CASE STUDIES INVOLVING THE APPLICATION OF IN-SITU OXIDATION TECHNOLOGIES TO REMEDIATE PETROLEUM HYDROCARBONS AND CHLORINATED SOLVENTS

REMEDIATION TECHNOLOGIES CONFERENCE -2016 BANFF, AB

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- Case Study #2: Ying Lang, P.Eng., Marina Makovetski, A.Ag., Lee Ringham, P.Geo.
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- APTWater Inc. (<u>www.aptwater.com</u>) for PulseOx[®]: Mr. Terry Applebury; Mr. Doug Gustafson
- Regenesis Inc. (<u>www.regenesis.com</u>) for RegenOx[®], ORC-A[®]: Ms. Ashley Cedzo (Marketing – Western Canada)



PRESENTATION OUTLINE

- BC Ministry of Environment Compliance Process
- Remediation Technologies
 - PulseOx Ozone and Peroxide
 - RegenOx and ORC-A[®]
- Case Study 1 Former Dry Cleaner
- Case Study 2 Former Gas Station
- Case Study 3 Gasoline, Diesel and/or Heating Oil Contamination from Leaky Underground Tanks
- Case Study 4 Old Brick Foundry









BC MINISTRY OF ENVIRONMENT – COMPLIANCE PROCESS



FACTORS INFLUENCING COMPLIANCE SOLUTIONS (NUMERICAL OR RISK-BASED)

- 1. Uncertainty with respect to site characterization
- 2. Site setting, sub-surface conditions, extent of contamination both onsite and offsite
- 3. Affected media and feasibility of different remediation options
- 4. Budget (\$\$\$ available to remediate or risk assess)
- 5. Time available to remediate
- 6. Consultant client relationship (confidence in the consultant to deliver the solution)

"COMPLIANCE SOLUTIONS EVOLVE AS THE PROJECT PROGRESSES"



Technology - PulseOx



PulseOx, a proprietary reagent injection methodology that maximizes the distribution of reagents, formation of hydroxyl radicals, and occurrence of chemical reactions which take place in the treatment zone.

- Individually, ozone and hydrogen peroxide react with organic contaminants due to their relatively high oxidation potentials (2.07 volts and 1.77 volts, respectively).
- Hydrogen peroxide and ozone also individually react with iron in the subsurface soils to form hydroxyl radicals.
- The formation of hydroxyl radicals through the introduction of ozone and hydrogen peroxide follows this reaction:

$$2\mathrm{O}_3 + \mathrm{H_2O_2} \rightarrow 2\mathrm{OH} + 3\mathrm{O_2}$$

- Hydroxyl radicals have a higher oxidation potential of 2.80 volts than either ozone or hydrogen peroxide individually.
- The PulseOx technology can be used to time the injection of ozone and peroxide into each well connected within a network.



Technology - PulseOx

Chemical oxidation using Ozone and Peroxide













Technology – RegenOx and ORC Advanced

RegenOx is a percarbonate-based *in-situ* chemical oxidation technology that rapidly destroys petroleum hydrocarbons and chlorinated contaminants through powerful chemical reactions. It directly oxidizes contaminants while a catalytic component generates oxidizing free radicals to destroy the target compounds.

ORC Advanced is a proprietary formulation of food-grade, calcium oxyhydroxide that produces a controlled release of molecular oxygen to enhance aerobic biodegradation.

ORC Filter Sock is a permeable filter sock containing calcium oxy-hydroxide based chemical which produces a controlled release of molecular oxygen (17% by weight) when hydrated.

