

Calcium Hydroxide (Activator of Sodium Persulfate)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Calcium hydroxide is a solid granular product commonly called hydrated lime or slaked lime. It is commonly mixed with soil, and then sprayed with water used to raise the pH of soil and water to act as an activator of sodium persulfate. When added to water, calcium hydroxide dissociates into calcium ions and hydroxide ions.
3. MSDS - See attached file
4. Number of Field Applications: 300 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Calcium hydroxide is used as a high pH activator of sodium persulfate. Calcium hydroxide is normally delivered in 50 pound or 1,000 pound bags. When added to soil or groundwater, calcium hydroxide will cause the pH of the surrounding treatment area to increase to over 10.5 pH units. A bench scale soil buffering test should be performed in the laboratory to determine the quantity of calcium hydroxide required to raise the pH to 10.5 units and to maintain that pH for up to 4 hours. A properly designed buffering test will determine the soil buffering capacity in units of grams of NaOH per kilogram of soil. Soil buffering capacity can vary greatly between sites (over 10 fold).

Immediately after injection, calcium levels will increase by approximately 20% over baseline levels within the radius of influence. Calcium ions are quickly diluted and dispersed by groundwater flow until the effects are no longer detectable.

Hydroxide ions will cause an immediate increase of pH that lasts about 30 days. At properly designed sites, the pH will typically return to normal within 30 to 60 days. The natural soil buffering capacity slowly neutralizes the high pH conditions and restores the groundwater to a neutral pH.

Calcium hydroxide is highly corrosive and must be handled with established safety precautions. Calcium hydroxide (in powder or liquid form) can cause serious burns to the skin, eyes, and lungs, so use of proper PPE is critical. A full face respirator, chemical resistant clothing, and gloves are required when handling calcium hydroxide.

Evaluation of Calcium Hydroxide for Inclusion in the General WDR Permit

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May 15, 2013

Physical Description of Calcium Hydroxide

- Simple molecular structure: $\text{Ca}(\text{OH})_2$
- Also known as Hydrated Lime or Slaked Lime
- Solid (granular) chemical that is commonly used for soil blending projects
- Mixed using excavation equipment with sodium persulfate into shallow soils to treat VOCs. Generates heat.
- Portland cement can also be used with lime (provides stabilization)
- Combined high pH and the heat generated provides dual activation of persulfate.

Testing to Ensure Effectiveness

- Soil buffering test should be performed initially
- Determines the amount of hydroxide required to raise and maintain the pH over 10.5 units
- A properly designed test will determine the soil buffering capacity in units of grams CaOH per kilogram of soil
- Soil buffering capacity can vary greatly between sites.

Impact on Water Quality

- Ca(OH)_2 disassociates into calcium ions and hydroxide ions
- Calcium levels may increase by approximately 20% within the treatment area
- Calcium hydroxide will cause an immediate increase of pH
- At properly designed sites, the pH will typically return to normal within 30 to 60 days, as the soil buffering capacity slowly neutralizes the alkaline conditions and restores the site to a normal pH

Minimize Health & Safety Issues

- Safe handling of calcium hydroxide requires close adherence to established safety precautions.
- Calcium hydroxide can cause serious burns to skin and lungs so use of proper PPE is critical.
- Dust generation is the primary route of exposure for soil blending projects.
- Chemical delivered in Super Sacks of 1,000 lbs

Case Study No. 1 - Turtle Bayou, Texas

- Former waste disposal facility contaminated with over 20 chlorinated VOC compounds and petroleum hydrocarbons
- Mixed 760,000 pounds of persulfate with Hydrated Lime into soil using a large diameter auger excavator
- Confirmation sampling verified a 84% mass reduction of VOCs was attained after 30 days (exceeded goal)

Case Study No. 1 - Turtle Bayou, Texas



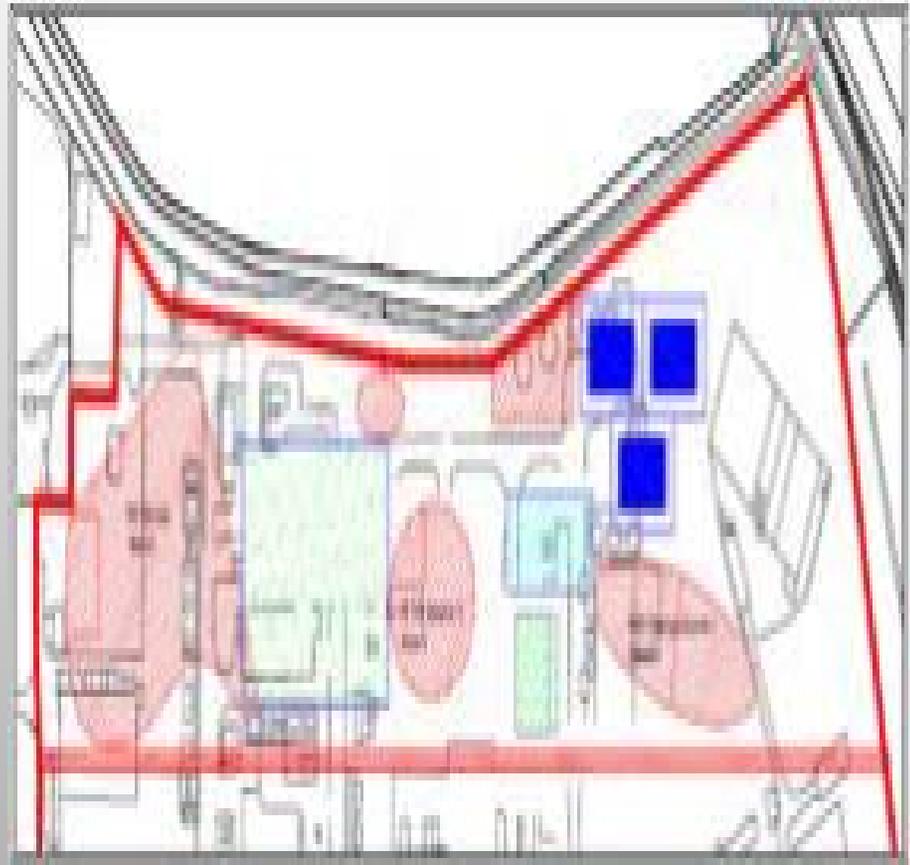
Case Study No. 1 – Mixing Head with Water Nozzle



Case Study No. 2. Thornton, England

- Lime activation of persulfate used to treat Chlorobenzenes and Dichlorobenzenes five large areas of soil contamination (7,300 m²)
- Used continuous flight augers
- Heat released from Lime resulted in enhanced mobilization from NAPL and sorbed contaminants.
- Soil concentrations of COCs were reduced by 10-fold using Lime Activation
- Estimated that 11,300 kg of COCs were destroyed
- Cleanup met the Environmental Quality Standards of UK. Site received Closure
- Churngold Remediation Limited won 2008 Brownfield Remediation Innovation Award for "Best Conceptual Design"

