In-Situ Thermal Treatment of MGP Waste and Creosote

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ABSTRACT: Remediation of coal tar at former Manufactured Gas Plant (MGP) sites, and creosote associated with wood preservative sites is challenging due to the viscous nature of the dense non-aqueous phase liquid (DNAPL) and the modest solubility and vapor pressure of the contaminants of concern (COCs). DNAPL seepage into surface water bodies, as well as groundwater plumes formed by the most mobile constituents like benzene, pentachlorophenol and naphthalene, are frequent environmental problems associated with coal tar and creosote. In Situ Thermal Remediation (ISTR) technologies have been shown to overcome these limitations through one or more of the following approaches: (1) decreasing DNAPL viscosity by one to two orders of magnitude, making the DNAPL pools recoverable; (2) removal of the most volatile and mobile COCs by steam stripping, making the residual mass immobile and non-leachable; and/or (3) complete removal of the COCs if the soil can be dried out and treated at temperatures above 300°C. Three case studies of thermal remediation of DNAPL sites are presented, covering the range of aggressiveness of heating and degree of treatment, as follows:

Approach (1) was demonstrated at full-scale at a former MGP site owned by National Grid in North Adams, MA. There, over 60,000 l of formerly highly viscous coal tar was recovered over a four-month period from a buried gasholder by thermally-enhanced free-product recovery, conducted by heating the gasholder contents to <100°C.

Approach (2) was initially developed through extensive laboratory testing of MGP-contaminated soil by the Gas Technology Institute, and named In Situ Thermochemical Solidification (ISTS). ISTS has recently been the subject of a comprehensive evaluation conducted under sponsorship of the Electric Power Research Institute (EPRI) on soil contaminated with coal tar from a former MGP site in the Southeast US. The results indicate that heating the subsurface to 100ºC is sufficient to remove the benzene, toluene, ethylbenzene and xylenes (BTEX) and naphthalene fractions from the soil and coal tar, thereby rendering the soil inert with respect to the potential for leaching of these constituents to groundwater. Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) tests on post-heated samples indicated that BTEX and naphthalene were not leachable (i.e., the leachate was non-detect for these constituents). This modest level of heating nevertheless solidifies and stabilizes the remaining, higher boiling coal tar residuals as an asphaltic material, no longer a NAPL.

Approach (3) was employed at full-scale at a former wood treater site owned by Southern California Edison in Alhambra, CA. In Situ Thermal Desorption (ISTD) was used to treat 12,400 m^3 of predominantly silty soil to a depth of 32 m without costly excavation. Heating the heavily PAH- and dioxin-contaminated soil to 325°C resulted in the CA Dept. of Toxic Substances Control granting a No Further Action letter, releasing the site for unrestricted land use.

INTRODUCTION

MGP coal tar and creosote are characterized as being relatively viscous DNAPL with toxic and carcinogenic constituents such as BTEX, pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs) such as benzo(a)pyrene (B(a)P). Spills and releases of these contaminants can degrade soil, sediment, groundwater and surface water bodies. NAPL can migrate long distances for decades before it finds its eventual position, evidenced by persistent seepage of NAPL to water bodies at many sites.

In addition, dissolution into flowing groundwater can create massive problems for drinking water aquifers, such as under the city of Visalia in central California, where PCP and naphthalene from a 43-m (140-ft) deep creosote DNAPL source zone threatened to close down the municipal groundwater production wells, until it was successfully cleaned and delisted from the National Priority List (NPL) using ISTR (USEPA 2009).

