

# RegenOx™

## Advanced Chemical Oxidation

### Contaminated Soils Treatment via Ex-Situ and In-Situ Mixing Methods

The treatment of contaminated soils by chemical oxidation processes can offer significant cost savings when compared to other treatment alternatives such as incineration or excavation and disposal. While often more expensive than biological soil treatment techniques such as landfarming, *in situ* and *ex situ* chemical oxidation techniques offer the advantage of expediency, which is often favored in today's real estate transaction-driven remediation market.

#### Advantages and Disadvantages of Chemical Treatment

Successful use of chemical oxidation technology to treat soils on site is generally accomplished by either the in-place mixing the soils with a chemical oxidant (*in situ* treatment) or by excavating the soil and mixing the chemical oxidant with the soils in above ground vessels (*ex situ* treatment).

The advantages of chemical oxidation employing ex-situ and in-situ soil mixing are:

1. Ensures direct and immediate contact with chemical oxidant;
2. Undergoes rapid oxidation reactions;
3. Eliminates uncertainties of subsurface geology and hydrogeology;
4. Minimizes liability as compared to off-site disposal.

The disadvantages of chemical oxidation employing ex-situ and in-situ soil mixing are:

1. Not all contaminants are degraded quickly and/or completely;
2. Predicting final treatment concentrations from bench-scale studies are often difficult;
3. *In situ* treatment via soil mixing may be limited by subsurface structures; and
4. *Ex situ* treatment may require significant on-site area.

#### Mechanisms of In-situ and Ex-situ Soil Mixing

Treatment of contaminated soils with chemical oxidants via *in-situ* and *ex-situ* soil mixing involves chemical oxidation as well as biological and/or physical processes to transform organic contaminants in soil. The soil mixing that occurs during an ex-situ or in-situ mixing treatment serves to homogenize the soil and contaminants at the same time it forces contact with the oxidant mixture. During this process the contaminant can be diluted and some amount may volatilize. These physical losses are difficult to differentiate from chemical oxidation losses, but can be significant.

The proportion of contaminant that is degraded by chemical, biological or physical processes will depend on:

- Soil type
- Contaminant distribution

- Contaminant type
- Oxidant Efficiency
- Soil/Water ratio
- Type & frequency of Mixing
- Temperature
- Treatment Duration.

The duration of the treatment program is very important to ensure that sufficient time has been allowed for the complete chemical reactions to occur. Additionally, many contaminants that are partially oxidized during the chemical treatment become more readily available for biological degradation. Thus, contaminant concentrations often continue to decline as a result of this post-chemical oxidation biological activity.

The table below gives an idea of the proportional effects of different processes. In a typical contaminated soil treatment employing mixing and chemical oxidation technology, the actual chemical oxidation reactions can account for 10 to 60% of the contaminant removal, less for TPH compounds and higher amounts for cVOCs. Biological activity can account for 20-60%, primarily depending of the time and water content. Physical processes can account for 10-90% of the contaminant removal, primarily depending on the type of mixing that is used and the volatility of the contaminant treated.

Treatment/Contaminant	Petroleum-based	Chlorinated-Solvents
Homogenization	Low to Medium	Medium to High
Volatilization	Low	High
Chemical	Low to Medium	Medium to High
Biological	Medium	Medium

In general, chemical treatment of soils employs chemical/biological treatment and homogenization to attain cleanup goals. Complete mineralization via chemical treatment should not be the goal and is almost never achieved.

In treating total petroleum hydrocarbons (TPH)-type contaminants, adding a stoichiometric amount of oxidant is usually not necessary or economical. Instead, a sub-stoichiometric dose of a chemical oxidant can partially oxidize the contaminant to more soluble intermediate products that are readily biodegradable. Often residual oxygen left behind will stimulate aerobic biodegradation of these compounds.

**When dealing with contaminants of very low solubility and low volatility, multiple chemical oxidant treatments may be required.** Despite superior contact with soil mixing, the chemical treatment still requires time to permeate the soil matrix and to react with the contaminant in aqueous solution. Chemical oxidation of low solubility contaminants will be desorption-limited. Therefore, soil mixing designs may require multiple passes to desorb and oxidized the sorbed mass that is released over time. This should be recognized before embarking on any chemical oxidation of soils in order to align treatment expectations with pending reality.

