



# A comparison of physicochemical methods for the remediation of porous medium systems contaminated with tar

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## ABSTRACT

The remediation of former manufactured gas plant (FMGP) sites contaminated with tar DNAPLs (dense non-aqueous phase liquids) presents a significant challenge. The tars are viscous mixtures of thousands of individual compounds, including known and suspected carcinogens. This work investigates the use of combinations of mobilization, solubilization, and chemical oxidation approaches to remove and degrade tars and tar components in porous medium systems. Column experiments were conducted using several flushing solutions, including an alkaline-polymer (AP) solution containing NaOH and xanthan gum (XG), a surfactant-polymer (SP) solution containing Triton X-100 surfactant (TX100) and XG, an alkaline-surfactant-polymer (ASP) solution containing NaOH, TX100, and XG, and base-activated sodium persulfate both with and without added TX100. The effectiveness of the flushing solutions was assessed based on both removal of polycyclic aromatic hydrocarbon (PAH) mass and on the reduction of dissolved-phase PAH concentrations. SP flushes of 6.6 to 20.9 PV removed over 99% of residual PAH mass and reduced dissolved-phase concentrations by up to two orders of magnitude. ASP flushing efficiently removed 95–96% of residual PAH mass within about 2 PV, and significantly reduced dissolved-phase concentrations of several low molar mass compounds, including naphthalene, acenaphthene, fluorene, and phenanthrene. AP flushing removed a large portion of the residual tar (77%), but was considerably less effective than SP and ASP in terms of the effect on dissolved PAH concentrations. Persulfate was shown to oxidize tar components, primarily those with low molar mass, however, the overall degradation was relatively low (30–50% in columns with low initial tar saturations), and the impact on dissolved-phase concentrations was minimal.

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## 1. Introduction

The remediation of former manufactured gas plant (FMGP) tars presents a number of challenges. These tars were generated during the historical gasification of coal and petroleum to produce “town gas,” a flammable gas used for heating, cooking and lighting between the early 1800s and the 1950s (Birak and Miller, 2009). Onsite disposal practices and leaks in plant infrastructure frequently resulted in the release of tars to the subsurface, and contaminated FMGP sites are estimated to

number in the tens of thousands (Harkins et al., 1988; U.S. EPA, 2004). FMGP tars are viscous, dense non-aqueous phase liquids (DNAPLs). They are mixtures of thousands of compounds, including mono- and polycyclic aromatic hydrocarbons (MAHs and PAHs), heterocyclic compounds, asphaltenes, and alkanes (Birak and Miller, 2009; Hauswirth et al., 2012b; Luthy et al., 1994). PAHs are the dominant compound class, but high molar mass, heterocyclic compounds, such as asphaltenes and resins, may account for up to 36% of the tar (Barranco and Dawson, 1999; Birak and Miller, 2009; Hauswirth et al., 2012b; Powers et al., 1996; Zheng and Powers, 2003).

Once released to the subsurface tars may become trapped in porous media due to capillary forces, forming a residual. The residual saturation of tars is typically higher than that of other

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NAPLs due to their high viscosity and ability to alter the wettability of porous media (Powers et al., 1996). Because tar components have low aqueous solubilities, they can persist in the subsurface for decades to centuries under natural conditions, thereby acting as a long term source of groundwater contamination. Remediation through direct extraction or pump-and-treat has proven largely ineffective (Abriola and Bradford, 1998; Atteia et al., 2013; Mackay and Cherry, 1989). Where NAPL-contaminated source zones are readily accessible, direct removal by excavation, followed by ex situ treatment or offsite disposal, is often a preferred approach (Luthy et al., 1994). However, in many cases excavation may be precluded due to onsite structures, utilities, or roads, the depth of the contaminated zone, geologic limitations, or other considerations. In such situations, *in situ* techniques provide an alternative approach. *In situ* remediation involves containing, treating, or removing contaminants without excavation, and encompasses a wide range of techniques, including surfactant or cosolvent flushing, *in situ* stabilization (ISS), enhanced bioremediation, vapor extraction, chemical oxidation or reduction, and thermal methods. We restrict our discussion here to chemical methods that result in removal of contaminants from the system through one of the following mechanisms: (1) mobilization of NAPL, (2) solubilization, and (3) chemical oxidation.

