in the vadose zone because of the potential to increase water content, which could increase infiltration of contaminants to the groundwater (Dresel et al. 2008).

2.1.5 Shear-thinning Fluids

The rheological properties of shear-thinning fluids (STF) have been harnessed for improved subsurface delivery and distribution. At high shear rates, such as those experienced as a fluid moves through soil pores, viscosity is low. However, as the shear rate decreases, the fluid will become more viscous. It is this rheological behavior that permits the use of relatively moderate injection pressures. Solutions of xanthan gum, guar gum, and Slurry Pro™[1] are STFs commonly used for remediation applications.

Non-Newtonian fluids have been used to enhance sweeping efficiency over heterogenous or layered media, to deliver amendments, and to increase the contact time between the amendment and pollutants (e.g., Silva et al. 2012; Zhong et al. 2009; Truex et al. 2015; Chokejaroenrat et al. 2013; Oostrom et al. 2014). The shear-thinning behavior tends to improve amendment placement in the subsurface because, as the STF moves away from the injection point, the shear rate decreases, causing the fluid viscosity to increase. This behavior is particularly helpful for low-permeability treatments. Low-permeability layers commonly contain contaminant sources and STFs can extend contact time in these zones. STFs can also be placed to hydraulically isolate a source zone because groundwater will bypass around the zone containing the high-viscosity fluid.

The viscous nature of STF has been used to improve delivery of particles by decreasing particle sedimentation and aggregation rates (e.g., stabilization of ZVI particles) (e.g., Tiraferri et al. 2008; Truex et al. 2011a). Decreases in amendment reactivity have not been reported when STFs were used as carrier fluids.

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[1] SlurryPro CDP, KB International, Chattanooga, Tennessee; www.kbtech.com

Laboratory STF testing has shown potential for further optimizing STF amendment delivery. Flow cell experiments have shown the potential for STF emplacement in variably saturated homogenous and layered heterogenous systems (Oostrom et al. 2014; Silva et al. 2012). Improved transport through low-permeability layers was a product of cross flow between layers result of the elevated fluid viscosity. Oostrom et al. (2014) also amended the STF with phosphate to test the potential to deliver amendments, finding that phosphate successfully transported with the STF.

In a field trial, micron-sized ZVI particle stability and subsurface distribution were enhanced when combined with a STF (Slurry Pro™) for treatment of a TCE source zone (Truex et al. 2011a). Additional field testing focused on STF transport behavior by quantifying the improvement in tracer distribution when using a STF over the distribution obtained with a standard aqueous injection (Truex et al. 2015). Tracer breakthrough and electrical resistivity tomography data showed that STF provided reduced transport through high-permeability regions, increased transport through low-permeability zones, and interrogated a larger subsurface cross-sectional area than aqueous solutions.

Laboratory and field tests confirm that STFs provide enhanced distribution through heterogenous aquifers. However, one possible limitation of this delivery approach is increased injection pressures, as evidenced by Truex et al. (2015) where a steady increase in injection pressure was experienced over the duration of the injection. The pressure caused the STF to break the well seal and infiltrate an untargeted higher-permeability zone. Additionally, some STFs may require additional pre-injection procedures, such as an overnight hydration period needed for a xanthan gum injection (Truex et al. 2015).

2.1.6 Gelling Liquids

Gelling liquids have been used in petroleum engineering to enhance oil recovery by physically blocking flow paths. In situ gelation has been extended to the remediation sector for contaminant containment and delivery of amendments. With in situ gelation, a solution (or a mixture of solutions) is injected into the subsurface, where either the prevailing conditions or temporal gelation will induce a change in the physical property of the injected material. Typically, a dramatic increase in viscosity in situ will be harnessed to create an impermeable barrier (Apps et al. 1998). Colloidal silica gels, waxes, polysiloxanes, and polybutenes have all been identified as potential materials to create in situ barriers (DOE/EM-O134P 1994; EPA 1999). Gelling liquids have been proposed for use in both saturated and unsaturated zones (Kim and Corapcioglu 2002).

2.1.6.1 Gelling Liquids for Encapsulation

Grout is considered to be a gelling liquid, because grout can be injected into the subsurface to encapsulate contaminants or as a barrier to prevent infiltrating water from coming into contact with contaminants. For deep vadose zone application at the Hanford Site, acrylamide and silicate grouts were identified as potential candidates for encapsulation because they have low injection viscosities and controlled gelling times (et al. 2011b). In the unsaturated zone, gelling liquids can be used to limit infiltration, thereby decreasing downward contaminant migration. In situ emplacement of grout can be completed via jet grouting or permeation grouting methods. With jet grouting, high energy injections are used to disturb and displace formation sediments while concurrently mixing in grout material. Permeation grouting involves injection of a liquid grout that permeates and fills the pore space of granular media, then gels over time, leaving a solid, cemented mass of reduced permeability. The achievable ROI, especially in the unsaturated zone, is rather limited and highly dependent on soil properties such as permeability and particle size, making the approach most applicable to targeted treatment of high-permeability zones.

2.1.6.2 Gelling Liquids for Amendment Delivery

Recently, colloidal silica suspensions have been investigated to deliver remedial amendments after gelling occurs in the vadose zone (Lee et al. 2014; Zhong et al. 2018). Batch and column testing indicated silica suspensions were able to provide a slow release of carbon (sodium lactate and molasses), and showed that gelation rates were a function of silica, salt, and amendment concentrations (Zhong et al. 2018). The suspensions had favorable, low injection viscosities of 2 to 6 cP (with the viscosity increasing over time as gelation occurred) and shear-thinning behavior. Similar proof-of-concept experiments have explored the potential of the natural polymer sclerogucan to simultaneously trap and treat Cr(VI) (Pensini et al. 2018). Preliminary testing shows that when the sclerogucan polymer comes into contact with Cr(VI) it cross-links and gels, increasing the fluid viscosity. The Cr(VI) is then trapped in place and subsequently reduced via the sodium thiosulfate contained in the gel.

2.1.7 Surfactants

Surfactants can aid in environmental remediation through contaminant mobilization and solubilization effects. Surfactants have been used to enhance bioremediation, phytoremediation, and electrokinetic remediation (Mao et al. 2015). Amphiphilic surfactant molecules contain a polar, hydrophilic group and a non-polar hydrophobic tail and, at concentrations above the critical micelle concentration, surfactant molecules will self-assemble in a specific formation where the non-polar groups face inwards and the hydrophilic polar part of the molecule face outwards into the aqueous solution. Surfactant molecules can reduce the interfacial tension between water and a non-polar phase or a contaminant, allowing for increased contaminant mobility. Additionally, due to micellar solubilization, the water solubility of hydrophobic contaminants (e.g., PCBs, PAHs, dyes, organics, etc.) can be increased 100 to 1000 times (Shah et al. 2016).

In situ treatment of contaminated soils using surfactant solutions is commonly done via an injection-extraction well setup or is allowed to infiltrate through the subsurface using a trench or pond, flushing pollutants into the groundwater. The surfactant solution facilitates solubilization of the metal, where the contaminant-containing surfactant/groundwater mixture is then recovered via extraction wells.

A major concern related to surfactant use is toxicity. Due to the toxic nature and low biodegradability of many surfactant solutions, the collection of solutions is critical, and a potential limitation. Biosurfactants have been gaining in popularity because they are less toxic and more biodegradable than traditional surfactants, decreasing the emphasis on post-treatment surfactant recovery. Consequently, when considering in situ use, surfactants with low critical micelle concentration are ideal for limiting the surfactant concentration and volume required for successful treatment. Likewise, surfactants with limited soil adsorption are preferable, because this decreases surfactant requirements (Mao et al. 2015).

Several review articles outline the mechanisms of surfactant-based contaminant removal, as well as the many studies that use surfactants for remediation of soils (Befkadu and Chen 2018; Mao et al. 2015; Shah et al. 2016). An Environmental Protection Agency (EPA) CLU-IN document on in situ soil flushing provides details on both contaminant properties (e.g., contaminant phase, water solubility, soil sorption, etc.) and site-specific factors that influence the likelihood of success (e.g., hydraulic conductivity, soil surface area, carbon content, cation exchange capacity, and clay content) (Roote 1997). Currently, most field-scale studies target hydrocarbons, NAPL (both LNAPL and dense non-aqueous phase liquid [DNAPL]), and PCBs (e.g., Childs et al. 2006). However, laboratory testing has been completed for removal of Cd, Zn, Cu, Ni, Pb, and other heavy metals, albeit predominantly in batch experiments (e.g., Torres et al. 2012; Mao et al. 2015).

A treatability test of soil flushing for mobilization of Cr(VI) was designed (and is being conducted) for the 100-K West Area on the Hanford Site (DOE/RL 2018). The intent of this treatability test is to apply treated effluent at a pH of 5.0-5.5 to the ground surface in a test area to infiltrate through the vadose zone and mobilize residual Cr(VI) from a seasonally rewetted zone into the groundwater where the existing pump-and-treat system can capture and treat the contamination. Preliminary monitoring data indicate that Cr(VI) is indeed being mobilized from the deep portions of the vadose zone.

2.2 Gases

Gases can be introduced to either the vadose or saturated zones, to initiate direct contaminant removal, deliver reactive amendments, or manipulate conditions to facilitate remedial technologies. Gases can be injected as pure gas (e.g., air, nitrogen) or as a mixture of gases. Gas amendments tend to have several advantages over liquid and solid injections in terms of cost, increased treatment area, and higher penetration of lower-permeability zones. As with all amendments, however, site-specific factors (e.g., subsurface geology, lithology, porous media types) will influence effectiveness. To some extent, gas flow can be manipulated with injection and extraction wells that push/pull gases through the subsurface environment to improve spatial distribution (Truex et al. 2012).

In saturated porous media, gas transport is dictated by gas buoyancy and the pressure applied at the injection well. When injected into unconsolidated porous media, gas will flow outwards and upwards through the path of least resistance. When injected into groundwater, gas will create channels for gas flow. However, once the injection is terminated, the channels may collapse back to their original state, thereby trapping residual gas. Because of low gas solubility, dissolution of gases into water at the air-water interface of the residual trapped gas can occur over weeks or longer, thus acting as a long-term amendment source (Kitanidis and McCarty 2012). Still, treatment is limited by gas solubility, and flow bypass can limit transport to low-permeability regions. In the unsaturated zone, amendment delivery via gas is frequently considered to be superior to liquid or solid delivery because gases have been found to be more efficient, predictable, and better able to permeate larger areas, as well as into low-permeability materials (Denham and Looney 2007).

Traditionally, air has been used to remove volatile organic compounds via air sparging in groundwater. However, other pollutants with high Henry’s law coefficients (e.g., mercury, ^{129}iodine) can also be successfully stripped from groundwater, although, such contaminants may require chemical manipulations to ensure the dominant species is the volatile form (Denham and Looney 2007). For instance, the addition of aqueous stannous chloride can reduce inorganic mercury (Hg(II)) to volatile Hg^0, which can then be removed via air sparging. Similarly, it has been proposed that an ozone-air mixture injected into groundwater containing ^{129}iodine could strip the containment from groundwater and be subsequently vacuum extracted for removal (Denham and Looney 2007).

Use of other gases has gained traction for remediation. For instance, gas injections of ozone are commonly used for delivery of a chemical oxidant for ISCO (ITRC 2005) and pure oxygen injections can be effective for enhanced aerobic bioremediation (EPA 2017). Recent investigations have been aimed at injecting reactive gases such as hydrogen, methane, propane, butane, ozone, pure oxygen, hydrogen sulfide, and ammonia (Evans et al. 2011; Kitanidis and McCarty 2012; Maire et al. 2019; Szecsody et al. 2015; Zhong et al. 2015). For instance, gaseous amendments (methane, nitrous oxide, and triethyl phosphate) have been used to stimulate bioremediation via sparging in groundwater located deep in the subsurface (160 ft bgs) using horizontal injection and vacuum extraction wells (Brockman et al. 1995). A mixture of gaseous electron donors (hydrogen, carbon dioxide, liquefied petroleum gas, and nitrogen) was injected into the vadose zone for perchlorate and nitrate remediation (Evans et al. 2011). Contaminant destruction was observed in a range of moisture contents (6.8 to 36%), as well as in both low- and high-permeability media with the ROI for perchlorate estimated to be between 3 and 4.6 m (10 and 15 ft), and over 17 m (56 ft) for nitrate treatment.

The pH, redox conditions, and water content of porous media can be adjusted with gas injections. Use of NH_3 to increase porewater pH has been examined for immobilization of inorganic contaminants such as uranium (Zhong et al. 2015) and technetium (in concert with H_2S gas) (Szecsody et al. 2015) in the vadose zone. Gas injections have also been used for desiccation of the vadose zone to reduce contaminant flux to groundwater (Truex et al. 2012). For example, dry N_2 gas has been used in a field demonstration to dry out the vadose zone at the Hanford Site, with the aim of reducing the infiltration of inorganics and radionuclides to groundwater (Truex et al. 2012). N_2 gas was injected into the vadose zone through a screened well (9 to 15 m (30 to 49 ft) bgs), with soil gas extracted from a screened well 12 m (39 ft) away at similar depths. Gas tracer tests and moisture monitoring (up to 15 m (49 ft) away from injection well) showed that gas did preferentially flow (and desiccate) the higher-permeability sand layers. However, adjacent loamy sand layers also showed a decrease in water content. Spatial non-uniform residual water content also affected distribution, hindering gas transport in wetter regions (Truex et al. 2012).

Gaseous amendments can have several advantages over other amendment types, including increased ROI, potential to infiltrate low-permeability zones, and lower cost. Gases may be effective for vadose zone treatment, although when targeting the unsaturated zone, high water contents may limit success. As with liquid reagents, formation heterogeneities may limit gas transport to lower-permeability regions, especially in the saturated zone. Gases can also collect in pockets under horizontal layers of low permeability because these zones can impede the upward flow. However, if reactive gas concentrations can be introduced and sustained at high concentration, then areas that would be bypassed by advective gas flow (i.e., low-permeability zones, high water content regions) may be more accessible over time via gas diffusion (Zhong et al. 2015). Another potential limitation for reactive gases is that some gases have a maximum concentration or total volume that can be safely introduced without creating an explosion or toxicity hazard.

2.2.1 Gaseous Encapsulation

Reactive gases encapsulated within layers of surfactants, as colloidal gas aphrons, have been proposed for use with bioremediation (Jauregi and Varley 1999; Molaei and Waters 2015). For example, microbubbles with ozone encapsulated within a non-ionic Tween-20 surfactant layer have been designed with in situ applications in mind. Initial testing where this ozone bubble suspension was injected into the bottom of a saturated sandy soil batch reactor contaminated with phenanthrene showed potential to pair surfactant soil washing with delivery of ozone for contaminant oxidation (Zhang et al. 2019). Colloidal bubbles are appealing for subsurface applications because they can act as a delivery vehicle and have good kinetic stability to facilitate injectability. The high interfacial area of aphrons also facilitates mass transfer of gases and provides enhanced micellar solubilization, while having water-like flow properties (Molaei and Waters 2015). However, bubble size, which is typically on the order of 10 to 100 µm, may limit distribution in porous media. Roy et al. (1995) found decreased efficiency in naphthalene removal from a sand column using colloidal gas aphron suspensions as opposed to a surfactant solution. Presumably the decrease was due to incompatibility of sizes between the suspension and pore throats which led to clogging of the porous media.

2.3 Solids/Particulates

Solids can provide treatment either through a reaction at the solid surface (e.g., reduction, sorption, etc.) or through dissolution that release solutes for aqueous reactions. Solid amendments provide treatment either through direct contact between amendment and the contaminant or by utilizing dissolution to create a long-term reactive zone downgradient. Relatively soluble solids have the potential to deliver large quantities of active ingredients while also providing an element of controlled, long-term release.

Although laboratory studies have found that solid particles can successful supply active reagents, particle delivery and distribution in the subsurface is problematic. For example, ZVI particles occupied much attention within the remediation community given the high reactivity of these particles in batch studies. However, the very limited mobility of the particles within porous media has been a major road block for implementation in the field (Kocur et al. 2014; O'Carroll et al. 2013). Suspensions or slurries of solid reactive particles also tend to be unstable, limiting the ability to inject and distribute amendments successfully in situ. These suspensions can be so unstable that clogging has occurred even before injection within the well.

Particle transport through the subsurface is governed by straining, attachment (or deposition) and detachment (or remobilization) of particles onto porous media. Particle straining becomes increasingly relevant as the distribution of particle size approaches and overlaps with the pore throat size distribution. If the mean particle size is greater than 0.5% of the mean grain size diameter (d_{50}) then straining will occur (Bradford et al. 2004). As straining and deposition occur, a reduction in porosity and permeability will follow as the particles fully or partially clog the pore throats. This reduction in aquifer permeability will subsequently create increased pressure gradients. Suspension stability also affects particle size through aggregation. Particle attachment and detachment is affected by electrostatic, chemical, and hydrodynamic forces between the particle and soil grain surface (e.g., surface charge, ionic strength, pH, particle density, particle concentration, etc.). In the case of ZVI, magnetic interactions also affect suspension stability and subsurface interactions.

Recently, activated carbon (AC)-based treatments that couple physical adsorption onto AC with amendments to support chemical and/or biological degradation processes (e.g., chemical oxidation, chemical reduction, bioremediation, etc.) have shown promise for in situ treatment (e.g., Fan et al. 2017). There are many available products, such as PlumeStop®[1], Carbon-Iron (Mackenzie et al. 2016), and BOS-100®[2] that pair granular, powdered, or colloidal-sized AC with additional amendments (e.g., microbes, ZVI, nutrients, etc.) to support contaminant degradation.

Overall, particle size is the major factor that controls injection and delivery of solid particulates. Course or granular particles, as well as some micron-sized particles, tend to have limited stability and injectability, whereas nano-size particles show improved mobility. Gravity feed methods, pressure injection, direct push, soil mixing, trenching, pressure pulse technology, jet grouting, and fracturing (both hydraulic and pneumatic) have all been used for subsurface placement of particulates and slurries (McGregor 2018; Comba et al. 2011; ITRC 2005). Delivery by injection tends to be only applicable for smaller particle sizes. Larger-sized solids are more commonly employed as PRBs (Obiri-Nyarko et al. 2014; Phillips et al. 2010), where a reaction or particle dissolution occurs as groundwater flows through the reactive zone. The EPA's "Field Applications of In Situ Remediation Technologies: Permeable Reactive Barrier" document details many field examples (EPA 2002). Larger particle sizes can also be introduced via methods other than in PRBs, although such applications tend to require more aggressive and disruptive techniques like fracturing, grouting, and in situ mixing. Although smaller particulates can travel through porous media more successfully, the porous media grain size distribution, presence of

[1] PlumeStop® Liquid Activated Carbon, Regenesis, San Clemente, CA; https://regenesis.com/en/remediation-products/plumestop-liquid-activated-carbon
[2] BOS-100 ®, Remediation Products, Inc., Golden, CO, https://www.trapandtreat.com/wp-content/uploads/2016/05/RPI-Spec-sheet-BOS-100-f.pdf

subsurface heterogeneities, such as textural interfaces, and particle concentration greatly influence the achievable ROI.