Source: www.regenesis.com









Technology - RegenOx

PRINCIPLES OF CHEMICAL OXIDATION TECHNOLOGY for the Remediation of Groundwater and Soil





- RegenOx[™] is a two part product. Part A (the oxidizer complex) and Part B (the activator complex).
- Part- A and Part-B can be mixed together without concern of excess heat or gas generation. The two part product is simply mixed together and pumped into the subsurface or can be injected using a drill rig. Typically 3-5% solution of RegenOx is used. It is recommended that no more than 10% solution be used.
- Molecule of sodium percarbonate (C₂H₆Na₄O₁₂ or 2Na₂CO₃.3H₂O₂) dissolved in water yields sodium carbonate and hydrogen peroxide creating an alkaline, oxidative environment. Reaction of ferrous ion and hydrogen peroxide generates hydroxyl radicals which can react with almost any hydrocarbon or chlorinated hydrocarbon.
- Can oxidize contaminants in both soil and in groundwater. A pound of RegenOx delivers approximately 0.15 lbs of O_2 . Approximately 20 lbs of RegenOx would be required to oxidize 1 lb of Toluene.
- Releases sodium into the water
- Leaves behind very little residue limited to carbonate and bicarbonate ions.
- More info: Principles of Chemical Oxidation Technology (www.regenesis.com)

Relative Electropotentials (source ITRC 2005)

Hydroxyl radical 2.8 V Ozone (gas) 2.1 V Sodium persulphate 2.0 V Sodium percarbonate 1.8 V Hydrogen Peroxide 1.8 V Permanganate 1.7 V Superoxide Ion -2.4 V



Technology – RegenOx (contd.)



Catalytic peroxide activation and contaminant degradation under alkaline conditions

- Desorption (detergent-like properties)
- Surfactants generated by oxidation of organics
- Surface-Mediated Oxidation
 - Adsorption Degradation
- Direct Oxidation
 - · Highly-active iron centers
- Free Radical Oxidation



Activated Sodium Percarbonate

Residuals after oxidation are carbonates, silicates, iron oxides, and other low-toxicity soil-like materials

Source: Principles of Chemical Oxidation Technology – RegenOx Design Manual (www.regenesis.ca)



Case Study #1: Former Dry Cleaner Chilliwack, BC

Comingled Plume: Petroleum Hydrocarbons and Dry Cleaning Chemicals

Initial findings by other consultants:

- Soil exceedances identified onsite (LEPH, Ethylbenzene, Toluene, Xylenes, VPH)
- Extensive groundwater contamination onsite and offsite into the laneway

Client: Ruth and Naomi's Mission (Not for profit Homeless Shelter) Project: Environmental Investigations and Remediation to support the Redevelopment of the facility



Case Study 1: Soil Characterization Results





Case Study 1: Groundwater Results

Maximum Concentrations in Groundwater (onsite):

Ethylbenzene: 2,140 μg/L (2,000 μg/L) Toluene: 3,850 μg/L (390 μg/L) Light Extractable Petroleum Hydrocarbons (LEPH_w): 5,600 μg/L (500 μg/L) EPH_{w 10-19}: 5,900 μg/L (5,000 μg/L) Volatile Hydrocarbons (VH_w): 33,000 μg/L (15,000 μg/L) Naphthalene: 340 μg/L (10 μg/L)

Maximum Concentrations in Groundwater (offsite):

LEPH_w: 1,800 µg/L (500 µg/L) VPH_w: 3,900 µg/L (1,500 µg/L) Naphthalene: 100 µg/L (10 µg/L) Toluene: 392 µg/L (390 µg/L) Tetrachloroethylene (PERC): 2,760 µg/L (1,100 µg/L)





Case Study#1: Conceptual Site Model











- Layers of fine and coarse sands
- Shallow groundwater (within 3M below grade)
- Conductive stratigraphy (K 10⁻⁵ m/s), Ground water speed – 23 m/Year or 2.3 km in 100 Year
- Onsite and offsite contamination
- Petroleum hydrocarbon contamination in groundwater localized, however, high concentrations present
- DNAPL or LNAPL not identified in wells
- Comingled plume of petroleum hydrocarbons, PERC and anaerobic degradation products (Trichloroethylene, cis, trans 1,2 Dichloroethene and Vinyl Chloride)



Conceptual Site Model (contd.)





