

Chemical Oxidation of Broad-Spectrum PAH Contamination Using Activated Persulfate

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Abstract

The project site was formerly a creosote-pentachlorophenol (PCP) wood preserving facility which included a former creosote treatment area, old treatment cylinders, aboveground storage tanks, a surface impoundment, a drip pad, and a former chipping/debarking area. The site investigation, initiated in 1986, has identified semivolatile organic compounds (SVOCs), primarily polynuclear aromatic hydrocarbons (PAHs) contamination in source areas and soil.

The soil below ground surface (bgs) consists of clayey sands from surface to 2 feet bgs, beige and orange clay and sand from 2-4 feet bgs. The soil from 4-8 feet bgs is primarily light silty clay. Underneath the light silty clay, loose white sand was observed from 8 feet to 12 feet bgs. The SVOCs, primarily PAHs, were detected in soil and groundwater at levels exceeding regulatory standards and required treatment. The contaminants of concern (COCs) include acenaphthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, chrysene, naphthalene, pentachlorophenol, and phenanthrene. Phenanthrene and naphthalene displayed the highest concentrations of COCs. The remaining SVOCs that were also detected include 2,4-dimethylphenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, methylphenol, acenaphthylene, anthracene, benzo(g,h,i)perylene, benzo(k)fluoranthene, bis(2-ethylhexyl)phthalate, dibenz(a,h)anthracene, diethyl phthalate, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, isophorone, phenol, and pyrene. Due to the massive contamination in soil, source areas and groundwater, the primary remedial objectives are source removal and reduction of COCs in soil and groundwater to levels below regulatory standards. A total of nearly 60,000 cubic yards of contaminated soil were removed and disposed of offsite between 2007 and 2008.

A treatability study for groundwater remediation was designed to verify the applicability of chemical oxidation, to select the most effective chemical oxidant(s), and to determine the worst-case scenario total oxidant demand on oxidizing the SVOCs, primarily PAHs. The bench-scale treatability study evaluated chemical oxidation processes in groundwater phase alone and in soil slurry phase. For the groundwater phase alone, contaminated groundwater samples were exposed to conditions with no chemical oxidants (i.e., controls), with sodium hydroxide (NaOH) activated persulfate and with NaOH-hydrogen peroxide [H2O2] activated persulfate. The duration of study in groundwater phase was 21 days. For the soil slurry phase (50 milliliters of groundwater and 200 grams of soil), a total of 4 chemical oxidation conditions (control, NaOH, NaOH activated persulfate, NaOH-H2O2 activated persulfate) were evaluated. The controls were evaluated at 0, 7 and 21 days. The NaOH condition was evaluated at 21-days. The NaOH activated persulfate and NaOH-H2O2 activated persulfate conditions were evaluated at two dosages for 7 and 21-day durations. Each condition was tested with duplicate runs. Although the reduction of COCs varied by treatment conditions and each individual COC, the overall treatment efficiency falls in order of NaOH-H2O2 activated persulfate > NaOH > NaOH activated persulfate > Controls. There was no notable difference between test durations of 7 vs 21 days. The reduction increased as the concentrations of NaOH and persulfate increased. Under the most efficient NaOH-H2O2 activated persulfate conditions, higher reductions (>80%) were identified for low-molecular weight PAHs (with three aromatic rings or less). However, 100% reduction was also found for benzo(a)pyrene, benzo(g,h,i)perylene. For other oxidation conditions, the treatment efficiency is not directly correlated to physicochemical properties of PAHs.

Site Background

- The Site is approximately 8.5 acres and was formerly a creosote-pentachlorophenol (PCP) wood preserving facility which included a former creosote treatment area, old treatment cylinders, aboveground storage tanks, a surface impoundment, a drip pad, and a former chipping/debarking area.
- The soil investigations identified PAHs as primary contaminants of concern exceeding regulatory standards. Approximately 16,000cy of contaminated soil was excavated and disposed of offsite.



- Groundwater investigation delineates the extent of PCP, naphthalene and other PAHs in groundwater
- Feasibility study was conducted to select in-situ chemical oxidation, enhanced bioremediation and phytoremediation as potential technologies

PAHs Treatability Using Persulfate

A ISCO treatability study was designed to:

- Verify applicability of ISCO to each specific PAH
- Select the most effective chemical oxidant(s) for saturated soil and groundwater treatment
- Determine the worst-scenario total oxidant demand on oxidizing the Site contaminants

The contaminated soil and groundwater samples were collected and blended in the laboratory for the ISCO treatability study.