Case Study No. 2. Thornton, England



Case Study No. 3 - Wood Treatment Facility, Lester Prairie, Minnesota

- Soils contained concentration of Pentachlorophenol (PCP) as high as 1,600 mg/kg and Diesel Range Organics as high as 17,000 mg/kg
- Designed Ex-Situ Chemical Oxidation Treatment system
- Used 7,000 pounds of lime combined with 6,000 pounds of persulfate to treat Location # 4
- Chemical oxidants were sprayed onto soils and then mixed with excavator
- Significant off-gassing and heat generation during treatment
- 340 tons of soil successfully treated to below Cleanup Standard (120 mg/kg PCP) for soil disposal

EX-SITU CHEMICAL OXIDATION AT A FORMER MANUFACTURING FACILITY

Introduction:

Geomatrix Consultants, Inc. (Geomatrix) contracted ORIN Remediation Technologies (ORIN) to treat pentachlorophenol (PCP) impacted soil at two former locations of a single aboveground dip tank (Locations #1 and #4). The dip tank was used to treat wood for the manufacturing of wood frame buildings from the mid-1960's to the mid-1980's in Lester Prairie, Minnesota. Soils at both Locations #1 and #4 with PCP concentrations greater than 120 milligrams per kilogram (mg/kg) were determined to be a listed hazardous waste (F032) by the Minnesota Pollution Control Agency (MPCA). The different contaminant chemistries at each Location #1 and #4 necessitated the design of two separate chemical oxidation treatments of these soils.

Objective:

The objective of the project was to treat the hazardous soils at each Location #1 and #4 by ex situ chemical oxidation (ESCO) to meet the treatment standards for a nearby Minnesota Subtitle D landfill as a non-hazardous waste.



Off-gassing and heat generation during treatment



Closeup of off-gassing

Treatment Approach:

Treatment Chemistries:

Iron-Activated Hydrogen Peroxide (aka Fenton's Reagent) at Location #1
Alkaline-Activated Sodium Persulfate at Location #4

Treatment application: Chemical oxidants were sprayed onto hazardous soils as the soils were returned to their original excavations, and then mixed with excavator.

Dosage Rate: 1% weight of hydrogen peroxide to weight of soil at Location #1
1% weight of sodium persulfate to weight of soil at Location #4

Dosage: 5,350 lbs of hydrogen peroxide were mixed with soils at Location #1
6,000 lbs of sodium persulfate were mixed to soils at Location #4

Method of Treatment:

The treatment chemistries at both Locations #1 and #4 were designed to oxidize PCP. The purpose of the treatments was to lower PCP concentrations to meet the requirements of the local waste disposal facility.

Bench-scale testing was conducted to determine the treatment chemistries and dosage rates for each Location #1 and #4. A commonly used oxidant called Fenton's Reagent successfully lowered PCP concentrations in site soil samples from Location #1 in a single application. However, the elevated petroleum concentrations at Location #4 compared to Location #1 proved to be more challenging, and Fenton's Reagent was unsuccessful despite multiple treatments. A different treatment chemistry called Alkaline-Activated Sodium Persulfate successfully lowered PCP concentrations in site soil samples from Location #4 in a single application.

Immunoassay testing completed during the soil treatment at Location #4 showed that the different Alkaline-Activated Sodium Persulfate chemistry was working at the full scale level.

Site Characteristics:

Site: Site was sold during the soil corrective action and redeveloped for the cold storage of boats

Geology: Soils are sandy to a depth of approximately 15 feet below ground surface (ft bgs) with an organic-rich silty layer (foc > 1%) between 3 and 6 ft bgs at Location #4. Dense clay till underlies the sandy soils.

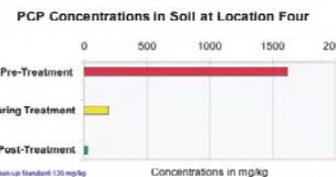
Groundwater: Depth to groundwater is approximately 5 ft bgs

Maximum Contaminant Concentrations and Treatment Standards:

| | Location #1 | Location #4 | Treatment Standard |
|---------|--------------|--------------|--------------------|
| DRO | 3,530 mg/kg | 17,100 mg/kg | N/A |
| PCP | 192 mg/kg | 1,620 mg/kg | 120 mg/kg |
| Dioxins | 0.0039 ug/kg | 1-2 ug/kg | 10 ug/kg |

Amount of soil treated:

Location #1: 316 tons
Location #4: 340 tons



Beginning treatment



Ending treatment

Summary

ORIN successfully lowered PCP concentrations in soils at Locations #1 and #4 using two different treatment chemistries. Post treatment laboratory confirmation sampling showed that PCP concentrations at both Locations #1 and #4 were below the treatment standard of 120 mg/kg, and the soils were disposed of at the nearby Minnesota Subtitle D landfill. The cost savings from the ESCO treatment of soils at Locations #1 and #4 is estimated to be on the order of \$500,000.



During treatment, 7,000 lb of lime were added to temporarily raise the pH and to reduce the moisture content before landfilling.

Case Study No. 4. - Industrial Site in North Carolina

- Co-mingled groundwater plumes containing 1,1,1-TCA, 1,1-DCE, and 1,4-dioxane
- Sodium persulfate and several activators used, including hydrated lime, sodium hydroxide, iron EDTA, and heat (steam).
- Utilized direct push injection and large diameter auger borings
- 30 injection points inside the building and another 60 injection borings outside the building
- 2,500 pounds of lime used, along with 100,000 pounds of persulfate
- COCs reduced by 90% to 100% across the site (some areas treated twice)