In general terms, there are three different levels of heating, and thus thermal treatment approaches applicable to MGP and creosote sites. One may be used alone, or two or more can be applied sequentially at the same site:

- Level 1. Thermally Enhanced Free Product Recovery (TEFPR). The subsurface is heated to temperatures above ambient, typically between 70 and 90°C, and the removal of DNAPL by pumping is enhanced. After cool-down, the residual DNAPL is relatively immobile. The subsurface can be heated using any one or a combination of the common ISTR technologies: thermal conduction heating (TCH), also known as In Situ Thermal Desorption (ISTD); electrical resistance heating (ERH) including the Electro-Thermal Dynamic Stripping Process (ET-DSP™); and/or steam injection/steam-enhanced extraction (SEE), selected based on hydrogeology and site considerations.
- Level 2. Treatment at boiling point temperature (100°C above the water table and steam temperature below). Steam stripping depletes the DNAPL of its more volatile and mobile constituents, rendering the DNAPL viscous and without significant leachability, which has been termed ISTS (Hayes 2002). Any one or a combination of the common ISTR technologies listed above (i.e., ISTD, ERH, SEE) can be used to achieve the target temperature, depending on the hydrogeology.
- Level 3. Treatment at temperatures above the boiling point of water, with drying of the subsurface. Of the prevalent heating techniques, only ISTD can accomplish this, as no moisture addition is needed to deliver the energy. Target temperatures range from less than 200°C for complete removal of naphthalene, to 335°C for treatment of high molecular weight PAHs, including B(a)P, PCP and dioxins.

CASE STUDIES

Level 1: Thermally-Enhanced Coal Tar DNAPL Recovery. TerraTherm employed all three levels of heating at full scale to remediate a gasholder containing residual coal tar at a former MGP site in North Adams, Massachusetts, which had operated from the 1860s to the 1950s. The abandoned subsurface gasholder was about 18.9 m (62 ft) in diameter and 5.5 m (18 ft) deep, with a Target Treatment Zone (TTZ) of approximately 1,530 m^3 (2,000 yd^3). Although for the purposes of this paper we shall focus on the Level 1

(TEFPR) portion of the project, papers by Baker and coworkers (2004; 2006; 2008) address other aspects of the project.

The COCs at the site included the following constituents and corresponding maximum concentrations: B(a)P (650 mg/kg), naphthalene (14,000 mg/kg), benzene (6,200 mg/kg), and Total Petroleum Hydrocarbons (TPH) (230,000 mg/kg). The surficial soil inside the former gasholder was a mixture of sand, gravel, cobbles, concrete, debris and other fill material. Perched water was found within the gasholder, although the regional aquifer was situated beneath its base. While the gasholder had not been known to leak, its proximity to underlying groundwater and the adjacent Hoosic River (and therefore the risk of a leak) were major factors prompting the cleanup.

The project goals, derived from a human health risk assessment, depended on the depth. Although the project included several levels of heating performed sequentially, we focus herein only on the lower-temperature, TEFPR part of the project (Level 1 heating). Prior to the project, several years of bailing of wells inside the gasholder had seldom produced more than a liter or so of the highly viscous coal tar from any of the wells at a time. Our laboratory tests performed during the design phase showed that increasing the temperature of the coal tar from the site from 25 to 60°C (77 to 140°F) would decrease its viscosity about 6-fold, from 130 to 23 Centipoise (Baker et al. 2004).

TerraTherm installed twenty-five TCH wells within the gasholder on 3.7-m (12-ft) centers, down to, but not through the concrete base of the gasholder. Thermocouple arrays were used to monitor and control subsurface temperatures during each phase of heating. The water produced during the initial dewatering step was treated by passing it through an oil/water separator followed by clay/carbon media and activated carbon. Then moderate heating (to about 80°C (175°F) was used to thermally enhance coal tar recovery, utilizing two Blackhawk-type piston pumps. During Level 1 heating, we recovered >60,000 l (16,000 gal) of coal tar/emulsion from the gasholder (Figure 1) (Baker et al. 2006).

