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Appendix B. Commonly Encountered Issues with In situ Remediation

Commonly Encountered Issues Associated with Remedial Design Characterization – Section 2				
Lithology	Contaminant	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
All		Reliance on MW data vs. a full understanding of contaminant mass distribution vs. lithology vs. permeability (K) available through higher resolution site characterization (HRSC) technology.	Continuous profiling tools such as MiHPT, MiHPT- CPT, LIF, LIF-CPT, LIF-CPT-MiHPT, MIP, MIP-CPT- MiHPT, etc., or continuous rock coring coupled with high density soil or rock sampling and physical and chemical analyses (<u>ITRC 2015</u>).	
		Reliance on older CSMs that have not benefited from current investigation best practices, specifically higher resolution.	Fill data gaps with HRSC and update as needed based on injection performance monitoring.	
		Unrealistic expectations without a full understanding of site-specific challenges, e.g., matrix back-diffusion, which can lead to contaminant concentration rebound after initial improvement in concentrations postinjection.	See <u>Section 2</u> . Knowledge of delivery and amendment limitations in achieving contact and adequate residence time with mass sorbed to the soil matrix.	
		Uncharacterized contaminant mass due to site constraints, existing structures, utilities, roads, or other access limitations, which can recontaminate areas treated by injections (e.g., rebound).	Remedial design characterization and monitoring to evaluate mass flux from areas inaccessible for direct characterization; incorporate contaminant mass flux from these areas into amendment dosing and delivery design (<u>ITRC 2010</u>).	
		Too much reliance placed on point permeability (K) measurement results and not enough on definition of transmissivity network, especially in fractured rock and in larger TTZs whether fractured rock or porous media.	Transmissivity network is directly related to mass flux concepts and can be better elucidated through tracer testing or aquifer pumping tests. Tracer testing conducted in drift mode is typically the most effective approach and, combined with continuous profiling or coring and selective groundwater sampling and analysis, can be highly effective in focusing remediation (ITRC 2010), (ITRC 2017a).	
		Focusing narrowly on basic hydraulics, aqueous geochemistry, and contaminant chemistry and overlooking importance of biogeochemical features and processes.	Sites exhibiting organic and/or metal-metalloid COCs whose fates are susceptible to transport and fate processes influenced directly or indirectly by biogeochemical processes (e.g., redox, precipitation, sorption) may benefit from biogeochemical characterization and treatment considerations. Here, the sessile and planktonic microbes (often quite different populations), their biofilms, and neoformed (authigenic) amorphous and crystalline minerals can offer insight to treatment potential or unintended consequences. Designs can be enhanced, optimization options broadened.	
Bedrock		The amount of contaminant mass sorbed into bedrock secondary porosity.	(ITRC 2017a)	

	Commonly Encountered Issues Associated with Remedial Design Characterization – Section 2				
Lithology	Contaminant	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links		
Soil		Lack of understanding of contaminant mass sorbed onto finer grained soils.	Application of MiHPT, MiHPT-CPT coupled with high density soil sampling to determine extent and distribution of contaminant mass (<u>ITRC 2015</u>).		
		Limitations of solvent extraction in quantifying mass sorbed into soil.	See <u>Discrete fracture network approach for</u> studying contamination in fractured rock		
Groundwater		Variability of K and calculated seepage velocity in contaminated intervals is needed to estimate ROI delivery approaches and residence time within ROI.	Higher resolution slug testing, tracer testing, or pilot testing with monitoring to determine amendment distribution in effective pore space.		
		Mischaracterization of mass flux to be targeted in a mass flux reduction strategy.	Higher resolution sampling to identify transmissive zones for injection based on defined targeted K values, contaminant mass, and heterogeneity within the TTZ.		
	NAPL or DNAPL	Mischaracterization resulting in not identifying the presence of LNAPL or DNAPL that overwhelms efficacy of in situ treatment.	Evaluate vertical extent of TTZ for presence of LNAPL or DNAPL (<u>ITRC 2015</u>) (<u>ITRC 2018</u>).		

C	Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
All		Reaction kinetics is consistent with time of contact.	See <u>Appendix A</u> for specific discussion of amendments, kinetics, and persistence of each amendment. Sections <u>3.3.2</u> and <u>3.5.1</u>	
		Sound design basis for ROI considering transportability within target intervals, e.g., liquids vs. solids, and seepage velocity.	See ROI, Section 3.3	
		Lack of QA/QC evaluation of amendment and water to be used for both dilution of amendment and flushing purposes may introduce new contaminant(s) such as PFAS to the formation other than the targeted COC.	Check Safety Data Sheets of amendments before injecting and request detailed laboratory results of amendment showing the composition from the vendor. If potable water or hydrant water will be used for dilution and as chase water, request a lab analysis for PFAS or other contaminants or inorganic parameters (TDS, TSS, hardness, cations/anions, etc.) that might interfere with the chemical reactions. The details of PFAS sources, fates, etc., can be obtained from the ITRC PFAS Guidance document (in progress).	
ISCO	All	Bench testing actual dosing vs. using default values to determine oxidant demand that is representative of full-scale implementation.	See <u>Appendix A</u> and <u>Klozur[®] Persulfate</u> <u>Oxidant Demand</u>	
		General lack of basis for designing the number of injection events but rather using a rule of thumb.	See Appendix A and Klozur [®] Persulfate Oxidant Demand	

Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design – Section 3			
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		Bench testing is representative, as close as possible, to full-scale remediation design, e.g., water to soil ratios and taking into account the perfect mixing that occurs at the bench scale and not at full scale in regard to contaminant contact.	See <u>Appendix A</u> and <u>Klozur[®]</u> <u>Persulfate Oxidant Demand</u>
	СНР	Injection of peroxide, with or without activation in close proximity to petroleum free product, results in safety risks.	Hydrogen Peroxide (H2O2) Safety and Handling Guidelines
		Improper venting of injection system to avoid overpressurization and safety risks.	See <u>Appendix A</u> and <u>Hydrogen</u> <u>Peroxide Safety and Handling</u>
		Injection of CHP at too high a flow rate, resulting in excessive daylighting and lack of contact within target interval	See <u>Appendix A</u> – Conduct pilot test to define maximum flow rates and pressures and manifold to multiple locations if flow rates are too low to support project budget.
		Sequential vs. concurrent injection of hydrogen peroxide and iron activator result in inefficient contact for complete activation for radical formation.	See <u>Appendix A</u> – USEPA- <u>USEPA In</u> situ Chemical Oxidation
		For chlorinated ethanes or methanes that require reducing radicals, bench testing is essential to determine percent reduction with this secondary treatment pathway from reducing superoxide radicals.	See <u>Appendix A</u>
	Persulfate	The background geochemistry, including TOD, is essential to identify the loading of base activator (NaOH). Persulfate can be used as direct oxidant or in an activation optimization process mode with multiple options for activation to generate radicals. If base activation is used, often with caustic NaOH, reactivity due to sulfate radical declines when pH falls below approximately pH 10. (Note: Some say 9.5, others 11). However, if following oxidation reaction residual pH is too high, this may adversely affect potential for further biodegradation without adjusting the pH.	See Chemical Oxidants Bench Testing (ITRC 2005) to determine buffering capacity of the soil <u>Klozur® Persulfate</u> <u>Activation Guide</u>
		Avoiding DPT injection of iron activated persulfate due to corrosion of carbon steel rods and tooling and comixing of iron and persulfate resulting in excessive heat generation.	See Section <u>3.3.2</u> ; and Chemical Oxidants Compatibility (<u>ITRC 2005</u>) Corrosion and Material Compatibility with Klozur [®] Persulfate and The Safe <u>Use of Klozur[®] Persulfate Activators</u> and <u>ReMox[®] ISCO Reagent Material</u> Compatibility Technical Brief and <u>ReMox[®] Liquid Material</u> <u>Recommendations and Compatibility</u> <u>Technical Brief</u>
		Avoiding overdosing caustic activated persulfate resulting in solids precipitation that could plug wells and injection tools (certainly reduce porosity of the formation).	See <u>Klozur[®] Crystal Formation in</u> Solutions of Klozur [®] SP and Klozur [®] Caustic

(Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
	Permanganate	Exceeding the solubility of potassium permanganate in water resulting in possible plugging (new) injection screen, filter pack, and formation.	See <u>ReMox[®] ISCO Reagent Solubility</u> in Distilled Water Technical Brief	
		Storing and mixing of incompatible materials can lead to serious adverse effects. Care should be taken when the chemical oxidants are stored and mixed. Follow manufacturer's guidelines.	Burn Injury Caused by Mixing Incompatible Chemical with Sodium Permanganate	
Anaerobic	AII	Anaerobic biotreatment technologies are typically effective when geochemical conditions such as relatively lower redox (e.g., lower than -200 mv) are achieved. Depending on specific geochemical conditions, oxygen and one or more AEA (anandamide externally added) such as sulfate may need to be eliminated or greatly reduced before desirable treatment response is observed. Residual electron acceptor concentrations (e.g., sulfate and nitrate) may exceed water quality standards.	It is essential to collect background and baseline geochemical data, including electron acceptor demand, and to understand the existing biodegradation pathways before designing the loading for the amendment. Use a highly soluble amendment to stimulate sulfate reduction prior to dosing with a longer lasting amendment that will facilitate development of methanogenic conditions. (Note: It is not always desired to achieve methanogenic conditions.) See Appendix <u>A1.3</u>	
	Soluble	Low persistence requires multiple injection events to overcome matrix back-diffusion.	Typically used to get anaerobic conditions started and then followed by nonsoluble. See Appendix <u>A1.3</u>	
	Solids	Mulch, chitin, or other solids must be emplaced by trenching, soil mixing, or fracturing.	Must achieve adequate loading to promote degradation reaction within treatment zone, which depends on width of PRB trench and groundwater flow rate.	
Aerobic	All			
	Solids	Estimating diffusive transport of slow-released oxygen source in finer grained soils to develop ROI.	Find the appropriate gas diffusion coefficient or conduct a treatability study (<u>Allaire 2008</u>). See Appendix <u>A1.1</u>	
	Liquids	Short-lived release of oxygen from hydrogen peroxide requires multiple events.	Develop a good design basis for the amount of hydrogen peroxide needed considering its persistence and residence time within ROI, and plan for multiple injection events or continuous feed system if warranted. Consider different oxygen source. See Appendix <u>A1.1</u>	

Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
	ZVI	Abiotic chemical reduction technologies of which ZVI and BiRD are two, typically express at least two reaction pathways: 1) beta elimination through acetylene series, and 2) hydrogenolysis through less chlorinated aliphatic DCE isomers and VC. Additionally, some fraction of PCE or TCE may concurrently transform via microbial hydrogenolysis. Often DCE and VC production is much less but still significant.	Evaluate potential for production of lower chlorinated compound and compare to regulatory goals. Often, effective understanding of chlorinated transformation product potential requires bench or pilot testing. Modifications might include sulfidization of the ZVI or bioaugmentation with Dehalococcoides spp. that (currently) are the only microbes known to promote direct and full dechlorination. See Appendix <u>A1.1</u>
	Chemical	Calcium polysulfide solution should not be diluted below a 5% concentration, otherwise precipitation issues with sulfur develop as the pH drops during dilution.	Adding a caustic to dilution water helps maintain pH above precipitation levels.
Sorption and sequestration	Activated carbon and biochar- based injectates	Limited data to evaluate long-term effectiveness of sorption/sequestration technologies and potential for contaminant leaching from carbon over time.	Develop monitoring program to assess long-term effectiveness See Section <u>4.4</u> and transition and contingency planning See Section <u>4.6</u> .
		Injection of activated carbon may limit viability of subsequent treatment by other technologies due to changes in porosity, carbon content.	Design should be sufficient to achieve remediation objectives, or consider applicability of suitable combined remedies, e.g., enhanced bioremediation following carbon injection. See Section <u>3.4.1</u>
Surfactant flushing	Surfactants, saponification agents, shear- thinning fluids (polymers), electrolytes	Surfactant flushing achieves contaminant mass recovery and can involve mobilization and solubilization, or only solubilization. However, surfactant flushing is most efficient when mass mobilization and recovery is the desired outcome. In this case, most mass would be recovered by mobilization and the balance by solubilization. A challenge is to correctly determine which mode to apply to site conditions and to provide sufficient recovery of mobilized and solubilized contaminants.	Bench testing and pilot testing are critical for surfactant selection and flushing and extraction design for full capture of mobile contaminants. See Section <u>3</u> , Appendix <u>A2.5</u> , and Section 4.3, Implementation and Optimization Staircase (ITRC 2002a).
		Formation porosity reduction via mobile phase gelling or silt-clay migration and plugging by flocculation or straining is possible if the aqueous and sediment geochemistry is not adequately considered in surfactant system specification (e.g., surfactant, cosurfactant, electrolyte, etc.).	An important objective of bench-scale testing is to assess for adverse formation damage. One indicator that porosity reduction is occurring is the marked increase in back pressure during column flushing tests. It is noted that bench treatability testing for surfactant assessment efficacy and developing scalable design specifications must include a mix of batch and column flushing experiments. See <u>Table 3-2</u>

C	Commonly Encountered Issues Associated with Amendment Delivery, Dose, and Design - Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
		Mobilization recovery is typically the most efficient means of LNAPL recovery if the hosting formation permeability/transmissivity is supportive (e.g., formation is porous media with average grain size of fine sand or larger and low clay and silt content). Shear-thinning fluids or polymers should be used in forced-gradient mode to help push the LNAPL, including previously immobile LNAPL at less than residual phase, out of the pores and toward the recovery well.	The bench treatability study should include tests for shear-thinning polymer selection and characterization, and polymer flushing stages should be included in column flushing tests. See <u>Table 3-2</u>	
		One of the optimization opportunities with mobilization flushing is selection of a surfactant package that achieves low interfacial tension, e.g., three orders of magnitude or lower than interfacial tension between water and the oil phase in question.	Many commercial products or commodities with some surfactancy effect can produce a noticeable outcome in terms of NAPL mobilization or increased dissolved- phase concentration. Despite a noticeable outcome these products are relatively ineffective technically and economically for mobilization flushing and even enhanced solubilization mass removal. Well designed and operated bench studies can readily demonstrate the relative benefits of different products. See <u>Table 3-2</u> Bench Testing: Objectives and Design Considerations	
Enhanced solubilization flushing	Co-solvent, surfactant, clathrate	Agents designed for enhanced solubility functionality such as co-solvents (e.g., alcohols) and chlathrates (certain complex sugars) are sometimes specified or applied for NAPL mobilization flushing mass removal. These should be applied only to enhanced solubilization flushing operations. Surfactants are a special case where mass removal is possible via both enhanced solubilization and mobilization.	Bench testing is an important design component and necessary for optimization (<u>ITRC 2018</u>).	