Case Study No. 4. - Industrial Site in North Carolina

| Compound concentration (ppb) | | Compound concentration (ppb) | | | | | | Compound concentration (ppb) | | | | | |
|------------------------------|---------|------------------------------|-----------|------------------------|-------|---------|-----------|------------------------------|----|---------|-----------|-----------------------|----|
| 8/27/2004 | | 7/11/2005 | | | | | | 3/13/2006 | | | | | |
| Aquifer zone | Well ID | 1,1 DCE | 1,1,1 TCA | Combin 1, 4 ed dioxane | | 1,1 DCE | 1,1,1 TCA | Combined 1, 4 dioxane | | 1,1 DCE | 1,1,1 TCA | Combined 1, 4 dioxane | |
| S | GP-4 | 14200 | 313 | 14513 | NT | <1 | 7.36 | <8.36 | NT | <1 | <1 | <2 | NT |
| S | MW-1 | 27800 | 96000 | 123800 | 29000 | <2 | 909 | <911 | <5 | <1 | 3740 | <3741 | NT |
| T | MW-1v | 89000 | 99800 | 188800 | 24.1 | <32 | 31.9 | <63.9 | <5 | <16 | 360 | <376 | NT |
| T,B | M2-1d | 4950 | 4390 | 9340 | <5 | 71.2 | 11700 | 11771.2 | <5 | <7 | 4220 | <4227 | NT |
| S | MW-2 | 94.1 | 52.3 | 146.4 | NT | 23.6 | 20.7 | 44.3 | NT | NT | NT | NT | NT |
| S | MW-3 | 24.3 | 5.93 | 30.23 | NT | 19.6 | 8.14 | 27.74 | NT | NT | NT | NT | NT |
| S | MW-7 | 5670 | 57700 | 63370 | 199 | 170 | 7560 | 77300 | <5 | <8 | 7240 | <7248 | NT |
| S | MW-9 | 0.418 | 0.47 | 0.888 | NT | <1 | <1 | <2 | NT | NT | NT | NT | NT |
| S | MW-11 | 711 | 1410 | 2121 | <5 | 841 | 1470 | 2311 | <5 | 770 | 1050 | 1820 | NT |
| S | MW-12 | 32.7 | 23.8 | 56.5 | NT | 136 | 43.3 | 179.3 | NT | NT | NT | NT | NT |
| T | MW-13v | <1 | <1 | <2 | NT | <1 | <1 | <2<2 | NT | NT | NT | NT | NT |
| S | MW-14 | 12000 | 9950 | 21950 | 3440 | <1 | 23.9 | <24.9 | <5 | <1 | 13.8 | <14.8 | NT |
| T | MW-14v | 58.9 | 76.2 | 135.1 | NT | 1490 | 1120 | 2610 | NT | NT | NT | NT | NT |
| T | MW-15v | 4.22 | <1 | <5.22 | NT | 7.84 | <1 | <8.84 | NT | NT | NT | NT | NT |
| S | MW-16 | 3.11 | 0.96 | 4.07 | NT | 3.31 | 0.5 | 3.81 | NT | NT | NT | NT | NT |
| S | MW-17 | 33700 | 73000 | 106700 | 3400 | <1 | 262 | <263 | <5 | <1 | 217 | <218 | NT |
| T | MW-17v | 18.9 | 23.7 | 42.6 | NT | <1 | 1910 | <1911 | NT | <2 | 491 | <493 | NT |
| B | MW-17d | 48.1 | 1.73 | 49.83 | <5 | 127 | <1 | <128 | <5 | NT | NT | NT | NT |
| S | MW-20 | 71400 | 63700 | 135100 | <5 | 46.1 | 3270 | 3316.1 | <5 | <4 | 3020 | <3024 | NT |
| T | MW-20d | 55300 | 124000 | 179300 | <5 | <5 | 4740 | <4745 | <5 | <4 | 751A | <7514 | NT |
| S | MW-21 | <1 | <1 | <2 | NT | <1 | <1 | <2 | NT | NT | NT | NT | NT |

In-Situ Chemical Oxidation with Klozur™ Activated Persulfate: Co-Mingled Plume Of Chlorinated Solvents and 1,4 Dioxane

Remediation Contractor: Redox Tech - Morrisville, NC
Chemical Supplier: FMC Corporation - Philadelphia, PA

1) Site Description

The site is located within the Piedmont (physiographic province) of North Carolina. The property contains a divided warehouse and active manufacturing building that is equipped with loading docks and a small office. The property is bordered by an active railroad track. A release of solvents or cleaning agents from an industrial process occurred primarily in the vicinity of the loading docks. The major contaminants were 1,1,1 -trichloroethane (1,1,1 -TCA), 1,1 -dichloroethene (1,1 -DCE), and 1,4 -dioxane. The site sits in a mixed zone of an industrial and residential area within a fairly large city. The impacted area is 1.5 acres or roughly 68,000 square feet. One-half of the treatment area was underneath an existing building (concrete/slab floor) and the other half was outside of the building. Based on initial sampling, there were very high concentrations of contaminants; some analytical results indicated the potential presence of Dense Non-aqueous Phase Liquid (DNAPL) in the vadose zone and in the saturated zone. Even though there were no known active drinking water wells near the site, there was potential receptor impact through vapor intrusion. The goal of the remediation was to reach realistic clean-up levels to allow the property to be resold.

2) Site Characterization

Contamination ranged from the surface down to 100 feet below ground surface. The subsurface materials in the target area consisted of Piedmont soils, including a heterogeneous mix of sand, silt and clay. In the lower treatment depths of 50-100 feet, there was some Saprolite, which is composed of layers of clayey silt and silty clay. Based on prior characterization performed at the site, there was a vertical gradient downward as well as some complicated geologic features, such as suspected clastic dykes, which produced significant flow path contrasts.

Activated persulfate was selected as the oxidant of choice because of its known ability to degrade the target contaminants. FMC Corporation's remediation grade persulfate, Klozur™, was used in conjunction with various activation methods. Target injection volumes of activated persulfate were selected based on the sum of the prior characterization data, which included multiple level groundwater data. Vertical intervals were determined based on layered isoconcentration contour maps. The bulk of the activated persulfate was injected in the area that was used to unload 1,1,1 -TCA from rail shipments, however discrete contaminant volumes were addressed that were some distance away from the shallow source area, at around 100 feet deep. Both the vadose and saturated zones were treated at this site.

Vadose zone treatment consisted of cluster wells in a small area, with a higher density of injection points to insure comprehensive lateral distribution, and better contact. Two years prior to activated persulfate treatment, Fenton's chemistry was used to treat a portion of the source area in a pilot study. This activity created many surface flow paths, which made

it difficult to laterally distribute the activated persulfate without daylighting. To overcome this, cluster wells were installed, and numerous re-injections at smaller volumes were performed to decrease the chance for surfacing of the oxidant. Because of high concentrations of contaminant were known to exist in the vadose zone, fairly high concentrations of persulfate were injected (15-25 wt% persulfate).

Saturated zone injections exhibited significant channeling, probably as a result of clastic dykes and other formation heterogeneity. Because of this, the injectate moved in significantly different flow paths, depending on whether they were inside or outside the dyke.

3) Treatment Selection/Design

The treatment selection and design consisted of combinations of multiple catalysts, such as hydrated lime, sodium hydroxide (for base-catalyzed remedies), FeEDTA (ferric), and steam activation used in conjunction with persulfate.

For both the vadose and saturated zone under the building, hydrated lime and steam activation, in combination with persulfate, were primarily used. These combinations have proven to be very economical. It should be noted that as a by-product of the reaction between the contaminant and activated persulfate sulfate will be formed. There is a secondary drinking water standard of 250 mg/L for sulfate (taste issue). In addition to catalyzing the persulfate, hydrated lime will combine with the sulfate in solution to form gypsum, thereby reducing the concentration of sulfate in ground water.

Within the main source area, which included the railroad tracks and loading dock next to the building, hydrated lime and steam activation with persulfate were used initially. Due to difficulties with daylighting, which is a surface pathway not associated with the well bore, it was difficult to effectively transfer the heat using steam. Instead, sodium hydroxide was used to catalyze the persulfate.

Well design and installation for the shallow source area included direct injection (Geoprobe™) and auger holes with a high density of application points. The need for a large number of points was due to daylighting to the surface as a result of prior remediation activities (Fenton's chemistry).

Well design and installation for the deep source area included direct injection (Geoprobe™ to a maximum depth of approximately 80 feet) and deep (100 feet) injection points installed using a mud rotary drill rig. A higher density of injection points was also used in the deep source area.