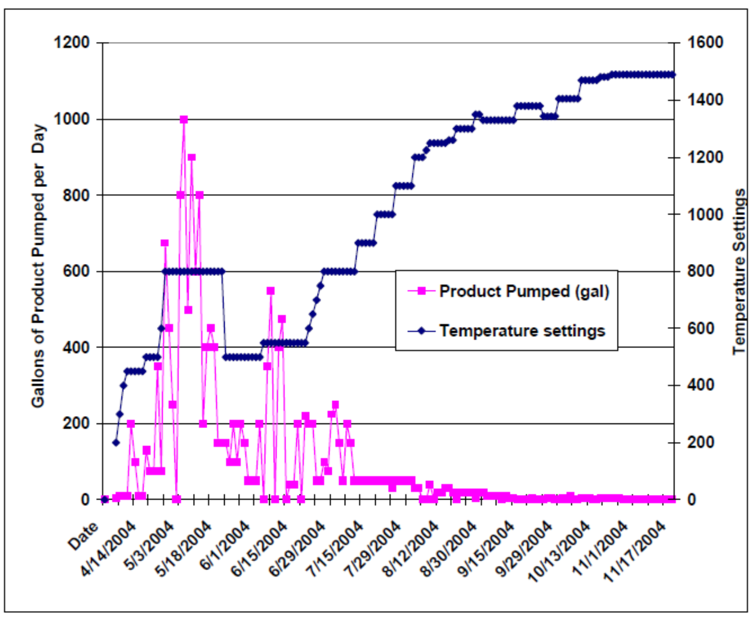

FIGURE 1. Product recovered as a function of temperature settings (°F) of thermal wells. The first three months comprised the Level 1 phase, after which the temperatures were ramped up to accomplish Level 2/3 heating.

Level 1 heating/TEFPR was a prerequisite step prior to higher-temperature (Levels 2/3) heating, which resulted in attainment of all project goals.

Level 2: In-Situ Thermochemical Solidification of Coal Tar. Under sponsorship of the Electric Power Research Institute (EPRI 2009), laboratory tests of soil samples from a coal tar site were performed to simulate thermal treatment and to evaluate chemical and physical behavior of the coal tar DNAPL during treatment. Four samples were collected from different depths and locations from a confidential coal tar-impacted site in the Southeast US. The site is underlain by a sandy fill, clay layers, a sandy aquifer, and a clay aquitard. Peat is found in isolated pockets. The DNAPL impacts extend under a rail yard with multiple railroad tracks, making assessment of thermal impacts on the geotechnical stability of the site important. In summary, the objectives of the testing were as follows:

- Determine the lowest effective treatment temperature for BTEX and naphthalene distillation from the sand and peat site materials;
- Evaluate DNAPL mobilization of the sand and peat site materials;
- Perform an assessment of the soil property changes induced by the thermal treatment of the sandy layer, peat and clay materials at temperatures of 100°C, 120°C and 150°C; and of the fill at a temperature of 100°C; and,
- Evaluate the potential for settlement of the site materials beneath the railroad tracks following thermal treatment; specifically, assessment of the sandy layer, peat and clay materials at temperatures of 100°C, 120°C and 150°C.

The findings (EPRI 2009) of the laboratory treatability study indicate the following:

- Materials collected from the site were fairly homogeneous silty sands, despite an effort to collect samples representative of the primary stratigraphic layers thought to be present beneath the treatment area: silty sand, peat, clay, and fill. These materials were impacted with MGP coal tar based on visual inspection and the results of pre-testing characterization data.
- The thermal treatment tests indicate that raising the temperature to 100ºC is sufficient to remove the volatile fraction from the coal tar (e.g., benzene and naphthalene) and render the tar inert with respect to the ability to leach constituents to groundwater. Figure 2 illustrates the reduction in leachable COCs, based on the TCLP method. Similar results

