Technology fusion for MGP remediation: surfactant-enhanced in situ chemical oxidation, pressure-pulse injections and advanced site investigation

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Abstract

An *in situ* treatment that combined VeruTEK Technology's patented surfactant-enhanced in situ chemical oxidation (S-SICO®) technology with Wavefront Technology Solutions US Inc's Primawave technology, a novel pressure-pulsing injection enhancement process, and a patent-pending process to quantify subsurface contamination and measure the effectiveness of full-scale treatment, successfully remediated coal tar-related contamination at a former lumber processing facility in New York City. This remedy overcame standard obstacles to effective in situ remediation: even distribution of the injected chemistry and effective transport at the pore-scale level; solubilization of NAPL contaminant into the aqueous phase where it can be oxidized; and identification of the amount and location of the contaminant mass for targeted treatment. Contamination at this site, the future location of a public library on the shore of a New York City river, included residual NAPL within the pore spaces of the soil matrix. Remediation was required reduce the mass of BTEX, naphthalene and PAHs in soil and reduce groundwater concentrations. The remedial process began with a laboratory treatability study that demonstrated the effectiveness of S-ISCO using VeruSOL and alkaline-activated sodium persulfate to destroy the recalcitrant coal tar contamination from site soils. Next, the three technologies (S-ISCO, Primawave and advanced investigation) were implemented during a one-month pilot test. The full-scale remediation that followed, under approval by the NYSDEC, included 5 months of injections accompanied by comprehensive groundwater monitoring at wells within and outside of the treatment area. Monitoring also included collection of soil samples halfway through the

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injection process to inform modifications to the final stage of injections. The success of the full-scale remediation will be presented, as well as an evaluation of the advantages to combining S-ISCO, Primawave and advanced site investigation to increase the effectiveness of *in situ* treatment of MGPs.
Keywords: coal tar remediation, in situ oxidation, surfactant enhanced oxidation.

1 Introduction

Manufactured Gas Plants (MGPs) burned coal and provided gas to urban areas from 1850 to 1950. The process resulted in a complex mixture of organic hydrocarbons known as coal tar. While the exact composition of coal tar varies at each plant due to unique processing temperatures and coal supply, the primary contaminants of concern at MGP sites are polyaromatic hydrocarbons (PAHs) specifically PAHs with between four to six rings. Because of their historic role MGP wastes are typically found in highly developed regions where residual coal tar may pose a threat to human and environmental health. The mixtures of PAHs found in coal tar have been shown to be more carcinogenic than an equivalent dose of a single compound (benzo[a]pyrene) in isolation. Weyand *et al*. [2] Persulfate (peroxydisulfate $S_2O_8^{2-}$) can be used to chemically oxidize and destroy MGP related contamination. Heat, peroxide, transition metals, high pH or UV light may be used to activate persulfate and generate the sulfate radical $SO_4^{\bullet-}$. Sulfate radical chemistry is more complex than hydroxyl radical chemistry produced by Fenton's reagents. Unlike hydroxyl radicals which add to C=C bond or abstract hydrogen from C-H, sulfate radicals react with organic contaminants to form organic radical cation intermediaries or may react with water to form hydroxyl radicals (Tsitonaki *et al*. [1]) While persulfate is effective at destroying PAHs upon contact, since PAHs are highly hydrophobic organic contaminants with low solubility in water achieving contact between sulfate radicals and the PAHs compounds is challenging. Concentrations of PAHs at coal tar contaminated sites may exceed concentrations predicted by their poor solubility in the form of colloids (Mackay and Gschwend [3]) but to access the bulk of PAH found at these sites it is necessary to use surfactants, solvents or combinations thereof to effectively solubilize the compounds into the aqueous groundwater phase. Nonionic surfactants have been shown to solubilize these compounds effectively (Yeom *et al*. [4]).

The VeruTEK surfactant enhance in situ chemical oxidation (S-ISCO) processes utilizes persulfate radical chemistry and nonionic surfactants to solubilize and oxidize hydrophobic organic contaminants like those found in MGP coal tar.