2.3.1 Granular-size Particles

Granular-sized particles are typically in the millimeter size range. These large particles tend to have lower reactivity than smaller-sized counterparts due to surface area effects, but are typically less expensive. These solids have particle sizes much larger than the soil grain pore throats, and thus are commonly physically placed in the subsurface as barriers. Granular ZVI and granulated activated carbon (GAC) are commonly placed in the subsurface via trenching or soil mixing to create PRBs. Direct placement of solids into a borehole (or contained in a filter sock) is one of the simpler introduction methods that can also be completed with larger, granular particles. This method has been used with oxygen releasing compounds for instance (EPA 2017). High-pressure methods such as fracturing have been used to place these larger particles in low-permeability zones.

2.3.2 Micron-sized Particles

Micron-sized particles can be successful transported through some subsurface environments. These particles (~ 1 µm) are smaller than sand pore throats (~ 10 µm) but similar in size to silt and clay pores (Nelson 2009), limiting transport in these materials. Although this size range of particle can be successfully injected in higher-permeability media, other introduction methods can also be used. AC particles can be been applied to low-permeability zones via high-pressure injection methods such as direct push or fracturing to deliver particles (Fan et al. 2017). For example, high-pressure jetting of BOS 100® slurry was used to reach a residual DNAPL plume sitting on a clay layer (Harp 2014).

2.3.3 Nano-sized Particles

Smaller nanoparticles have two benefits over larger particles: increased reactivity due to higher surface area to volume ratios, and improved subsurface mobility. Low-pressure injection methods can deliver nano-sized particles because particles of this size are able to transport with groundwater. Still, these materials have also been delivered by pressure pulse technology and fracturing (Comba et al. 2011). Delivery of solids can be enhanced by using physical mixing or following an injection with a water chase or another slurry to “push” solids away from the injection site.

Nano-scale zero-valent iron (nZVI) is widely used for remediation, with the majority of nZVI delivery completed via injection techniques. Although most applications target the saturated zone, some investigations have reported injections into variably saturated zones (Chowdhury et al. 2015; Wei et al. 2010). Bare or unstabilized nZVI was used in early field-scale testing, although recently most nZVI suspensions are stabilized with a polymer coating to improve the ROI. The smaller-sized particles have been injected into bedrock, coarse-medium sand, silty sand, and stiff clay with sand and gravel deposits (e.g., Chowdhury et al. 2015).

2.3.4 Surface Modified Reactive Particles

To combat the major issues related to delivery of solids, particle surfaces can be modified to improve both the stability and transport behavior of a particle suspension. Modifications provide increased control over the physical and chemical properties of particles (both micro- and nano-sized) for enhanced subsurface distribution. Surfactants, polymers, and polyelectrolytes have all been used to improved stability and transport of particles, most notably ZVI, in the subsurface. Other nanoparticles such as zinc oxide and titanium dioxide have also been stabilized with surface coatings (e.g., Lowry et al. 2012). Irreversible polymer coatings (i.e., covalently bonded or physically adsorbed) provide permanent stabilization. In contrast, surfactant coatings tend to be reversible, which may limit particle transport as the coatings desorb over time.

Stabilized particulates have been injected into many different subsurface environments, including saturated environments ranging from bedrock to stiff clays to sand and gravel (Chowdhury et al. 2105). Many field studies show successful delivery of solids through particle modifications. A review by O'Carroll et al. (2013) found that the field ROI for nZVI injections had been reported from 0.45 to 2 m (1.5 to 6.6 ft), depending on the subsurface formation, injection method, injection rate, the solution formulation, and the method of nZVI stabilization. Beyond nZVI, a suspension of Carbo-Iron colloids was stabilized with carboxymethyl cellulose for improved stability and injectability into a sandy aquifer. The suspension was injected 0.5 m below the groundwater table, where particles were subjected to gravitational and natural groundwater flow in the hope of spreading iron along the same flow paths that TCE contamination had previously followed (Mackenzie et al. 2016).

Stabilized nZVI particulates have been introduced via gravity at field scale, with reported injection rates from 1 to 20 L/min depending on the subsurface geology and hydrogeology (Chowdhury et al. 2015; Wei et al. 2010). A 1 g/L suspension of nZVI stabilized with 0.8% carboxymethyl cellulose was transported at least 1 m within a sandy aquifer in Ontario using gravity-fed injections and a recirculation system to improve nZVI movement (Kocur et al. 2014). Pressure injections have also been used to deliver nZVI at many field sites, although, in some cases, pressure injection has resulted in daylighting (Chowdhury et al. 2015).

Wei et al. (2010) delivered stabilized nZVI via gravity feed to a 15 m (49 ft) screen well, where, due to preferential flow, it appeared much of the material was delivered to the unsaturated zone 3 to 4 m (10 to 13 ft) bgs right above the water table (at 4 m [13 ft] bgs). The injection resulted in decreasing iron concentrations with depth as nZVI was retained on the soil. A field-scale gravity-fed injection of carboxymethyl cellulose stabilized nZVI near the water table in a shallow sandy silty aquifer resulted in a ROI in the saturated zone of approximately 0.6 m (2 ft). Because the injection was completed near the water level, mounding of the water table occurred, which inadvertently placed nZVI in the unsaturated zone (Chowdhury et al. 2015). The nZVI accumulated in the variably saturated zone did not appear to be highly mobile, and thus may have the potential to be placed as a PRB in the unsaturated zone or capillary fringe for remedial applications.

2.3.5 Solid Encapsulation

Another method to improve delivery of solids is through encapsulation of reactive particles in a material (e.g., alginate, paraffin wax, gellan gum, etc.) that enables more successful injection, delivery, and potentially provides targeted delivery or controlled release. Although encapsulation has the potential to be tailored for very specific needs, most encapsulation technology investigations to date have been conducted at the laboratory scale. While encapsulation can improve subsurface mobility, this often comes with the tradeoff of increased particle size. Many encapsulation methods result in the creation of macrocapsule carriers with diameters on the order of millimeters (e.g., Flora et al. 2008; Kang et al. 2004; Rust et al. 2002). These large particles can limit delivery via PRBs or screened wells. Encapsulation of nanoparticles still increases particle diameters. However, the final particle sizes can be on the nano- to micron-scale, allowing for additional introduction methods to be used (e.g., Bezbaruah et al. 2011; Luo et al. 2014).

The materials used for encapsulation can be tailed for specific uses. For example, paraffin wax dissolves only when in contact with hydrophobic phases such as NAPL (Kang et al. 2004) and pH-sensitive polymers only dissolve over a specific pH range (Flora et al. 2008; Rust et al. 2002). Other materials provide non-specific but long-term release through degradable polymers such as alginate (Bezbaruah et al. 2011; Luo et al. 2014). Alginate, the most commonly used encapsulant, has been proposed for encapsulation of ZVI (e.g., Bezbaruah et al. 2011; Luo et al. 2014), zinc oxide nanoparticles (Motshekga et al. 2018), and bacteria (Owsianiak et al. 2010). nZVI particles have recently been incorporated within silica nanospheres for improved subsurface transport and distribution while not decreasing iron reactivity (Lu et al. 2018).

Many amendments have been successfully encapsulated including bacteria, ZVI, zinc oxide, potassium permanganate, and phosphate buffer solids. Encapsulation of bacteria, most commonly in alginate, shows potential for enhancing biostimulation or augmentation efforts by protecting the cells from high levels of toxic contaminants encountered in source zones (Gentry et al. 2004; Moslemy et al. 2002; Rahman et al. 2006). With the aim of encapsulating bacteria, gellan gum microbeads with diameters between 10 to 40 μm were injected into one-dimensional sand columns of varying size fractions. As expected, the microbeads transported the furthest in the coarser sands, and more deposition and hydraulic conductivity loss was experienced in the finer sands (Moslemy et al. 2003). Targeted release of potassium permanganate was attempted by encapsulating the oxidizing particles within paraffin wax. The wax coating is largely insoluble in water, but dissolves when in contact with hydrophobic organics. In theory, the wax matrix protects the reactive ingredients from dissolving in water en route to the targeted NAPL source zone where treatment is aimed (Kang et al. 2004).

KH_2PO_4 powder was encapsulated within a pH-sensitive degradable polymer and tested for use to regulate pH during microbial denitrification. The 1 mm diameter macrocapsules were investigated for use in PRBs or placement within a screened well for long-term release as the polymer degrades in sand column experiments (Rust et al. 2002). Comparable macrocapsules containing $Ca(H_2PO_4)_2$ and K_2HPO_4 housed in degradable polymers were able to release their active ingredients to alter pH conditions (Flora et al. 2008). Similar marocapsules were employed at field scale via an in-well system, where the capsules were held within a SoakEase^{TM} canister. Groundwater flow through the slotted well screen infiltrated the canister and the pH-sensitive capsules slowly degraded to provide treatment. An in-well recirculation system was used to enhance mixing. The pH control via these microcapsules was only successful for a short time, which was attributed to high groundwater flow rates and the small-scale application that limited how many macrocapsules could fit within the well (Aelion et al. 2009).

2.4 Summary of Amendment Types

A summary of amendment types used in subsurface remediation is given in Table 3. The advantages and limitations highlight the site-specific factors and contaminant properties that determine the potential effectiveness of each amendment type. The case studies provided are not an exhaustive list but rather give a representative example (ideally a field case study, when available) of each amendment classification. A development/implementation maturity rating of low, medium, or high has also been provided for each amendment type (Table 1). Foam, gelling liquids for amendment delivery, encapsulated gases, and encapsulated solids are identified as being of low maturity.

The following amendment types are identified as being of **high** maturity:

- Aqueous solutions
- Emulsions
- STF
- Gases
- Solids (granular, micron, nano-sized, and surface modified)
- Gelling liquids for encapsulation

The following amendment types are identified as being of **medium** maturity:

- NAPL
- Surfactants

The following amendment types are identified as being of **low** maturity:

- Foam
- Gelling liquids for amendment delivery
- Encapsulated gases
- Encapsulated solids

Table 3. Overview of Amendment Types.

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
Liquids							
Aqueous Solutions	• Aqueous solutions are injected into the aquifer. • Solids can be dissolved and injected as aqueous solutions	• Gravity-fed injections • Pressure injections • Horizontal wells • Direct push • Hydraulic control • In-well recirculation • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Surface application • Multicomponent pulsed injection • Electokinetic • Density driven	• Microbes • Electron donors and nutrients for biological processes • Chemical oxidants (e.g., sodium permanganate) • Chemical reductants (e.g., ferrous sulfate) • Surfactants • NAPL • Amendments for geochemical manipulation (e.g., pH, etc.)	• Widely used in field applications • General subsurface injection and distribution documents (Kitanidis and McCarty 2012; NAVFAC 2013; Pac et al. 2019; New Jersey Department of Environmental Protection 2017)	• Widely used in field applications for treatment of groundwater • Applicable for most amendment materials (i.e., most amendments can take aqueous/liquid forms)	• Hydrogeologic heterogeneities make amendment distribution difficult • In fast moving groundwaters, only can provide a short contact time between amendment and contaminant • Can mobilize contaminants (esp. from vadose zone) including NAPL • Injected amended water can displace contaminated water thus only providing treatment at the small mixing boundary between the fluids • Density differences can create unsuccessful distribution and mixing • Fouling of injection wells may occur	• **High**. Widely used in field applications for treatment of groundwater

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
						(bio, mineral and gas fouling) • Requires use of dilute amendment solutions (i.e., provide low mass loadings) to limit solute precipitation, increased viscosity and high backpressures • Generally, not ideal for hydraulic conductivities less than 5 ft/day because slow injection rates are required to not fracture the formation (Divine et al. 2018)	
NAPL	• Non-aqueous phase liquids used to sequester organics and/or provide electron donor to support bioremediation activities	• Gravity-fed injections • Pressure injections • Direct push	• Edible oils (can be used as electron donor)	• Neat oils injected into aquifer (Borden 2006) • Applied to the vadose zone where oil formed thin layer on groundwater to intercept, partition and enhance degradation of organics (DOE, 2014; Riha et al. 2012)	• Can supply large quantities of amendment (high NAPL saturations) • LNAPL will float on water table creating a physical barrier between unsaturated and saturated portions of the aquifer • Organic contaminants become sequestered in NAPL	• Difficult to inject large volumes due to high backpressure • High permeability loss has potential to create flow bypass • Limited distribution away from injection site • NAPL can float or sink in the aquifer, potentially spreading contaminants that	• **Medium**. Some field-scale testing for the water table and saturated zones

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
					• Oil can be used to clog aquifer pores to promote flow bypass of a source zone	become sequestered in NAPL • Oil can clog aquifer, making multiple injections difficult	
Emulsions	• Oil-in-water emulsions are introduced typically to improve injectivity and distribution of edible oils • Reactive amendments can be housed within oil droplets	• Gravity-fed injections • Horizontal well • Pressure injections • Direct push • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Surface applications • Jetting technology	• Edible oil (electron donor) • $CaCO_3$/MgO particles • ZVI	• Field examples of source zone treatment or used as a PRB for treatment of groundwater (Borden 2006) • Direct push, pneumatic and hydraulic fracturing with injection, and pressurized pulse technology evaluated for distribution of emulsified zero-valent iron (EZVI) in sandy aquifer (Quinn et al. 2004) • Gravity-fed injections into chlorinated solvent contaminated aquifer (DOE, 2014; Riha et al. 2012)	• More effective method to inject and distribute edible oils • Can pair contaminant sequestration with bioremediation support • Viscous nature of emulsions improves sweeping efficiency • Some emulsions can be shear-thinning which improves delivery to low-permeability zones • Remedial amendments can be delivered via emulsions • Can be used to treat source zones or used to create a PRB	• High permeability loss has potential to create flow bypass • Oil can clog aquifer making multiple injections difficult • Soil type dictates maximum oil retention • A water chase is commonly needed to effectively distribute oil droplets into the aquifer • Potential to solubilize heavy metals or generate gases • Sufficient emulsion kinetic stability is required for successful injections (may require on-site preparation) • Larger-sized emulsion droplets have lower ROI compared to nano-sized droplets	• **High**. Field-use mainly for treatment of the saturated zone

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
						• If housing amendments within emulsion droplets, encapsulation may affect: (i) reactivity and (ii) limit the maximum concentration/mass of amendment that can be delivered	
Foam	• Foams have been used for mobility control, delivery of amendments, and to block highly permeably flow paths	• Pressure injections • Direct push	• Surfactants • Calcium polysulfide • Sodium phosphate • ZVI	• Used foam to divert groundwater flow around DNAPL source zone (Portois et al. 2018) • Laboratory testing using foams to deliver amendments (Zhong et al. 2011)	• Improved lateral distribution as compared to aqueous injections in laboratory tests • Vadose zone transport is less influenced by gravity than liquids • Viscosity enhances sweeping efficiency especially to low-permeability zones • Surfactant foams are widely used for enhanced oil recovery • Foams can clog pores which can be used to divert flow	• High viscosity creates high backpressures that limit injectability • Potential to increase water content of unsaturated zone • Foams can clog pores which can be problematic	• **Low**. Limited field testing for site remediation
Shear-Thinning Fluids	• Non-Newtonian fluids (i.e., fluids that decrease in viscosity with increased shear rate).	• Pressure injections • Horizontal well • Direct push • Hydraulic fracturing injection	• Surfactants • Edible oils • ZVI	• Field injection of micro sized ZVI with a shear-thinning fluid enhanced suspension stability and subsurface	• Viscous nature can enhance delivery to low-permeability zones • Rheological behavior facilitates	• Injections require moderate pressure due to solution viscosity which may limit applicability to	• **High**. Demonstrated success in field applications

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
		• Pneumatic fracturing injection		distribution for TCE source zone treatment (Truex et al. 2011)	subsurface emplacement • Increases contact time between the amendment and pollutants • Can act as a carrier fluid for solid amendments	perched-water zones • Injection pressures can increase over the course of injection • Water table mounding during injection can occur	
Gelling Liquids-Encapsulation	• Solution(s) will solidify over time or under specific in situ conditions. Gelation drastically increases fluid viscosity which can be used to create an impermeable barrier or divert flow	• Pressure injections • Horizontal well • Direct push • Jelling technology	• Acrylamide grout • Silica grout • Waxes • Cement	• Field testing of permeation grouting in heterogeneous gravel quarry using colloidal silica and polysiloxane at 10 to 14 ft bgs in the unsaturated zone (Moridis et al. 1995)	• Grouting is widely used at field scale • Shear-thinning properties are favorable for injection • Delayed gelation allows for encapsulation to target zones away from the injection point	• The temporal increase in viscosity required solutions to be made onsite • Rheological behavior effected by pH, temperature, ionic strength, and minerals • Limited ROI	• **High**. In situ grouting is routinely completed
Gelling Liquids-Amendment Delivery	• Solution(s) will solidify over time or under specific in situ conditions. Gelation drastically increases fluid viscosity which can be used deliver and emplace amendments	• Pressure injections • Horizontal well • Direct push • Jelling technology	• Permanganate • Carbon source (lactate, molasses)	• Column testing on gelation properties and amendment release (Lee et al. 2014; Zhong et al. 2018) • Proof-of-concept experiments where gelation occurs when solution contacts a specific containment (e.g., Cr(VI)) (Pensini et al. 2018)	• Potential for controlled release applications • Shear-thinning properties are favorable for injection • Delayed gelation allows for delivery and emplacement to target zones away from the injection point	• Amendment delivery via suspensions has only been tested in columns • The temporal increase in viscosity required solutions to be made onsite • Rheological behavior effected by pH, temperature, ionic strength, and minerals	• **Low**. Only laboratory testing completed for amendment delivery

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
Surfactants	• Surfactant solutions can aid in contaminant (e.g., organics, heavy metals, radionuclides) dissolution, desorption, mobility and solubilization	• Pressure injection (with extraction)	• Surfactants (ionic, nonionic, biosurfactants, etc.)	• tetrachloroethylene (PCE) saturation reduced from 0.7 to 0.2% at field-scale site (Childs et al. 2006) • Batch solubilization testing of various heavy metals (Torres et al. 2012)	• Enhances treatment of other widely used technologies	• Many surfactants can be toxic and need to be removed from the subsurface after use (i.e., require an active pumping setup) • High cost of surfactants can be prohibitive • Same flow issues as aqueous solutions unless solutions are of higher viscosity	• **Medium**. Limited number of full-scale field operations. Application to metals only tested in the laboratory
Gases							
Gases	• Gases are delivered either below the groundwater table or to the vadose zone to directly remove contaminants, • deliver reactive amendments, or manipulate conditions to facilitate remedial technologies	• Pressure injections • Horizontal wells • Hydraulic control • In-well recirculation • Pneumatic fracturing with injection • Multicomponent pulsed injections	• Air • Steam • N_2 • NH_3 • H_2 • H_2S • Ozone • Propane • Phosphate	• Field-scale desiccation of vadose zone with N_2 (Truex et al. 2012) • Laboratory studies using ammonia gas to immobilize inorganics in the vadose zone via dissolution and re-precipitation (Zhong et al. 2015) • Gaseous electron donor was injected into the vadose zone (Evans et al. 2011)	• Improved vadose zone distribution as compared to liquids • ROI can be enhanced with paired extraction wells	• Low solubility of gases can limit amendment delivery • Geologic heterogeneities can make gas distribution difficult • High water content in the vadose zone can limit treatment of the porewater • Non-uniform water contents effect gas distribution • Gases will flow via pre-existing flow paths (i.e., previously drilled wells, etc.)	• **High**. Used at many field sites