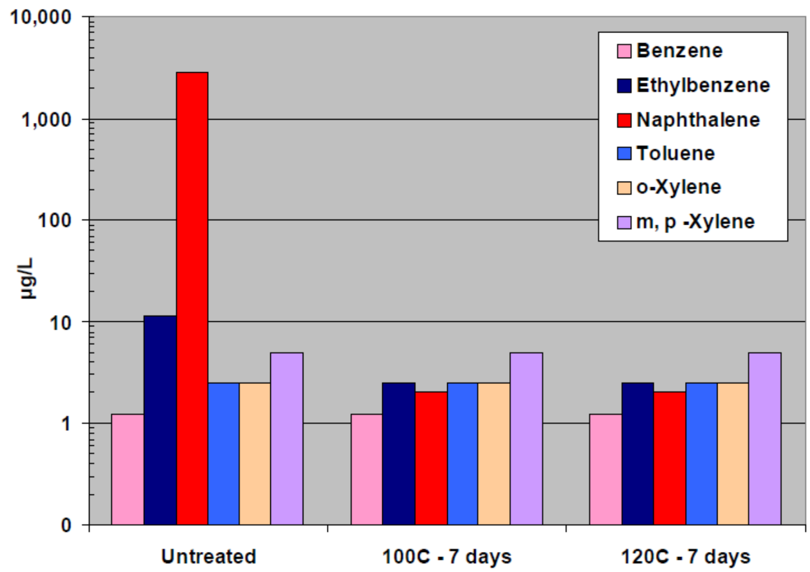

FIGURE 2. TCLP leaching results for untreated and thermally treated soils from a coal tar site in the Southeast US (EPRI 2009).

were obtained using the SPLP method. Treating to 120ºC did not result in a significant increase in the removal efficiency, since treatment at 100ºC was highly effective (>99.9% reduction for naphthalene).

- Based on the results of other treatability tests and field experience at full-scale sites, treatment temperatures >300ºC would be required to result in a significant removal of higher molecular weight compounds such as B(a)P.
- The DNAPL mobilization tests indicate that some of the NAPL will likely be mobilized during heating due to viscosity reductions and that a multiphase extraction and containment system would be required as part of any thermal remedy for the site.
- The results of the geotechnical and volume tests indicate that the structural integrity of the materials tested from the site will not be affected by heating to temperatures of 150ºC (the maximum expected target treatment temperature). Thus, the stability of the railroad tracks will not be affected during heating.

Based on these results, application of ISTS with a target temperature of 100ºC at the site would be effective at removing the volatile compounds, rendering the remaining tar inert, reducing the mass transfer rate of chemicals dissolving into the groundwater, lowering groundwater concentrations within and downgradient of the treatment area, and protecting off-site surface water. In addition, these results indicate that thermal treatment will not adversely affect the geotechnical properties of the soil and/or result in subsidence beneath the railroad tracks.

These results were consistent with earlier laboratory research done by GTI (Hayes 2002), which had showed that for various MGP coal tar-contaminated soil samples, heating to the boiling point of water or slightly above would distill off the BTEX and naphthalene, leaving a residual material that is no longer leachable for those COCs, that has the appearance of asphalt, and that is no longer a NAPL. These results were also consistent with the Level 2 results achieved at the full-scale North Adams, MA site (see above) inside the confines of a gasholder (Baker et al. 2006). Significantly, though, the EPRI study expanded the paradigm, indicating that ISTS can be accomplished for this coal tar within a highly transmissive aquifer setting, without dewatering.

Level 3. Complete Removal of PAHs by Higher-Temperature ISTD. The largest in situ TCH project ever undertaken at a wood treatment (creosote and dioxin) site was for Southern California Edison (SCE) in Alhambra, CA (Baker et al. 2007). ISTD treated approximately 12,400 m^3 (16,200 CY) of predominantly silty soil to a maximum depth of 32 m (105 ft). The subsurface soils were contaminated primarily with PAHs, PCP, and dioxins and furans, with soil treatment standards of 65 µg/kg B(a)P Toxic Equivalents (TEQ), 2,500 µg/kg PCP, and 1.0 µg/kg dioxin, expressed as 2,3,7,8-tetrachlorodibenzo-dioxin (TCDD) TEQ. Because of the size of the treatment area and projected power demand, the site remediation was divided into two phases. Phase 1 treatment ended in early 2004, at which time Phase 2 construction commenced. Phase 2 treatment was completed in September 2005, with complete site demobilization by March 2006.