2 Project overview

VeruTEK Technologies (VeruTEK) successfully implemented its patented surfactant-enhanced in situ chemical oxidation (S-ISCO®) technology to destroy coal tar contamination at a former roofing products manufacturing site in New

York City (the Site). The urban parcel, surrounded by dense residential and commercial development along the shores of the East River, was contaminated by coal tar repurposed from a nearby Manufactured Gas Plant (MGP) for the roofing manufacturing process. VeruTEK conducted five months of S-ISCO injections that destroyed greater than 90% of the BTEX, PAHs and naphthalene contaminants in the targeted interval. The S-ISCO treatment consisted of injections of VeruSOL®, VeruTEK's patented plant-based surfactant and co-solvent mixture, and alkaline-activated sodium persulfate that used Wavefront Technology Solutions US Inc's (Wavefront) Primawave pressure-pulsing injection enhancement technology (Hoag and Collins [6]). The patent-pending RemMetrik℠ process was used to quantify subsurface contamination, target the treatment and measure its effectiveness. S-ISCO was an integral part of the remedial strategy at the Site that resulted in the New York State Department of Environmental Conservation (NYSDEC) issuing a Certificate of Completion (COC) to confirm the success of the cleanup, and enable the Site's redevelopment as a public library and park ranger station. The successful destruction of MGP-related coal tar at this urban Brownfield site demonstrates the effectiveness of S-ISCO as a remedy for MGP-related contamination.

Figure 1: Site location.

2.1 Site background

Located on the bank of the East River in a densely developed residential and commercial area in New York City, this 0.73-acre parcel is part of an urban revitalization project and will be redeveloped as a public library and park ranger station. During historic roofing products manufacture at the Site, MGP coal tar was brought onto the Site and entered the subsurface, contaminating the soil and groundwater with volatile organic compounds (VOCs) including benzene, toluene, ethylbenzene, total xylenes (BTEX), and semi-volatile organic compounds (SVOCs) including naphthalene, and polycyclic aromatic hydrocarbons (PAHs). Contaminant concentrations in the soil and groundwater exceeded the NYSDEC regulatory limits, including in several groundwater locations by orders of magnitude. SVOCs comprised greater than 95% of the total contaminant mass; naphthalene alone accounted for 65% of the total mass. The majority of contamination was present as residual non-aqueous phase liquid (NAPL) held within the pore spaces of the heterogeneous soil matrix which consisted predominately of sand and silts but which also included lenses of silt and silty clay. Traditionally these NAPL droplets, especially in fine soils such as the silts and clays present at this site, present a challenge to in situ treatment.

Figure 2: NAPL-stained boring from center of treatment area (11–13 ft bgs), 2008.

2.2 Site challenges

Full-scale excavation is the conventional remedy for sites such as this one which have coal tar-related NAPL contamination. Because of the unique and challenging characteristics of the Site and its location, however, this approach was neither feasible nor practical. A dig-and-haul solution would have involved removal of thousands of truckloads of soil, from depths extending below 22 ft bgs, as well as concomitant de-watering operations. Such a large-scale excavation would have required comprehensive infrastructure to stabilize the subsurface, and may still have compromised the stability of the high-value residences on surrounding parcels especially since this parcel was constructed from landfill brought in over the history of the property. Because of the frequent high-wind conditions associated with the river, a tent or covering would have been necessary to prevent the exposed soil from affecting the humans living, working and traveling in the area. Finally the traffic generated by the continuous stream of construction vehicles to and from the Site would have added congestion to the local roadways and as well as emissions to the air.

2.3 Remedial technologies for in situ treatment

An *in situ* remedy based on VeruTEK's S-ISCO technology was selected to overcome the standard obstacles to effective *in situ* remediation: solubilization of NAPL contaminant into the aqueous phase where it can be oxidized; even distribution of the injected chemistry and effective transport at the pore-scale level; and identification of the magnitude and location of the contaminant mass for targeted treatment. This remedy included S-ISCO with Wavefront Technology Solutions US Inc's (Wavefront) Primawave Pressure-Pulsing Injection Enhancement tool, and the patent-pending RemMetrik^{SM} contamination identification and quantification process.

2.3.1 S-ISCO

S-ISCO is one of VeruTEK's patented remedial technologies that use VeruSOL surfactant and co-solvent mixtures to bring NAPL and sorbed contaminants into contact with free radical oxidants. VeruSOL desorbs NAPL contaminants, bringing them into a stable oil-in-water emulsion in the aqueous phase. High-performing activators generate free radicals, including sulfate radicals ($SO_4{\bullet}^-$ or SO_4^{-2}) from sodium persulfate and hydroxyl radicals (OH·) from hydrogen peroxide, which then oxidize the aqueous-phase contaminants. Because S-ISCO is able to target the source of contamination, the treatment yields a permanent solution and prevents contaminant rebound.