Case Study#1: Actual Well Connections





PulseOx Trailer

Typical expected radius of influence – 2-3 m from each well in a sandy conductive aquifer



Case Study#1: The PulseOx Oxidation System

PulseOx Reactor: This gets inserted into each well



View inside the Trailer: Ozone generator, electronically controlled injection valves for peroxide and ozone





Well head: connections into the PulseOx reactor. Ozone in Transparent Tube, Peroxide through the black tube.





Case Study#1: PulseOx Application Summary

| Well # | Monitoring Wall ID | Treatment Setup Configuration (min.) | | | | | | |
|--------|--------------------|--------------------------------------|-----------|-----------|-----------|--------------|--|--|
| | | 5-Apr-10 | 28-Jul-10 | 08-Sep-10 | 24-Sep-10 | 30-Sep-10 | | |
| Well 1 | 08-MW10 | 10 | 10 | 10 | 10 | Disconnected | | |
| Well 2 | 08-MW7s | 10 | 10 | 10 | 10 | Disconnected | | |
| Well 5 | 08-MW14 | 10 | 10 | 10 | 10 | Disconnected | | |
| Well 6 | 08-MW18 | 10 | 10 | 10 | 10 | Disconnected | | |
| Well 7 | 08-MW12 | 10 | 60 | 10 | 60 | 60 | | |
| Well 8 | 08-MW13 | 10 | 10 | 10 | 10 | Disconnected | | |

Notes:

1. PulseOx System stopped between 28 July 2010 to 8 September 2010 when soil remediation activities were undertaken

2. 10-PR-MW3S was connected to the system on 24 Sept 2010, replacing 08-MW12

Total Operation Hours (5 April 2010 – 26 October 2010): 3,470 Hours = 144 days = 4.8 months Total volume of Hydrogen Peroxide (H_2O_2) injected into the ground: 2,100 L Rate of Ozone application: 0.9 kg / day Rate of H_2O_2 use: ~ 200 L / week



Case Study #1: pH and DO in Offsite Wells



Offsite Treatment Monitoring

Oxidation Reduction Potential (ORP) vs. Monitoring Date

Initial Trends: pH: 6.21 to 8.05 ORP: -104.1mV to 261.5mV Dissolved Oxygen: 1.49mg/L to 8.9mg/L

Trends during System Application:

pH: 4.98 to 6.98 ORP: -117mV to 391.72mV Dissolved Oxygen: 0.57mg/L to 28.04mg/L

Trends following Conclusion of Remedial Activities onsite:

pH: 2.71 to 6.39 ORP: -23.2mV to 533.3mV Dissolved Oxygen: 0.33mg/L to 30.81mg/L

Case Study #1: Onsite Excavations and RegenOx Addition

Total Volume of Excavation Water Pumped and Treated: 180,000 L (over 4 days, 27-30 August 2010 inclusively)

Approximately 500 Kgs of RegenOx – Parts A and B mixed within the base. Key observations included elevated pH – 9.81, desorption of petroleum hydrocarbons evident in the form of sheen in the groundwater

Case Study #1: Onsite Monitoring Results

Maximum Concentrations at 10-PR-MW3S: September 14, 2010 VHw: 15,500 µg/L VPHw: 5,400 µg/L Toluene: 3,530 µg/L Xylenes: 5,960 µg/L Naphthalene: 235 µg/L LEPH: 4,020 µg/L Trichloroethylene: 201 µg/L

Concentrations decreased: October 13, 2010 after 1 additional month of treatment by PulseOx.

Maximum Concentrations at 10-PR-MW2

VPHw: 1,600 µg/L Naphthalene: 11.1 µg/L LEPH: 2,250 µg/L

Offsite Monitoring Results

Trichloroethylene AW standard – 200 µg/L

Case Study#1: Offsite Monitoring Results

BC CSR – No Aquatic Life Water Use Std. for cis – 1,2 dichloroethene

BC Hazardous Waste Reg. Leachate Quality Standard – 200 µg/L for Vinyl Chloride

Case Study #1: Offsite Monitoring Results

WSP

ORC Socks in Wells – Post-Remediation

Case Study #1:

1. PulseOx can rapidly oxidize petroleum hydrocarbons and chlorinated compounds and is effective in conductive sub-surface conditions (high K values).