3-a) Energy and Oxidant - Target Temperature

A threshold number of calories (amount of heat) is needed to catalyze a persulfate molecule. The selected average target temperature for this site was 45 degrees C for 1,1,1 -TCA (primary contaminant) based on FMC literature. The oxidant concentration was based on Total Oxidant Demand (TOD) Test (ref: Haselow et. el, *Estimating the Total Oxidant Demand for In Situ Chemical Oxidation Design*, Remediation Autumn 2003). Temperatures achieved in the subsurface ranged from 25-60 degrees C on average. Higher temperatures (up to

100 degrees C) occasionally occurred at monitoring points due to preferential flow of steam. Subsurface temperatures were monitored in existing monitoring wells at multiple depths using thermocouples.

3-b) Injection/Transfer of Heat in the Subsurface

Steam injection was used to heat up the subsurface. Steam was injected into the subsurface through injection wells. The same injection points that were used for the steam activation were also used for the injection of persulfate. Steam was injected under pressure, ranging from 20-150 psi. Convection and conduction were the delivery mechanisms relied upon for heat distribution in the treatment zone.

3-c) Injection of Persulfate in the Subsurface

Due to the variable permeability encountered at the site, pressure injections were used. Pressure injections for persulfate ranged from 20-200 psi depending on the geology encountered within the injection interval. The control of lateral spreading is generally accomplished by injection from the down gradient plume toward the source. The vertical injection interval ranged from 20-100 feet. For all but the deep injection wells, single point injection wells with approximately 1-2 feet injection intervals were used.

3-d) Limits of Free Product

With separate phase product and chemical oxidation (in this case, persulfate oxidation) there generally has to be a mass transfer of the contaminant to the aqueous phase. Then, the (required stoichiometric amount of) oxidant has to come in contact with the contaminant of concern in order for the oxidation to occur. Source reduction is always advised when the source is accessible and removal is economically feasible. Source reduction can be achieved by direct removal, soil vapor extraction (SVE), air sparging or other methods.

4) Remedy Implementation/Performance Monitoring

4-a) Remedial Action Objectives/Cleanup Goals

The Remedial Action Objectives were to reduce the contaminant concentrations to set target concentrations:

Starting Concentrations:

1,1,1 - TCA - 203 mg/L
1,1 -DCE - 82 mg/L
1,4 Dioxane exceeding 50 mg/L,

Reduction of the contaminants, to the following concentrations, had to be met in order for the property to be sold:

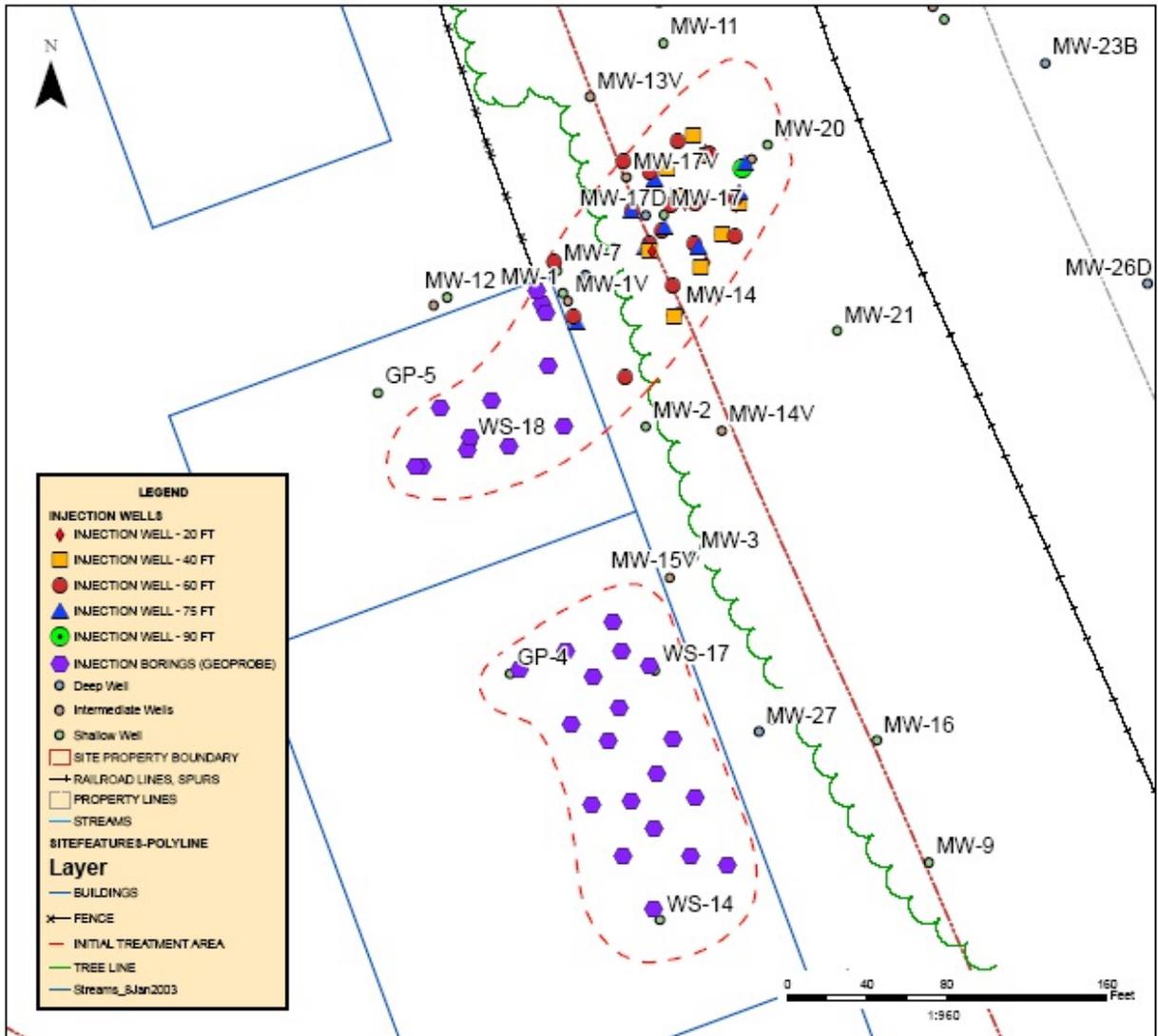
1,1,1 -TCA & 1,1 -DCE combined < 16 mg/L
1,4 Dioxane < 5 µg/L

4-b) Vapor Release

A SVE system was used during injection at locations inside the building. No contaminant vapor exceedences were measured through the duration of the project.

4-c) Number of Injection Points (picture/diagram)

There were a total of 30 injections points installed inside the building, which encompassed one-half the treatment plume. Outside the building, approximately 60 injection points were installed.