2.3.2 Primawave™ pressure-pulsing process

The Primawave pressure-pulsing process uses a sidewinder tool attached to the injection well head that generates subsurface pressure waves to open soil pore spaces. Particularly in tight clayey and silty soils, this tool enhances the uniformity of chemical dispersion and affects the treatment's radius of influence.

2.3.3 RemMetrik^{SM} contamination investigation and characterization method

The RemMetrik process includes a method and process for calculating the mass and three-dimensional location of subsurface contamination using a grid and random sampling system. The contamination information is used to target the treatment to areas with the most significant impacts. Data collected using this method after treatment, informs an assessment of treatment effectiveness.

2.3.4 Remedial design process

The S-ISCO approach was approved as part of the Brownfield Cleanup strategy for the site after the results of VeruTEK's bench-scale treatability tests and pilot-scale field implementation demonstrated that the S-ISCO process could effectively contact and destroy Site contamination, including sorbed NAPL. The laboratory and field-scale testing, typical components of the S-ISCO design process, indicated that a S-ISCO remedy composed of VeruSOL-3 and alkaline-activated sodium persulfate (FMC Corporation [5]) was the optimal remedy for site contaminants, while the results of the pilot test indicated that the combination of Primawave pressure-pulsing with S-ISCO injections could affect the radius of influence and dispersion for the injected chemistry. The following sections describe the treatability study and field pilot test.

2.3.5 VeruTEK lab treatability study

Using soil and groundwater from the Site, VeruTEK conducted bench-scale testing to determine the optimal S-ISCO remedy for Site contaminants. The investigation included surfactant-screening tests to identify the optimal VeruSOL blend to maximize contaminant solubilization; aqueous-phase oxidation tests to identity the most effective oxidant and activator system to destroy the solubilized contaminants; and finally, soil column tests to simulate application of the S-ISCO surfactant and oxidant system under field conditions. The results of these tests indicated that an S-ISCO remedy consisting of VeruSOL-3 and alkaline-activated sodium persulfate was optimal for this Site. Figure 3 shows how VeruSOL-3 increased the solubility of VOCs and SVOCs from Site soils by up to 29 times. The column tests demonstrate how the S-ISCO remedy with VeruSOL-3 and alkaline activated persulfate destroyed 96% of SVOCs and 99% of PAHs in 28 days of treatment.

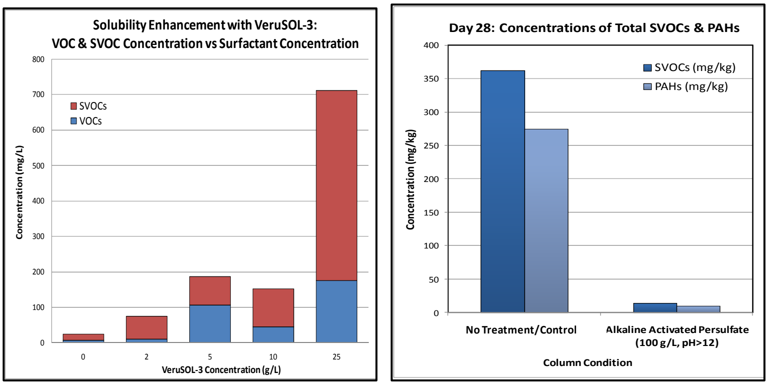

Figure 3: VeruSOL solubility enhancement (left) column tests (right).

2.3.6 Pilot test

The S-ISCO Pilot Test consisted of ten days of injections into four areas of the Site using the Primawave sidewinder Figure 4 shows these Pilot Test areas (blue circles). Soil analytical data indicated that the S-ISCO chemistry achieved significant contaminant mass removal, including up to 93% in Cell 27. Groundwater data indicated effective chemical transport in the subsurface and also that no NAPL was mobilized beyond the treatment areas – a priority at this Site given its proximity to the East River. In addition the treatment yielded significant reductions in soil gas impacts, including 96% for benzene. The pressure-pulsing sidewinder was used in three of the four areas. By comparison, the pressure-pulsing improved the vertical dispersion and distribution of the injected chemistry, reducing the density-driven tendency of the persulfate chemistry. In addition, it increased the rate at which the chemistry could be injected and appeared to provide more even coverage of the treatment area.