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
All		Hydraulic design basis for ROI taking into account effective or mobile porosity and seepage velocity vs. persistence.	Ensure dosing and number of applications are consistent with projected advective distribution of amendments.
ISCO	All	Using vendor dosing calculator default values.	Suggest that you bracket the vendor estimates with science-based oxidant demand calculations and include a safety factor. (Note that chemical sellers are motivated to be conservative (include <i>safety</i> factors) so very much agree on independent work but the quantity may actually be less than proposed.) See Appendix <u>A.2</u>
		Issues with amendment safe handling concentrations.	Follow guidelines and recommendations from vendor. See Appendix <u>A.2</u>

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
		Consider solubilities of amendments in water.	If reagent exceeds aqueous solubility, not all of amendment will dissolve, resulting in precipitation of chemicals, which may reduce effective porosity of aquifer. Appendix <u>A.2</u>
	Catalyzed hydrogen peroxide	Using vendor dosing calculator default values vs. site specific values for peroxide concentration.	Determine dosing during bench scale testing with site soils. See Section <u>3.5</u>
	Persulfate	Using vendor dosing calculator default values vs. site-specific values, e.g., buffering capacity, oxidant demand.	Determine dosing during bench-scale testing with site soils. See Section <u>3.5</u>
	Permanganate	Using vendor dosing calculator default values vs. site-specific values, e.g., effective oxidant demand.	Determine dosing during bench-scale testing with site soils. See Section <u>3.5</u>
BIO	All	Using vendor dosing calculator default values.	Make sure you bracket the vendor estimates with science-based calculations of electron donor/acceptor and include a safety factor.
		Lack of degraders present to use the nutrients in a useful manner.	Evaluate use of biological/chemical testing (e.g., PetroTrap, CSIA). See <u>Table 3-2</u>
		Apparent lack of nutrients to sustain degradation.	Determine dosing during bench-scale testing with site soils. Verify during pilot testing. See Appendix <u>A.1</u>
Anaerobic	All	Overdosing resulting in creating methanogenic conditions.	Develop a design based on pilot testing and don't use rule of thumb concentrations. See Section <u>3.3.3</u>
	Soluble	Substrate does not last long enough in subsurface to conduct performance monitoring or see reductions in target compounds.	Electron donor demand is higher than what can be provided with a soluble donor. Consider pilot testing a combination of soluble and less-soluble substrates. Another possibility is that the soluble substrate is not adequately distributed or the monitoring locations are not adequately placed. See Section 3.3.3
	Nonsoluble	Not adding or not adding enough buffering amendments to maintain pH in optimal range for CVOC biodegradation.	Determine during bench-scale testing with site soils. Verify during pilot testing and test pH and adjust as necessary when pH drop reduces remedy effectiveness. See Section 3.3.2
	Solids	Solid substrates, such as mulch or chitin, must be emplaced by trenching or soil mixing.	Consider adding mechanism to replenish PRB with a liquid substrate. See Appendix <u>A1.3</u>
	Gas	Hydrogen gas can serve as source of hydrogen for ERD.	Hydrogen gas is flammable and can be an explosive hazard. Consider how hydrogen gas will be mixed with groundwater and how often hydrogen gas cylinders must be replaced. See Appendix <u>A1.2</u>
Aerobic	All	Consider stoichiometry for release of oxygen compared to demand from NAPL, solid, and dissolved contaminant phases, reduced minerals, and NOD.	Determine oxygen release rates and distribution in bench scale or pilot testing. See to Appendix A1.2 Sections $3.3.2$ and $3.3.3$