2. Notable changes in the sub-surface include high DO levels in the order of 20-30 mg/L, changes in redox potentials and pH. Radius of influence can be up to 3.0 m from a single reactor in sandy aquifers.

3. RegenOx and ORC-A are also effective in oxidizing petroleum hydrocarbons and chlorinated compounds. Dosage of these compounds would depend upon the mass of contaminants that would need to be treated. The groundwater pH becomes alkaline when RegenOx is used and reactivity can range from days to weeks with most of the immediate oxidation occurring within a few days.

4. Use of a combination of remedial technologies is required at times when there is a limit on the time and budget to achieve compliance.

Redeveloped Site Risk Based Compliant, No Vapour Barrier required

Case Study #2: Former Gas Station Site West Vancouver, BC

CHEMICAL OXIDATION OF PETROLEUM HYDROCARBONS

History and Contaminants:

- 1930s to 1990, the site was used as a gas station (Diesel and Gasoline).
- Soil (BTEX, VPHs-870µg/g , LEPHs -3730µg/g)
- Groundwater (Mainly BTEX and up to 56 mg/L of xylenes, VPHw- 6.5 mg/L, LEPHw 2.97 mg/L, Naphthalene, Pyrene and Benzo(a)pyrene)

Date: 2011-2013

Case Study #2:

Site location Plan: Capilano River. West Vancouver, BC is located towards the east

Case Study #2: Soil Zones of Contamination (after a DSI)

Maximum Concentrations of Petroleum Hydrocarbons in Soil:

Benzene = $1.2 \mu g/g (0.04 \mu g/g)$ Ethylbenzene = $180 \mu g/g (7 \mu g/g)$ Toluene = $10 \mu g/g (2.5 \mu g/g)$ Xylenes = $1,100 \mu g/g (20 \mu g/g)$ VPH = $2,600 \mu g/g (200 \mu g/g)$

Soil Contaminants present 6-10 m below grade

Groundwater Contamination

Maximum Concentrations of Petroleum Hydrocarbons in Groundwater:

Benzene = 390 µg/L (DW-5 µg/L, AW -1,000 µg/L) Ethylbenzene = 9,200 µg/L (2.4 µg/L, 2,000 µg/L) Toluene = 3,840 µg/L (24 µg/L, 390 µg/L) Xylenes = 79,700 µg/L (300 µg/L, NS) VPH = 39,000 µg/L (NS, 1,500 µg/L) VH = 85,000 µg/L (15,000 µg/L) LEPH = 4,300 µg/L (NS, 500 µg/L) Acridine = 1.7 µg/L (NS, 500 µg/L) Benzo(a)pyrene = 0.12 µg/L (0.01 µg/L, 0.1 µg/L) Naphthalene = 240 µg/L (NS, 10 µg/L) Phenanthrene = 4.6 µg/L (NS, 3 µg/L) Pyrene = 1.9 µg/L (NS, 0.2 µg/L)

Well depths up to 12 m below grade. Most between 6-8 m below grade.

IW – Injection wells

Case Study #2: Cross-Section & Conceptual Site Model

- Fill in the area of the former underground tanks underlain by sands, silts and gravel. Buried logs encountered at depth.
- Soil contamination extended from 6.0 to 10.0 m below grade, mainly BTEX, VPH.
- Groundwater contaminants included BTEX, VPH (gasoline), LEPH and PAHs (diesel)
- Groundwater contamination localized within the site and immediately adjacent area.
- Highly conductive sub-surface (K~10⁻⁵ m/s)
- Local groundwater flow towards SW @ 190 m/year

CASE STUDY#2: CHEMICAL OXIDATION OF PETROLEUM HYDROCARBONS USING REGENOX

- As contaminants were primarily in groundwater and soil beneath the water table, chemical oxidation was chosen to reduce contaminant concentrations.
- The groundwater plume was found not to have migrated beyond the immediate west bound lane along Marine drive, West Vancouver.
- The objective was to aggressively reduce contaminant concentrations so a numerical or risk –based Certificate of Compliance could be obtained through the BC Ministry of Environment.

