CHEMICAL OXIDATION OF CHLORINATED DNAPL USING ACTIVATED PERSULFATE, BOTANY BAY, AUSTRALIA

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I. Botany Industrial Park Area

II. Project Background

This study was conducted to evaluate the feasibility of using chemical oxidation processes for remediation of a DNAPL-contaminated site at the Botany Industrial Park (BIP) located near Sydney, Australia. The DNAPLs and the dissolved-phase plumes in the subsurface are the result of almost 60 years (since the 1940s) of chlorinated solvent and polymer manufacturing at this site.

DNAPL in the source area is approximately 68% tetrachloroethene (PCE), 30% carbon tetrachloride (CT), 7% hexachloroethane (HCE) plus a broad range of other volatile chlorinated compounds (VOCs) and semi-VOCs. In Situ Chemical Oxidation (ISCO) using activated persulfate was selected as the treatment method to be evaluated for this project. Additionally, chemical oxidation including VeruTEK's Surfactant-Enhanced In Situ Chemical Oxidation (S-ISCO™) was also tested.

The ISCO process included activation of persulfate with Fe(II)-EDTA, heat (35ºC and 50ºC) and high pH (pH>11). Various experimental systems were investigated including DNAPL dissolution and oxidation tests, batch aqueous, batch soil slurry and continuous flow soil column tests. Each of the activation methods was tested in combination with biodegradable, food-grade co-solvents and surfactants (VeruSOL-3™) leading to simultaneous dissolution of the DNAPL and chemical oxidation known as S-ISCO™.

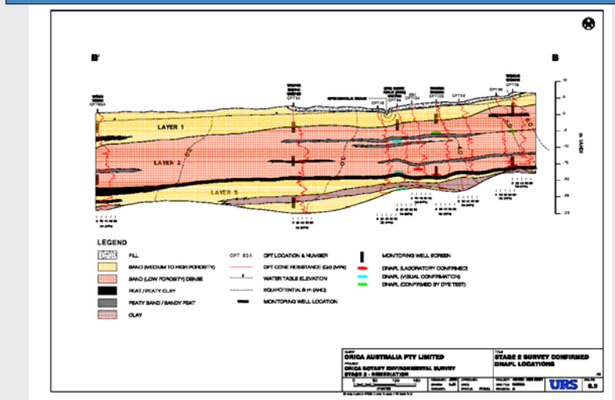
The following two types of bench scale tests were used in the study:

1. Idealized experimental models representing physical and chemical conditions of the site were conducted using batch aqueous and soil slurry equilibrium tests. These results were used to screen the chemistry of the persulfate remedial process and to select the preferred activation method.
2. Continuous flow soil column test experimental models were used to more closely simulate kinetic and transport conditions operable at pilot- and full-scale.

III. Key Objectives of the Study

- Assess the ability of activated persulfate processes (i.e., ISCO) and surfactant enhanced activated persulfate (i.e., S-ISCO™) to treat sorbed-phase and DNAPL target compounds.
- Assess and characterize the formation of by-products and the results of native soil interactions with persulfate.
- Determine the amount of persulfate soil oxidant demand (SOD) for two composite soil types (i.e. sandy and clayey peat material) collected from the source area.
- Determine optimal treatment processes for target compounds using S-ISCO™ processes.

IV. Site Characterization-Contaminants of Concern

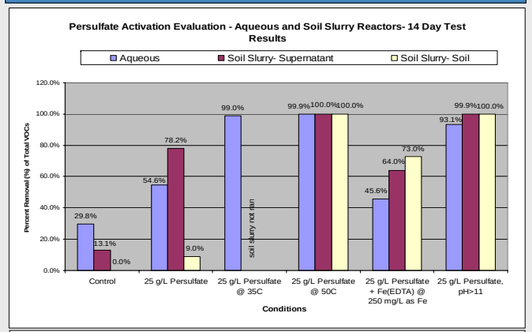


IV-1. Contaminants Detected in Soils

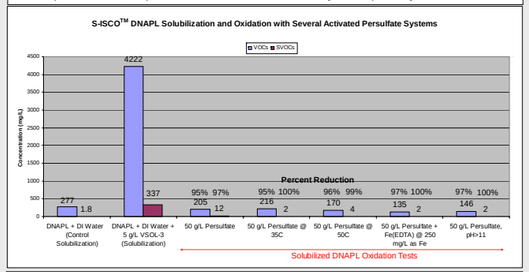
VOCS (ug/kg)	Sandy Soil	Clayey-Peat Soil
Carbon Tertrachloride	50000	450
Chloroform	1705	BRL (<150)
Total Chlorinated Methanes	**51705**	**450**
1,1,2,2-Tetrachloroethane	300	2950
1,1,2-Trichloroethane	430	BRL (<150)
Total Chlorinated Ethanes	**730**	**2950**
Tetrachloroethene (PCE)	230000	9600
Trichloroethene (TCE)	725	280
Total Chlorinated Ethenes	**230725**	**9880**
Acetone	3900	BRL (<2900)
Total VOCs (ug/kg)	**287060**	**13280**
SVOCs (ug/kg)	**Sandy Soil**	**Clayey-Peat Soil**
Hexachlorobenzene (HCB)	27500	2550
Hexachlorobutadiene	25500	4150
Hexachloroethane	3950	1550
Phenol	3500	1600
Total Semi-VOCs (ug/kg)	**60450**	**9850**
Total VOCs and SVOCs (ug/kg)	**347510**	**23130**