Injections occurred periodically from September 2004 through June 2005. Approximately 100,000 lbs of Klozur™ persulfate was used. To catalyze the persulfate, multiple activators were used. Their quantities are as follows:

Activators

- * 2,500 lbs of calcium hydroxide
- * > 500 million BTU's steam
- * 17,700 lbs of sodium hydroxide (25 wt%)

Oxidant

* 100,000 lbs Klozur™ persulfate

Per injection point (total of 90 points, 30 inside the building and 60 outside the building), on average;

- * 5 million BTU's of steam
- * 25 lbs of calcium hydroxide
- * 200 lbs of sodium hydroxide
- * 1,200 lbs of Klozur™ persulfate

Again, the quantities above were averaged; however more mass and energy were put in to some points versus others, depending on the contaminant mass and amenability of the subsurface.

4-d) Hot Sampling

Temperatures were typically not high enough in the monitoring wells to warrant special sampling procedures. So, no hot sampling was required.

4-e) Timing Between Injections

The timing between activator (steam, NaOH, Ca(OH)₂) injection and oxidant injection occurred from hours to days depending on injection location specific conditions (e.g. daylighting concerns).

4-f) Issues with Drilling into DNAPL Zones ("drag down")

There were no issues with drilling into NAPL or DNAPL zones. No "drag down" was observed based on well concentration data.

4-g) Groundwater Rebound Data

| BASELINE GROUNDWATER ANALYTICAL RESULTS | | | | | | POST-REMEDATION GROUNDWATER ANALYTICAL RESULTS | | | | | | | |
|-----------------------------------------|---------|------------------------------------------|-----------|----------|-------------|------------------------------------------------|-----------|----------|-------------|------------------------------------------|-----------|----------|-------------|
| AQUIFER ZONE | WELL ID | 8/27/2004 COMPOUND CONCENTRATION, PPB | | | | 7/11/2005 COMPOUND CONCENTRATION, PPB | | | | 3/13/2006 COMPOUND CONCENTRATION, PPB | | | |
| | | 1,1-DCE | 1,1,1-TCA | Combined | 1,4 Dioxane | 1,1-DCE | 1,1,1-TCA | Combined | 1,4 Dioxane | 1,1-DCE | 1,1,1-TCA | Combined | 1,4 Dioxane |
| S | GP-4 | 14200 | 313 | 14513 | NT | <1 | 7.36 | <8.36 | NT | <1 | <1 | <2 | NT |
| S | MW-1 | 27800 | 96000 | 123800 | 29000 | <2 | 909 | <911 | <5 | <1 | 3740 | <3741 | NT |
| T | MW-1v | 89000 | 99800 | 188800 | 24.1 | <32 | 31.9 | <63.9 | <5 | <16 | 360 | <376 | NT |
| T, B | MW-1d | 4950 | 4390 | 9340 | <5 | 71.2 | 11700 | 11771.2 | <5 | <7 | 4220 | <4227 | NT |
| S | MW-2 | 94.1 | 52.3 | 146.4 | NT | 23.6 | 20.7 | 44.3 | NT | NT | NT | NT | NT |
| S | MW-3 | 24.3 | 5.93 | 30.23 | NT | 19.6 | 8.14 | 27.74 | NT | NT | NT | NT | NT |
| S | MW-7 | 5670 | 57700 | 63370 | 199 | 170 | 7560 | 7730 | <5 | <8 | 7240 | <7248 | NT |
| S | MW-9 | 0.418 | 0.47 | 0.888 | NT | <1 | <1 | <2 | NT | NT | NT | NT | NT |
| S | MW-11 | 711 | 1410 | 2121 | <5 | 841 | 1470 | 2311 | <5 | 770 | 1050 | 1820 | NT |

| | | | | | |
|---|--------|-------|------------|--------|------|
| S | MW-12 | 32.7 | 23.8 | 56.5 | NT |
| T | MW-13v | <1 | <1 | <2 | NT |
| S | MW-14 | 12000 | 9950 | 21950 | 3440 |
| T | MW-14v | 58.9 | 76.2 | 135.1 | NT |
| T | MW-15v | 4.22 | <1 | <5.22 | NT |
| S | MW-16 | 3.11 | 0.96 | 4.07 | NT |
| S | MW-17 | 33700 | 73000 | 106700 | 3400 |
| T | MW-17v | 18.9 | 23.7 | 42.6 | NT |
| B | MW-17d | 48.1 | 1.73 | 49.83 | <5 |
| S | MW-20 | 71400 | 63700 | 135100 | <5 |
| T | MW-20d | 55300 | 12400 0 | 179300 | <5 |
| S | MW-21 | <1 | <1 | <2 | NT |
| B | MW-26d | <1 | <1 | <2 | NT |
| S | WS-14 | 81700 | 5180 | 86880 | NT |
| S | WS-17 | 44400 | 23600 | 68000 | NT |
| S | WS-18 | 32500 | 1060 | 33560 | NT |

| | | | |
|------|-------|--------|----|
| 136 | 43.3 | 179.3 | NT |
| <1 | <1 | <2 | NT |
| <1 | 23.9 | <24.9 | <5 |
| 1490 | 1120 | 2610 | NT |
| 7.84 | <1 | <8.84 | NT |
| 3.31 | 0.5 | 3.81 | NT |
| <1 | 262 | <263 | <5 |
| <1 | 1910 | <1911 | NT |
| 127 | <1 | <128 | <5 |
| 46.1 | 3270 | 3316.1 | <5 |
| <5 | 4740 | <4745 | <5 |
| <1 | <1 | <2 | NT |
| <1 | <1 | <2 | NT |
| <2 | 1090 | <1092 | NT |
| <10 | 11800 | <11810 | NT |
| <2 | 664 | <666 | NT |

| | | | |
|----|------|-------|----|
| NT | NT | NT | NT |
| NT | NT | NT | NT |
| <1 | 13.8 | <14.8 | NT |
| NT | NT | NT | NT |
| NT | NT | NT | NT |
| NT | NT | NT | NT |
| <1 | 217 | <218 | NT |
| <2 | 491 | <493 | NT |
| NT | NT | NT | NT |
| <4 | 3020 | <3024 | NT |
| <4 | 7510 | <7514 | NT |
| NT | NT | NT | NT |
| NT | NT | NT | NT |
| <1 | 928 | <929 | NT |
| <4 | 7270 | <7274 | NT |
| NT | NT | NT | NT |

Aquifer Zones (Note: Zones are interconnected with one another, distinction is for reporting purposes only)

S = Saprolite Zone

T = Transition Zone

B = Bedrock Zone

<1 = Result less than laboratory practical quantitation limit (shown in PPB).

1,1-DCE = 1,1-Dichloroethene

1,1,1-TCA = 1,1,1-Trichloroethane

NT= Not Tested For This Compound

PPB - Parts per Billion or micrograms per liter (ug/L)

 indicates source area

Keeping the pH of the aquifer as close to neutral as possible to decrease metals solubilization/mobilization.