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
						• Explosive risk may dictate maximum concentration and volume of certain reactive gases (can minimize risk by doing pulse injections or limiting the volume of gas injected) • Without paired gas extraction, soil gas may discharge to the ground surface in some cases, creating potential vapor intrusion into existing structures (can be mitigated with gas-impermeable surface barrier)	
Encapsulated Gases	• Gases are encapsulated within layers of surfactants as colloidal gas aphrons	• Pressure injections	• surfactants • ozone	• Colloidal gas aphron suspensions tested as means to flush naphthalene from sand in 1-d column experiments (Roy et al. 1995)	• High interfacial area provides large contact area between contaminant and amendment	• Large size suspensions may not transport well in porous media which can result in clogging • Studies using aphrons to deliver surfactants show mixed results for soil remediation outcomes	• **Low**. Laboratory studies only

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
Solids							
Granular solids	• Millimeter sized solids (e.g., GAC)	• In-well emplacement • Horizontal wells • Pressure injections • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Soil mixing • Trenching • Surface application • Jetting technology	• GAC • ZVI • Apatite	• A Funnel-and-Gate trench system was created using granular iron for reductive dechlorination of chlorinated solvents in a shallow aquifer. Groundwater was funneled into a 3 m wide x 4.5 m long x 6 m deep granular iron gate (Morkin et al. 2000)	• Large size particles can be used to create a PRB • Can deliver large quantities of amendments • Solids with limited solubility may be able to provide long-term treatment	• Particle size are larger than pore throats making non-fracturing injection unfeasible • Can easily clog the aquifer creating flow bypass zones	• **High**. Routinely used to create PRB or mixed into the shallow subsurface
Micron-sized solids	• Solid particles are injected or mixed into the subsurface as aqueous suspensions or as a slurry	• In-well emplacement • Horizontal wells • Pressure injections • Direct push • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Soil mixing • Trenching • Surface application • Jetting technology	• ZVI • $CaCO_3$ • Activated Carbon	• Carbon-Iron (d_{50}=1.3 µm) particles stabilized with carboxymethyl cellulose injected at 6 m bgs for PCE treatment in a shallow, high hydraulic conductivity, sandy saturated aquifer (Mackenzie et al. 2016) • Powdered apatite was mixed into an injectable slurry at a pilot-scale Hanford test site (CHPRC 2010)	• Can deliver large quantities of amendments • Solids with limited solubility can provide long-term treatment	• Particle size limits injectability and distribution of micron-sized solids through an aquifer • Large particles tend to be unstable in suspensions • Interactions with soils dictate ROI (straining, attachment, detachment, etc.) • Can clog the aquifer	• **High**. Routinely used at field-scale

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
Nano-sized solids	• Solid particles are injected or mixed into the subsurface as aqueous suspensions or as a slurry	• In-well emplacement • Horizontal wells • Pressure injections • Direct push • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Soil mixing • Trenching • Surface application • Jetting technology	• nZVI • Ferric iron • Activated Carbon	• nZVI injection into variable saturated media (Wei et al. 2010)	• High amendment reactivity • Small size allows for increased mobility in a range of porous media types • Delivery can be enhanced with a water chase	• Interactions with soils dictate ROI (straining, attachment, detachment, etc.) • ROI is improved with smaller particles. However, clogging can still occur depending on the porous media present • Smaller particles tend to be more stable in suspension which can improve injectability	• **High**. Routinely used at field-scale
Surface modified Solids	• Reactive particles are coated to improve stability of the particle suspension	• In-well emplacement • Horizontal wells • Pressure injections • Direct push • Hydraulic fracturing with injection • Pneumatic fracturing with injection • Soil mixing • Trenching • Surface application • Jetting technology	• ZVI • Carbon-Iron	• Field-scale injection of carbon-iron suspension stabilized with carboxymethyl cellulose for improved injectability into sandy aquifer (Mackenzie et al. 2016)	• Improved suspension stability allows for better injectability and distribution • Can deliver large quantities of amendments • Solids with limited solubility can provide long-term treatment	• Particle size can limit distribution through the aquifer • Some surface modifications are temporary which can limit distribution • Interactions with soils dictate ROI (straining, attachment, detachment, etc.)	• **High**. Most ZVI applications are stabilized through surface modifications

Amendment Type	Description	Access Methods	Amendments delivered	Example Case Studies	Advantages	Limitations	Maturity
Encapsulated Solids	• Solids are housed within a different material to improve injectivity, distribution or to provide controlled release of active ingredients	• In-well emplacement • Trenching • Soil mixing	• ZVI • Phosphate buffer	• Macrocapsules containing phosphate buffer were placed in a Soakease™ canister down a well for passive release (Aelion et al. 2009)	• Can aid in long-term controlled release applications	• Some encapsulation techniques create macrocapsules, which are too large for subsurface injection and instead are limited to use in-well or as PRBs	• **Low**. Limited field testing

3.0 Subsurface Access Methods

Multiple methods can be used to deliver, distribute, and emplace amendments in the subsurface. The applicability of an access method depends on many site-specific factors such as soil characteristics (e.g., soil type, particle size, lithology, fracture potential), contaminant location (e.g., groundwater vs. soil, shallow vs. deep in the subsurface), the amendment being delivered (e.g., gases vs. liquids vs. solids), aboveground constraints (e.g., infrastructure), limitations on applied pressure (e.g., presence of perched water, depth to water table), and more. A brief description of each subsurface access method, along with the associated, advantages, challenges, applicable amendment types, and field examples is provided in this section. That information is also summarized in Table 4.

3.1 Injections

3.1.1 Injection Wells

Injection wells contain a vertically screened section for direct injection of a specific zone. Nested injection wells or a multi-screen well can also be used to simultaneously target different depths within a single well bore. There are generally no depth limitations for installation of wells. Flowing sands or a significant amount of cobbles can make well installation difficult, depending on the drilling method employed. Wells can be placed in shallow groundwater or in the deep subsurface. Drilling methods include continuous flight auger (hollow or solid), sonic, rotary, cable tool, hollow rod, and jetting. Hollow-stem augers and sonic drilling are often used for installation of injection wells (In Situ Remediation Reagents Injection Working Group 2009), but the specific method often depends on administrative or physical conditions that favor specific types of drilling.

3.1.1.1 Horizontal Wells

Horizontal wells can be installed using slant boreholes and directional drilling techniques to place a long well screen along a linear or curved path in the subsurface. The main benefit of horizontal wells is that they provide access to a greater length of formation and to a longer lateral extent than traditional vertical wells. Horizontal wells are typically 20 cm (8 inch) or less in diameter, although wells up to 60 cm (24 inch) in diameter have been installed. Wells over 305 m (1000 ft) long are commonly used, making this technique applicable for groundwater or soil treatment at large or deep sites (Divine et al. 2018; Lubrecht 2012). Additionally, because wells interrogate the subsurface horizontally, there can be less disturbance aboveground (i.e., fewer penetrations), which allows for deployment in areas with aboveground structures.

This type of well has been used for technologies such as soil vapor extraction, air sparging, chemical treatments, and bioremediation (Lubrecht 2012). At a Savannah River Site where TCE contamination was located deep in a layered sand and clay, horizontal injection and extraction wells were used to deliver gaseous carbon (methane), nitrogen (nitrous oxide), and nutrients (triethyl phosphate) to support bioremediation, with ancillary air stripping effects as well (Brockman et al. 1995). Horizontal injection and extraction wells were used, respectively, to bubble gaseous amendments through the saturated zone and the gases were collected in the vadose zone. The reported zone of influence from this well configuration, via indirect evidence of increased microbial activity, was at least 18 m (60 ft) from the injection well, radially.

Beyond using horizontal wells to inject amendments, large-diameter horizontal wells can be drilled parallel to groundwater flow, and subsequently filled with reactive materials, as explored in laboratory and modeling efforts by Divine et al. (2018). The concept here is that the fully-screened wells create new passive preferential flow paths for groundwater to travel, directing flow through a reactive treatment zone. Furthermore, Divine et al. (2018) proposed that this well design could be used to direct groundwater flow around a contaminated zone. In this instance, the well could be filled with uncontaminated high-permeability porous media, as opposed to reactive material.

Well diameter and length can be altered to increase: (i) the ROI of the injected amendments, (ii) residence time in the treatment zone (if filling with solid reactive materials), and/or (iii) the hydraulic capture zone of the well (if using for flow alteration). Although horizontal wells do increase the area over which amendments are delivered relative to traditional vertical wells, distribution of reagents is still dependent on formation hydrogeology. Groundwater pumping can also be used to help focus flow into the horizontal well, and groundwater can be recirculated to complete multiple treatment passes. Although horizontal wells can deliver amendments, or provide passive treatment via flow focusing, there is the possibility that the newly created flow path will provide a fast-flowing conduit, spreading contaminants further from the points of injection. In areas of high heterogeneity, use of horizontal wells for focused flow may be less successful.

3.1.1.2 In-well Emplacement

Active reagents can be placed into open boreholes or wells for the purpose of allowing amendments to dissolve and release into the well bore water and be carried into the aquifer as groundwater flows through the well. In-well emplaced solid amendments (e.g., oxygen release compounds such as powdered magnesium peroxide) will slowly dissolve, providing long-term treatment of groundwater because release rates are controlled by particle dissolution kinetics (EPA 2017).

3.1.1.3 Gravity-fed Injection

Gravity can be used for introduction of amendments via injection wells, but the injection rate is contingent upon permeability, depth of the well screen, and the height of the water column in the well. When injections are gravity-fed, introduction into zones of low hydraulic conductivity or into layers with permeability contrasts can be very difficult. Thus, gravity feed, is only recommended for use in homogenous, high-permeability aquifers. Furthermore, issues of clogging and fouling via in situ precipitation or biological growth can impede amendment injectability because injection flow rates are low and amendments spend an extended time in or near the well.

3.1.1.4 Pressure Injection

Pressure injection involves the active pumping of a fluid into an injection well, in contrast to gravity feed. When injecting liquids, no additional measures are required if the well screen is deep enough to allow an elevated water column within the well bore without overflowing the well. To avoid overflowing the well, a well seal may be used at the well head so that the desired pressure for injection may be attained. However, such approaches may be undesirable because amendments may react within the well bore before they reach the formation. To minimize the volume of injected liquid in the well bore, an inflatable packer can be placed at a suitable location (e.g., just above the well screen) to seal off the well bore and allow the pressurized injection. Well seals and inflatable packers are also relevant to pressurized gas injections.

A concern when using a pressurized injection is the potential for unplanned fracturing of the formation or surfacing of the injected fluid. Higher pressures may be either desired to improve amendment distribution or may be necessary to maintain a particular flow rate as well fouling occurs due to precipitation or biological growth. Design calculations involving fluid properties, soil density, vadose zone thickness, and the depth of the saturated zone above the injection point (In Situ Remediation Reagents Injection Working Group 2009) should be completed to determine a maximum allowable pressure that will avoid fracturing the formation. Surfacing may still occur if there are existing preferential pathways (utility conduits, poor well construction, old nearby wells, etc.). Pressure injections thus involve a feedback of monitoring pressures and surface observations, while adjusting pump/blower speeds to maintain the desired injection flow rate, yet staying under the maximum injection pressure.

3.1.1.5 Direct Push with Injection

Direct Push (DP) methods involve forcing a hollow rod into the subsurface. Well diameters are typically smaller than boreholes at around 2.5 to 3.8 cm (1 to 1.5 inches) (In Situ Remediation Reagents Injection Working Group 2009). DP can reach depths of 15 to 30 m (50 to 100 ft) and potentially deeper, depending on the porous media. DP is not recommended for use with depths greater than 50 m (In Situ Remediation Reagents Injection Working Group 2009). DP is also not appropriate for tight geologic formations such as silts and clays (NAVFAC 2013), materials with a lot of gravels and cobbles, or consolidated media. DP injection rods can be fitted with an expendable point that allows an amendment to be injected out the end of the rod, but this method tends to force reagents downwards and can potentially fill higher-permeability zones and not reach other units. Horizontal injection can be better achieved using a lead rod that contains pressure-activated ports beneath a retractable sleeve (In Situ Remediation Reagents Injection Working Group 2009).

3.2 In-well Operational Approaches for Enhanced Distribution

3.2.1 Hydraulic Control

To enhance in situ mixing and distribution, flow can be modified to facilitate amendment movement to the target area. An injection/extraction well pair (dipole) oriented transverse (perpendicular) to the direction of groundwater flow can be used to increase the ROI by distributing amendments cross gradient to ambient groundwater, with the intent of enhancing mixing in the aquifer (e.g., Suthersan et al. 2009). For example, biostimulation by means of injecting nitrate (as an electron acceptor) and ammonium phosphate (as a key nutrient) using a recirculating dipole well configuration was successful for hydrocarbon remediation in a high-permeability gravel aquifer (Ponsin et al. 2014).

3.2.2 In-well Recirculation

A circulating well (or vertical dipole well) can be used to enhance vertical mixing in an aquifer. Circulating wells contain two screened sections within a single well. Groundwater is extracted through one screen and then injected back into the formation through the other screened interval, typically with amendments added before injection. Issues of heterogeneity can be overcome using this recirculation approach and it can be particularly useful for a vertically extensive source zone (Suthersan et al. 2009). Contaminated groundwater can also be treated within the recirculation well itself (e.g., air stripping, carbon adsorption, or biological treatment). As with many well-based approaches, fouling of the well and near-well formation can diminish the ROI over time (Borden and Cherry 2000). In-well recirculation systems have been effective for treatment of volatiles or increasing groundwater oxygen levels, where water is pulled from the bottom of the well, aerated, and reintroduced at or above the water table (EPA 1998).and may require well rehabilitation efforts for sustained use (Suthersan et al. 2009). In-well recirculation systems have been effective for treatment of volatiles, and for increasing groundwater oxygen levels by extracting water from a lower well screen, aerating the water, and reintroducing the water through a screen at or above the water table (EPA 1998).

3.2.3 Multicomponent Pulsed Injections

Mineral precipitation, biofouling, and/or gas formation at the well or within the aquifer can lead to permeability reductions and decreased ability to inject amendments over time. When multiple chemicals are required for the desired reaction to take place, it is possible to employ alternating, or pulsed, injections of the different amendments. This encourages mixing of the amendments and the associated chemical or biological reactions to take place within the aquifer away from the injection well, as opposed to the reaction starting within the injection well bore. Pulsed injections of acetate and nitrate for in situ bioremediation of carbon tetrachloride have been used at the Hanford Site to create a large biologically active zone (Hooker et al. 1998). For the Hanford Site, acetate and nitrate nutrient injection pulses were offset by two hours as groundwater was recirculated using a dipole well system. Although this approach can reduce fouling near the injection point and improve mixing within the aquifer, it may only be applicable to a limited set of circumstances, such as for treatments requiring multiple solutes or aerating and maintaining an oxidative environment. Many of the same issues that plague aqueous amendment delivery and distribution also apply.

3.2.4 Pressure Pulsing Technology

Pressure pulsing technology (PPT) injects an aqueous solution via a quick releases of a pressured solution (Gale et al. 2015). In theory, pressure perturbations create a sudden increase in fluid pressure (for fluids with low compressibility), momentarily dilating porous media pores in response to the pressure wave, thereby enhancing movement of the injected solution. Spanos and Davidson provide laboratory and field case-study examples where PPT has been used, citing positive outcomes of PPT over conventional injection methods. One example outlines improved tracer distribution when using PPT, both up and down gradient from the injection point, as compared to a conventional pressure injection for a low-permeability silt-clay site. Other pilot-scale testing using PPT, in this case for EZVI distribution, resulted in a 1 m (3.5 ft) ROI. However, investigators noted this technique is vulnerable to short circuiting due to preferential flow paths. Such short circuiting was observed when injected EZVI came up around the well liner after two injections, causing subsequent injections to be terminated (Quinn et al. 2004).

3.3 Physical Displacement Approaches

3.3.1 Jetting Technology

Jetting involves using high pressures to inject amendments through the subsurface, typically via a small diameter drill rod placed at the desired subsurface depth. The high pressures facilitate mixing of amendments into the soil because the formation is disturbed and physically mixed. However, the limited ROI of this technique makes it only applicable for targeted treatment or for locations that larger drill rigs cannot access (NAVFAC 2019). Jet grouting has been used to create subsurface barriers where a grout mixture is injected at very high pressure and velocity into the pore spaces of the formation (EPA 1999). Also, ZVI slurry has been introduced via jetting (NAVFAC 2013). In situ grouting (via jet grouting and permeation grouting) has been evaluated as a potential remediation technique that may be applicable for focused locations in the deep vadose zone at the Hanford Site (Truex et al. 2011b).

3.3.2 Formation Fracturing

Fracturing involves injecting a liquid (hydraulic) or gas (pneumatic) into the subsurface at a pressure that surpasses the cohesive strength of the formation or at an injection rate that exceeds subsurface permeability. In response, a new flow path, or facture, is created (or enhanced) through which the injectate can travel. The properties of the porous media determine the amount of pressure required to facture. Clays, for example, tend to have higher cohesive strength than sands (In Situ Remediation Reagents Injection Working Group 2009). Fracturing with injection can be accomplished using DP paired with a high-pressure pump system and is well suited for either unconsolidated or consolidated media. Fracturing can also be completed from open boreholes. Many remediation technologies have used fracturing (e.g., bioremediation, soil vapor extraction, ISCO, etc.), particularly for treatment of low-permeability soils and bedrock (ITRC 2005). The inability to control fracturing patterns limits the treatment effectiveness. Fracturing patterns are hard to predict, and surface deflections are common which may be problematic if aboveground structures are present. Additionally, fracturing is generally not applied at depths greater than 30 m (100 ft) (EPA 2019).

Convention wisdom submits that hydraulic fracturing produces a larger ROI and the propped fractures allow for multiple injections to be completed, whereas pneumatic fracturing produces a smaller, albeit denser, fracture network. Recently, an ESTCP report (ER-201430 2019) tested these assumptions by directly comparing the performance of hydraulic and pneumatic fracturing to facilitate amendment delivery to low permeability areas at the Lake City Army Ammunition Plant Site. Unfortunately, the limitations of pneumatic fracturing were exhibited at the test site, where the pneumatic approach resulted in daylighting, and thus, a direct comparison between the methods could not be completed. Instead, a hybrid pneumatic approach was used, where fracture initiation was performed pneumatically but amendment delivery was completed hydraulically. Overall, the ESTCP report found that hydraulic permeability enhancement increased injection rates and volumes by orders of magnitude over conventional injection methods.

3.3.2.1 Hydraulic Fracturing

Many injectable fluids can be used to initiate and then sustain fractures. A viscous biodegradable slurry (e.g., guar gum) containing sand is commonly used to create and fill fractures. Over time, the guar gel degrades, leaving sand to support the integrity of the facture while allowing for fluids to more easily penetrate through the newly created fracture network (ITRC 2005). Slurries containing solid amendments can also be used as the fracturing fluid itself.