### Sites Appropriate for Chemical Oxidation of Contaminated Soils

Typical applicable sites are:

- Abandoned tank farms, bulk plants, where diesel fuels, gasoline and other petroleum distillates have been handled

- Old dry cleaner sites
- Industrial facilities

Typical site conditions are that the contamination is usually less than 20 ft. in depth. The bulk of the contamination may reside in the upper portion of the vertical interval, e.g. ground surface to 10 feet in depth. The soil can be sandy or clay, vadose or below the water table groundwater. Large objects and debris must be generally less than 4” in diameter. There must be an ample water source to maintain desired soil moisture during treatment. There should be ample space and an adequate buffer area around the excavation/treatment zone so as to not impact infrastructure, foundations, or neighbors.

### Considerations for Treatment Design

When designing an approach for implementing chemical oxidation of soils one should attempt to maximize the surface area in contact with the chemical oxidant. Typical soil particles need to be below one centimeter in size. Most soils will require the addition of water and other amendments before treatment. In soils with high clay content, soil shredding and/or blending with a bulking agent may be needed to improve the soil structure and porosity. Prior to any soil shredding, a screening step should occur to remove rocks and debris. Lime and/or bulking agents, such as wood chips or sand may be needed to improve both material handling as well as to maximize biological degradation after the chemical oxidation.

### In Situ Mixing

Use of typical construction equipment (e.g. track hoe) often does not adequately break up soil matrices and homogenize the mixture. This approach to mixing chemical oxidants often results in untreated soil in clumps, even after many passes. Specialized soil mixing equipment is available. Shallow mixing rigs that can access the top 20’ are available that can operate at costs in the range of \$10/CY to \$25/CY. Deep soil mixing typically requires large diameter drill rigs that operate in excess of \$25+/CY.

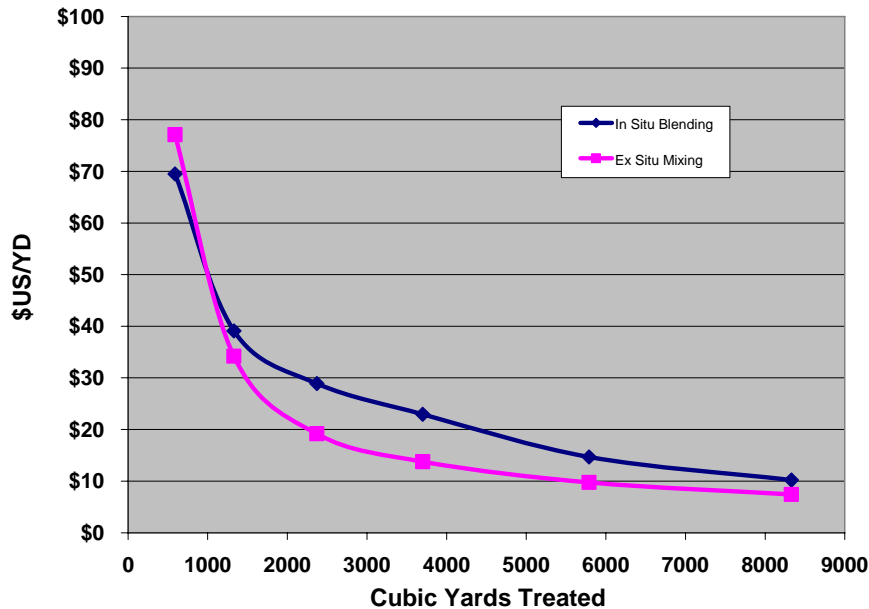
### Ex Situ Mixing

Excavation methods can use conventional equipment to transfer contaminated soils surface piles or windrows where chemical oxidants are applied followed by surface mixing by compost-turning type equipment. Alternatively, the soil once excavated can be processed in a trommel screen or pug mill to shred the soil and ensure contact /mixing. Soil shred costs are typically <5\$/CY. Other Ex-mixing costs are shown below in the cost analysis assumptions.