4-h) In-Situ Process Control

Monitoring nearby wells for water level changes, presence of persulfate, concentrations of sulfate (by-product of the reaction), ORP, pH and temperature depending on the activator) can all be used to evaluate the progress and success of oxidant application. An increase in electrical conductivity is an important way to understand the zone of influence of the injection. Other process controls include logging of volumes injected and depths, chemical probing with depth information and surface geophysics, such as ground penetrating radar where appropriate.

Process control changes were implemented due to daylighting issues in the source area (utilized higher density injection points and sodium hydroxide). Interim field screening was used because some contaminants had more mass in

specific areas than previously identified. Within these areas, the amount of persulfate was increased to account for the higher contaminant mass. The use of process control optimization allowed the site to be remediated.

4-i) Intermediates Monitored

Concentrations of 1,1,1 - TCA and 1,1 - DCE were monitored after injection events using an SRI portable GC. Short-lived and relatively low concentrations of oxidation intermediates were occasionally observed and included less chlorinated ethanes and methanes (e.g. chloromethane, chloroethane). 1,4 dioxane was periodically monitored due to the need for lab testing versus field testing.

5) Cost Information

This was a guaranteed fixed price contract for < \$1 million. The consultant who performed the work for this site met the guaranteed fixed price financial requirement. Concentrations have remained below target levels for a year after completion of remediation costs.

Overall cleanup costs were approximately \$5/ton of saturated soil. The chemical cost for treatment was roughly \$2/ton of soil. The remaining cost was steam and injection costs.

6) MNA or ENA Component

Monitored natural attenuation (MNA) was a component of the remedy used at this site. MNA was used to negotiate treatment levels above MCLs

A by-product of the persulfate reaction is sulfate. Sulfate could potentially hinder full reduction of the contaminants with the addition of sulfate to the system but this is very site specific. Dissolved sulfate ions are highly soluble and generally move rapidly through the aquifer, so ambient sulfate conditions usually return in a few months. Sulfate concentrations at the site have remained below 250 ppm, which is the secondary drinking water standard.

Use of In-situ Soil Mixing as the delivery tool for Lime activated Sodium Persulphate for the in-situ chemical oxidation of chlorobenzene contamination.

Authors: Ross Pollock (Technical Director, Churngold),
Wayne Davies (Technical Director, RPS)

Churngold Remediation Limited (Churngold) were selected as a specialist remediation contractor for remediation works required on part of the former ICI Burnhall Facility, Thornton. This part of the Site is being developed as part of the Lancashire Waste Partnership PFI Project to enable the construction of an innovative green and brown waste composting facility. Churngold worked alongside RPS Planning & Development and Waste 2 Resources (W2R), the principal contractor for the project, in developing a remediation strategy for the Site.

Extensive Site Investigation works undertaken by RPS identified hotspots of elevated Chlorobenzene (MCB), all isomers of Dichlorobenzene (DCB), Trichloroethene (TCE) and Tetrachloroethene (PCE), which when combined totalled just over 0.7 hectares. The investigation data indicated that the contamination occurred within the saturated zone, both as Dense Non-Aqueous Phase Liquid (DNAPL) and dissolved phase contamination. A subsequent Detailed Quantitative Risk Assessment (DQRA) using ConSim determined that the Contaminants of Concern (COC's) posed an unacceptable risk to the environment. The key receptor at risk was a non-tidal ditch that forms the northern boundary of the Site.

Best assessment of the remediation options

Based on detailed discussions with the principal stakeholders (including Lancashire County Council, the Environment Agency, Wyre Borough Council, W2R, Bovis Lend Lease and Global Renewables) criteria were developed to determine the most appropriate remediation strategy. The key criteria were as follows:

- Capable of reducing contaminant concentrations below the remedial target concentration
- Will fit in with the timescales of the development programme
- Will not cause unacceptable issues during remediation such as nuisance, particularly contaminant odours
- Costs in keeping with the objectives of the remediation

A detailed review of remedial options was undertaken to assess what techniques could be applicable at the Site. Each option was assessed based on a simplified Site Characterisation Model, which was designed to highlight the difficulties faced by any attempt to treat the encountered contamination thus focusing the decision making process. The key considerations of the model were:

- Low permeability geology and low hydraulic groundwater flow;
- Heterogeneity of the geology;
- The physiochemical properties of the COCs;
- Concentrated pockets of contamination indicative of residual NAPL;
- Limited timeframe and logistical restrictions associated with the overall Site development;
- Scale of required treatment; and
- Depth and geometry of treatment zones.

Assessed technologies included Dual Phase Vacuum Extraction, In-situ Biological Techniques, Enhanced 'Pump and Treat', Ex-situ Methods and Reactive Barriers. Methods based on extraction/abstraction would be hampered by the low permeability geology and rate limiting release of gross contamination within the source zones. The engineering solution required to overcome these issues would be cost prohibitive. Other techniques were also ruled out on cost, timeframe and performance issues.

The most favourable technique, which was known to be very effective for the destruction (oxidation) of the COC's, was In-situ Chemical Oxidation (ISCO). ISCO however, relies on contact between the oxidant and contaminant to ensure destruction of the COC's. As contamination was partitioned within soil and as NAPL often in organically rich silt sand bands, conventional methods of injection would not provide sufficient certainty of this being achieved. An innovative method of delivery and selection of the most appropriate chemical oxidants was required to maximise the effectiveness of ISCO. The solution offered was based on an innovative combination of soil mixing and high strength oxidants, which would offer the following advantages:

- The addition of mechanical mixing together with conventional injection would increase the contact of oxidant and contaminant;
-

- The treatment intensity could be varied by altering the rate of mixing, the speed of advancing the mixing head, the oxidant injection rate and column spacing;
- The process would be rapid, capable of covering large treatment areas;
- It would avoid fixed infrastructure i.e. injection wells;
- It would be capable of targeting specific horizons within the subsurface, thereby minimising wastage of oxidant solution;
- It would not generate any waste streams or VOC emissions.

Represents best, rather than good or average practice

Churngold undertook detailed literature reviews, laboratory studies and a pilot study in order to optimise treatment design. The first stage involved the selection of the most appropriate chemical oxidant. A literature review determined that modified hydrogen peroxide and catalysed sodium persulphate (persulphate) were likely to be the most effective oxidants. Preliminary experimental results, using soil and groundwater samples collected from site, demonstrated that lime activated persulphate was the most effective oxidant, routinely reducing COC masses by >95% in each test microcosm. It was therefore agreed that work should advance to a site scale Pilot Study using this oxidant. The pilot study comprised the use of a modified Continual Flight Auger (CFA) linked to an oxidant mixing and injection system and confirmed that this type of delivery was effective with groundwater and soil contaminants being reduced by an average of 97% and 49% respectively.

With the concept proven, work began on refining the process. A further laboratory study concluded that the use of hydrogen peroxide based oxidants were not as effective as activated persulphate. A more detailed refinement of the activation of the persulphate helped improve the performance of the process. High ratios of hydrated lime and buffers were used to maintain a strongly alkaline pH, which was shown to be critical in extending the activation lifetime of the oxidant.