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
	Solids	Consider stoichiometry for release of oxygen from solid oxygen-releasing compounds compared to demand from NAPL, solid, and dissolved hydrocarbon phases, reduced minerals, and NOD.	Many solid oxygen-releasing compounds are very alkaline and the elevated pH can impact microbial populations. See Appendix <u>A.1.1</u> , Section <u>3.5.2</u>
	Liquids	Hydrogen peroxide is a source of oxygen as it decomposes. Too high of a dose of peroxide can be toxic to microbes or wasted if decomposition rate is too fast.	Start out with low hydrogen peroxide dose and increase over time. See Appendix <u>A.1.1</u>
	Gas	Oxygen can be provided from air or purified oxygen and sparged into groundwater or introduced by bioventing.	Determine ROI for gas distribution. If sparging, consider pulsed injections to avoid preferential pathways. See Appendix <u>A1</u>
ISCR	All		
	ZVI	Using vendor dosing calculator default values versus site-specific values, ZVI weight percent to soil.	Determine dosing during bench-scale testing with site soils. See Section 3.5
		ZVI reducing equivalents may be funneled to water reduction up to ~99% and CAH (chlorinated aliphatic hydrocarbon) reduction as low as ~1%. The dose calculations portion of the design may not factor this in.	Bench or pilot testing can confirm ZVI efficiency for direct reduction versus H_2 (hydrogen) dissolved gas generation that might promote enhanced biotic reduction. Sulfidization of ZVI has been shown to effectively reverse the reducing equivalent flow (Semprini 1992).
	Liquids	Chemical reductants such as sodium dithionite, calcium polysulfide, or solutions of ferrous iron-containing compounds can provide ISCR reagents to subsurface or reduce existing iron in soil, and create reactive minerals such as ferrous sulfide.	Bench scale or pilot testing recommended to determine appropriate loading and confirm effectiveness in treating COCs. See Section 3.3.2 and 3.3.3
Sorption and sequestration	Activated carbon and biochar-based injectates	Dosing should be based on estimated contaminant mass across area and vertical profile of TTZ, including saturated zone soils.	Complete RDC soil sampling See Section 2.3
Surfactant flushing	Surfactants, saponification agents, shear- thinning fluids (polymers), electrolytes	Surfactant flushing can be applied to both LNAPL and DNAPL source zones. LNAPL sources are typically addressed through mobilization and DNAPL through enhanced potentially super-solubilization. It is desirable to mobilize LNAPL, and solubilization with increased contaminant dissolved phase concentrations will occur concurrently. Adverse impact will be minimal to nonexistent if the recovery well network is designed appropriately. Unlike LNAPL source zones, DNAPL source zones are often more complex and more difficult to fully characterize, and uncontrolled contaminant mass migration is more likely. Surfactant flushing is rarely applied to DNAPL.	Bench testing can generate data offering insights into the magnitude and extent of enhanced solubilization and desorption under either mobilization or enhanced solubilization approaches. The types of contaminants and concentrations, as well as other characteristics such as surfactant concentrations, pH, salinity, etc., are important for selecting effluent management approach and developing treatment specifications as appropriate. Field pilot testing is critical to effective assessment of magnitude and extent of contaminant mobilization. The pilot test should evaluate mass recovery approach and details including extraction well design for full capture.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Delivery and Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
All		Misapplying reagents not suitable for specific lithologies, e.g., solids in sands or liquids in clays.	Sands compact, rather than fracture, limiting the amount of amendment that can be emplaced. Injection velocities may need to be consistent with fluidization to obtain adequate distribution.
		Poor areal and vertical distribution.	Integrate delivery approach with amendment's physical form and the target lithology.
		Delivery in shallow intervals results in daylighting.	Possible in all types of geology, sometimes due completely to anthropogenic features. Possible with coarse-grained soils at low flow rates and pressures.
		Delivery of liquids in soils that need to be fractured.	Typically liquids don't have the residence time required to be effective in low pore volume applications required while fracturing.
		Determine whether injections will be advanced top-down or bottom-up and select appropriate injection tooling. Consider target lithology, injection pressures, and injectate type (e.g., aqueous solution or slurry).	For DPT injections a top-down approach generally results in more uniform distribution of reagent than a bottom-up approach. In a bottom-up approach, the borehole created by the rod and screen as they are raised can act as a conduit for downward migration of the reagent. Hence, a pyramid-shaped distribution of the amendment can result (<u>NAVFAC 2013a</u>). An exception would be in some flowing sands because the formation immediately collapses back into the void created by pulling up on the rods. Special injection tools can also help make bottom-up injections more successful in all lithologies. Injections using straddle packers, especially when sealing off directly onto the rock, are generally done bottom-up to increase the likelihood that the packer can be retrieved.
		Percent pore volume required for injection or emplacement for vadose zone remediation.	Vadose treatment requires injecting enough water to allow reactions to occur in the dissolved phase. Typically this would require 100% of pore volume to be displaced with diluted amendments. Liquids may drain from vadose zone.
		Groundwater displacement due to injection/emplacement of amendments that results in untreated contaminated groundwater leaving the site.	Develop a sound basis for ROI taking into consideration whether hydraulic control (e.g., extraction and recirculation) of groundwater used for dilution water to inject higher volumes is required for low seepage velocity sites. Also consider sequence of injections, specifically starting at the periphery and working in to mitigate migration risk.
	< fracture pressure injection	Not controlling and accurately recording injection pressures throughout the injection process.	Best practice would be an automated injection and injection performance data recording system.
	> fracture pressure injection	Unrealistic expectations on ROI.	Verification of amendment distribution during pilot testing. The design is not finished until the design is first implemented.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Delivery and Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
	> fracture pressure solids emplacement	Unrealistic expectations on ROI.	Verification of amendment distribution during pilot testing. The design is not finished until the design is first implemented.
	DPT delivery	Not factoring in compaction around the piping when controlling pressure and loss of pressure control as rods are added or removed.	Demonstrating compaction pressures during pilot testing and using inner hose direct push tooling to maintain constant injection pressure throughout the target interval and keeping the rods under pressure while advancing to the next injection depth. Monitoring of "breakout" pressure, and resultant drop (with increase in flow) is important to note during injection, and equipment must be sized to overcome initial injection resistance.
	Injection wells	Wells are not screened in the correct intervals that could have been optimized through high-resolution characterization.	Define target intervals for well screens with HRSC approaches before installation. Shorter screen intervals are often better but longer screen intervals can allow for more formation distribution and the possibility of acceptable performance.
ISCO	All		
	Catalyzed hydrogen peroxide	Increases in pressure when injecting rapidly reacting reagents, like H_2O_2 , may signify gas generation and improper dosing/delivery. Safety risk by not venting all valves in contact with peroxide.	Vent all equipment in contact with hydrogen peroxide to prevent gas generation that has nowhere to escape and could cause a rupture of equipment and injury to operators.
		Low pH iron activation is incompatible with DPT drill pipe. Must inject through PVC.	pH < 2 will corrode pipe threads and they will not be retrievable.
	Persulfate	Iron activation incompatible with DPT drill pipe, must inject through PVC wells.	pH < 2 will corrode pipe threads and they will not be retrievable.
			Distribution can be verified by electrical conductivity logging, ORP, and pH readings during injections.
		Exceedance of auto decomposition concentrations.	> 30% concentration will react with itself and persulfate will be wasted.
	Permanganate	Mixing potassium permanganate above 2.5% without creating a slurry.	2.5% still requires good mixing and greater than2.5% will require heating dilution water.Reconsider sodium permanganate.
			Distribution can be verified by soil coring and photo spectrometer to determine concentration.
Anaerobic	All	Pulsing of bioaugmentation cultures with an anaerobic blanket vs. mixing with anaerobic dilution water.	Ensure good in situ mixing of both amendments to obtain the same ROI.