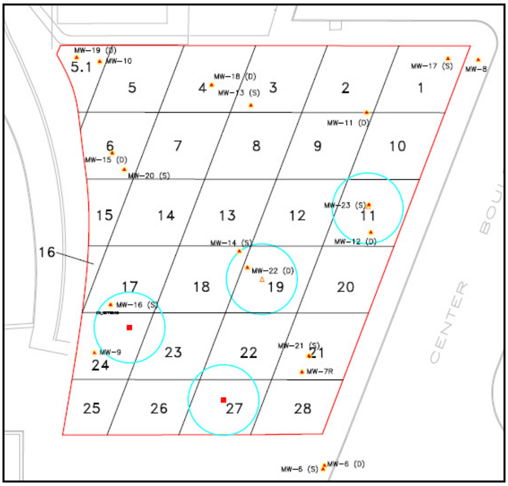

Figure 4: S-ISCO pilot test areas.

3 Full-scale S-ISCO remediation

Under the approval of the NYSDEC, the full-scale remediation took place between October 2010 and March 2011. During 100 days, the S-ISCO chemistry – VeruSOL-3, sodium persulfate and sodium hydroxide, was injected using the Primawave sidewinder into 34 wells installed in the areas in which the greatest contamination had been identified. These 2-inch wells were variably screened across 6–7 foot lengths within the 10 and 22 ft bgs treatment interval. Injections took place at an average rate of 8 gallons per minute (GPM) per well into 4 wells at a time (32 GPM overall). Table 1 summarizes the injection parameters, including concentrations and total amounts injected all injection system components were housing in a bermed exclusion area that was lined with impermeable plastic and secured with fencing.

Table 1: Injection summary.

Injection summary		
Chemical	**Amount**	**Injected concentration (g/L)**
VeruSOL-3	29,545 kg	5 g/L
Sodium Persulfate	152,000 kg	25 - 50 g/L
Sodium Hydroxide	61,950 kg	20 g/L
Total Fluid	1,201,900 gal	--

3.1 Monitoring

Monitoring was conducted before, during and after S-ISCO injections to track the progress and performance of the injected chemistry in the subsurface and to confirm that the treatment was not negatively impacting sensitive receptors such as the adjacent river. Monitoring was essential to understanding the treatment and informed continuous modification to the process that optimized results. Monitoring included: continuous tracking of water quality parameters including oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature and conductivity using *in situ* data loggers; collection of groundwater samples for analysis of parameters including oxidant concentration, interfacial tension (IFT), total petroleum hydrocarbons (TPH) and pH in VeruTEK's on-site laboratory; observation of all wells on and off-site for indications of NAPL; and collection of soil and groundwater samples for contaminant analysis.

4 Results

4.1 Contamination destruction

Approximately 5 months after the end of injections, when the results of groundwater monitoring indicated that the sodium persulfate reactions had subsided, VeruSOL had largely degraded and pH conditions were approaching pre-injection levels, 114 soil grab samples were collected from the treatment area and analyzed for total VOCs and SVOCs. The RemMetrik process was used to identify sampling locations and intervals. These results were used to calculate the mass of contamination remaining that was then compared to the mass calculated before treatment.

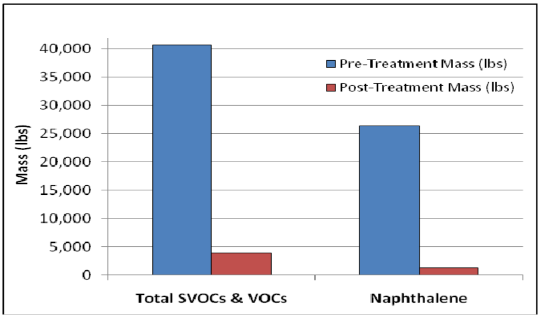

Figure 5: Contaminant mass reductions.

This analysis indicated that the S-ISCO treatment destroyed 90.3% of the mass of total VOCs and SVOCs present before treatment, including more than 95% of the naphthalene present (Figure 5), and in doing so, exceeded the remedial objective for soil – that is, to destroy 50% of the contaminant mass between 10 and 22 ft bgs. Naphthalene, a principal component of coal tar, was the primary SVOC affecting Site soils and groundwater; it accounted for almost 65% of the total pre-treatment contaminant mass. Table 2 shows additional reductions for priority contaminants, including benzene, toluene, ethylbenzene and total xylenes (BTEX).