Injection of Oxidant and Angular Drilling of Boreholes for Installation of Injection Wells

- RegenOx application Batch delivery at temporary well points (injection wells) and direct push methods (injection rod). Mud bay drilling, Surrey, BC used for RegenOx injections.
- Installation of 24 Injection wells (vertical and angled)– Schd. 40 PVC, nested, screened within 6-10 m below grade.
- Multiple applications (of RegenOx in 2011 and 2012.
- 7800 Kgs of Part A and 3180 Kgs of Part B along with 163,000 L of water (6.7% solution) applied in total within the most contaminated zone.

Case Study 2: Results for select wells within the Treatment Zone

CASE STUDY#2: CHEMICAL OXIDATION: Results for PHH-10-BH102

CASE STUDY#2: CHEMICAL OXIDATION Results for PHH-10-BH102 (BTEX)

| Time Frame | Prior To LGRCO | | Post-LGRCO | | | | | | | | |
|-------------------|----------------|---------------|--------------|---------------|--------------|--------------|---------------|------------------------|-----------|------------|------------|
| Parameters | 30-May- 11 | 23-Aug- 11 | 4-Nov- 11 | 15-Dec- 11 | 8-Feb- 12 | 8-Mar- 12 | 11-Apr- 13 | 11-Apr- 13 (Dup) | CSR DW | CSR AWf | CSR AWm |
| Benzene | 18 | 360 | 42 | 49.5 | 4.6 | 25.2 | 50.7 | 84.3 | 5 | 4000 | 1000 |
| Ethylbenzene | 5100 | 3600 | 21 | 2010 | 270 | 541 | 700 | 1310 | 2.4 | 2000 | 2500 |
| Toluene | 230 | 480 | 76 | 245 | 20.6 | 44.4 | 51.1 | 82.7 | 24 | 390 | 3300 |
| Xylenes (total) | 29000 | 26000 | 36000 | 34900 | 13800 | 7790 | 6710 | 9570 | 300 | NS | NS |
| NOTES | | | | | | | | | | | |
| ND - Not detected | | | | | | | | | | | |

BOLD Sample concentration exceeds the applicable standard.

CASE STUDY#2: SITE CONDITIONS FOLLOWING DEMOLITION **AIP ISSUED**

APPROVAL IN PRINCIPLE (Pursuant to Section 53 of the Environmental Management Act)

THIS IS TO CERTIFY that the remediation plan described herein submitted by Mr. Amir Khalili for the contaminated site identified below has been approved.

Summary of Site Condition, prepared by Reidar Zapf-Gilje, P.Eng. and Laura H. Koch, P.Ag., Ven Huizen Consultants Ltd., November 19, 2013;

Risk Assessment and Remediation Plan, 675 Marine Drive, West Vancouver, British Columbia, Jas Minhas, M.E.T., R.P.Bio., Ying-Lang Chang, B.A.Sc., E.I.T., Jay Rao, M.A.Sc. P.Eng., Levelton Consultants Ltd. and Scott Steer, M.E.T, R.P.Bio., Steer Environmental Associates Ltd., 14 November 2013;

Extended Stage 2 Preliminary Site Investigation, Limited Groundwater Remediation by Chemical Oxidation and Detailed Site Investigation. 675 Marine Drive, West Vancouver, BC, Ying-Lang Change, B.A.Sc., E.I.T., Ram Maddur, M.A.Sc., P.Eng., Jay Rao, M.A.Sc., P.Eng., Levelton Consultants Ltd. 14 November, 2013; and

Stage 1 Preliminary Site Investigation, 675 Marine Drive, West Vancouver, BC, Marina Makovetski, B.Sc., Ying-Lang Chang, B.A.Sc., E.I.T., Jay Rao, M.A.Sc. P.Eng., Levelton Consultants Ltd., 14 November, 2013.

This remediation plan is for remediation to numerical and risk-based standards.

A site plan is attached as Schedule "A" to this Approval in Principle.