Commonly Encountered Issues Associated with Amendment Delivery – Section 3				
Amendment Class	Delivery and Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
		Poor distribution, resulting in discrete zones of concentrated mass of injectate, can lead to chemical and biological plugging of formation or at least low efficiency.	Design for undesirable concentration resulting from heterogeneous distribution with reduced injectate concentration or strength.	
	Soluble	Distribution	Can be verified by changes in electrical conductivity in nested wells, or by temporary temperature changes. A tracer can be added to aid in visual determination, if site conditions do not include risk of daylighting.	
	Nonsoluble	Distribution	Can be verified by changes in electrical conductivity in nested wells, or by temporary visual or temperature changes. A tracer can be added to aid in visual determination, if site conditions do not include risk of daylighting.	
		Calculating an EVO (emulsified vegetable oil) loading only on hydrogen demand and not factoring in enough water to achieve ROI.	Factor in total volume of injectate, accounting for percent water in any vendor product, and the required volume of makeup water necessary to reach your design ROI. Make sure your calculations are checked by a third party.	
	Solids	Poor mixing resulting in clogging and inconsistent delivery.	Define mixing equipment and time required to create homogenized slurry during preplanning or pilot testing event.	
		Using emplacement tools not designed for solids.	Use pressure-activated emplacement tooling rather than screened tools. Anecdotal evidence suggests pressure-actuated injection points often fail to work.	
Aerobic				
	Solids	Emplacement at low flow rates resulting in not achieving ROI, unless ROI is just diffusion based.	Distribution requires exceeding fracture pressures at higher flow rates to create new pathways in order to approach design ROI.	
	Liquids	Dilute hydrogen peroxide or dissolved oxygen in other forms can lead to biofouling of injection wells.	Consider pulsed injections of higher doses or incorporation of biofouling control reagent to prevent microbial growth on well screens.	
ISCR	All			
	ZVI	Emplacement at low flow rates resulting in not achieving ROI.	Distribution requires exceeding fracture pressures and higher flow rates to create new pathways and achieve ROI.	
		Emplacement of higher volumes than location can assimilate, leading to daylighting.	Verification of amendment distribution during pilot testing.	