Hydraulic fracturing was tested to enhance delivery of EZVI at NASA's Launch Complex 34 on Cape Canaveral Air Force Station. A cross-linked guar gel was first injected into a sandy aquifer to open and propagate the fracture network before injection of EZVI, but with limited success (Quinn et al. 2004). At the F.E. Warren Air Force Base (former Atlas "E" Missile Site No. 12) in Windsor, Colorado, a perched-water zone containing TCE was targeted for treatment in a pilot-scale setup using hydraulic fracturing to deliver a mixture of granular ZVI and organic carbon in a biodegradable gel carrier to the sandstone formation (Swift et al. 2012). Fractures were induced from boreholes placed 18.3 m (60 ft) apart in the source zone, where 1.2 m (4 ft) intervals were isolated with straddle packers within 11 – 20 m (35 – 65 ft) bgs of the targeted zone. The factures covered the entire saturated thickness of the formation, with an average fracture propagation radius of 24 m (79 ft) vertically, 20 m (65 ft) horizontally, and 0.85 cm (1/3 inch) in aperture. The delivered amendments were able to successfully reduce TCE concentrations by 90%. Another field study compared DP, hydraulic and pneumatic fracturing to deliver a tracer mixture to a low-permeability basal clay till (Christiansen et al. 2010). Hydraulic fracturing was completed using a sand-guar mixture that produced elliptical, asymmetrical fractures with an ROI of 3.5 m (11.5 ft) at 3 m (10 ft) bgs. Due to the large aperture size of the fractures, the authors concluded that hydraulic fracturing may be a successful way to create a PRB in low-permeability formations.

3.3.2.2 Pneumatic Fracturing

Gases can be forced into a formation via controlled pulses of high-pressure gas to fracture the media, followed by injection of the desired reagent. However, with pneumatic fracturing, no proppant is used to sustain fractures, and so is only successful for formations where created fractures will remain open without assistance. Compressed air can be used where an oxidative environment is desired. For remediation technologies requiring a reducing environment, nitrogen gas is used to prevent addition of oxygen to the subsurface (In Situ Remediation Reagents Injection Working Group 2009). Amendment delivery via pneumatic fracturing has been applied to sands, silts, silty clays, and highly weathered fractured bedrock to depths of 49 m (160 ft) (In Situ Remediation Reagents Injection Working Group, 2009). Pneumatic fractures tend to be of smaller aperture than hydraulic fractures (Christiansen et al. 2010). Pneumatic fracturing was tested for EZVI delivery at NASA's Launch Complex 34 test site. N_2 gas was used to fluidize the subsurface and generate fractures, followed by EZVI injection. This method resulted in a 1.2 to 1.4 m (4 to 4.5 ft) ROI in the unconsolidated sandy sediments, providing higher ZVI concentrations than desired in the target zone (Quinn et al. 2004). The previously mentioned Christiansen et al. (2010) study found that pneumatic fracturing with nitrogen gas produced a fracture network with an ROI of less than 2 m (6.6 ft).

3.3.3 Soil Mixing

Soil mixing can be used for in situ barrier formation and amendment delivery and distribution. Physical mixing of the subsurface environment can also be used to create a more homogenous subsurface by altering existing preferential pathways. In situ barrier formation (or deep soil mixing) involves mixing reagents into the soil to produce a solid barrier. A column of soil and reagent is created using a special auger with a mixing shaft that simultaneously drills and injects barrier amendments. Bentonite, cement, lime, and other binders are commonly used in barrier formation for containment and contaminant stabilization efforts. The deep soil mixing technique can produce walls up to 30 m (100 ft) deep. Typically, the approach is only applied to depths of 18 m (60 ft) or less due to cost constraints (NAVFAC 2019), making it only applicable for shallow contamination zones. Soil mixing is commonly done either via large-diameter augers (up to 3 m in diameter) that are mounted to conventional drilling rigs or using rotary drum blenders that are mounted at the end of an excavator. Large diameters augers can mix well at depth but are not efficient at treating large areas. Conversely, blenders are good at integrating larger areas but not suited for treatment at depth (Markesic et al. 2018).

In situ soil mixing for amendment delivery has been used to deliver a wide range of amendments, such as reagents to promote biodegradation (nutrients, microbes, oxygen releasing compounds), chemical oxidants, and reductants. Amendments can be distributed for source zone treatment or placed to create PRBs. It is common practice to mix solids with water to create slurries, although introduction of solids is also done (mainly with permanganate additions). Crane-mounted mixers or drill rigs with a special drill bit have been used for mixing activities, with drill bits ranging from 0.9 to over 3.7 m (3 to 12 ft) in diameter, reaching depths of 30 m (100 ft) or more (NAVFAC 2019). Deployment of calcium polysulphide (CaS_x) via soil mixing was investigated for the treatment of hexavalent chromium (Cr(VI)) contaminated soils and groundwater in Glasgow (CL:AIRE 2013). Cr(VI) was successfully reduced in both soil and groundwater, but mixing decreased soil stability.

The main advantage of soil mixing is that it can be applied to many types of soils (sands, silts, clays); though large cobbles are problematic (NAVFAC 2019; EPA 1999). The in situ nature of this technique is beneficial because soil does not need to be excavated, thereby decreasing disposal costs. However, as with any mixing method, the major concerns include altering the subsurface and groundwater flow conditions, as well as potentially spreading contaminants. Mixing efforts modify soil parameters such as density, compressibility, permeability, void ratio, and moisture content, which may benefit, or inhibit, remedial efforts. Additionally, mixing may make soils (especially low-permeability soils like clays) unstable for an extended period of time (Markesic et al. 2018).

3.3.4 Trenching

Trenching can be used to create a PRB by removing soil replacing it with reactive amendments. This passive treatment can be successful for shallow zones. However, trenching has limited applicability when contaminants are deeper in the subsurface due to equipment limitations and formation stability issues. In addition to depth limitations, constraints include requirement of a large working area, the need to dispose of excavated soil, and limited ability to treat large soil volumes. Furthermore, trenching is not feasible for very hard formations or fractured bedrock.

Trenching commonly relies on groundwater flowing through the reactive trench zone. This method can be particularly effective for low-permeability sites, as long as the PRB additive mixture has a higher permeability than the surrounding formation so as to promote flow through the created reactive zone (He and Su 2015). Detailed PRB guidance is available to describe trench construction techniques, site considerations, and potential costing information (Gavaskar et al. 2000).

Large size granular ZVI (particle size $> 200\ \mu m$) is commonly placed in a PRB via trenching because the large particle size is unsuitable for injection (NAVFAC 2013). Other zero-valent metals, granular iron with amendments, GAC, bentonite slurries, mulch, and vegetable oil have all been used for PRB creation via trenching (Gavaskar et al. 2000). The EPA (EPA 1999) lists field-scale applications of PRBs (both pilot and full-scale examples), many of which include barrier creation via trenching.

3.4 Other Approaches

3.4.1 Electrokinetics

Electrokinetics (EK) involves applying a low-voltage direct current electric field via placement of a positively charged anode and a negatively charged cathode in the subsurface. Migration of contaminants then occurs via electroosmosis (i.e., fluid movement of either soil moisture or groundwater through pores), electromigration (i.e., ion transport to the electrode of opposite charge), and/or electrophoresis (i.e., charged, dissolved, or colloid particle movement from the electric field). Once pollutants have transported to the electrodes, they can be removed by pumping, precipitation, electroplating, or with ion-exchange resins (Virkutyte et al. 2002).

This rather non-invasive EK method has been used for remediation of organics, inorganics, and heavy metals. However, contaminants need to be either dissolved or attached to mobile particulates. Charged contaminants (e.g., metal cations, nitrates, etc.) are transported mainly by electromigration, whereas non-ionizable compounds (e.g., organics) rely on electroosmosis where the contaminant comes along with the water as it migrates to the cathode. EK has been shown to enhance contaminant desorption, and contaminant mobility can be further improved via surfactant additions (Gill et al. 2014). EK can also enhance in situ biodegradation by increasing contaminant bioavailability.

The strength of EK is that electromigration and electrophoresis processes are independent of hydraulic conductivity, and thus contaminants can be mobilized from areas that are not reachable via advective water flow. For low hydraulic conductivity or fine-grained soils, especially clays, EK is more successful than relying on a natural or induced hydraulic gradient (Gill et al. 2014). Although EK is well suited for low-permeability formations, and has potential application for the unsaturated zone, implementation at field scale, particularly at depth, may be problematic (Dresel et al. 2008). This technique lends itself to be paired with enhancement techniques that either solubilize contaminants to more mobile states or control soil pH to facilitate electrochemical processes. Surfactants, chelating agents, complexing agents, oxidizing/reducing agents, and cation solutions have all been used as enhancement agents (Yeung and Gu 2011).

The transport of ions in the vadose zone via EK has been found to be highly dependent on the spatial water content distribution, with preferential transport through heterogenous layers having higher soil moisture content and higher electrical conductivity. A six-month field deployment in a layered, heterogeneous, unsaturated zone found that EK transport was proportional to a power function of the effective moisture content (Mattson et al. 2002).

EK has been used to deliver amendments, as opposed to removing contaminants directly. Microbial degradation has been facilitated using EK to deliver and distribute nutrients (e.g., phosphate) and electron acceptor/donor (e.g., nitrate, lactate), as well as delivering bacteria to less hydraulically accessible target zones, which frequently hold significant contaminant mass (e.g., Gill et al. 2014). This technique is particularly intriguing for delivery of amendments to low-permeability regions because delivery rates via EK are greater than for simple diffusion.

Because H+ ions are generated at the anode and travel to the cathode during EK, an acidic water front is inherently developed and acidification of the subsurface is common. This can be exploited for remediation of metals because most metals are more soluble at lower pH. However, low pH conditions can have many adverse effects, such as stalling microbial activity for bioremediation. An additional limitation is that reactive transport processes such as sorption and precipitation continue to occur while contaminants migrate through the subsurface, which can result in significant retardation of contaminant transport. Furthermore, issues related to long-term efficiency may be problematic. Over time, the gas generated from electrolytic dissociation will accumulate at the electrode surface, decreasing the overall effectiveness (Virkutyte et al. 2002). Major limitations of EK include that contaminant concentrations must be above the sorption capacity of the soil, a limited ROI requires that electrodes to be placed relatively close together, and creation of a pH front in the subsurface (Alshawabkeh 2009).

To counteract some of the limitations and enhance remediation, additives can be used, primarily to enhance contaminant desorption and subsurface mobility. Also, many variations on EK have been developed. For example, the Lasagna™ process layers treatment zones between electrodes. In this configuration, the polarity of the electrodes can be switched, allowing for multiple passes through the treatment zone, as well as counteracting any developed pH gradient. A small field-scale test of this Lasagna process showed promise for remediation of TCE-contaminated soils with a moisture content of 15 to 18% in a sandy clayey loam. However, large changes in pH and temperature were still induced (Ho et al. 1999).

3.4.2 Density-Driven Delivery

In some cases, density differences between amended solutions and groundwater can be harnessed to support amendment delivery and mixing. Collection of contaminants on and within low-permeability materials is common, especially at DNAPL sites. The concept with density-driven delivery is that injection of a solution denser than groundwater could infiltrate the subsurface along a path similar to that taken by the original contamination. The injected solution could then settle and spread on top of an aquitard layer (Kitanidis and McCarty 2012), just like the contaminant DNAPL. Potassium permanganate (KM_nO_4) was delivered at a field site via density-driven flow, with amendments being transported through the sandy aquifer to the underlying confining layer holding the TCE-DNAPL source zone (Henderson et al. 2009).

3.4.3 Surface Application

Infiltration ponds, infiltration galleries, and sprinkler systems have all been used to deliver amendments to the subsurface environment. Although infiltration basins, ponds, and galleries are typically used to recharge aquifers, amendments can also be added though a surface application. Infiltration will follow the most permeable flow paths, and if there are strong preferential flow paths through the subsurface, limited distribution through the vadose zone. Because application can be completed over a large surface area, it can be effective for treating large amounts of soil and groundwater. If contamination is present in the vadose zone, a major concern is the potential to spread contamination to groundwater. However, soil flushing of the vadose zone (which can be done via infiltration techniques) uses this exact process for cleanup (but includes capture of the contaminated groundwater) (e.g., Truex et al. 2010; DOE/RL 2018).

Surface applications were used to support a 4.5-year field-scale in situ bioremediation operation where KNO_3, $NH_4H_2PO_4$, and oxygen were pumped into groundwater before it was returned to the aquifer via an infiltration gallery (Hunkeler et al. 2002). A sprinkler system was used to infiltrate an amendment nitrate solution for bioremediation of shallow sandy aquifer where the water table was located 1 to 1.2 m (3 to 4 ft) bgs (Hutchins et al. 1998). Liquid infiltration alone provided a reduction in contaminant concentrations due to soil washing. However, surface vegetation had to be removed because it consumed the applied nitrate, limiting subsurface distribution. Surface application of a soybean oil and peat moss mixture to promote perchlorate biodegradation in the vadose zone has been proposed, though only laboratory microcosm testing has been completed (ESTCP/ER-200435 2011). The oil/peat moss blend would be mixed into the surface soils and watered to promote distribution through the vadose zone; however, only laboratory microcosm testing has been completed (Diebold 2011). These investigators also suggested introduction of dilute emulsified vegetable oil via infiltration galleries to enhance unsaturated zone bioremediation by percolating electron donor through the formation (Hutchins et al. 1998).

3.5 Summary of Subsurface Access and Amendment Emplacement Methods

A summary of subsurface access and amendment emplacement methods are given in Table 4. The advantages, limitations, and designated maturity of the amendment introduction methods are also provided. The applicable amendment types (liquid, gas, solid) for each access method are also given. The case studies provided are not an exhaustive list, but rather give a representative example of each amendment introduction and emplacement approach.

Additional information can be found in the Naval Facilities Engineering Command technical report entitled "Best Practice for Injection and Distribution of Amendments," which details liquid and solid phase injection methods, along with site-specific considerations that determine overall effectiveness (NAVFAC 2013). The NAVFAC document focuses on pressure injections, DP injections, fixed vertical and horizontal wells, recirculation well systems, and pneumatic and hydraulic fracturing. Specific design, installation, and operational considerations are discussed for each method.

The following access and emplacement methods are considered **high** maturity:

- Injection Wells
- Horizontal Wells
- In-well Emplacement
- Gravity-fed Injections
- Pressure Injections
- Direct push Injections
- Hydraulic Control
- Multicomponent Pulsed Injection
- Jetting Technology
- In-well Recirculation
- Hydraulic Fracturing with Injection
- Pneumatic Fracturing with Injection
- Soil Mixing
- Trenching
- Surface Application

The following access and emplacement methods are considered **medium** maturity:

- Electrokinetics
- Density Driven

The following access and emplacement methods are considered **low** maturity:

- Pressure Pulse Technology

Table 4. Subsurface Access and Amendment Emplacement Techniques.

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
Injections						
Injection Wells	• Vertical or horizontal wells are screened for subsurface introduction of amendments to a target zone	• Gases • Liquids • Solids or suspensions	• CaSx injected for Cr(VI) treatment (CL:AIRE 2013)	• Well established technique	• Difficult for low hydraulic conductivity zones • Limited success for highly heterogeneous sites • Layered heterogeneity can be problematic • Clogging or fouling (biological or mineral) can occur • May require manipulation of flow field to successfully deliver amendments, especially for large treatment areas	**High**. Routinely used in field applications.
Horizontal Wells	Long, typically fully-screened wells are drilled in linearly or along a curve path in the subsurface	• Gases • Liquids • Solids or suspensions	• Proposed to use horizontal wells for flow focusing for increased contact time with reactive solid material placed within the well (Divine et al. 2018) • Field demonstration using horizontal wells to deliver methane, air, nitrous oxide, and triethyl phosphate gaseous	• Provides a larger contact area than vertically placed wells • Can be paired with any solid reactive material to create a PRB • Flow focusing can be used to bypass contaminated zones • Can treat large zones and create long residence times in	• Can result in spreading of contaminants especially once reactive material is exhausted • Treatment efficiency is diminished by heterogeneities, formation layering, and hydraulic stagnation zones • Reactive materials can clog over time	**High**. Widely used in field applications

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
			reagents 49 m (160 ft) bgs to the saturated zone (Brockman et al. 1995)	the created treatment zone • May be applicable to homogenous low-permeability zones • Minimal aboveground disturbance • Can be used to target zones under existing structures		
In-well Emplacement	• A passive delivery technique where solids are placed down a borehole and allowed to diffuse into the flowing groundwater	• Solids	• Oxygen release compound socks (0.3 m tall x 0.15 m diameter) were placed vertically in a barrier 0.3 m bgs (Schmidtke et al. 1999) • Macrocapsules containing phosphate buffer were placed in a Soakease™ canister down a well for passive release (Aelion et al. 2009)	• Passive treatment • Typically, low cost • Can use existing boreholes	• Diffusion limited • Only suited for highly permeable formations • Only applicable for amendments that do not require additional pressure beyond hydraulic head to induce flow into the formation • Fouling can occur at the well screen or near the injection site • Reliant on existing flow paths for delivery	• **High**. Widely used in field applications.
Gravity-fed	• Amendments are placed in open boreholes where gravity introduces amendments to the aquifer	• Liquids • Solids or suspensions	• CaSx introduced via gravity for Cr(VI) treatment (CL:AIRE 2013)	• Simple technique that can be done using existing boreholes	• Only suited for highly permeable formations • Only applicable for amendments that do not require additional pressure beyond hydraulic head to	• **High**. Widely used in field applications

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
					induce flow into the formation • Fouling can occur at the well screen or near the injection site • Reliant on existing flow paths for delivery	
Pressure Injection	• Pressure is used to inject amendments into formation	• Gases • Liquids • Solids or suspensions	• Pilot-scale injections of Carbo-Iron to in a highly permeable sandy aquifer (Mackenzie et al. 2016) • nZVI was injected into a variably saturated soil (Chowdhury et al. 2015)	• Method can deliver amendments to lower-permeability regions and extend ROI	• Maximum injection flow rate may limit delivery and distribution • Daylighting of injected amendments can occur	• **High**. Routinely used in field applications.
Direct Push with Injection	• Small diameter hollow rods are forced into the subsurface. Can be paired with expendable tip or horizontal injection ports	• Gases • Liquids • Solids or suspensions	• EZVI into sandy aquifer (Quinn et al. 2004) • CaSx injected for Cr(VI) treatment (CL:AIRE 2013) • EVO to create pilot-scale bio-barrier (Borden, 2007)	• Ideal for shallow, thin target zones or for delivery of a small volume of amendment	• Limited on depth of wells • Limited ROI • Daylighting of injected amendments can occur	• **High**. Routinely used in field applications
In-well Operational Approaches						
Hydraulic Control	• Series of injection and extraction wells are used to modify ambient groundwater flow	• Gases • Liquids • Solids or suspensions	• CaSx injected and distributed for Cr(VI) treatment (CL:AIRE 2013) • Pilot scale use of injection-extraction wells. Wells placed	• Increases vertical and horizontal mixing within the aquifer	• Flow is still dominated by preferential flow paths	• **High**. Widely used in field applications

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
			in a square grid to deliver and distribute sodium permanganate (Lowe et al. 2002)			
In-well Recirculation	• Well is screened in two vertical locations where injection and extraction are completed within one well	• Gases • Liquids • Solids or suspensions	• Pilot testing of in-well air stripping via in-well recirculation wells for treatment of chlorinated solvent plumes (Ryan et al. 2000)	• Promotes vertical mixing • Can overcome some aquifer heterogeneities	• Susceptible to fouling and clogging • May have limited ROI	• **Medium**. Used in some field applications
Multicomponent Pulsed Injections	• Solute injections are spaced out in time out to promote mixing within the aquifer, away from the injection point	• Gases • Liquids	• Pulsed injections of acetate and nitrate for bioremediation (Franzen et al. 1997)	• Decreases potential of clogging at the injection well • Facilitates creation of a larger treatment zone	• Only applicable when multiple amendments are needed	• **Medium**. Uses well established methods, but has had limited number of applications
Pressure Pulsing Technology	• Injects aqueous solution via quick released of pressured solution to momentarily dilate pores for enhanced delivery and distribution	• Liquids • Suspensions	• EZVI into sandy aquifer (Quinn et al. 2004)	• Dilation of pore throats should increase ROI without fracturing media	• Vulnerable to short circuiting through preferential flow paths • Can cause clogging near injection point	• **Low**. Limited field testing
Physical Displacement Approaches						
Jetting Technology	• Amendments are injected at high pressures into the pore spaces which also mix amendments into the formation	• Solids or suspensions	• ZVI slurry introduced via jetting (NAVFAC 2013)	• Useful for very targeted delivery • Applicable for low permeability	• Limited ROI (especially in the unsaturated zone) • High cost (due to limited ROI) • Low applicability for zones where limited pressured can be	• **High**. Widely used, in particular for in situ grouting applications.