The application of *in situ* remediation techniques for FMGP tars has received relatively little study compared to petroleum, chlorinated solvents and other NAPLs. A summary of previous studies investigating mobilization- and solubilization-based methods for FMGP tars is provided in Table 1. A relatively early

field trial used hot water flooding to remove 1500 gal of FMGP tar from a site in Stroudsburg, PA, however, mobile tar remained after the project (Johnson and Fahy, 1997; U.S. EPA, 2000). Subsequent research on mobilization-based approaches has focused on modifying interfacial properties (contact angle and interfacial tension) by varying the aqueous phase pH (Barranco and Dawson, 1999; Hauswirth et al., 2012a; Hauswirth et al., 2012b; Hugaboom and Powers, 2002) or viscosity (Giese and Powers, 2002), or by adding surfactant (Dong et al., 2004). Of these studies, only Hauswirth et al. (Hauswirth et al., 2012a), which used a NaOH-xanthan gum (XG) solution (alkaline-polymer; AP solution), resulted in large reductions of tar mass (80–93%), with final tar saturations of 0.018 to 0.048.

Studies of the application of solubilization techniques for FMGP tars were initially directed at the use of cosolvents (Table 1), however, the mixed results and difficulty associated with injecting large volumes of potentially hazardous solvents at field sites shifted focus away from this approach (Hayden and Van der Hoven, 1996; Luthy et al., 1994; Peters and Luthy, 1993; Roy et al., 1995). Although no studies have used surfactants to solubilize separate-phase tar, researchers have reported the removal of 60–80% of PAHs from FMGP soils, supporting the use of surfactants to solubilize tar components (Joshi and Lee, 1996; Pinto and Moore, 2000; Wu et al., 2010; Yeom et al., 1995).

A number of researchers have investigated the use of *in situ* chemical oxidation (ISCO) techniques for the remediation of FMGP soils, with widely varying results (Table 2). Fenton's

**Table 1**

Summary of literature studies of mobilization and solubilization approaches applied to FMGP tars and soils.

Study	Major findings	Ref.
<i>Mobilization</i>		
Johnson and Fahy, 1997	Hot water flushing removed 1500 gal of tar from a field site, but significant quantities of mobile tar remained after the project.	EPA (2000); Johnson and Fahy (1997)
Barranco and Dawson, 1999	Tar–water interfacial tension (IFT) and quartz–water–tar contact angle are decreasing functions of pH.	Barranco and Dawson (1999)
Hugaboom and Powers, 2002	NAPL-wetting conditions observed at low pH, water-wet at high pH. IFT is decreasing function of pH. Tar saturations of 0.47, 0.30, and 0.29 reported for flushing solutions of pH 4.7, 7.2, and 9.2, respectively.	Hugaboom and Powers (2002)
Giese and Powers, 2002	In tar-wet columns, increasing viscosity of water flushing solution ( $\kappa = 0.1$ ) decreased tar saturation from ~ 0.45 to ~ 0.19. Tar saturation in water wet columns was ~ 0.19 regardless of flushing solution viscosity.	Giese and Powers (2002)
Dong et al., 2004	Polaxamine surfactants reduced tar-water IFT and altered wetting behavior, and were qualitatively shown to mobilize tar in sand-packed 2D cell.	Dong et al. (2004)
Hauswirth et al., 2012a	NaOH + xanthan gum solutions mobilized >90% of residual tar in column studies, with final tar saturation of 0.018–0.048.	Hauswirth et al. (2012a)
<i>Solubilization</i>		
Peters and Luthy, 1993 Roy et al. 1995	Tar solubility greatly increased in n-butylamine, acetone, isopropanol. Flushing tar-contaminated sand columns (tar saturation = 0.04–0.25) with 80–100% n-butylamine removed large quantity of tar, but tar remained in effluent after 40 PV (Roy et al., 1995)	Peters and Luthy (1993)
Hayden and Van der Hoven, 1996	Field-collected, tar-contaminated soil columns flushed with 100% isopropanol, resulting in a maximum tar removal of 19.4%	Hayden and Van der Hoven (1996)
Birak et al. 2011	Field-collected, FMGP soil-packed columns flushed with 95% methanol resulted in 80–90% removal of total PAHs after 10 PV	Birak et al. (2011)
Wu et al., 2010	PAHs extracted from FMGP soil using biodiesel, Tween 80, and cyclodextrin. Biodiesel most effective, removing 80–100% of PAHs.	Wu et al. (2010)
Pinto and Moore, 2000	Very high concentrations (> 1000 × CMC) of Tween 80 resulted in removal of >50% of PAHs from aged, PAH-contaminated soils in batch experiments.	Pinto and Moore (2000)
Joshi and Lee, 1996	Nonionic surfactant (Igepal) at concentrations up to 10% removed up to 80% of PAHs from FMGP soil in column studies.	Joshi and Lee (1996)
Yeom et al., 1995	Nonionic surfactants (Brij 30, Triton X-100, Tween 80) at concentrations up to 3% removed a maximum of 25% of total PAHs from aged FMGP soil.	Yeom et al. (1995)

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