Commonly Encountered Issues Associated with Amendment Delivery – Section 3			
Amendment Class	Delivery and Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
		Adequate mixing of ZVI and guar is required to prevent settling in tanks and injection hoses.	Educt guar into mixing tanks rather than applying by hand to avoid clumping of guar <i>fish</i> <i>eyes</i> . Replace guar with shear-thinning fluid or consider adding an emulsifier. Mixing equipment and injection pumps must be designed to work with slurries. The slurry must not be allowed to 'settle' anywhere within the injection equipment.
		Combining conflicting remedies (e.g., permanganate injection upgradient of ZVI barrier).	Manganese Dioxide can plug ZVI reaction sites.
		Distribution can be verified by soil coring and measuring magnetic responses.	Use of Magnetic Susceptibility to Map Amendment Distribution in the Subsurface, (<u>Harkness</u>).
	Liquids	Pulsing of calcium polysulfide with water flush may not result in uniform distribution within ROI.	Inject a diluted solution of at least a 5% concentration at the volumes required to achieve ROI based on advective flow.
		Using emplacement tools not designed for solids.	Use pressure-activated emplacement tooling rather than screened tools.
Sorption and sequestration	Activated carbon and biochar-based injectates	Injection of carbon as a slurry often requires high-pressure injection, which may exceed fracture pressures.	Verification of amendment distribution during injection via presence in wells, coring.
Surfactant flushing	Surfactants, saponification agents, shear- thinning fluids (polymers), electrolytes	Surfactant flushing can be applied to both LNAPL and DNAPL source zones. LNAPL sources are typically addressed through mobilization and DNAPL through enhanced, potentially super- solubilization. It is desirable to mobilize LNAPL, and solubilization with increased contaminant dissolved-phase concentrations will occur concurrently. Adverse impact will be minimal to nonexistent if the recovery well network is designed appropriately. Unlike LNAPL source zones, DNAPL source zones are often more complex and more difficult to fully characterize, and uncontrolled contaminant mass migration is more likely. Surfactant flushing is rarely applied to DNAPL.	Field pilot testing is critical to effective assessment of magnitude and extent of contaminant mobilization. The pilot test should evaluate mass recovery approach and details including extraction well design for full capture (ITRC 2002b).

Commonly Encountered Issues Associated with Field Implementation – Section 4				
Amendment Class	Field Implementation- Technology, Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
All		Utilizing pumps that don't meet the specifications for effective distribution.		

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	Field Implementation- Technology, Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
		Utilizing mixing equipment that doesn't meet the specification for effective mixing required for effective distribution.	
		Defining downhole pressures based on pressure readings at the injection pump.	Have a good understanding of pressure losses throughout the injection system from the pump pressure gauge to the exit from the injection tool.
	< Fracture pressure injection	The inability of the injection system, as designed and operated, to maintain injection pressures below fracture pressures required for distribution.	Do not exceed fracture pressures to maintain controlled distribution.
	> Fracture pressure injection	The inability of the injection system, as designed and operated, to maintain injection pressure and flow rates above fracture pressures required for distribution.	Review pump curves of pressure vs. flow.
		Ensure all injection hose and pipe connection is pressure-rated for maximum pressures of the pump.	
	> Fracture pressure solids emplacement	The inability of the emplacement system, as designed and operated, to maintain injection pressures above fracture pressures required for distribution.	Review pump curves of pressure versus flow and size of solids it can pump.
		Ensure all emplacement hose and connections are pressure-rated for maximum pressures of the pump.	
	DPT delivery	Losing pressure control as rods are added or removed to achieve target depths.	Utilization of an <i>inner hose</i> system to maintain constant pressure.
		Ensure injection or emplacement tools are at target depth.	
		Ensure boring is straight to avoid daylighting around rods.	
		If injection rods are left in overnight, make sure they won't plug and require excess pressures and fracturing to restart injection.	
		Develop specific procedures on how to complete locations should daylighting or refusal prevent meeting dosing specifications.	
	Injection wells	Don't exceed pressure rate of well seal to avoid compromising well for future injection.	