Addition of high strength lime slurries had several major benefits. The first was that their surfactant properties increased the surface area of NAPL available to the oxidant and added to the dissolution of the contaminant in the dissolved phase (where oxidant reactions are at their optimum). The excess of lime also helped to improve the geotechnical stability of the treated soils by reacting with any by-products, including free sulphate to form benign minerals such as gypsum.

Work was also undertaken to improve the CFA mixing rigs. This included modifications to the mixing heads and auger strings, inclusion of GPS, process control and data logging of all key operational parameters. The rigs also featured a number of modifications to improve health and safety, including better seals and splash guards.

Cost effectiveness and durability over the period of operation

Although extensive site characterisation was completed by RPS, it was agreed with them that additional information on the vertical distribution of the contamination was important. A Membrane Interface Probe (MIP) investigation was therefore undertaken by Churngold to help identify depths to contamination in the subsurface. The results of the survey were used to ensure the treatment was focussed and/or intensified at the most impacted depths, between 1.5 and 12.0 metres below ground level (mbgl).

The flexibility of the mixing and injection system (varying injection rates, ability to adjust column spacing, ability to inject at specific depths and ability to create chemical oxidant batches of varying concentrations) enabled Churngold to intensively target those areas which had been identified as heavily impacted without wasting valuable resources on those areas which were less impacted. Where results indicated the presence of NAPL the injection programme was modified to allow for two rounds of treatment. This was one of the keys to the success of the project as very little oxidant was wasted, making the process highly efficient and cost effective.

Significant reduction of pollution burden rather than transferring it

Baseline mass balance calculations estimated that approximately 17,400 kg of contamination was partitioned in soil and NAPL, with a further 210 kg in groundwater. Calculations completed post remediation indicated that 11,715 kg of contamination was destroyed in-situ as part of the process. Philip Block, the technical manager for FMC who hold the worldwide patent on the use of persulphate for remediation purposes, suggests '*...that this is one of the largest, if not largest, destruction of contamination at any site using persulphate oxidation*'.

Application of in situ chemical oxidation using this method prevented approximately 48,400 tonnes of contaminated from soil being sent to landfill. Table 1 summarises some of the key parameters from the operational phase.

| Hotspot | Area Requiring Treatment (m ²) | Total No. of Columns | Mass of Injected Oxidant Solution (kg) |
|---------|--------------------------------------------|----------------------|----------------------------------------|
| A | 3,974 | 1,438 | 106,921 |
| B | 194 | 139 | 13,810 |
| C | 1,080 | 946 | 146,306 |
| D | 624 | 238 | 10,101 |
| E | 1,446 | 113 | 4,937 |
| Total | 7,318 | 2,874 | 282,077 |

Table 1. Treatment Areas and Oxidant Injection Masses

Compliance with Health and Safety

Robust health and safety practices were put in place and policed by W2R throughout the works. All operatives involved in the mixing process who could come into contact with the oxidants wore full chemical, suits, full face masks and long gloves in accordance with the PPE requirements identified as part of the risk assessment process. Regular toolbox talks were undertaken and all personnel involved in the process were fully inducted. Operations were run in accordance with detailed method statements and designed to ensure safe operation. Consideration of health and safety was also a determining factor in the selection of persulphate, which is less hazardous to store and handle when compared to other oxidants such as hydrogen peroxide.

Community and stakeholder acceptance

In-situ remediation techniques were promoted by the regulators as a way of managing the potential risks and nuisance that could have been presented by ex-situ methodologies. The injection of the chemical oxidant over a single round or minimum number of rounds of injection was also a key design aim to reduce the treatment timeframes.

The use of alternative techniques employing extraction/abstraction would have meant extending the remediation to several years and presented potential long- term nuisance within the local environs, thus not meeting the requirements of W2R in terms of delivery of their PFI scheme. Similarly the use of barriers would have resulted in a long-term solution due to the slow travel of groundwater in the impacted zone and hence would not have satisfied the long term liability issues of Lancashire County Council who would ultimately take back ownership of the site back including any latent environmental liability. The techniques would also have required maintenance and on-going monitoring. The solution addressed all parties' requirements.

Throughout the project the regulators and client were regularly engaged with updates, including several on-site presentations to interested parties involved in the project. Stuart McDonald, overseeing the project for the Environment Agency, concluded the following within his site sign-off correspondence: *'In reviewing all available documents, I am satisfied that the remediation scheme has resulted in a massive reduction in the bulk contamination at the defined 'hotspots', and I consider this process to be particularly successful, as demonstrated in your validation reports...I would like to take this opportunity to thank RPS, Churngold and W2R for all the assistance given during this period of the remediation. It is this that has enabled us to have considerable faith in both remediation methods employed and the validation of results.'*

Considerations of Sustainability (including the wider stakeholder impacts on and off site)

Remediation works took place in order prevent contamination impacting on the "Non-Tidal Ditch" running to the north of the site. It has been estimated that in total 11,493 kg of chlorobenzene and dichlorobenzene isomer contamination was destroyed by ISCO within both soil and groundwater. Destruction of this contamination has potentially prevented an estimated 7,183,125 m³ of water in the Non-Tidal Ditch from becoming impacted beyond Environmental Quality Standards.

The Non-Tidal Ditch was sampled in three locations before and throughout the works in order to assess the impacts of the remediation process on the ditch. Average contaminant concentrations pre and post works are provided in Table 2.

| Sample Location | Average concentration of chlorobenzene and dichlorobenzene isomers (mg/l) | |
|-----------------|---------------------------------------------------------------------------|------------------|
| | Sept – Nov 2007 | Feb – March 2008 |
| 1 (upstream) | 1.0 | 0.1 |
| 2 (midstream) | 1.9 | 0.1 |
| 3 (downstream) | 1.9 | 0.04 |

Table 2: Average concentrations of chlorobenzene and dichlorobenzene isomers within water samples taken from 3 locations within the Non-Tidal Ditch during two different time periods.

Results from water samples taken from the surface water feature show that concentrations of chlorobenzene and dichlorobenzene isomers have reduced more than ten fold since completion of the ISCO treatment.

Genuine Novelty

Traditional chemical oxidation delivery and its effectiveness is limited by a number of factors including:

- Works best in permeable homogeneous geologies
- Limits mass of oxidant that can be delivered
- Does not guarantee oxidiser/contaminant contact
- Treatment duration may extend due to multiple rounds of treatment due to difficulty of injection and achieving dispersion into the treatment zone

The use of soil mixing negated each of these concerns. Despite the impermeable, highly heterogeneous geology, remedial targets were achieved within 80% of the injected footprint after only one round of injection. All works were completed within the 20 week strict timeframe.

To our knowledge the innovative combination of soil mixing and use of an emerging oxidant, selected and developed to overcome a series of site-specific restrictions, has not been used in the UK or European markets before and therefore should be considered novel. The unique use of high strength lime activators aided the process by making more contamination available for oxidation adding to the innovative nature of the solution. Phil Block has confirmed that this project is the second largest application of persulphate to be undertaken worldwide. The largest, which is currently being undertaken in Texas, is using a similar soil mixing delivery technique.