### Cost Comparison of Common Mixing Methods

<u>Criteria</u>	<u>In Situ Mixing</u>	<u>Ex Situ Mixing</u>
Mixing Efficiency	Low- Medium	High
Mixing Equipment Cost	High	Low-Med
Mixing Throughput	Medium	High
Space Requirements	Low-Medium	High

General Cost Comparison for various mixing technologies is summarized in the figure below.



General assumption for cost comparison:

- CY treated per day: In-situ= 750, Ex-situ= 5,000
- Assumed Daily Rate of \$4,500 for in-situ blending (e.g Lang Tool), Other costs are support vehicles. Monthly rate assumptions used.
- Assumed Daily Rate of \$4,000 for ex-situ mixing (e.g. H&H Micro-enfractionator®), Other Costs are Support Vehicles. Monthly Rate Assumptions Used
- Caveats, if soil blending usage is greater than 10 business days, rate equal to \$35,000 per month, other support equipment at \$20k per month
- Caveats, if ex situ blending usage is greater than 10 business days, rate equal to \$45,000 per month, other support equipment at \$20k per month.
- Since Mixing is so quick, may need to mobilize equipment twice and therefore mob charges reflect a double mob, mixing perhaps 3 weeks apart

The overall costs for both ex-situ and in-situ mixing applications require a minimum 2,000 to 5,000 cu. Yds. to get to a economical cost of <\$20/ cu. Yd.

### Need for Bench Testing

Bench-scale testing, although not an absolute guarantee of success can substantially reduce the risk of unexpected costs or poor performance in the field. Bench-scale tests are not scalable to full-scale designs, but can point out problems early in the process to improve the final design. Fully characterizing site soils in the laboratory for contaminant type (especially important with petroleum-based contaminant) and concentration. In addition the following characterization may be helpful:

- Metals--Fe, Mn, Al, Cu, Ni, Zn, Cr, Cd, Co, As, Se
- Base Cations--Na, Mg, K, Ca
- Anions-- NO<sub>3</sub>/NO<sub>2</sub>, PO<sub>4</sub>, SO<sub>4</sub>
- pH (optimum 6-9)
- Moisture content (optimum 70 to 95% field capacity)
- Particle-size distribution (optimum soil void volume >25%)

- TOC and COD

If the initial values for pH, TOC, COD, and moisture are not within the optimal criteria, adjustments should be made and tested at the bench-scale to determine the importance of these criteria to the performance of the treatment option and to determine the feasibility of scaling up these adjustments for full-scale design. Other parameters mentioned above may be important in identifying unusual geochemistry which may also affect performance.

### **Need for Field Pilot Testing**

Pilot-scale testing provides scalable information on the effectiveness of a given technology applied to a given soil. Critical parameters for estimating full-scale design are typically unknown. For example, unless the soils have already been stock pile and a statistical robust sampling has been done, the average starting concentrations are not known. Therefore, pilots or phased applications with intensive performance monitoring can be used to avoid uncertainty and performance problems during full-scale operations.

### **Estimating RegenOx™ Application Rates**

Typically for a cVOC contaminated site the amount of oxidant used can be calculated from the stoichiometry of the average concentrations. These sites use 20-40lbs/CY of RegenOx which is usually economical. With TPH based contamination, the design starts with 1/10 the average concentration stoichiometry, and to be economical this usually needs to be 10 to 20 lbs/CY. We have gotten good results with lower percentage of the stoichiometry (i.e. 1/50) with some sites. So, if the calculated amount is greater than 20 lbs./CY for a TPH-based site, a pilot application might be tried to see with a less amount of oxidant can the treatment goal still be met.

### **Summary**

There are many successful applications and sites where *in situ* mixing/blending technology is applicable and has been applied with RegenOx. The attached table summarizes those examples of these applications. Success for each of these applications is very site specific. Some sites only needed modest reduction from 1000 ppm to 400ppm, while other sites needed reduction to below 20 ppb to be considered successful. Therefore, to be successful with chemical oxidation of vadose zone contaminated soils, one must have reasonable expectations up front, and verify results through pilot/phased applications in the field.