Test Controls (no chemical oxidant addition):

- Total PAHs at day 0: 270.4 mg/kg (Phenanthrene: 57 mg/kg)
- Total PAHs at day 21: 290.1 mg/kg (Phenanthrene: 82 mg/kg)

Each slurry test condition below include duplicates and three time points (t=0, t=7 days, t=21 days):

- NaOH addition only
- NaOH activated persulfate (low dosage 30 g/kg)
- NaOH activated persulfate (high dosage 60 g/kg)
- Peroxide activated persulfate (low dosage 30 g/kg)
- Peroxide activated persulfate (high dosage 60 g/kg)

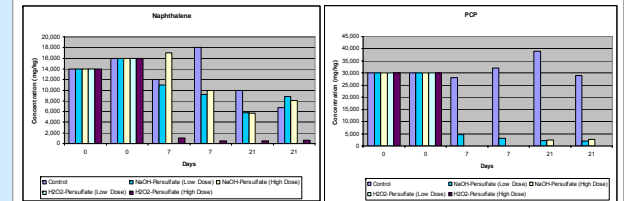
Results

Test Conditions for Groundwater

Groundwater was effectively treated by both base catalyzed and peroxide catalyzed persulfate (data not shown). Nearly all contaminants were reduced below reporting limits.

Test Conditions for Slurries

- Both base catalyzed persulfate and hydrogen peroxide catalyzed persulfate were effective in treating the soil contaminants although the peroxide catalyzed persulfate achieved better reduction over most PAHs.
- There was little difference in contaminant reduction between treatments for 7 or 21 days.
- There was little difference in contaminant reduction between treatments with 30 g/kg persulfate and 60 g/kg persulfate dosages.
- The base only (25 wt % sodium hydroxide with a total dose of 9 ml/kg) treatment was effective in reducing concentrations of many PAHs.
- Although the reduction of COCs varied by treatment conditions and each individual COC, the overall treatment efficiency falls in order of NaOH-H2O2 activated persulfate > NaOH > NaOH activated persulfate > Controls.
- Naphthalene and PCP are two primary chemicals of concern in groundwater and can be treated effectively using peroxide activated persulfate



Remedial Option Using Persulfate:

- Effective soil blending will be extremely difficult to achieve in zones consisting of contiguous portions of dense clay.
- Groundwater treatment will be effectively achieved by injecting either base catalyzed persulfate or peroxide catalyzed persulfate.
- Although a higher initial dose of persulfate did not appear to significantly enhance soil contaminant reduction, multiple sequential applications of peroxide catalyzed persulfate at the lower treatment dose (30g/kg) should effectively enhance contaminant reduction. This can be achieved either by soil blending (where possible) or direct injection.

Test Controls

Control ID	C0	C0R	C1	C1R	C3	C3R
Time	0	0	7	7	21	21
2-Methylnaphthalene	12,000	13,000	12,000	15,000	11,000	9,000
Acenaphthene	26,000	25,000	22,000	26,000	24,000	22,000
Dibenzofuran	19,000	18,000	16,000	20,000	18,000	17,000
Fluoranthene	34,000	30,000	28,000	40,000	33,000	39,000
Fluorene	25,000	25,000	20,000	26,000	25,000	24,000
Naphthalene	14,000	16,000	12,000	18,000	10,000	6,700
Pentachlorophenol	30,000	30,000	28,000	32,000	39,000	29,000
Phenanthrene	57,000	56,000	50,000	83,000	76,000	82,000
Pyrene	20,000	18,000	17,000	26,000	21,000	24,000
Total	237,000	231,000	205,000	286,000	257,000	252,700

*Only PAHs >10,000 mg/kg are shown

PAH Reduction (%)

Oxidant	NaOH	HP1D1	HP3D1	HP1D2	HP3D2	PP1D1	PP3D1	PP1D2	PP3D2
Time	21	7	21	7	21	7	21	7	21
Persulfate	Low	Low	High	High	Low	Low	High	High	High
H2O2						√	√	√	√
NaOH	√	√	√	√	√	√	√	√	√
2-Methylnaphthalene	74	27	34	9	41	84	85	72	75
Acenaphthene	74	59	75	64	83	89	87	84	82
Dibenzofuran	71	30	14	19	19	56	54	44	48
Fluoranthene	66	28	11	22	19	52	47	45	47
Fluorene	70	46	48	44	54	59	56	55	52
Naphthalene	88	33	51	10	54	100	100	95	96
Pentachlorophenol	100	87	93	100	92	100	100	100	100
Phenanthrene	61	28	-7	20	-6	51	41	43	35

Remedial Technology Selection

- The treatability results indicated that the treated slurries contained some PAHs exceeding the regulatory standards even the most aggressive chemical oxidation conditions are used.
- Based on the treatability study results, the overall treatment efficiency and the total treatment costs required to cleanup the contaminated soil, chemical oxidation is not considered as a feasible technology for unsaturated soil. Soil excavation and disposal is the remedy selected for the unsaturated soil.
- The groundwater monitoring has indicated that the primary COCs in groundwater are PCP and naphthalene. These two contaminants can be treated effectively using peroxide activated persulfate. Chemical oxidation in the source area has been retained as a feasible technology and will be combined with aerobic biodegradation and phytoremediation for dissolved plume downgradient from the source areas.