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
					applied (e.g., Perched-water zone)	
Hydraulic Fracturing with Injection	• Liquids are pressure injected into a formation creating new (temporary or permanent) flow pathways. Amendments can be then delivered to the newly hydraulically accessible zones. Proppants (e.g., sands) are used to keep fractures open	• Liquids • Solids or suspensions	• EZVI into sandy aquifer (Quinn et al. 2004) • ZVI-GAC emplaced in low-permeability media via hydraulic fracturing (Swift et al. 2012)	• Well suited for low-permeability zones, bedrock, and consolidated media • Not well suited for highly permeable porous media • Applicable for unsaturated and saturated zones • Liquids used for fracturing can house remedial amendments	• Produced fractures are unpredictable • Potential to damage existing structures or sensitive areas • Surface deflections can limit where fracturing can be used • Potential for contamination to spread via newly created flow paths	• **High**. Widely used in field applications
Pneumatic Fracturing with Injection	• Gases are used to create new (temporary or permanent) flow pathways. Amendments can be then delivered to the newly hydraulically accessible zones	• Gases • Liquids • Solids or suspensions	• EZVI into sandy aquifer (Quinn et al. 2004) • Pilot-scale demonstration using pneumatic fracturing to enhance subsurface airflow to enhance in situ bioremediation in low-permeability soil (Venkatraman et al. 1998)	• Well suited for bedrock and consolidated media • Applicable for unsaturated and saturated zones	• Less control over fracture patterns than with hydraulic fracturing • Produced fractures are unpredictable • Potential to damage existing structures or sensitive areas • Surface deflections can limit where fracturing can be used • Potential for contamination to spread via newly created flow paths • Only applicable for use in formations where fractures will	• **High**. Widely used in field applications

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
					remain open without support of a proppant (i.e., not applicable for swelling clays and low strength porous media).	
Soil Mixing	• Soil is mechanically mixed using soil blenders or large augers to create in situ barriers, deliver amendments or homogenize the subsurface	• Liquids • Solids or suspensions	• CaSx mixed into soils for Cr(VI) treatment (CL:AIRE 2013)	• Can be used in all soil types • Can place amendments throughout the subsurface or in a PRB • Homogenizes subsurface to reduce preferential flow	• Mixing at significant depths is not feasible or practical • Mixing over large areas can be impractical • Large buried objections (e.g., cobbles and rocks) impede mixing • Mixing can further spread contaminants • Can alter subsurface conditions and groundwater flow • Homogenizing subsurface can alter soil properties and groundwater flow • Mixing can make soils unstable	• High. Routinely used in field applications
Trenching	• Soil is dug up and replaced with reactive solid materials	• Solids or suspensions	• Large size granular ZVI has been placed for remediation via trenching (NAVFAC 2013)	• Large quantities of amendments can be added	• Only applicable for shallow treatment	• **High**. Routinely used in field applications
Other Approaches						
Electokinetics	• An electric field is applied to soil increasing	• Liquids	• Lasagna method for heterogeneous or	• Can remove contaminants from zones that are	• Field deployment, particularly at depth and over a large area	• **Medium**. Some field testing.

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
	contaminant (or amendment) mobility via electroosmosis, electromigration, and/or electrophoresis		low-permeability soils (Ho et al. 1999) • Unsaturated acetate transport (Mattson et al. 2002) • Transport of negativity charged amendments is improved through heterogeneous and low-permeability regions (Gent et al. 2001)	hydraulically unreachable (e.g., low-permeability lenses) • Can distribute amendments (e.g., aqueous solutions, microbes) • Not contaminant specific (i.e., would simultaneously migrate organics, inorganics, and heavy metals) • Can be paired with other technologies such as soil flushing and bioremediation • Applicable for remediation of heavy metals from unsaturated soils	may be problematic (limited ROI) • Required relatively close spacing of electrodes • Acidification of the subsurface is common • Reactive transport processes (i.e., sorption/desorption, precipitation/dissolution) still dictate contaminant migration rates • Contaminant must be in a mobile state (in aqueous phase or attached to mobile particulates) • Metal objects in the subsurface can influence the applied current • May required introduction of carrier fluid which may be problematic for vadose zone treatment • Precipitation at cathode can decrease efficiency • May requires collected contamination to be	

Technique	Description	Applicable Amendment Types	Example Case Studies	Advantages	Limitations	Maturity
					retrieved and disposed of	
Density Driven	• Solutions denser than groundwater will sink through aquifer until reaching low-permeability lenses, ideally co-locating source zones with amendments	• Liquids • Suspensions	• Potassium permanganate delivered utilizing density contrasts to treat DNAPL source zone on lower-permeability lens (Henderson et al. 2009)	• Potential to target contamination sitting on a low-permeability lens/layer	• Density contrasts can limit mixing inhibiting uniform distribution throughout the aquifer (i.e., amendment solution floating or sinking in comparison to groundwater)	• **Medium**. Some field applications
Surface Application	• Surface application and infiltration uses sprinklers, drip irrigation, trenches, ponding, and shallow basins to introduce reagent to the subsurface	• Liquids • Solids or suspensions	• Long-term field-scale application of KNO_3, $NH_4H_2PO_4$ and oxygen via an infiltration gallery (Hunkeler et al. 2002)	• Straightforward method	• Not applicable for low-permeability soils • Infiltration can spread contaminants from vadose zone to groundwater • Distribution limited to preferential flow paths • Unwanted lateral spreading of amendments or contaminants can occur in the vadose zone	• **High**. Routinely used in field applications.

4.0 Target Zones for Amendment Delivery and Applicability in the Hanford Context

In addition to the factors related to specific amendments and access/emplacement methods discussed above, applicability of delivery mechanisms for specific subsurface target zones is also a key consideration. Amendment delivery to five types of subsurface zones, each with their own challenges, is discussed in the subsections below, both in general terms and relative to the context of Hanford Central Plateau applications. That Hanford context is first described to set the stage for determining relevant amendment delivery approaches. At the end of this section, after description and discussion of the target zones, the applicability of amendments by target zone, and the associated relevant access/emplacement methods are compiled in a Table 5.

4.1 Hanford Site

The DOE Hanford Site is a 1,516 km^2 (586 mi^2) facility located in Washington State along the Columbia River. Historical waste disposal practices included discharge of waste streams to surface structures (e.g., cribs, trenches) and chemical spills and leaks into the soil. In certain areas of the Hanford Site, these historical events have resulted in contamination in the vadose (unsaturated) zone of the subsurface, with some contaminants infiltrating into the water table aquifer. Much of the liquid waste discharged into the vadose zone occurred in the Central Plateau, a 190 km^2 (75 mi^2) area that includes approximately 800 waste sites. The Central Plateau deep vadose zone begins at a depth of approximately 15 m (50 ft) bgs and extends to the top of the groundwater at about 76 m (250 ft) bgs. Major lithologic units in the subsurface include the Hanford Unit (a permeable sandy/sandy gravel material), the Cold Creek Unit (which includes low-permeability fine grained and cementitious material), and the Ringold E Unit (relatively permeable sandy material). A more detailed description of the geology and lithology of the Hanford Site can be found in the DOE/RL-2017-58, *Technology Evaluation and Treatability Studies Assessment for the Hanford Central Plateau Deep Vadose Zone* report.

A range of contaminants (radionuclides, non-radioactive metals, inorganics, and organics), with many co-located within a specific target zone exist at the Hanford Site. In the Central Plateau, some of the contaminants have infiltrated to the deep vadose zone, where direct exposure pathways are not of concern, but where remediation may be required to protect groundwater. In general, the unsaturated zone (within both high and low-permeability zones) can be contaminated with uranium, technetium-99, iodine-129, hexavalent chromium, nitrate, strontium-90, cyanide, carbon-14, and organics. Specific contaminants of concern that may include these or other contaminants are identified for each operable unit and waste site

One feature at the Hanford Site that is rather unique is the existence of a perched-water zone. A perched aquifer exists underneath the B-Complex in the 200-DV-1 OU in the Central Plateau. The conceptual model developed for this site is of a 1.8 to 3.4 m (5.9 to 11.2 ft) thick perched-water layer atop a low-permeability silt layer and located 69 m (225 ft) bgs (about 5 m [15 ft] above the regional water table). The total volume of perched water is estimated to be 1.62×107 L (Oostrom et al. 2013). This perched water is primarily contaminated with nitrate, uranium, technetium-99, and carbon-14 (DOE/RL-2017-58 2019).

4.1.1 Hanford Site Considerations

Multiple site-specific factors influence the potential applicability and appropriateness of remediation strategies and access methods for Hanford. General Hanford Site considerations are listed below, and, where appropriate, are used to indicate specific technologies that are not considered applicable:

- The Hanford Central Plateau has a vadose zone that ranges in thickness from 67 to 104 m (221 to 340 ft). DP, soil mixing, trenching, and surface application have low applicability for these deep vadose zone areas.
- A relatively thin perched zone (< 5 m [15 ft] thick) is located a few meters above the unconfined aquifer, on top of a low-permeability perching unit. Methods that significantly disturb the formation, including high-pressure injection of high volumes or jetting, cannot be applied to the Hanford perched-water zone.
- Heterogenous formations contain both high-permeability (Hanford formation, Ringold Formation, and Cold Creek gravel unit) and low-permeability (Cold Creek silt and caliche units) zones.
- Contamination includes a range of chemicals (radionuclides, non-radioactive metals, inorganics, and organics), with many co-located within a specific target zone.
- The cost of well installation is very high, driving high relative costs for remedies needing numerous boreholes. A sparse spatial coverage of wells requires a large achievable ROI to span larger areas of contamination, though targeted remediation of source areas may be more feasible. Access methods such as DP, foams, and jetting have low applicability because of their small ROI.
- Aboveground structures are present above many waste sites, notably above the perched-water zone. Structures limit where wells and equipment can be placed and may not allow for amendments to be introduced via surface application.

Encapsulated gases, encapsulated solids, and PPT were all recognized as having too low of a maturity status to be applicable for Hanford at this time.

4.2 Subsurface Target Zones

The five subsurface target zones considered are: unsaturated high permeability, unsaturated low permeability, perched water, saturated high permeability, and saturated low-permeability zones. A general description of each zone is provided before discussing the specific conditions and considerations for the Hanford Site. Potential methods applicable for each Hanford specific target zone are also provided.

4.2.1 Unsaturated Zone

The vadose zone is the unsaturated portion of the subsurface above the water table. In this region, the pore space is filled with both air and water, making the soil moisture content less than fully saturated. Water movement through the vadose zone is dominated by infiltration and recharge events from the ground surface. However, at Hanford, the semi-arid conditions limit the amount of natural infiltration and recharge. Soil permeability, subsurface heterogeneities, and lithology can all have a substantial impact on how remedial technologies are deployed, and how effectively in situ treatment amendments can be delivered to this zone.

4.2.1.1 Unsaturated High-Permeability Zone

Highly permeable porous media such as sands and gravels allow for relatively easy flow of gas and infiltrating liquids through the unsaturated zone. In general, higher-permeability soil strata are more amenable to delivery of in situ treatment reagents, although any subsurface heterogeneities or regions with permeability contrasts may be bypassed as liquids infiltrate through the vadose zone.

4.2.1.2 Unsaturated Low-Permeability Zone

Low-permeability zones contain finer-grained materials such as silts and clays. Contaminants can enter low-permeability zones, making remediation challenging because it is difficult to remove or interact with the contaminants in the low-permeability zone. Gas (and liquid) flow is more difficult because of the lower permeability, forcing treatments to rely primarily on diffusion. In the unsaturated zone, it is expected that low-permeability regions have higher moisture content, which can limit the distribution of gases.

4.2.1.3 General Constraints

In the unsaturated zone, liquid delivery is constrained by wettability and permeability, and lateral distribution of liquids is typically limited. Aqueous injections increase the water content of the vadose zone, with the potential unintended consequence of connecting contamination in the unsaturated zone to the aquifer (Zhong et al. 2010; Zhong et al. 2009). Transport and distribution of gas through the vadose zone tend to be superior to liquid or solid delivery. Gases have been found to be more efficient, predictable, and better able to permeate a larger area, as well as low-permeability materials (Denham and Looney 2007). However, high water content in vadose zone sediments may limit success of gas treatments. Emplacement of solid amendments (e.g., as a PRB) or mixed directly into the soil has proven to be successful, although such approaches have limited application at depth or for large areas. Injection and distribution of solid reagents is very difficult because of the limited ROI. Thus, solids may only be appropriate for a targeted vadose zone injection. Furthermore, solids and NAPL/emulsion droplets can clog the pores, dramatically decreasing the ROI.

4.2.1.4 Methods Potentially Applicable Hanford

- Gaseous amendments are well suited for deployment in high-permeability vadose zones, but are more difficult to use in lower-permeability zones, forcing treatments to rely more on diffusion than advection. Non-aqueous phase liquids may have some potential for vadose zone treatment, although such amendments have not been tested.
- Granular particulates can be successful, although introduction may be limited to soil mixing and trenching. Such methods can be successfully applied to shallow vadose zones, but are infeasible for the deep vadose zone of the Central Plateau.
- Pneumatic fracturing may be an option for the vadose zone. However, the benefit of increased flow paths created through fracturing also potentially increases the connectivity to groundwater.

4.2.2 Perched Water

A perched-water zone is a vertically isolated, body of water that is separated from the regional water table by a layer of unsaturated material. In general, a perched aquifer is formed when infiltrating water collects on top of a low-permeability unit. Arid and semi-arid regions with deep water tables and high subsurface heterogeneity are susceptible to temporary or permanent perched-water zones. When surface discharges of liquid wastes take place above low-permeability units in the vadose zone, a perched aquifer can be contaminated (or created, if not previously present). Contamination in perched water can slowly infiltrate through the underlying low-permeability layer or can move horizontally off the edge of the underlying unit (though lateral movement can be inhibited if the perching layer is bowl shaped).

4.2.2.1 General Constraints

Amendment delivery to the perched-water zone has unique concerns. The main concern for perched water is the access method, as opposed to the amendment type. Substantial applied pressure and added volume (e.g., from an injection) to the thin perched-water zone has the potential to displace perched water laterally over the edges of the confining layer or to enhance migration through the confining layer, making some amendment delivery techniques unsuitable for the perched-water zone. For the Hanford Site, the perched water is within relatively low-permeability materials, which limits injection flow rates and the ability to extract water from this perched region. Thus hydraulic manipulation and reliance on intense extraction such as use of dipole configurations and surfactant solutions is precluded.

4.2.2.2 Potential Methods Applicable for Hanford

- Aqueous amendments (including emulsions, STF, and surfactants) could potentially be used to directly target perched-water zones, but total injection volume would need to be within constraints designed to avoid enhancing contaminant flux toward the aquifer.
- NAPL could potentially be emplaced above or at the surface of the perched-water table, as has been done with water table aquifers. However, this approach is untested for perched-water applications.
- Smaller-sized solid amendments (i.e., micro- or nano-size particles) could be applicable, if they can be introduced using low-volume, targeted injections.
- Horizontal wells may be an appropriate access method for targeting perched-water zones due to the constraints of aboveground structures, though the perched water is a relatively thin target.
- Targeted hydraulic fracturing may be applicable to the perched-water zone. However, a careful assessment would be required to ensure fracturing would not disturb the underlying confining layer and result in an increased contaminant flux towards groundwater.

4.2.3 Saturated Zone

The saturated zone is the fully saturated portion of the subsurface where all the pore spaces are filled with water. Water flow through the saturated zone is dependent on the permeability of the aquifer materials, preferential flow paths, subsurface heterogeneities, and lithology. The saturated zone is connected to the vadose zone through water infiltration and recharge. However, infiltration rates at Hanford are limited due to the semi-arid conditions. At Hanford, groundwater generally flows toward the Columbia River. In situ remediation considered here is for targeted application to Hanford source zones, not for the large dilute contaminant plumes. Thus, the in situ treatment would be for a limited lateral extent and focus on a thin vertical interval near the water table.

4.2.3.1 General Constraints

Soil permeability, subsurface heterogeneities, and lithology can all have a substantial impact on how effectively amendments are delivered to this zone. Considerations for high- and low-permeability zones, as described for the unsaturated zone, are also relevant for the saturated zone. Generally, delivery and distribution to low-permeability regions is more challenging and relies more heavily on diffusion. Introduction of higher viscosity fluids (such as emulsions and STF) can provide improved sweeping efficiencies to low-permeability areas and can potentially be used to emplace amendments within these regions. NAPL distribution in the saturated zone is affected by soil properties (e.g., pore throat size, textural interfaces, etc.) and material properties (e.g., density, viscosity, wettability, etc.). Transport of particulates is highly dependent on the size of the solid particle, as well as the size of the pore throats. Clogging of pores with either solids or NAPL/emulsion droplets can drastically decrease the ROI, potentially inhibit injectability, and alter ambient groundwater flow paths. Fouling of wells due to mineral precipitation and/or biological growth can also limit amendment delivery.

4.2.3.2 Potential Methods Applicable for Hanford

- The saturated zone is amenable to transport of aqueous solutions including emulsions, STF, and surfactants.
- Gases can be applied to the saturated zone, although gas lock can occur when gas i.e., either injected or generated in situ (biogenic or chemically). Gas treatment is also constrained by gas solubility in groundwater.
- Solid particles can migrate through the porous media with groundwater. Particle size is the key factor that determines the ROI for particle distribution, with smaller particle sizes having improved mobility through a range of pore sizes.
- Hydraulic and pneumatic fracturing are amenable access methods for the saturated zone, primarily in lower-permeability zones. Amendment delivery and the ROI can be improved by increasing soil permeability and providing access to low-permeability units.