Commonly Encountered Issues Associated with Field Implementation – Section 4				
Amendment Class	Field Implementation- Technology, Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
		Monitor groundwater elevations at nearby wells to assess degree of mounding remains within design specifications and adjust injection rates and pressure as needed.	Consider automated injection systems that can be controlled based on groundwater elevations in nearby wells.	
	Adequate distribution of amendments	Include adequate monitoring locations (wells or Geoprobe borings) and equipment in the design workplan to capture distribution. Downhole monitoring can be conducted using a variety of instruments to capture changes in physical and geochemical parameters during and immediately after injection.	See Section <u>4.4.1</u>	
	Performance monitoring	Postinjection monitoring data indicate an increase in concentrations following an initial decrease in contaminant concentrations, commonly referred to as "rebound."	Re-evaluate CSM and potential causes of rebound, which may include back-diffusion from within the TTZ, recontamination of the TTZ from impacted areas outside of the ROI (see Section 2), inadequate dosing/persistence of reagents relative to contaminant mass (see Section 3).	
ISCO	All	Maintaining injection pressures and flows during startup at multiple manifolded injection locations.	Ensure system design and operating procedures prevent fracturing of the formation. Consider automated systems as best practice.	
		Health and safety plan, personal protective equipment (PPE), and associated Safety Data Sheets don't address site-specific safety considerations.	Generic information is often not adequate to ensure safety. Focus on heat stress during hot weather.	
		Ensure adequate protection of public when establishing work areas.	Public should never be in close proximity to injection locations that could spray them with oxidants and activators during equipment malfunctions.	
		Injection while site is active for business.	Avoid this situation if adequate safety systems can't be implemented, e.g., injection at active gas station.	
	СНР	Daylighting events do not stop once flow is shut down. Exothermic energy input has been excessive and is driving pressure release for a period of time until pressure has declined enough.	Maintain injection rates, according to demonstrated specification to minimize daylighting.	

Commonly Encountered Issues Associated with Field Implementation - Section 4			n - Section 4
Amendment Class	Field Implementation- Technology, Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
		Installation of thermal couples to ensure groundwater temperature specifications are not exceeded.	Excess heat not only leads to daylighting but also decomposes the hydrogen peroxide quickly. Don't inject into NAPL zones. Cause and effect – excess H_2O_2 and catalysis lead to heat that leads to pressurization that leads to vaporization and concurrently leads to H_2O_2 decomposition, which leads to gas generation and to more pressurization and destabilization.
	Permanganate	Have adequate neutralization chemicals available for daylighting or spill events.	
BIO	All	No indications of change after amendment injection.	Verify groundwater flow direction, velocity, and lithology. Ensure that sampling locations and sampling depths are downgradient of the treatment area. Install temporary borings to check on distribution.
Anaerobic	All	Not achieving anoxic and pH specification for dilution water.	Note: pH may drop at least one order of magnitude (one pH unit) after mixing with amendment.
		Not achieving in situ redox conditions necessary for bioaugmentation culture to survive.	Check your site's ambient redox conditions, DO, pH, alkalinity, and dosing calculations to verify that the correct amendment and dosing are being used. Continue to monitor for change.
		An excess of methane is being generated in the surface as a result of amendment dosing.	Stop injection amendment and carefully monitor methane gas concentration in and around the wellheads. Provide supplemental mixing with air to reduce concentrations to below explosive limit. Research and implement safety precautions to prevent oxygen deprivation to potential receptors.
	Solids	Daylighting events do not stop once flow is shut down.	Maintain emplacement rates as those specified and demonstrated to minimize daylighting.
ISCR	All		
	ZVI	Plugging of injection tools due to inadequate mixing and suspension of ZVI.	Review mixing design and test during and verification of amendment suspension during pilot testing.
		Abrasion of emplacement tools from ZVI increasing emplacement port diameter.	Inspect tools after each location and replace as necessary. Inject port size directly impacts emplacement exit velocity, which impacts distribution.

Commonly Encountered Issues Associated with Field Implementation – Section 4			
Amendment Class	Field Implementation- Technology, Amendment Specifics	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links
		Adequate measurement of injection rates.	Consider mag flow meters vs. estimating tank level reduction over time.
	Liquids	Continuous monitoring of H_2S during calcium polysulfide injection.	H ₂ S generation occurs as calcium polysulfide is diluted with water.
Sorption and sequestration	Activated carbon and biochar- based injectates	Carbon presence in monitoring wells provides real-time evidence of amendment distribution during injection; however, carbon-impacted wells will need to be redeveloped to remove carbon from the well and filter pack, or replaced to ensure that groundwater samples provide contaminant concentration data representative of the aquifer for performance monitoring.	See Appendix <u>A.2.4</u>

Overall Challenges Associated with Section 5 Regulatory Perspectives & Section 6 Community and Tribal Stakeholder Considerations			
	Challenges, Lessons Learned, and/or Best Practices	Discussion, Document Section, Links	
The traditional linear evaluation and decision-making process prevents implementation testing of an in situ treatment alternative.	Understanding that the successful application of in situ technologies is an inherently iterative process, that the regulatory process can allow for iterations within the traditional regulatory process, and that the early and close coordination of all stakeholders is essential, it is possible to optimize the regulatory process by building needed iterative assessments and adjustments into a project's decisions documents.	Section <u>5</u> and Section <u>6</u>	

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