Selection of a Remediation Alternative which is Best for Your Site

The Hepure team has over 100 years of environmental site remediation planning, design, and execution. Each day we work with project managers to help select the best remedial alternative for their site conditions. This paper discusses how to evaluate chemical and biological treatments to determine which may be the best alternative for your site. This paper will focus on the treatment of chlorinated ethenes (VOC), each technology has a proven record of success with these compounds.

Zero Valent Iron (ZVI): ZVI is the newest of the technologies, first discovered about 25 years ago the primary use was flow through barriers. Once technologies became available to produce fine iron powders which are injectable as a slurry, ZVI became a major player in plume and source area treatment.

Figure 1 Fine Iron Powder

Two key advantages of ZVI are its abiotic reaction and longevity. The abiotic pathway removes two electrons and prevents the formation of daughter products. For example, PCE is reduced to dichloroacetylene (Pathway 2) without formation of intermediaries such as dichloroethane and vinyl chloride (Pathway 1). Another advantage is a typical longevity of over 10 years of reactivity depending on the particle size.

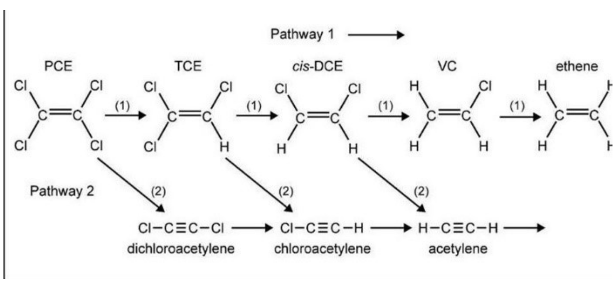

Figure 2 Abiotic Pathway

Chemical Oxidation

Permanganate and persulfate are the two chemical oxidants of choice for remediation of VOC. Each has a long history of efficacy in treatment of VOC. Selection is based mostly on characteristics of the contaminant.

Permanganate comes in two forms, solid (potassium permanganate) and liquid (sodium permanganate). The chemistry and usage of each Figure 3 Potassium Permanganate. Potassium Permanganate is provided as a 97% solid and sodium permanganate can be provided in a solution up to 40%.

Figure 3 Sodium Permanganate

Figure 4 Potassium Permanganate

Permanganate is the preferred chemical oxidant for chlorinated solvents. It is highly effective and has a reasonable period of effectiveness and does not require activation. Permanganate's solubility allows it to diffuse into the aquifer providing a larger area of treatment. It may be placed into the aquifer by high- and low-pressure injection or back fill into an excavation and soil mixing.

Persulfate is typically applied with an activator, although, in some conditions an activator may not be needed. Persulfate advantage is that it can treat a broader range of recalcitrant contaminants if present with VOC. Activating with caustic or hydrogen peroxide is typically performed in two stages.

Figure 5 Persulfate

The aquifer is conditioned with the activator and then the persulfate is applied. Various forms of iron activation are now available which do not require pre-conditioning, the persulfate and iron activator can be applied together. Due to its ability to corrode injection equipment, persulfate is usually not preferred over permanganate unless there are compounds present which permanganate cannot treat.

Bio-Treatment: Bio-Treatment is really bio-augmentation. The current biology of the aquifer is augmented with a carbon source, necessary nutrients and sometimes a bacteria culture. Bio-Treatment is the work horse of chlorinated solvent remediation, it has more site applications than ZVI and Chemical Oxidation combined. Bio-Treatment has a reasonable longevity of about 3-5 years but a weakness that daughter products can be formed if the treatment is incomplete.

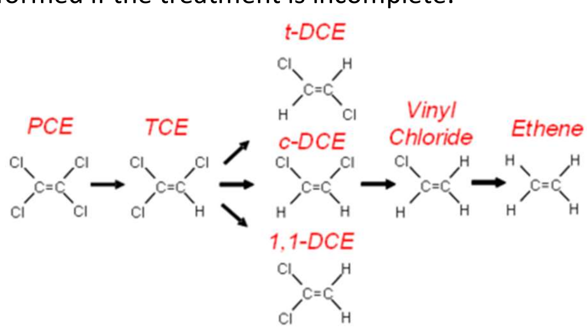

Figure 6 Biotic Pathway

A newer preferred approach to Bio-Treatment is the dual application of ZVI and a carbon source. The ZVI helps condition the aquifer by scavenging oxygen and minerals which have negative effects on the efficacy of Bio-Treatment. Most often Bio-Treatment is only recommended where data show that biological degradation of contaminants is already occurring. This is typically shown as the presences of degradation daughter products TCE, DCE, and VC.