TerraTherm installed a total of 785 thermal wells (654 heater-only wells and 131 heater-vacuum wells) within the TTZ, the area of which was approximately 2,920 m^2 (31,430 ft^2). The well field (Figure 3) was laid out in a hexagonal grid pattern with heaters being 2.1 m (7.0 ft) on center. A heater-vacuum well was at the center of each hexagon of heater-only wells. The average thermal well depth was 6.1 m (20 ft), but the thermal well depths at the site ranged from 2.1 m (7.0 ft) to 32 m (105 ft).

FIGURE 3. ISTD well field and process equipment, Alhambra, CA.

TerraTherm installed a light cement aggregate as the well field surface cover, to: (a) insulate the surface to prevent heat loss from the TTZ, (b) shed rainfall, and (c) provide a vapor seal to prevent any escape of steam or vapors to the atmosphere. Two 2,500-kVA transformers provided power to the heaters and the Air Quality Control (AQC) system. Approximately 2,650 m (8,700 ft) of heaters were operated at approximately 984 W/m (300 W/ft) for a total heater power demand of approximately 2,600 kW. The heaters were configured to automatically maintain a set point temperature. Silicon controlled rectifiers and temperature controllers regulated the power application to the ISTD heaters using temperature input from thermocouples located on each heater circuit.

The AQC system included a regenerative thermal oxidizer (RTO) with 99% Destruction and Removal Efficiency (DRE), a heat exchanger, and two 2,268-kg (5,000-lb) granular activated carbon (GAC) vessels (plus an installed 1,361-kg (3,000-lb) spare). Vapors were pulled through the AQC system by two blowers and then discharged to the atmosphere through a stack containing sampling and monitoring ports, with a third blower installed as a spare. The AQC system operated with a continuous emission monitoring system (CEM), staffed 24 hr/d, 7 d/wk.

The soil clean-up standards for the Alhambra site were established by the site-specific Risk Characterization performed as part of the Remedial Action Plan (Table 1).

TABLE 1. Site Specific Cleanup Goals for Alhambra, CA Wood Treater Site.

Compound	Soil Cleanup Standard
PAHs, expressed as B(a)P toxicity equivalents	65 µg/kg
Dioxin, expressed as 2,3,7,8-TCDD toxicity equivalents (TEQ)	1.0 µg/kg
Pentachlorophenol (PCP)	2,500 µg/kg

To enable the progress of subsurface heating to be monitored, 164 temperature monitoring points were installed, many at representative centroids (coolest locations in the center of each equilateral triangle of heaters) to observe the progression of heating through the subsurface. The target treatment temperature of 335°C (635°F) at the centroids was attained within each phase (Figure 4). The curves show initial soil heat up/ start of super-heating, attainment (or exceedance) of target treatment temperature, shut-down of the heaters, and ultimate soil cool-down. As seen in Figure 4 at left, the cool-down stage was much more pronounced in Phase 2 due to active cooling measures that were implemented to facilitate well abandonment.