4.3 Applicability of Delivery Mechanisms for Target Zones at Hanford

Table 5 provides a summary of potentially applicable remediation amendments and access methods for each target zone and which are relevant to remediation in the Hanford Central Plateau.

Table 5. Applicability of Amendments and Access/Emplacement Methods by Target Zone and Relevant to the Hanford Central Plateau.

Amendment	Unsaturated High-Permeability Zones	Unsaturated Low-Permeability Zones	Perched Water	Saturated High-Permeability Zones	Saturated Low-Permeability Zones
Aqueous Solutions/Liquid Amendments	Applicability: **Low**. Poor distribution in vadose zone and could mobilize contaminants to groundwater.		Applicability: **Medium**. Injection of liquids could directly target perched-water zones but has potential to transfer contaminants to other areas of the aquifer. Applied pressure with high volume to this zone has the potential to displace perched water laterally around the confining layer or enhance infiltration through confining layer. Access Methods: gravity-fed injections, pressure injections, horizontal wells, targeted hydraulic fracturing	Applicability: **High**. Standard method in high permeability zones, but with some limitations in heterogeneous aquifers. Access Methods: gravity-fed injections, pressure injections, horizontal wells, hydraulic control, in-well recirculation, hydraulic fracturing with injection, pneumatic fracturing with injection, multicomponent pulsed injection, electrokinetics, density driven	Applicability: **Low**. Flow will bypass low-permeability regions
NAPL	Applicability: **Medium**. Largely untested in the unsaturated zone due to very limited ROI, but neat oil has been injected directly above the water table to create a thin barrier on groundwater table to intercept any transfer from the vadose zone to groundwater (Riha et al. 2012) Access Methods: gravity-fed injections, pressure injections		Applicability: **Medium**. Untested for perched water but neat oils could be placed on perched-water table as a film (e.g., Gent et al. 2001; Riha et al. 2012) Access Methods: gravity-fed injections, pressure injections, horizontal wells	Applicability: **Low**. High-viscosity limits injectability (limited ROI) and causes aquifer clogging	Applicability: **Low**. High fluid viscosity and oil retention inhibit injectability and distribution (limited ROI)

Amendment	Unsaturated High-Permeability Zones	Unsaturated Low-Permeability Zones	Perched Water	Saturated High-Permeability Zones	Saturated Low-Permeability Zones
Emulsion	Applicability: **Low**. Although untested in the vadose zone, emulsions have same limitations as aqueous solutions including the potential to mobilize contaminants		Applicability: **Medium**. Same limitations and concerns as with aqueous solutions especially for use in perched-water zones Access Methods: gravity-fed injections, pressure injections, horizontal wells, targeted hydraulic fracturing	Applicability: **Medium**. Improves transport for some amendments and retains amendment loading by deposited emulsion droplets. Some limitations in heterogeneous aquifers Access Methods: gravity-fed injections, pressure injections, horizontal wells, hydraulic control, hydraulic fracturing with injection, pneumatic fracturing with injection	Applicability: **Medium**. Increased viscosity can improve sweeping efficiency to low-permeability areas, but may still have pore size constraints for emulsion delivery Access Methods: gravity-fed injections, pressure injections, horizontal wells, hydraulic control, hydraulic fracturing with injection, pneumatic fracturing with injection
Shear-Thinning Fluids	Applicability: **Low**. Limited ROI in the unsaturated zone		Applicability: **Medium**. Same limitations and concerns as with aqueous solutions especially for use in perched-water zones Access Methods: gravity-fed injections, pressure injections, horizontal wells	Applicability: **High**. Desirable injection properties and effective distribution Access Methods: pressure injections, horizontal wells	Applicability: **High**. Desirable injection properties and rheological properties facilitate effective distribution and emplacement in low-permeability zones Access Methods: pressure injections, horizontal wells,
Gelling Liquids-Encapsulation	Applicability: **Low**. Limited ROI		Applicability: **Low**. Limited ROI and injection pressure limitations in perched water	Applicability: **Medium**. Transports readily in high permeability, but with limitations for gelling time Access Methods: pressure injections, hydraulic fracturing with injection	Applicability: **Medium**. Increased viscosity can improve sweeping efficiency to low-permeability areas Access Methods: pressure injections, hydraulic fracturing with injection

Amendment	Unsaturated High-Permeability Zones	Unsaturated Low-Permeability Zones	Perched Water	Saturated High-Permeability Zones	Saturated Low-Permeability Zones
Gelling Liquids-Amendment Delivery	Applicability: **Low**. Promising laboratory testing with manageable injection viscosity and pressures	Applicability: **Low**. Promising laboratory testing shows gels can also have shear-thinning behavior which could potentially helpful for delivery to low-permeability zones	Applicability: **Low**. Limited ROI and injection pressure limitations in perched water	Applicability: **Medium**. Promising laboratory testing with manageable injection viscosity and pressures, but with limitations for gelling time Access Methods: pressure injections, horizontal wells, hydraulic fracturing with injection	Applicability: **Medium**. Increased viscosity can improve sweeping efficiency to low-permeability areas Access Methods: pressure injections, horizontal wells, hydraulic fracturing with injection
Surfactants	Applicability: **Low**. Poor distribution in vadose zone. Same limitations and concerns as using aqueous solutions in the unsaturated zone. Additionally, can mobilize contaminants to groundwater which would require extraction (which depending on treatment may or may not be desired)		Applicability: **Low**. Mobilizing contaminants via surfactants requires extraction which has rate limitations in the perched water	Applicability: **Medium**. Same limitations and concerns as using aqueous solutions in addition to potentially mobilizing contaminants which would require extraction (which may or may not be desired) Access Methods: pressure injections (with paired extraction)	Applicability: **Low**. Same limitations as aqueous solutions in addition to potentially mobilizing contaminants which would require extraction (which may or may not be desired) Access Methods: pressure injections (with paired extraction)
Gases	Applicability: **High**. Successful field and lab testing but high and non-uniform water contents can limit uniform delivery Access Methods: pressure injections, horizontal wells, hydraulic control, pneumatic fracturing with injection, multicomponent pulsed injection	Applicability: **Medium**. Diffusion limited Access Methods: pressure injections, horizontal wells, hydraulic control, pneumatic fracturing with injection, multicomponent pulsed injection	Applicability: **Low**. Limited ROI	Applicability: **Low**. Limited ROI	Applicability: **Low**. Limited ROI

Amendment	Unsaturated High-Permeability Zones	Unsaturated Low-Permeability Zones	Perched Water	Saturated High-Permeability Zones	Saturated Low-Permeability Zones
Granular Solids	Applicability: **Low**. Large particle size limits introduction to methods like soil mixing and trenching, which have depth constraints		Applicability: **Low**. Large particle size limits introduction to methods like soil mixing and trenching which have depth constraints	Applicability: **Medium**. Large particle size limits introduction to methods like soil mixing and trenching which have depth constraints Access Methods: in-well emplacement	Applicability: **Medium**. Large particle size limits introduction to methods like soil mixing and trenching which have depth constraints Access Methods: in-well emplacement
Micron-sized Particles	Applicability: **Low**. Limited ROI in the unsaturated zone, but can be mixed into the subsurface to create a PRB		Applicability: **Medium**. Focused low-volume high-pressure methods would be required to deliver Access Methods: targeted hydraulic fracturing	Applicability: **Medium**. Can inject into aquifer but at lower ROI than aqueous solutions. Distribution is sensitive to heterogeneity. Access Methods: pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection	Applicability: **Medium**. Particle size allows transport in sands, but particles will get stuck in silt and clay pore throats. May create clogging and regions of flow bypass. Access Methods: pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection
Nano-sized Particles	Applicability: **Low**. Limited ROI, but can be introduced via soil mixing techniques to create a PRB	Applicability: **Low**. Limited ROI, but can be introduced via in situ soil mixing techniques to create a PRB	Applicability: **Medium**. Similar to aqueous liquid injection but need to manage particle agglomeration and deposition that limit ROI Access Methods: in-well emplacement, gravity-fed injection, pressure injections, horizontal wells targeted hydraulic fracturing	Applicability: **High**. Increased subsurface mobility over large particles. Similar to aqueous liquid injection but need to manage particle agglomeration and deposition that limit ROI Access Methods: in-well emplacement, gravity-fed injections, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection	Applicability: **Medium**. Particles will transport better in a wider range of pore throats sizes, however, still limited in low-permeability zones. Similar to aqueous liquid injection but need to manage particle agglomeration and deposition that limit ROI Access Methods: in-well emplacement, gravity-fed injections, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection

Amendment	Unsaturated High-Permeability Zones	Unsaturated Low-Permeability Zones	Perched Water	Saturated High-Permeability Zones	Saturated Low-Permeability Zones
Surface Modified Particles	Applicability: **Low**. Limited ROI, but can be introduced to create a PRB	Applicability: **Low**. Limited ROI, but can be introduced to create a PRB	Applicability: **Medium**. Modification likely improves ROI over bare particles Access Methods: in-well emplacement, gravity-fed injection, pressure injections, horizontal wells, targeted hydraulic fracturing	Applicability: **Medium**. Modifications should increase ROI although transport and distribution is mainly dictated by particle size and grain size distribution Access Methods: in-well emplacement, gravity-fed injections, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection	Applicability: **Medium**. Modifications should increase ROI although transport and distribution is mainly dictated by particle size and grain size distribution Access Methods: in-well emplacement, gravity-fed injections, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection
Encapsulated Solids	Applicability: **Low**. Limited ROI, but can be introduced to create a PRB	Applicability: **Low**. Limited ROI, but can be introduced to create a PRB	Applicability: **Medium**. Encapsulation should improve ROI, although method may be limited by particle size Access Methods: in-well emplacement, gravity-fed injection, pressure injections, horizontal wells, targeted hydraulic fracturing	Applicability: **Medium**. ROI is mainly dictated by particle size and grain size distribution. Some encapsulation methods increase particle size and thus will have limited mobility Access Methods: in-well emplacement, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection	Applicability: **Medium**. ROI is mainly dictated by particle size and grain size distribution. Some encapsulation methods increase particle size and thus will have limited mobility Access Methods: in-well emplacement, pressure injections, horizontal wells, hydraulic fracturing with injection, pneumatic fracturing with injection

5.0 Conclusions

Most subsurface remediation technologies rely on successful delivery and distribution of amendments to the subsurface. While the underlying mechanisms of a remediation technology may show promise at the laboratory scale, issues related to subsurface delivery and distribution are typically responsible for limited effectiveness when implemented in the field. For success in the field, the implementation method needs to be considered alongside the remediation technology. This document is intended to support technology selection by providing information on the site-specific factors that determine field-scale application and subsequent treatment effectiveness. This document does not provide information on specific remediation technologies or guidance on selecting the appropriate amendment, but does provide information on the amendment delivery methods and subsurface access methods, which are critical for overall remediation success.

Overall, this document provides a broad overview and summary of the available amendment delivery and distribution methods, as well as subsurface access methods. After surveying the existing methods, amendment types, and access methods, approaches were given a maturity rating of high, medium, or low. Each of the amendment delivery approaches was then assessed for applicability to specific subsurface target zones, including unsaturated high permeability, unsaturated low permeability, perched water, saturated high permeability, and saturated low permeability zones. The techniques were then further evaluated for specific applicability to the Hanford Site zones where site-specific factors including limitations related to depth, the presence of a thin perched-water zone, and existing aboveground structures were considered. Encapsulated gases, encapsulated solids, and PPT were all recognized as having too low of a maturity status to be applicable for Hanford at this time. DP, soil mixing, trenching, and surface application were deemed as having low applicability for any of the mentioned subsurface zones at Hanford. Furthermore, any methods that significantly disturb the formation are not appropriate for the perched-water layer (e.g., high-pressure injection of high volumes and jetting technology). Generally, delivery methods that have a limited ROI (e.g., foams, DP, and jetting) have low applicability for the Hanford Site because of the high cost of well installation, although there could be some applicability to treat a small contaminated region. However, a number of potential delivery methods were identified and may be suitable to developing remedial alternatives that include in situ remediation.

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This work represents a review of the literature. The information associated with this report should not be used as design input or operating parameters without additional qualification.

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Appendix A – Laboratory and Field Implementations

Laboratory and field case-study examples are given in Tables A.1 and A.2, respectively. Recent laboratory experiments were only provided for delivery and distribution approaches that are considered less mature, or if a recent improvement to the method is being investigated (Table A.1). The many approaches that are more mature and widely used in field implementations were not included. Table A.2 provides an example field case for each delivery method. Some approaches (e.g., use aqueous solutions, hydraulic control, trenching, etc.) are so common and widely used in practice that very few examples of the technique are reported in the peer-reviewed literature. Each field implementation example provides a brief description and information on the target contaminant, general site information, amendment utilized, access and distribution method, reported radius of influence, along with pros and cons (Table A.2).

Table A.1. Summary of Laboratory Tests.

NAPL	• Pilot-scale test using soybean oil as a denitrifying barrier in a sand tank where sand was coated with oil using a cross-flow blender. Permeability reduction was directly correlated with oil percentage in column experiments (Hunter 2001).
Emulsion	• Encapsulation of ZVI in oil-in-water emulsions. Transported well in sandy 1-d columns (Berge and Ramsburg 2009). • Alkalinity releasing particles ($CaCO_3$ and MgO) were successfully encapsulated within highly concentrated (up to 23% wt. oil) oil-in-water emulsion droplets. Emulsions transported well in 1-d column experiments and alkalinity release from deposited droplets sustained pH for 30+ PVs (Muller 2016).
Foam	• Foam injection prior to delivery of an oxidant solution improved the radius of influence (ROI) in unsaturated soils with permeability contrasts in 1-d column and 2-d aquifer cells (Bouzid et al. 2018). • Column and flow cell experiments showed improved uniform distribution in heterogeneous vadose zone sediments while minimizing mobilization (Zhong et al. 2011). • Foam transport in unsaturated sediments was studied in column experiments finding that transport was influenced by foam injection pressure, foam quality and sediment permeability (Zhong et al. 2010). • In column experiments, foam generating surfactant solutions were used to deliver calcium polysulfide to immobilization Cr(VI) in vadose zone sediments. Delivery of amendments via foam decreased contaminant mobilization as compared to aqueous solutions (Zhong et al. 2009).
Shear-Thinning Fluids	• Sweeping efficiency through a heterogenous vadose zone was improved using STF in column and flow cell experiments. Amendment distribution to low-permeability zones was also improved (Zhong et al. 2011). • Xanthan gum shown to stabilize highly concentrated iron suspensions preventing aggregation and sedimentation (Comba et al. 2011). • Micron-size droplets of vegetable oil were stabilized using xanthan gum. Column tests demonstrated oil suspensions could be successfully injected (Zhong et al. 2015).
Gelling Liquids	• Batch and column testing showed successful delivery and slow release of carbon sources to vadose zone sediments via a suspension of colloidal silica that gelled and grouted in the porous media after injection. Low viscosity of freshly made suspension allowed for easy injection with rheological behavior showing viscosity increased with time as gelation occurs (Zhong et al. 2018). • Sodium thiosulfate held within a Scleroglucan polymer, gelled upon contact with Cr(VI) allows for simultaneous trapping and treating of Cr(VI) in batch studies. Proof-of-concept results show potential to tailor materials to target specific contaminants (Pensini et al. 2018).
Surfactants	• An average removal rate of 61-67% for As, Cd, Cu, Pb, Ni, and Zi from a highly contaminated industrial soil using three surfactants in batch reactors over a 23-hr period (Torres et al. 2012).

Reactive Gases	• Column and 2-d aquifer cell experiments quantified ammonia transport in unsaturated media and the resulting geochemical changes occurring when NH_3 gas is introduced to vadose zone sediments (Zhong et al. 2015). • H_2S and NH_3 gases reduced the mobility of ^{99}Tc in contaminated vadose zone sediments in column experiments (Szecsody et al. 2015).
Gas Encapsulation	• An ozone bubble suspension encapsulated within a surfactant layer was injected into the bottom of a saturated sandy soil batch reactor contaminated with phenanthrene. Results show potential to pair surfactant soil washing with delivery of ozone for contaminant oxidation (Zhang et al. 2019). • 1-d columns test efficiency of colloidal gas aphron suspensions to flush naphthalene from sand (Roy et al. 1995).
Solid Encapsulation	• Potassium permanganate particles were encapsulated within biodegradable paraffin wax that has low water solubility but high solubility in hydrophobic liquids. Encapsulation increased particle size from 15 to 874 µm. The wax encapsulation protects reactive ingredients from dissolving in water and wax only dissolves away when reached the targeted NAPL source zone (Kang et al. 2004). • Microbeads made from gellan gum (10-40 µm) injected into a 1-d column showed hydraulic conductivity loss in fine sand (Moslemy et al. 2003). • KH_2PO_4 powder was encapsulated within a pH-sensitive degradable polymer creating 1 mm macrocapsules (Rust et al. 2002). • $Ca(H_2PO_4)_2$ and K_2HPO_4 were encapsulated in degradable polymers were results show were able to release their active ingredients to successfully alter pH (Flora et al. 2008). • nZVI incorporated within channels of mesoporous silica nanospheres did not appear to effect particle reactivity while improving mobility in columns as compared to bare nZVI (Lu et al. 2018).
Electrokinetics	• EK facilitated transport of negativity charged amendments (lactate, citrate, permanganate) through heterogenous and low-permeability regions in 2-d aquifer cell experiments as compared to traditional aqueous solutions (Gent et al. 2001).

Table A.2. Field Application Examples.