Table 2: Mass reduction for priority contaminants.

Mass reduction for priority contaminants		
Contaminant	**Pre-treatment mass (kg)**	**S-ISCO reduction**
Naphthalene	26,389	95 %
Benzene	30	85 %
Toluene	267	81 %
Ethylbenzene	348	75 %
Total Xylenes	1,028	60 %
BTEX	1,674	67 %
Total SVOCs and VOCs	40,621	90.3 %

4.2 Groundwater

4.2.1 Controlled desorption and destruction process

Analysis of groundwater for S-ISCO performance parameters, including IFT, electrolytic conductivity, and concentrations of sodium persulfate and TPH, as well as regular inspection of all on and off-site wells for the presence of either NAPL or the injected chemistry, confirmed that the S-ISCO desorption and destruction process proceeded in a safe, controlled and effective manner. At no time during injections was any indication of either the injected chemistry or the targeted contamination, including NAPL, solubilized NAPL, odours or sheen, observed in off-site groundwater.

4.2.2 Contaminant reductions

Groundwater samples from the nine on-site monitoring wells screened across the treatment interval (10–22 ft bgs) were analyzed before and after treatment. This data indicated that the S-ISCO treatment achieved the groundwater objective – asymptotic decreases in VOCs and naphthalene. VOC reductions included 92% for xylenes; 87% for benzene, the most toxic and mobile VOC at the site; 90% for ethylbenzene; and 91% for BTEX overall. 80% naphthalene reductions were also measured.

4.2.3 Soil gas contamination reductions

Soil vapor samples collected from three areas adjacent to the site were analyzed before (October 2010) and after (April 2011) injections. Because regular measurement of soil gas pressure indicated that the injected oxidant was not causing any measurable increase in pressure, additional rounds of vapor sampling during injections were deemed unnecessary. Reductions in soil gas concentrations are shown in Figure 6, and included 100% for benzene, ethylbenzene, and naphthalene. Improvement in soil gas contamination included reductions at a sampling location more than 100 feet from the southeastern corner of the injection area, indicating that the effects of the treatment extended far beyond the immediate injection area.

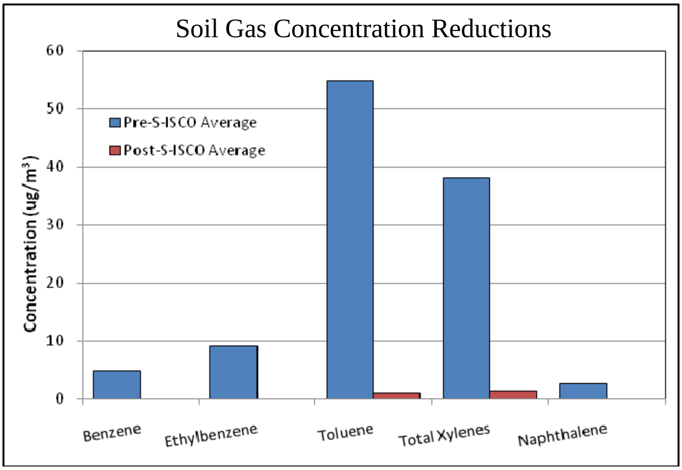

Figure 6: Soil gas concentration reductions

5 Conclusion

During this project, VeruTEK's largest S-ISCO remediation to date, VeruTEK gained significant insight into the remedial process that will inform future successes. The following section summarizes these lessons.

6 Outcomes

This S-ISCO remediation marks the first time a Green Chemistry solution of this kind has been used to remediate MGP-related contamination in New York City and sets a precedent for the use of innovative technologies to achieve a COC within the state's Brownfield Cleanup Program. S-ISCO provided a low-impact solution that benefits the health and safety of the community and environment. Specifically this treatment:

- Destroyed contamination in place, avoiding digging and hauling thousands of truck-loads of contaminated soil through the community while preserving the stability of the subsurface and high-rise buildings on adjacent parcels;
- Prevented surrounding businesses and residents from exposure to dust and emissions related to large scale excavation, and also reduced soil gas contamination;

- Took place during a short time frame (five months), without disturbing the community; and
- Provided a permanent solution to site contamination, preparing the site for safe and productive reuse as a public library and park ranger station.

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