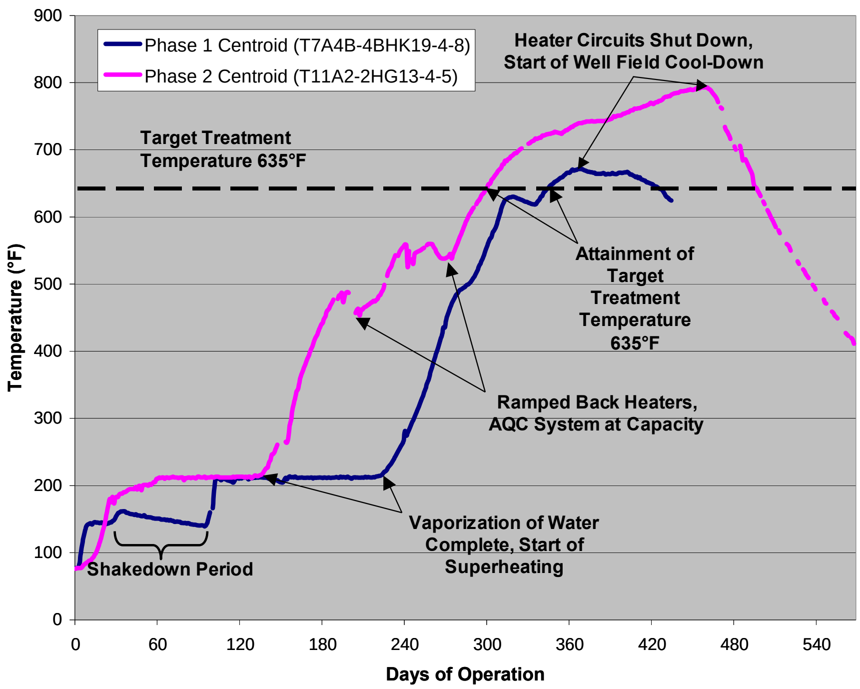

FIGURE 4. Phase 1 and Phase 2 centroid temperature progressions in degrees Fahrenheit (typical of many).

Results. The Soil Sampling and Analysis Plan specified collection of 60 post-treatment soil samples (60 for PAHs, 18 for dioxins) from 25 centroids within the TTZ, chosen at locations where the most contaminated pre-treatment samples had been collected. Soil samples were analyzed from shallow, mid-depth, and deep soil cores. The use of ISTD achieved all the site-wide treatment goals listed in Table 1 (Figure 5), while it also met all emission standards (Baker et al. 2007).

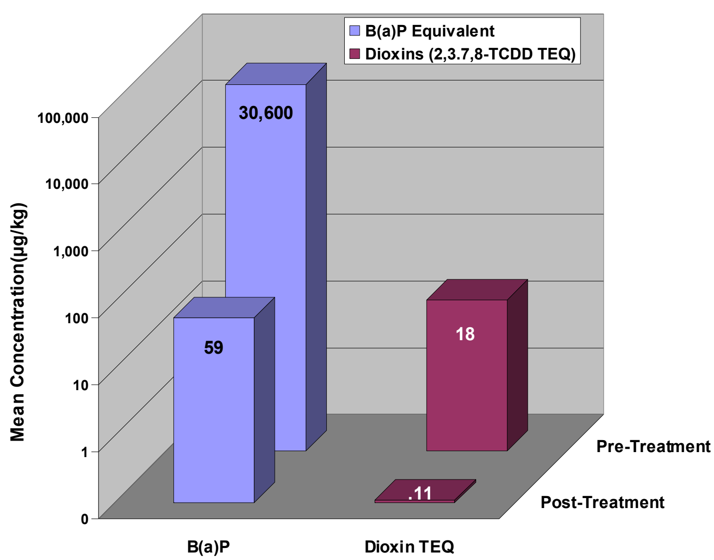

FIGURE 5. Comparison of pre- and post-treatment contaminant concentrations (all goals achieved).

CONCLUSIONS

A range of ISTR treatment approaches is now available for MGP and wood treater sites, selected on the basis of project goals: *Level 1* low-temperature heating, as illustrated by the North Adams, MA MGP site can be employed to greatly facilitate the removal of coal tar, which at ambient temperatures can be highly viscous and difficult to recover; *Level 2* moderate-temperature heating, as shown by the EPRI-sponsored study can effectively remove BTEX and naphthalene from coal tar at ~100°C without dewatering, leaving behind a residual material that is neither leachable nor mobile; and *Level 3* higher-temperature heating, as illustrated by the Alhambra, CA project can attain even very stringent cleanup goals for high-boiling COCs such as B(a)P and dioxins. There, the California Department of Toxic Substances Control (DTSC 2007) issued a No Further Action letter granting unrestricted land use, an unprecedented outcome for an in situ remediation technology at such a highly contaminated wood treater site.

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