V. Selected Testing Results

V-1. Solubilization-Oxidation Results

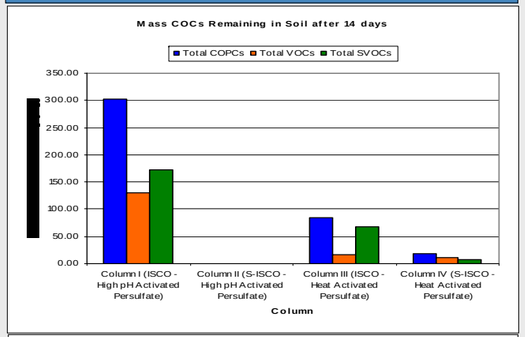


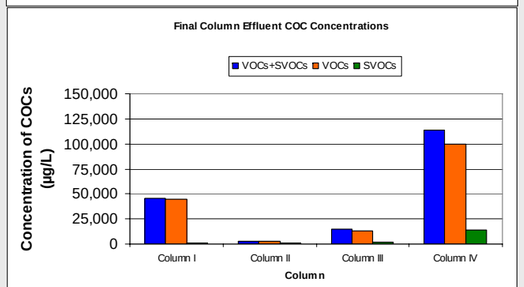
Notes:
1) Aqueous batch tests run in 500 mL reactors at 25ºC unless otherwise noted and at 120 RPM on a shaker table, test results for 14-day period.
2) Soil slurry batch tests run in 500 mL reactors with 100 g site soil at 25ºC unless otherwise noted and at 120 RPM. Test results for 14-day period upon which the experiment was separated from soils and each analyzed separately.



Notes:
1) DNAPL Solubilization Tests were run with a) 2.5 ml DNAPL in 500 ml D.I. water, and b) 2.5 ml DNAPL in 500 D.I. water with 500 g/L VeruSOL-3™. Solubilization period was 7 days at 25ºC and 60 RPM shaker table.
2) Activated persulfate oxidation tests were run on VeruSOL-3™ solubilized DNAPL in 500 ml reactors at 25ºC for 21 day period at 120 RPM on shaker table.

V-2. Column Test Results

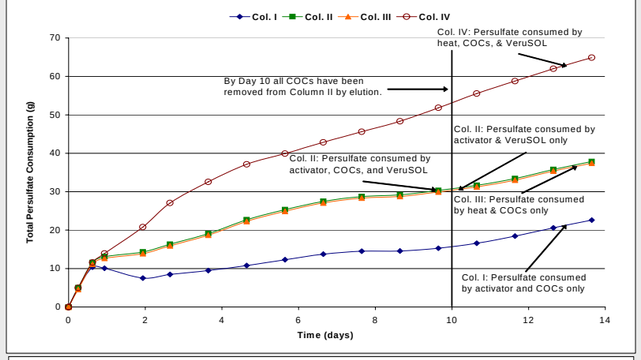




Notes: Final column effluent concentrations were a full composite from day 11 to day 14

Test Conditions: Persulfate 50 g/L, Flow = 0.5 mL/min, for 14 days.
Column I: pH>12
Column II: 5 g/L VeruSOL™, pH>12
Column III: Temp. = 35ºC VeruSOL™,35ºC
Column IV: Temp. = 5 g/L
Each Column of site soil was spiked with 3 (g) DNAPL dyed with Suidan-IV
Columns: 30 cm L x 5 cm dia. Q= 0.5 mL/min
Oxidation Test Results: *At the end of the 14-day column tests, target contaminants were greatly removed/degraded.* S-ISCO™ with alkaline persulfate was the most effective process soil column tested process.

V-3. Persulfate Consumption in Column Simulation



Cumulative persulfate consumption. Note that Column I has the lowest persulfate consumption and that consumption increases with the addition of either VeruSOL™ or heat.

V-4. Column Test Photos

Column 1: Alkaline persulfate; Column 2: VeruSOL™-enhanced alkaline persulfate (S-ISCO™).
Test Conditions: 50 g/L persulfate, Room temperature, Time = 8 days.

VI. Selected Key Findings

- Conventional ISCO processes, using alkaline or heat activation, can oxidize contaminants but are hampered by transport constraints observed in column tests. These constraints make complete remediation using conventional ISCO unlikely.
- Soil slurry treatability tests over-predicted DNAPL COC removal in comparison to soil column tests.
- The S-ISCO™ process effectively increased the rates of DNAPL solubilization, allowing for greater removal of sorbed- and dissolved-phase contaminants in soil column tests.
- Alkaline persulfate activation combined with S-ISCO™ appears to be an effective method of COC removal based on results of the soil column experimental model.
- Heat activation may decrease DNAPL viscosity, leading to undesirable downward transport of the DNAPL during field application.
- With the application of alkaline persulfate S-ISCO™ process, rates of solubilization and oxidation could be controlled such that targeting and destruction of subsurface DNAPL and sorbed residuals may be achieved during field implementation.