When this Approval in Principle is implemented, the implementation must be in accordance with the conditions specified in Schedule "B" which is attached to and is a part of this Approval in Principle. The substances for which remediation will be conducted arc listed in Schedule "C".

December 17, 2013 Date Issued

Colm Condo For Director, Environmental Management Act

Site Identification Number 13381

1 of 7

CASE STUDY#2: CONCLUSIONS

- Oxidation of petroleum hydrocarbons in groundwater could be achieved up to 70% of the initial concentrations of BTEX using RegenOx, a sodium percarbonate based oxidant.
- Depending upon the stratigraphy, injections can be completed using direct push rigs or under pressure using existing monitoring wells.
- The effectiveness of oxidation depends upon the level of mixing of the RegenOx slurry and the amount of the oxidant injected.
- In this case, due to budget and time constraints (property was sold), additional injections were
 not required and an AIP was obtained as the plan was to construct a building with
 underground parkade (two to three levels) which required a vapour barrier.

Case Study #3: Old USTs – General Construction Contractor Burnaby, BC (2013-2014)

Underground Tanks – Fuel – Diesel, Gasoline, Heating Oil (?) Maximum Initial Contaminant Concentrations in Groundwater before Application (Dec 2013): Benzene: 7.4µg/L >CSR DW (5 µg/L) Ethylbenzene: 5.7µg/L > CSR DW (2.7 µg/L) Benzo(a)pyrene: 0.17µg/L (0.01 µg/L) Stratigraphy: Dense Glacial Till Mode: Gravity feed into boreholes, injection wells and test pits Objective – Numerical Standards Compliance (DW) Maximum Contaminant Concentrations in Groundwater following Application (Aug 2014):

Benzene: 25 µg/L Ethylbenzene: 44.2µg/L Benzo(a)pyrene: Below Laboratory Detection Limits **Total Volume of RegenOx Applied:** 27,500 L of 3-5% v/v RegenOx Parts A & B **Conclusions: Minor rebound, concentrations in** groundwater did not go down below detection limits.

Case Study #4: **Former Brick Foundry** Langley, BC (2009 – 2013)

Maximum Initial Contaminant Concentrations in Groundwater before Application (Dec 2009): LEPH: 620µg/L> BC CSR Awf (500 µg/L) MTBE: 26.8µg/L> BC CSR DW (15 µg/L) Vinyl Chloride: 3.1µg/L >BC CSR DW (2 µg/L) CSR – Contaminated Sites Regulation Soil contamination from Petroleum Hydrocarbons (light and heavy extractable petroleum hydrocarbons)

Mixing recipe as per RegenOx® application manual. Approximately: 10 kg/m of Part A + 5 Kg/m of Part B + 7.5 kg/m of ORC-Advanced (ORC-A) applied over a 2 m vertical length at each borehole location.

This converts to 1.5 buckets of Part A, 0.75 bucket of Part B and 1.4 bags of ORC-A.

Total of eight borehole injection locations down to a maximum depth of 10.7 m below grade.

Case Study #4: **Former Brick Foundry** Langley, BC (2009-2013)

Maximum Contaminant Concentrations in Groundwater following RegenOx and ORC-A® Application (19, 20 Aug 2010): LEPH: 370µg/L (Awf - 500µg/L) MTBE: 26.5µg/L DW (15 µg/L) Vinyl Chloride: 1.7µg/L

DO – 19-35 mg/L following application of ORC-A, +ve Redox potentials in groundwater

Maximum Contaminant Concentrations in Groundwater following Application (Jan 2011) and later in 2013:

LEPH: Below Laboratory Detection MTBE: 17µg/L – 9 µg/L (in Nov 2013) Vinyl Chloride: Below Laboratory Detection

Conclusions:

RegenOx and ORC-A together can help oxidize trace concentrations of petroleum hydrocarbons and chlorinated compounds as long as the oxidant can mix well within the subsurface. Time frame can range from a week to months dependent upon the area and density of application, initial concentrations and sub-surface hydrogeological conditions.

Questions

to the states

-Seja

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