Figure 1: CFA Rigs In full swing

The work represents a significant technological advance for the industry, with the opportunity for widespread application

Until the design of this soil mixing technique, traditional ISCO was limited in its application by geological setting and cost of trying to achieve dispersion of sufficient oxidant into the sub-strata in order to affect contaminant breakdown without having to apply further expensive rounds of chemical injection. For oxidisable organic contaminant compounds, delivering chemical oxidants to the subsurface via in situ soil mixing is an excellent way of simultaneously destroying contaminant mass in both the soil or free phase source area and within dissolved phase. Remediation can be carried out to an extremely high standard within a reduced timeframe compared to traditional ISCO injection techniques and other technologies, which is a considerable advantage for projects which require short clean up times to meet development requirements. An overriding advantage of this technique however, is that it has been proven successful for use in challenging geological and hydrogeological environments and is flexible enough to be able to specifically target locally impacted areas within hotspots meaning that the chemical costs can be reduced. The many benefits of this novel technique certainly make it a viable option for increased application throughout the industry as a whole and will help promote more widespread uptake of ISCO technology.



Univar USA Inc Material Safety Data Sheet

MSDS No:

Version No:

Order No:

Univar USA Inc., 17425 NE Union Hill Rd., Redmond WA 98052
(425) 889 3400

Emergency Assistance

For emergency assistance involving chemicals call
Chemtrec - (800) 424-9300

The Version Date and Number for this MSDS is : 03/10/2006 - #008

PRODUCT NAME: CALCIUM HYDROXIDE HYDRATED LIME
MSDS NUMBER: P16782V
DATE ISSUED: 01/01/2006
SUPERSEDES: 01/01/2003
ISSUED BY: 008654

MATERIAL SAFETY DATA SHEET

OSHA HAZARD COMMUNICATION

PRODUCT IDENTIFICATION CALCIUM HYDROXIDE HYDRATED LIME

CHEMICAL ABSTRACT

CAS 1305-62-0

Distributor:

UNIVAR USA
6100 Carillon Point
Kirkland, WA 98033
425-889-3400

Section II - Hazardous Ingredients / Identity Information

| Specific Chemical Identity; | OSHA | ACGIH | Other | % |
|-----------------------------|-----------|------------|-------------|------------|
| Common Names | PEL | TLV | Recommended | (Optional) |
| Calcium Hydroxide; | | | | |
| Slaked Lime; | 5 mg/m3 | 5 mg/m3 | | |
| Hydrated Lime | | | | |
| Crystalline Silica (Quartz) | 0.1 mg/m3 | 0.05 mg/m3 | Respirable | < 0.10 % |

Calcium Hydroxide is not listed on the NTP, IARC, or OSHA lists of carcinogens. Univar recommends using personal protection equipment when handling this product.

Section III - Physical / Chemical Characteristics

| | |
|-------------------------------|------------|
| Boiling Point (Calcium Oxide) | 5162 deg F |
| Specific Gravity (H2O) = 1) | 2.2 |
| Vapor Pressure (mm Hg) | NA |
| Melting Point - Loses CO2 | 1076 deg F |
| Vapor Density (Air = 1) | NA |
| Evaporation Rate | NA |

Annotation:

Solubility in Water 0.185 % @ 0 deg C; 0.077 % @ 100 deg C
Appearance and Color Odorless; White as a dry powder or wet slurry.

Section IV - Fire and Explosion Hazard Data

Flash Point NA Flammable Limits - NA
Extinguishing Method NA
Special Fire Fighting Procedures NA
Unusual Fire and Explosion Hazards NA

Section V - Reactivity Data

Stability: Stable Conditions to Avoid: NA

Incompatibility (Materials to Avoid): Water, Acids, Inter-halogens,
Phosphorus (V) Oxide

Hazardous Decomposition or Byproducts: None

Hazardous Polymerization: Will Not Occur Conditions to Avoid: NA

Section VI - Health Hazard Data

Route(s) of Entry Inhalation? YES Absorption Through Skin? YES
Ingestion (swallowing)? YES

Health Hazards

Acute

Prolonged contact may irritate or burn skin - especially in the presence of moisture. Inhalation of dust may irritate mucous membranes or respiratory passages. Direct eye contact may cause permanent damage.

Chronic: Long term exposure can cause irritation

| Carcinogenicity | NTP? | IARC Monographs? | OSHA Regulated? |
|--------------------|------|------------------|-----------------|
| Calcium Hydroxide | NO | NO | NO |
| Crystalline Silica | YES | YES | YES |

Signs and Symptoms of Exposure: Irritation of skin, eyes, and respiratory tract.

Medical Conditions Generally Aggravated by Exposure: Respiratory disease, skin condition.

Emergency and First Aid Procedures: Provide fresh air. Wash off dust with soap and water. Drink plenty of water if swallowed. Flush eyes with water immediately and contact physician.

Section VII - Precautions for Safe Handling

Annotation:

Steps to Be Taken in Case Material is Released or Spilled: Normal clean-up procedures. Care should be taken to avoid causing dust to become airborne. Vacuum cleaning systems are recommended.

Waste Disposal Method: Dispose of product in accordance with Federal, State and Local regulations. See Section IX.

Precautions to Be Taken in Handling: Store away from water and acids.

Other Precautions

Section VIII - Control Measures

Respiratory Protection - Dust filter masks are recommended for personal comfort and/or protection

Ventilation: Local Exhaust - To maintain TLV's and PEL's Special - None
 Mechanical - To maintain TLV's and PEL's Other - None

Protective Gloves - Cloth or leather gloves when handling dry material-rubber gloves when wet or damp

Eye Protection - ALWAYS wear shielded glasses and/or fitted goggles around product to reduce eye injury

Other Protective Clothing - Wear long sleeve shirts and pants to minimize contact with product.

Work / Hygienic Practices - Maintain dust exposure limits below TLV's and PEL's. Whenever necessary wear respiratory protection

Section IX - Regulatory Compliance Guidance

CONEG

Materials used to manufacture bags that containing products are CONEG compliant.

CWA

Product contains alkaline material potentially toxic to aquatic life if concentration is high for extended periods of time. Minimize contact with storm water runoff.

DOT

Product is not regulated by U.S. Dept of Transportation.

EPA

Waste derived from unused products is not subject to RCRA. Solid waste is acceptable at landfills as a "special waste" but can often be beneficially reused for other purposes.

SPILLS

Annotation:

Whenever possible contain and sweep up spillage in dry form rather than flushing with water. Fire may occur in containers if damp product is placed in direct contact with combustible materials.

TSCA

Product is listed on Toxic Substance Control Act, Canada DSL and all other International Inventories

Prop65

Product is subject to California Proposition 65 warning labeling requirements for trace metals and Crystalline Silica.

NAFTA

Product qualifies under HS Tariff No 2522.20 as 100% US Origin, Preference Criteria A. Annual certification will be provided upon request.

Univar USA Inc Material Safety Data Sheet

For Additional Information contact MSDS Coordinator during business hours, Pacific time: (425) 889-3400

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