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Aqueous Solutions								
Vermeul et al. 2014	• Aqueous Ca-citrate and Na-phosphate solutions were injected to create an in situ apatite barrier for immobilization of Strontium-90 at the Hanford Site	• Strontium-90	• Gravel and sand aquifer at the 100-N Area at the Hanford Site	• Ca-citrate complex and a Na-phosphate solution (to form apatite in situ)	• 16 injection wells were spaced 9 m (30 ft) apart along the 91 m (300 ft) transect	• 6.1 m (20 ft) (at this distance, the concentration was ~ 50% of the injected concentration)	• Approximately 90% reduction in ^{90}Sr concentrations	• Limited vertical distribution • Incomplete distribution in the lower permeability formation
CL:AIRE 2013	• Gravity fed, direct push injections, and soil mixing of CaSx for treatment of Cr(VI) contaminated soil and groundwater	• Cr(VI)	• Site description not provided	• Calcium polysulphide	• Gravity fed at 4.9 L/min over 3 days	• Very limited due to clogging	• Amendment showed high reactivity	• Reaction products clogged aquifer near the injection well
Truex et al. 2009	• Substrate was injected to create a bio-barrier for supplemental treatment upgradient from the In Situ Redox Manipulation barrier previously installed at the 100-D Area	• Chromium	• Sandy gravel to silty sand aquifer with depth to water table between 1 m to 25 m (3 ft to 82 ft) • 100-D Area at the Hanford Site	• Molasses (soluble, miscible substrate)	• Process water was injected at ~ 40 gallons per minute amended with 40 g/L molasses through a fully-screened injection well	• 15 m (50 ft)	• Successfully stimulated microbial activity and reduced target species over the 2-year monitoring timeframe	• Microbial growth could limit the ability to inject additional substrate or treat a larger zone • Amendment uniformity was affected by subsurface heterogeneities
Thomson et al. 2008	• Pilot-scale delivery of permanganate to contain and treat a coal tar plume at the Borden site. Goal to bypass flow around source zone via magnesium oxide precipitation	• Coal tar creosote NAPL source zone	• 10 m (33 ft) thick unconfined aquifer at CFB Borden	• Permanganate	• Six semi-passive injection pulses upgradient of source zone • Hydraulic control via injection/extraction wells	• Not directly quantified. Monitoring at 0.3 m (1 m) shows solution traveled that far	• Mass discharge decreased over first two years of operation	• Precipitation of manganese oxides significantly reduced permeability creating issues for each subsequent injection • Injections created localized groundwater mounding • Contaminant rebounding 4 years post treatment

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Peterson and Hedquist 2006	• Liquid calcium polysulfide was injected to directly reduce chromium as well as reduce the aquifer materials to create an in situ PRB at the Hanford Site	• Chromium	• Depth to groundwater is 19.8 m (6 5ft) in the 100-K Area at the Hanford Site	• 29% calcium polysulfide (CPS) aqueous solution	• Four injection wells and one centrally located extraction well were used to treat a 30 m by 30 m (98 ft by 98 ft) area of the aquifer	• 30 m (98 ft)	• Successfully removed chromium from the groundwater and created reducing conditions in the aquifer	• Precipitation occurred within the pipes, flowmeters and pumps which caused a reduction in flow
Su and Ludwig 2005	• Field testing of combined reductant solutions for Cr(VI) reduction	• Cr(VI)	• Olin Chemical site in Charleston, TN • Characterization not provided	• Iron sulfate ($FeSO_4$) and sodium dithionite ($Na_2S_2O_4$)	• Pressure injection	• Less than 1.5 m (4.9 ft) (treatment zone)	• No well or formation clogging during injection	• Lack of pH control limited ROI
Fruchter et al. 2000	• Proof-of principle field test where buffered sodium dithionite solution was injected to create a reduced sediment zone for chromium immobilization	• Cr(VI)	• Hanford 100 H area unconfined aquifer 12.5 m (41 ft) bgs and 3 m (10 ft) thick comprised of sand/sandy gravel confided below by sandy clay/clayey silt	• Sodium dithionite ($Na_2S_2O_4$) with pH buffer (potassium carbonate/ bicarbonate)	• Injection into groundwater well, paused to let reaction occur (18.5 hours), then groundwater was extracted via the same well to remove any unreacted reagents, reaction products or mobilized metals	• 15 m (49 ft) diameter (target)	• No significant permeability reduction within the formation	• Small zone of reduced permeability near the well, hypothesized to have occurred from groundwater extraction that clogged well sand pack • Decreased treatment with increased distance from injection point

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
NAPL								
Riha et al. 2012	• Injected neat oil spread laterally on the surface of the water table creating a barrier to intercept vadose zone contaminations from transferring to groundwater. Oil also stimulated biological activity	• Chlorinated solvent residual source zone in deep vadose zone	• Site description is not available • Deep vadose zone treatment	• Neat soybean oil with 0.2% triethyl phosphate	• Gravity fed into deep vadose wells • Injection rates between 2.3 – 3.8 L/min for total of volume of $1.02x10^5$ L (27,000 gal)	• Insufficient monitoring wells to quantify ROI • ROI was estimated to be between 8 - 17 m (25-55 ft)	• Easy injection via gravity • Results indicate edible oil treatment is a viable technology	• ROI and oil distribution not quantified and likely less than the estimated values
Emulsion								
Watson et al. 2013	• EVO injected to sustain uranium bioreduction in high permeability, fast-flowing, gravel layer	• Uranium	• Highly permeable gravel aquifer	• Soybean oil (electron donor) • Phosphate buffer	• Injected via three wells at 9.5 L/min	• 50+ m (164+ ft)	• Majority of oil was retained or adsorbed to porous media providing a long-term source of electron donor • Reducing conditions sustained for over 1 year	• ~ 1 µm EVO droplets transported mainly through larger pores due to size exclusion effects • Density effectives where EVO floated on groundwater
Riha et al. 2012	• Injected commercially available emulsified oil (EOS™ and AquaBupH™) into chlorinated solvent groundwater plume	• Chlorinated solvent groundwater plume	• Site description is not available	• EVO	• Groundwater was extracted from a down gradient well, treated with a portable air stripper, and mixed with EVO before up gradient injection • Water chase used to enhance distribution (50:1 – 75:1 water to oil)	• Limited monitoring wells did not allow for quantification of ROI • ROI was estimated to be between 11 – 17 m (35-55 ft)	• Decreased plume size and mass • Facilitated enhanced attenuation	• Decrease in flow (from 11 to 4 L/min) was attributed to decrease in permeability from oil injection or clogging by clays
Truex et al. 2009	• Substrate was injected to create a bio-barrier for supplemental treatment upgradient from the In Situ Redox Manipulation barrier previously installed at the 100-D Area	• Chromium	• Sandy gravel to silty sand aquifer with depth to water table between 1 m to 25 m (3 ft to 82 ft) • 100-D Area at the Hanford Site	• EOS® 598 soybean oil emulsion (EOS Remediation, LLC)	• Seven pulse injections were completed over a 17-hour period where process water was injected at ~ 40 gallons per minute amended with 60 g/L emulsion through a single screened injection well	• 8 m (25 ft)	• Successful stimulation of microbial activity •	• Amendment distribution was affected by subsurface heterogeneities • Moderate reduction in aquifer permeability

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Quinn et al. 2004	• EVO injection methods were tested for distribution in a sand	• N/A	• NASA Launch Complex 34	• EZVI	• Tested PPT, hydraulic fracturing, and pneumatic fracturing	• Maximum of 1.4 m (4.6 ft) and varied based on injection method	• Hydraulic fracturing showed greatest potential	• None of the methods were particularly successful
Foam								
Portois et al. 2018	• Pre-generated surfactant foam was injected into chlorinated solvent source zone to increase permeability and divert groundwater flow around source zone	• Chlorinated solvent source zone	• Heterogeneous subsurface with two distinct clay layers	• None • Biodegradable surfactant used to create foam	• Injection wells (80 mm (3.1 inch) diameter, 7.5 m (25 ft) deep) were used to target a 2 m (7 ft) thick aquifer • Injected foam into areas surrounding low-permeability zones • To avoid air leaks, injection wells were isolated with a bentonite seal	• Not directly measured • Modeling efforts estimate maximum ROI to be 3.2 m (10.5 ft)	• Reduced hydraulic conductivity over 100-fold	• Foams were able to block the fully area • Foam efficiency needed improvement • Need to add bentonite seal to injection well
Shear-Thinning Fluids								
Truex et al. 2015	• Transport and distribution behavior of STF was compared to aqueous solutions with resulting showing improvements in an aquifer with moderate permeability contrasts	• Trichloroethyl ene (TCE)	• Heterogenous aquifer of glacial outwash and till with silt	• Ethyl lactate	• Injection well screened 15 to 21 m (50 to 69 ft) bgs	• 3+ m (10 ft) (breakthrough occurred in 3 m (10 ft) well but not 6 m (20 ft))	• Moderate improvement in fluid distribution	• Increased injection pressures associated with STF (1.75x than aqueous solution) broke the well seal and STF discharged into a high-permeability zone • STF required additional pre-injection steps
Truex et al. 2011a	• ZVI was injected into top 2 m (7 ft) of a TCE source zone with a shear-thinning fluid (SlurryPro) to enhance ZVI suspension stability and distribution within the aquifer	• TCE source zone	• Shallow aquifer containing gravel, outwash and till	• 2 µm ZVI	• Pressured injection (~ 80 L/min)	• ~ 4 m (13 ft)	• Effective distribution of ZVI • Shear-thinning fluid carrier did not affect ZVI reactivity	• Moderate pressure required for injection due to solution viscosity • Mounding of water table during injection

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Gelling Liquids								
Moridis et al. 1995	• A field-scale demonstration of permeation grouting using a cross-linking polymer (PolySiloXane) and temporal gelling colloidal silica	• N/A	• Heterogenous unsaturated gravel quarry containing coarse sand, silt, and gravel	• Colloidal silica • PolySiloXane	• Jet grouting via four injection wells at depths of 3.0, 3.7, 4.3 m (10, 12, and 14 ft) bgs	• Not reported	• No significant increase in pressure during injection • Created rather uniform zones that grouted both large and small pores • Successful permeability reduction (~ 4 orders of magnitude reduction)	• Colloidal silica did not fully saturate voids • Surface displacement observed during injection
Surfactants								
Childs et al. 2006	• Field demonstration for removal of PCE via mobilization and solubilization of DNAPL in a hydraulically isolated test cell	• PCE-DNAPL	• Silty clay with thin layers of silt and fine sand	• Surfactants	• Vertical circulation wells used to enhance mixing	• 4.6 m (15 ft) (distance between injection and extraction wells)	• Only 10% of surfactant was lost during treatment • 66% of PCE was removed with flooding	• Low-permeability lenses limited contact between amendment and contaminant • Flow bypassing likely occurred • High potential to mobilize contaminants requires extraction
Gases								
Truex et al. 2012	• Field testing where dry N_2 gas injected into the vadose zone for desiccation of sandy aquifer with loamy sand lenses	• N/A	• Sandy vadose zone with loamy sand lenses	• Dry N_2 (g)	• Pressured injection (at 510 m^3/hr) while extracting gas 12 m (39 ft) away (at 170 m^3/hr) • Gas-impermeable membrane barrier installed at ground surface	• 8.25 m (27 ft) (6.1 m (20 ft) depth for a total treated volume of approx. 1300 m^3)	• Highly permeability layers started to desiccate over time (loamy sand)	• Preferential flow through sand layers • Non-uniform moisture contents impeded gas flow through wetter regions • Drying was dependent on initial water content and distance from well

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Evans et al. 2011	• Gaseous electron donor was injected into the heterogenous vadose zone of fine and coarse grain materials for treatment of perchlorate and nitrate	• Perchlorate • Nitrate	• Fine-grained and coarse-grained soils (clay, sand and gravel) • Water table at 42 m (140 ft) bgs	• Gas mixture of 79% nitrogen, 10% hydrogen, 10% liquefied petroleum gas and 1 % carbon dioxide	• Gas injected at two depths (5.5 and 8.5 m [18 and 28 ft] bgs)	• 3 to 4.6 m (10 to 15 ft) for perchlorate destruction • Over 17 m (56 ft) for nitrate treatment	• Effective for low and high moisture content soils (6.8 to 36%) • Large ROI • Simultaneously destruction of perchlorate in low permeability and high-permeability soils • Hydrogen gas was not detected aboveground (i.e., hydrogen can be safely introduced)	• Heterogeneities could have decreased the ability to achieve uniform distribution (heterogeneities made actual assessment of perchlorate destruction rates difficult) • Decreased removals with depth
Brockman et al. 1995	• Field demonstration using horizontal wells to deliver methane, air, nitrous oxide, and triethyl phosphate gaseous reagents 49 m (160 ft) bgs to the saturated zone and extracted 21 m (70 ft) bgs in a paired extraction well	• TCE	• Layered sand and clay subsurface with TCE 30 – 43 m (100 – 140 ft) bgs • Water table at 40-43 m (130-140 ft) bgs	• Methane • Air • Nitrous oxide • Triethyl phosphate	• Horizontal injection well placed at 49 m (160 ft) bgs in the saturated zone with paired vacuum extraction well 21 m (70 ft) bgs in the unsaturated zone • Gaseous reactants (methane, nitrous oxide and triethyl phosphate) injected and bubbled below water table and extracted in unsaturated zone	• Treated zone 18 m (60 ft) from injection well (both horizontally and vertically, albeit determined by indirect measure-ments)	• Large treatment zone • Successful application deep into the subsurface • Treated both saturated and unsaturated zones	• Dried out top portion of the saturated zone (40-50% reduction in water content in the 40 – 43 m (130-140 ft) bgs zone

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Solids & Particulates								
McGregor 2018	• Field-study where colloidal activated carbon was introduced into a shallow aquifer for treatment of low to moderate levels of poly- and perfluoroalkyl substances (PFASs)	• Perfluorooctanoate (PFOA) and perfluorooctane sulfonic acid (PFOS)	• Shallow silty-sand aquifer	• Colloidal activated carbon • Oxygen-releasing materials	• 20 temporary direct push injections (pressures less than 25 psi) • Target treatment zone was 0.9 m to 1.7 m (3.0 ft to 5.6 ft) bgs	• 4.6 m (15 ft)	• Successful treatment of PFOA and PFOS using activated carbon • Effective amendment distribution within the target treatment zone (92% of samples collected had detectable TOC concentrations)	• Only monitored for 18 months, so contaminant levels could still rebound in the future
Mackenzie et al. 2016	• Pilot-scale injections of Carbo-Iron to target contaminants in a highly permeable sandy aquifer using 18 well to create a "ring" around a highly contaminant zone	• PCE	• Sandy aquifer with high hydraulic conductivity	• Carbo-Iron (i.e., nano-iron (~50 nm) embedded in activated carbon colloid particles stabilized with CMC)	• 18 pressure injection at 8.3 L/min to create a ring around a high contaminant area • Injected 0.5 m (1.6 ft) below water table to induce particle transport into same high-permeability zones as contaminants	• 3 - 4 m (10 – 13 ft)	• Iron showed high reactivity	• PCE rebounding occurred 2 to 3 months post injection
Truex et al. 2011a	• ZVI was injected into top 2 m (7 ft) of a TCE source zone with a shear-thinning fluid (SlurryPro) to enhance ZVI suspension stability and distribution within the aquifer	• TCE source zone	• Shallow aquifer containing gravel, outwash and till	• 2 µm ZVI	• Pressured injection (~ 80 L/min)	• ~ 4 m (13 ft)	• Effective distribution of ZVI • Shear-thinning fluid carrier did not affect ZVI reactivity	• Moderate pressure required for injection due to solution viscosity • Mounding of water table during injection
DOE/RL-2009-35	• nZVI was injected to increase the effectiveness of the In Situ Redox Manipulation barrier at the 100-D Area of the Hanford Site	• Cr(VI)	• Sandy gravel to silty-sandy gravel aquifer with the depth to water table between 1 m (3 ft) and 25 m (82 ft)	• RNIP-M2 nZVI slurry	• 370,970 L of nZVI slurry was injected under 2.5 psi of pressure over a 5-day period	• 7 m (23 ft)	• Cr(VI) was reduced/immobilized in the aquifer	• Decreased hydraulic conductivity of the aquifer by a factor of 2.7
Solids & Particulates- Surface modification								

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Chowdhury et al. 2015	• nZVI was injected into a variably saturated soil for TCE treatment. Mounding during injection placed nZVI in both the saturated and unsaturated zones of a shallow sandy-silt aquifer	• TCE	• Shallow sandy-silt aquifer	• nZVI	• Gravity fed (142 L at 3.3 L/min) • nZVI Injection followed by water flush (110 L at 3.3 L/min) followed by groundwater recirculation (50 min at 5 L/min)	• ~ 0.6 m (~2 ft) • Simulations show ROI is governed by injection velocity and fluid viscosity	• Water flush and recirculation increased ROI • CMC used to stabilize also likely enhanced microbial activity • nZVI injected into unsaturated zone attached to soil and remained immobilized	• Significant increase in water table during injection (2.8 to 1 m (9.2 to 3.3 ft) bgs) • thus, a portion of the injection was above water table • Carrier fluid migrated further than nZVI due to particle attachment
Wei et al. 2010	• Pilot-scale demonstration nZVI (commercially available and manufactured onsite) injections for degradation of chlorinated compounds in a variably saturated zone	• TCE and daughter products	• Medium to coarse sand with silt lenses • Hydraulic conductivity of 0.275 cm/sec	• Polymer coated nZVI (80-120 nm)	• Three gravity-fed injection wells (18 m (60 ft) deep with 15 m (40 ft) screens) at injection rate of 20 L/min • Gravity-fed injection caused the nZVI to travel through channels in unsaturated zone where it accumulated	• Estimated at 3 m (10 ft) • nZVI created onsite had larger ROI than commercial likely due to particle size effects	• Likely enhanced bioremediation	• Undesired nZVI accumulation in the unsaturated zone

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Solid Encapsulation								
Aelion et al. 2009	• Macrocapsules containing phosphate buffer were placed in a SoakeaseTM canister down a well for passive release	• Acidic conditions caused by coal pile runoff	• A fine to medium-grained sand shallow aquifer	• Alkalinity	• SoakEase^{TM} canister containing macrocapsules was placed within a groundwater well at a depth of 7.4 m (24 ft)	• Not quantified	• Easy, passive, implementation	• Provided limited pH treatment (initial pH increased to above 6, followed by a decrease back to baseline pH of 2.5 within 10 days) • Unable to provide sufficient amendment mass for successful treatment
Hydraulic Control								
CL:AIRE 2013	• CaSx injection for treatment of Cr(VI) contaminated soil and groundwater	• Cr(VI)	• Site description not provided	• Calcium polysulphide (CaSx)	• Four injection and one extraction wells (150 mm diameter) used to re-circulate groundwater	• 113 m^3 treatment zone (5 x 5 x 4.5 (LxWxD) created 1.5-6 m (4.9 – 20 ft) bgs	• Groundwater was successfully treated	• Amendment was observed in monitoring wells outside of recirculation zone
Horizontal Wells								
Brockman et al. 1995	• Field demonstration using horizontal wells (injection and extraction) to deliver gaseous reagents 49 m (160 ft) bgs	• TCE	• Layered sand and clay subsurface with TCE 30 – 43 m (100-140 ft) bgs • Water table at 40 – 43 m (130-140 ft) bgs	• Methane • Air • Nitrous oxide • Triethyl phosphate	• Horizontal injection well placed at 49 m (160 ft) bgs in the saturated zone with paired vacuum extraction well 21 m (70 ft) bgs in the unsaturated zone • Gaseous reactants (methane, nitrous oxide and triethyl phosphate) injected and bubbled below water table and extracted in unsaturated zone	• Treated zone 18 m (60 ft) from injection well (both horizontally and vertically, albeit determined by indirect measurements)	• Large treatment zone • Successful application deep into the subsurface for saturated and unsaturated zone treatment	• Dried out top portion of the saturated zone (40-50% reduction in water content in the 40-43 m (130-140 ft) bgs zone