Remedy Selection

The key to selecting the best remedial solution is to evaluate each alternative for compatibility with site conditions. Although there are many solutions which are effective in treating chlorinated solvents selection of the best alternative achieves that remediation goals with the least cost. This scoring system can be used as a preliminary evaluation to see which technology may be preferred for the given site conditions. For each condition select one row of criteria which best matches site conditions. Sum the score for each technology in the selected rows.

Example site:

The example site contains a dissolved VOC plume requiring treatment. The site is scheduled to be sold within 3 years and the client wishes to have remediation complete and natural attenuation demonstrated prior to transfer. DCE and VC are present in low concentrations indicating some biological degradation of VOC is taking place. The soil is a silty sand with an estimate annual flow rate of >100 feet per year. Dissolved oxygen has been measured at 4 ppm in most wells, VOC concentrations are moderate at about 500 µgL and TOC is relatively high at 15 ppm and low concentration of other minerals present.

One row in each evaluation criteria is highlighted in red to reflect the example site conditions. These rows are added together and the result place in "**Sum of Selected Rows".** The highest sum represents the preferred remedial alternative. A brief discussion of the evaluation follows the selection criteria.

Presence of Biodegradation Daughter Products

The presence of biodegradation daughter products (TCE, DCE and VC) indicate the site is a good candidate for continued biotreatment aided by bio-augmentation. Although the primary pathway for ZVI is abiotic there is an enhancement of the biotic pathway as well.

Presences of Daughter Products	ZVI	Chemical Oxidation	Bio-Treatment
Yes	7	2	10
No	10	7	2

Soil Type

The soil type plays and important role in selection of a remedial alternative. ZVI prefers sandier soils where the particles can easily be distributed into the soil matrix. Once in place ZVI will not mobilize, the contaminant must flow to the ZVI for effective treatment. Chemical Oxidations can be applied in sandy soils and in soils of moderate density and will mobilize with groundwater flow. Tighter soils are better suited for bio-treatment. Once in place the augmentation is highly mobile and will move within the soil matrix over time to help increase plume area coverage.

Soil Type	ZVI	Chemical Oxidation	Bio-Treatment
Tight Soils(Silt Clay)	2	7	10
Moderate Soils(Silty Sand)	7	10	7
Permeable Soils(Sand Gravel)	10	7	7

Aquifer Flow

Groundwater flow can have a detrimental effect on remedial alternatives. ZVI may require more product to be applied but will not be diluted or washed away in high flow conditions. Chemical Oxidation will be diluted but can be applied as a slurry to help mitigate this effect. Also give the short duration of Chemical Oxidation treatments it will not have time to highly dilute. Bio-Treatment is the most effected by high flow rates. Bioaugmentation products will move with the aquifer and may leave the treatment area. Water flow can also bring in additional oxygen which is detrimental to the anerobic process.

Aquifer Flow	ZVI	Chemical Oxidation	Bio-Treatment
High Flow(>100 ft/Year	10	7	2
Moderate Flow (20 -100 ft/yr)	10	7	7
Low Flow (<20 ft/year)	2	7	10

Mass of VOC

Selection of a remedial alternative can be greatly affected by the concentration of VOC in the groundwater. High concentrations are very difficult for Bio-Treatment but easily treated by chemical oxidation. ZVI may require additional time but due to its longevity can handle high concentrations. .

VOC Concentration	ZVI	Chemical Oxidation	Bio-Treatment
High (>1ppm)	7	10	2
Moderate (100 – 1000 µg/L)	10	7	7
Low <100 µg/L)	7	2	10

Geochemistry

Geochemistry plays an important role in the selection of remedial alternatives. High dissolved oxygen levels are detrimental to anaerobic Bio-Treatment and may consume excess amounts of ZVI. In addition, there are other chemistries which will affect the remediation process such as Total Organic Carbon and Dissolved Minerals.