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
In-well Recirculation								
Ryan et al. 2000	• In-well air stripping was used to treat volatile organic compounds	• A large dissolved chlorinated solvent plume	• Sands and gravel overlying low-permeability fine sand and silts with depth to water table at 3 to 18 m (10 to 60 ft) bgs. High hydraulic conductivity of 30 to 152 m/day (100 to 500 ft/day)	• Air	• NoVOCs™ in-well recirculation wells. Wells were 25-cm (10-inch) diameter, 64 m (210 ft) deep, spaced 30 m (100 ft) apart, with 4.5 m (15 ft) screened sections separated vertically by 14 m (45 ft), extending 44 - 67 m (145 - 220 ft) bgs	• 30 m (100 ft) radius of recirculation • Capture radius of over 137 m (450 ft)	• 91 – 98 % trichloroethylene treatment efficiency • No effect of water table elevation or adverse hydraulic effects on nearby surface water bodies • No significant fouling occurred at well screens • Groundwater passed through recirculation 3 to 4 times before exiting treatment zone	• Size of circulation zone, number of recirculation cycles, and well fouling are all dependent on heterogeneity, contaminant concentration, pumping rate and well spacing making success highly site specific
Multicomponent Pulsed Injections								
Hooker et al. 1998	• Pulsed injections of acetate and nitrate were offset by 2 hrs to create biological active zone within the aquifer for bioremediation of carbon tetrachloride treatment	• Carbon tetrachloride	• Highly stratified with depth but mostly sand and gravel aquifer (with portions of silt and clay) located 75 to 185 m (246 to 607 ft) bgs	• Nutrients (acetate, nitrate)	• Nutrients were injected in 1 hr pulses, separated by 2 hrs • Distribution is enhanced using a recirculation well system (injection and extraction wells 12 m (39 ft) apart)	• Simulations indicate nutrient mixing occurred 1 to 2 m (3.3 to 6.6 ft) from the injection well	• Biomass accumulated throughout the formation as opposed to at the injection well • More effective use of added electron donor	• Distribution has same limitations as all aqueous solutions

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Pressure Pulse Technology								
Gale et al. 2015	• Field testing comparing PPT to traditional injection methods using tracer solutions	• None	• Testing completed at two sites: (1) fine sand with limited heterogeneities (2) fine sand and silt with moderate heterogeneities and layering	• None	• Injection well screened over 1 m from 7.5 to 8.5 m (25 to 28 ft) bgs • Pulse rate of 2-3 pulses per second	• Not quantified	• Simulations suggest PPT increases mixing and transport to low-permeability zones, however significant enhancements were not seen in field measurements	• Only minor benefit of PPT over traditional injections • Daylighting of injected fluids occurred • Risk of fracturing or liquefaction
Quinn et al. 2004	• Field demonstration of injection technology for EZVI	• N/A	• Sandy aquifer	• EZVI	• 5 injections where 76 L EZVI was injected followed by 151 L water	• < 0.6 m (2 ft)	• Did not fully saturate pores	• Flow highly suspectable to preferential or pre-existing flow paths • Had to terminate after three injections due to EZVI coming up the well liner • EZVI traveled vertically as opposed to horizontally through path of least resistance (targeted at 5 m (15 ft) bgs, observed at 2 m (7 ft) bgs)
Electrokinetics								
Ho et al. 1999	• Field demonstration of electokinetic remediation using the Lasagna method with a GAC treatment zone	• TCE	• Sandy clay loam soils	• GAC	• Electrodes were 3 m (10 ft) apart with four GAC treatments zones created between the electrodes • Fluid was circulated by pumping from the cathode to supply the anode	• 4.6 x 3 x 4.6 m (15 x 10 x 15 ft) (length, width, depth) treatment zone	• Over 98% of TCE was removed • Successful removal from low-permeability clay	• Large pH gradient (2 to 12 at the anode and cathode, respectively) • Subsurface temperature increased from 15 to 45°C)

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Jetting Technology								
CHPRC 2010	• A pilot-scale demonstration using jet injection to deliver a phosphate solution, a pre-formed apatite slurry and a combination of pre-formed apatite and phosphate solutions to create a permeable reactive barrier (PRB) in the vadose zone and upper unconfined aquifer	• Strontium-90	• 100-N at the Hanford Site • Ringold and Hanford formations containing gravel with a fine to coarse-grained sand matrix and sand and silt interbeds with groundwater flowing towards the Columbia River	• Phosphate solution • Pre-formed apatite slurry • Phosphate solution with the pre-formed apatite	• Jet injection boreholes were used to deliver amendments using a proprietary jet injection system	• Expected radial distance of at least 1 m (3 ft) from the injection nozzle	• Successful emplacement of both phosphate and pre-formed apatite in the vadose zone as a PRB	• Amendment concentrations varied vertically with higher concentrations in the finer-grained sediments and lower concentrations in the coarser-grained regions • Gravitational “draining” of amendment through the unsaturated zone
Fracturing- Pneumatic								
Christiansen et al. 2010	• Comparison of pneumatic fracturing, hydraulic fracturing and direct push methods to deliver amendments to low-permeability media in the both the vadose and saturated zones	• Uncontaminated site	• Clay till with water table at 4 to 6 m (13 to 20 ft) bgs	• None (aqueous tracer solutions)	• Fracturing was completed with nitrogen gas in a single borehole at five depths (4, 5, 6, 7, and 8 m (13, 16, 20, 23, and 26 ft) bgs) using a bottom up approach where 50 L of tracer mixture was injected at each depth	• > 2 m (7 ft) • Produced a dense fracture network from 0-3 m (0-10 ft) bgs and wider spaced fractures at depths > 3 m (10 ft) bgs	• Can create smaller aperture fractures that would be useful for in situ mass removal	• High uncertainty in fracturing patterns • Unable to produce dense fracture network • Delivery intervals needed to be spaced more closely • Not as successful as direct push
Quinn et al. 2004	• Nitrogen gas was used to first fluidized sandy porous media followed by an EZVI injection	• N/A	• Sandy soil	• EZVI	• N_2 gas injected first to fluidize formation followed by EZVI • Injection nozzle (with 90-degree coverage) was rotated between injections to achieve 360-degree distribution	• 1 to 1.4 m (3 to 5 ft)	• No evidence of droplet deformation due to injection	• The injection saturated pore spaces with EZVI, providing higher than needed concentrations and potentially clogging the formation

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Fracturing- Hydraulic								
Swift et al. 2012	• Pilot-scale treatment using hydraulic fracturing to deliver a mixture of granular ZVI and organic carbon in a biodegradable gel carrier for TCE treatment in a sandstone perched-water zone	• TCE-contaminated perched-water zone (up to 9 m (30 ft) thick and 274 m (900 ft) long)	• Fine-grained sandstone and siltstone where groundwater (9 – 14 m (30-45 ft) bgs) is perched on a lower-permeability shale region	• EHC-G® (i.e., granular ZVI and organic carbon) delivered using a fracturing slurry with a biodegradable gel carrier	• Hydraulic fracturing with fracture boreholes placed within source zone 18 m (60 ft) apart (because fractures were expected to propagate 9 m (30 ft)) • 4 ft intervals were isolated with straddle packers within 11 – 20 m (35 – 65 ft) bgs targeted zone	• Average fracture propagation radius was 24 m (79 ft) (vertical), 20 m (65 ft) (horizontal), and 0.85 cm (1/3 inch) in aperture • Fractures covered entire saturated thickness of sandstone formation with an average of 1 fracture per 1.8 m (6 ft)	• Over 90% reduction in TCE concentrations	• Inability to control or predict fracture network limits control over amendment placement
Christiansen et al. 2010	• Comparison of pneumatic fracturing, hydraulic fracturing and direct push methods to deliver amendments to low-permeability media in the both the vadose and saturated zones	• N/A	• Clay till with water table at 4 – 6 m (13 – 20 ft) bgs	• None (aqueous tracer solutions)	• Fracturing was done in three boreholes at three depths (3, 6.5 and 9.5 m (10, 21, and 31 ft) bgs) (one fracture per borehole) with a sand-guar mixture. • 250 L of tracer mixture was injected with each fracture	• ~3.5 m (11.5 ft) (although fractures were elliptical and asymmetrical)	• Can create large distinct fractures that might be useful for creating PRBs	• Difficult to achieve sub horizontally oriented fractures below 3 m (10 ft) bgs for this site • Not as successful as direct push
Quinn et al. 2004	• Tested injection of EZVI into unconsolidated media using guar as fracturing fluid. Method resulted in very limited ROI	• N/A	• Sandy soil	• EZVI	• Cross-linked guar gel used to initial and propagate fractures followed by EZVI injection	• Could not locate injected EZVI	• No evidence of droplet deformation due to injection	• Very limited ROI • Guar gel may not have successfully propped open sand formation

Study	Description	Target Contaminant(s)	Target Geological Zone/Site Information	Amendment Delivered	Access & Distribution Method	ROI	Pros	Cons
Soil Mixing								
Kakarla et al. 2017	• Treatment of volatile organic compound (VOC) superfund site where Fenton's reagent was delivered via soil mixing	• VOCs (Trichloroethane, dichloroethane, 1,4-dioxane)	• Silt and clay soils	• Modified Fenton's reagent	• Rotating dual axis blending	• Treatment areas was 85 m^3 (3,000 ft^3), 2 to 5 m (7 to 15 ft) bgs	• Successful reduction of soil and groundwater levels • Amendment was entirely consumed	• Issues related to loss of soil structure and high liquid content that required in low bearing capacity of mixed soil
CL:AIRE 2013	• Injection and soil mixing of CaSx for treatment of Cr(VI) contaminated soil and groundwater	• Cr(VI)	• Site description not provided	• Calcium polysulphide	• 0.9 m (3 ft) diameter auger drill used to mix soil while injecting CaSx solution to create 39 columns (10 m (33 ft) deep x 0.9 m (3 ft) diameter) to over treatment zone	• Treatment area of 5 m x 5 m x 10 m (16 x 16 x 33 ft) deep (250 m^3)	• Provided treatment above and below water table	• Changes to groundwater beyond mixing zone were reported • Treatment area sunk 1 m (3 ft) into the ground requiring the addition of fill material
Trenching								
EPA 2002	• Continuous trenching was used to create a granular ZVI PRB for treatment of chlorinated solvents at a former plating facility	• Chlorinated solvents	• Sand and gravel aquifer with water table 1.2 to 1.5 m (4 to 5 ft) bgs	• Granular ZVI	• Continuous trenching via a large cutting chain excavator combined with a trench box and loading hopper	• Trench was 0.3 m (1 ft) thick and 5.5 m (18 ft) deep	• Minimal construction requirements • Extracted soils could be disposed of onsite	• Settling of iron particles dictates installation time and process
Surface Application								
Hutchins et al. 1998	• Sprinkler application of nitrogen for bioremediation of a fuel contaminated aquifer	• Jet fuel (i.e., benzene, toluene, ethylbenzene, xylenes, and trimethylbenzenes) located in the groundwater 1 to 2 m (3 to 7 ft) bgs	• Shallow, sandy aquifer with water table 1 - 1.2 m (3 – 4 ft) bgs	• Nitrate	• Surface application via five sprinklers to produce recharge rate of 6 cm/day	• 30 x 30 m (98 x 98 ft) treatment cell	• Solution did not pond once vegetation was removed	• Nitrate infiltration was not uniform • Infiltration caused water table to mound • Surface vegetation effected infiltration

Appendix B – Relevant Literature and Reports

Relevant literature and reports for each amendment delivery and distribution approach are listed in Table B.1.

Table B.1. List of Relevant Literature and Reports.

Approach	Relevant Literature and Reports
Aqueous Solutions	• Williams, M.D., Vermeul, V.R., Szecsody, J.E., Fruchter, J.S. 2000. 100-D Area in Situ Redox Treatability Test for Chromate-Contaminated Groundwater. PNNL-13349, Pacific Northwest National Laboratory, Richland, Washington. • Vermeul VR, JE Szecsody, BG Fritz, MD Williams, RC Moore, and JS Fruchter. 2014. "An Injectable Apatite Permeable Reactive Barrier for In Situ ^{90}Sr Immobilization." *Groundwater Monitoring & Remediation* 34: 28-41. doi:10.1111/gwmr.12055. • DOE/RL-2008-10. 2007. In Situ Redox Manipulation (ISRM) Annual Report Fiscal Year 2007, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. • Saslow, S.A., Lawter, A.R., Gartman, B.N., Zhang, Z., Snyder, M.M.V., Zhong, L., Cantrell, K.J., Brown, C.F. 2018. Evaluation of Perched Water Post-Extraction Remedy Technologies: Interim Status Report. PNNL-28054, Pacific Northwest National Laboratory, Richland, Washington. • Peterson SW and KA Hedquist. 2006. Treatability Test Report for Calcium Polysulfide in the 100-K Area, Rev. 0, U.S. DOE/RL-2006-17. Department of Energy, Richland Operations Office, Richland, Washington. • SGW-38255. 2008. Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site, Rev. 0, Fluor, Richland, Washington. • Ludwig, RD., CM Su, TR Lee, RT Wilkin, SD Acree, RR Ross, and A Keeley. 2007. "In Situ Chemical Reduction of Cr (VI) in Groundwater Using a Combination of Ferrous Sulfate and Sodium Dithionite: A Field Investigation," Environ. Sci. Technol. 41(15):5299-5305. • SGW-56970. 2015. Performance Report for the 2011 Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit, Rev.0, CH2M HILL Plateau Remediation Company, Richland, Washington • Truex, M.J., et al. 2009. Hanford 100-D Area Biostimulation Treatability Test Results. PNNL-18784, Pacific Northwest National Laboratory, Richland, Washington • NAVFAC. 2013. "Best practices for injection and distribution of amendments". Available at: https://clu-in.org/download/techfocus/chemox/Inject-amend-tr-navfac-exwc-ev-1303.pdf (accessed 08/27/2019). • ITRC. 2005. "Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater". Available at https://www.itrcweb.org/GuidanceDocuments/ISCO-2.pdf (accessed 08/27/2019).

NAPL	• SRNL-STI-2012-00290. 2012. Treatability Study for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina. • AFCEE. 2007. Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil. Air Force Center for Engineering and the Environment, Brooks AFB, San Antonio, Texas. • DOE/LMS/MND/S11745 2014. "OU-1 Enhanced Attenuation Field Demonstration Edible Oil Deployment Design, Mound, Ohio, Site". Available at:https://www.lm.doe.gov/cercla/documents/mound_docs/AR/2104XXXXXX-1410240003.pdf (accessed 08/27/2019).
Emulsions	• SRNL-STI-2012-00290. 2012. Treatability Study for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina. • AFCEE. 2007. Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil. Air Force Center for Engineering and the Environment, Brooks AFB, San Antonio, Texas. • Borden, RC. 2006. "Protocol for Enhanced in situ Bioremediation Using Emulsified Edible Oil". Available at: https://clu-in.org/download/contaminantfocus/dnapl/Treatment_Technologies/Edible-Oil-Protocol.pdf (accessed 08/27/2019) • Quinn, J., O'Hara, S., Krug, T., Geiger, C., and Clausen, C. 2004. "Evaluating the distribution of emulsified zero-valent iron for four different injection techniques". Paper presented at the Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds. • Truex MJ, et al. 2009. *Hanford 100-D Area Biostimulation Treatability Test Results*. PNNL-18784, Pacific Northwest National Laboratory, Richland, Washington. • Quinn, J., Geiger, C., Clausen, C., Brooks, K., Coon, C., O'Hara, S., Krug, T., Major, D., Yoon, W., Gavaskar, A., Holdsworth, T. 2005. "Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron". Environmental Science & Technology, 39(5): 1309-1318. doi:10.1021/es0490018 • Lee, T. H., Cao, W. Z., Tsang, D. C. W., Sheu, Y. T., Shia, K. F., and Kao, C. M. 2019. "Emulsified polycolloid substrate biobarrier for benzene and petroleum-hydrocarbon plume containment and migration control – A field-scale study". Science of The Total Environment, 666: 839-848. doi:https://doi.org/10.1016/j.scitotenv.2019.02.160 • Watson, D. B., Wu, W.-M., Mehlhorn, T., Tang, G., Earles, J., Lowe, K., Gihring, T. M., Zhang, G., Phillips, J., Boyanov, M. I., Spalding, B. P., Schadt, C., Kemner, K. M., Criddle, C. S., Jardine, P. M., Brooks, S. C. 2013. "In Situ Bioremediation of Uranium with Emulsified Vegetable Oil as the Electron Donor". Environmental Science & Technology, 47(12): 6440-6448. doi:10.1021/es3033555 • Riha, B., Looney, B., Noonkester, J., and Hyde, K. 2009. "Treatability Study for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site: Interim Report- Year One". Available at: https://pdfs.semanticscholar.org/b433/f4345388717b839f4fcffec59dcb9ae01c08.pdf (accessed 08/27/2019). • Riha, B., Looney, B., Noonkester, J., Hyde, W., and Walker, R. 2012. "Treatability study for edible oil deployment for enhanced cVOC attenuation for T-Area, Savannah River Site". Available at: https://digital.library.unt.edu/ark:/67531/metadc839723/m1/1/ (accessed 08/27/2019).

Foam	• Shen, X., L. Zhao, Y. Ding, B. Liu, H. Zeng, L. Zhong, and X. Li. 2011. "Foam, a promising vehicle to deliver nanoparticles for vadose zone remediation," Journal of Hazardous Materials 186(2-3): 173-1780. • Zhong, L., J. Szecsody, M. Oostrom, M. Truex, X. Shen, and X. Li. 2011. "Enhanced remedial amendment delivery to subsurface using shear-thinning fluid and aqueous foam," Journal of Hazardous Materials 191(1-3): 249-257. • Zhong, L., J. Szecsody, Z. Zhang, and S. Mattigod. 2010. "Foam Delivery of Amendments for Vadose Zone Remediation: Propagation Performance in Unsaturated Sediments," Vadose Zone Journal 9(3): 757-767. • Zhang, Z.F., Freedman, V.L., Zhong, L. 2009. Foam Transport in Porous Media - A Review. PNNL-18918, Pacific Northwest National Laboratory, Richland, Washington. • Zhong, L., N. Qafoku, J. Szecsody, P. Dresel, and Z. Zhang. 2009. "Foam Delivery of Calcium Polysulfide to the Vadose Zone for Chromium(VI) Immobilization: A Laboratory Evaluation, Vadose Zone Journal 8(4): 976-985 • Karthick, A., Roy, B., and Chattopadhyay, P. 2019. "A review on the application of chemical surfactant and surfactant foam for remediation of petroleum oil contaminated soil". Journal of Environmental Management, 243: 187-205. doi:https://doi.org/10.1016/j.jenvman.2019.04.092 • Bouzid, I., Maire, J., Ahmed, S. I., and Fatin-Rouge, N. 2018. "Enhanced remedial reagents delivery in unsaturated anisotropic soils using surfactant foam". Chemosphere, 210: 977-986. doi:https://doi.org/10.1016/j.chemosphere.2018.07.081
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Gelling Liquids-Encapsulation	• Truex, M.J., Pierce, E.M., Nimmons, M.J., Mattigod, S.V. 2011b. Evaluation of In Situ Grouting as a Potential Remediation Method for the Hanford Central Plateau Deep Vadose Zone. PNNL-20051, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/pnnl-20051.pdf. • Moridis GJ, P Persoff, JA Apps, L Myer, K Pruess, and P Yen. 1995. "A Field Test of Permeation Grouting in Heterogeneous Soils Using a New Generation of Barrier Liquids". LBL-37554, Lawrence Berkeley National Laboratory, Berkeley, California. • ORNL/ER-401/V1. 1997. "Field Grouting Summary Report on the WAG 4 Seeps 4 and 6 Removal Action Project". Vol. 1 and 2, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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