Dissolved Oxygen	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	2	7	2
Moderate (1-5 ppm)	7	10	7
Low <1ppm)	10	7	10

Total Organic Carbon	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	7	2	10
Moderate (1-5 ppm)	10	7	7
Low <1ppm)	10	10	7

Dissolved Minerals	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	2	2	10
Moderate (1-5 ppm)	10	7	10
Low (<1ppm)	10	10	10

Site Access

We would like to think of remedial applications to be one and done, that is rarely the case. ZVI with its longevity (10+ years) can be applied and left to do its work for a long time. Second in longevity is Bio-Treatment, however, it will typically require an additional application of a carbon source in 3-5 years. Chemical Oxidation treatment can remove a lot of mass, however, does not possess much longevity. Typically, at least 2 and possible 3 applications of Chemical Oxidation will be needed, requiring site access over a few years.

Site Access	ZVI	Chemical Oxidation	Bio-Treatment
Good (No Time Limit)	10	10	10
Moderate (2-5 Years)	10	2	7
Low (<2Years)	10	2	2

Lead Into Natural Attenuation

In order to achieve very low closure criteria (Drinking Water) Natural Attenuation (NA) will typically be the last treatment technology applied to a site. Most treatment technologies are very effective at reducing mass, however, become less effective as the mass decreases. This can result in post treatment concentration over the regulatory limits. Part of the selection criteria is if a treatment technology will be a better lead into natural attenuation (NA).

Natural Attenuation	ZVI	Chemical Oxidation	Bio-Treatment
Required	7	2	10
Not a Factor	10	10	10

Technology Ranking Score

Below is the Ranking Score for the example site. The score, red highlighted rows, shows which technology may have advantage over other technologies but is not meant to be a final selection. It does point out the potential strengths and weaknesses of each technology if you go back to each selection criteria and see why it was scored high or low. This also allows for looking at me to deal with some of the limitation identified.

	ZVI	Chemical Oxidation	Bio-Treatment
Sum of Selected Rows	**78**	**62**	**67**

The preferred treatment for the example site is Zero Valent Iron. This is largely due to the high aquifer flow, high TOC, and the need for natural attenuation. Since a single application is needed site access will not be an issue. Bio-Treatment could also be considered; however, additional application may be needed due to the high aquifer flow rate. Bio-Treatment is the best lead into natural attenuation, however, ZVI can also provide a augmentation to natural bio-treatment as a lead into natural attenuation. Chemical Oxidation can be considered; however, the treatments will need to be planned carefully to be complete in the time allowed. There will not be a good lead into NA.

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Remediation Alternative Selection Worksheet

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Tight Soils(Silt Clay)	2	7	10
Moderate Soils(Silty Sand)	7	10	7
Permeable Soils(Sand Gravel)	10	7	2

Aquifer Flow	ZVI	Chemical Oxidation	Bio-Treatment
High Flow(>100 ft/Year	10	7	2
Moderate Flow (20 -100 ft/yr)	10	7	7
Low Flow (<20 ft/year)	2	7	10

VOC Concentration	ZVI	Chemical Oxidation	Bio-Treatment
High (>1ppm)	7	10	2
Moderate (100 – 1000 ug/L)	10	7	7
Low <100 ug/L)	7	2	10

Dissolved Oxygen	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	2	7	2
Moderate (1-5 ppm)	7	10	7
Low <1ppm)	10	7	10

Total Organic Carbon	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	7	2	10
Moderate (1-5 ppm)	10	7	7
Low <1ppm)	10	10	7

Dissolved Minerals	ZVI	Chemical Oxidation	Bio-Treatment
High (>5ppm)	2	2	10
Moderate (1-5 ppm)	10	7	10
Low (<1ppm)	10	10	10

Site Access	ZVI	Chemical Oxidation	Bio-Treatment
Good (No Time Limit)	10	10	10
Moderate (2-5 Years)	10	7	7
Low (<2Years)	10	2	2

Natural Attenuation	ZVI	Chemical Oxidation	Bio-Treatment
Required	7	2	10
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