Remediation of Coal Tar Contaminated Porous Medium Systems

Seth C. Rylander

A technical report submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Environmental Engineering in the Department of Environmental Sciences and Engineering, School of Public Health.

Chapel Hill
2010

Approved by:

Advisor: Dr. Cass T. Miller

Reader: Dr. Michael Flynn

Reader: Dr. Stephen C. Whalen

Abstract

Seth Rylander: Remediation of Coal Tar Contaminated Porous Medium Systems

(Under the direction of Cass T. Miller)

The legacy practice of municipal gas production has led to thousands of tar contaminated subsurface systems, which have resulted from the disposal and handling practices of combustion by-products formed during gas manufacturing. These tar wastes can vary widely in composition, but they are essentially always complex mixtures that contain all of the 16 poly-nuclear aromatic hydrocarbon (PAH) priority pollutants, and 100's of other compounds as well. Conventional physicochemical remediation methods have not proven effective for remediating such sites. In this work, a novel approach is investigated based upon alkaline flushing to mobilize the residual tar contamination using a one-dimensional column. A follow-up approach is performed with an ethanol flush to further reduce the flux of PAHs from the treated source zone. More than 50% of the tar residual was removed during the alkaline flushing. Mechanistic understanding of the effects of alkaline solution flushing on wettability and tar mobilization deserve further consideration.

Acknowledgments

I express my gratitude and appreciation to my advisor, Dr. Cass T. Miller for his guidance and expertise. I also thank my thesis committee members Dr. Michael Flynn, and Dr. Stephen C. Whalen for serving on my committee. I appreciate the substantial assistance and support from the people in the groundwater research lab: Pamela S. Birak, Scott Hauswirth, Dr. Joseph A. Pedit, and Dominion Rognstad. I would like to acknowledge Scott Hauswirth assistance in the coal tar, soil extract, and interfacial tension analysis. I would have not been able to conduct laboratory research without their assistance.

This work was supported by the National GEM Consortium Fellowship (National Consortium for Graduate Degrees for Minorities in Engineering and Science Incorporated) through a consortium with the following entities: 3M Company, University of North Carolina at Chapel Hill, the UNC Graduate School and the Department of Environmental Sciences and Engineering. This support allowed me the opportunity to explore my aspirations and pursuits in continuing my graduate education in Environmental Engineering.

I also thank my family and close friends (Jacqueline Arrambide, Nakita Bowman, Adrian Delancy, Manuel Lugo, Velvet Fitzpatrick, Elizabeth Smith, and Kenneth Wilson) for helping me mentally, emotionally, and financially during my time here at UNC.

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List of Abbreviations and Symbols

AC	Alternating current
ACN	Acetonitrile
ACS	American Chemical Society
AD10	Anthracene-deuterium
BTEX	Benzene, toluene, ethylbenzene, and xylene
°C	Degrees Celsius
°C/min	Degrees Celsius per unit minute
C_2H_6O	Ethanol
CFC	Chlorinated fluorocarbons
C^a_{ei}	Species concentration of NAPL present in aqueous solution at equilibrium
C^a_i	Aqueous phase species concentration in bulk solution
C^i_{aq}	Aqueous concentration of component i in equilibrium
C^i_{sol}	Aqueous solubility of the pure component
cm	Centimeter
cm^3	Cubic centimeter
cm/sec	Centimeter per second
CO_2	Carbon dioxide
cP	Centipoise
ct/w	Mineral surface/coal tar IFT
DC	Direct current
DCE	Dichloroethene

DNAPL	Dense nonaqueous phase liquid
DUS	Dynamic underground stripping
ERH	Electrical resistive heating
EOR	Enhanced oil recovery
EPA	Environmental Protection Agency
FGMP	Former gas manufacturing plant
FID	Flame ionization detector
FR_i	Solid/liquid fugacity ratio of component i
g	gram
GC	Gas chromatography
g/cm^3	Gram per cubic centimeter
h	Sand column height
HPLC	High-performance liquid chromatography
IAS	In-situ air sparging
IFSV	Interfacial shear viscosities
IFT	Interfacial tension
I.S.	Internal standard
ISB	In-situ biodegradation
ISCO	In-situ chemical oxidation
ISTD	In-situ thermal desorption
ITRC	Interstate Technology Regulatory Council
K_{ai}	Mass transfer rate coefficient of the species in aqueous phase
k_{ai}	Mass transfer coefficient

L/T	Length per unit time
LNAPL	Light nonaqueous phase liquids
m	Meter
mM	Millimolar
m_{sand}	Mass of sand added to column
M/L^3	Mass per cubic unit length
M/L^3T	Mass per cubic length-time
$M^{in \to ia}$	Mass transfer exchange
$MeCl_2$	Methylene chloride
mg/g	Milligram per unit gram
mg/L	Milligram per unit liter
MGP	Manufacture gas plant
mL	Milliliter
mL/hr	Milliliter per hour
mL/min	Milliliter per minute
mm	Millimeter
MNA	Monitored natural attenuation
mN/m	MilliNewton per meter
n	NAPL phase
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate
NAPL	Non-Aqueous Phase Liquids
ND	Not detectable

nm	Nanometer
OERR	Office of Emergency and Remedial Response
ORD	Office of Research and Development
OTA	Office of Technology Assessment
PAH	Polycyclic aromatic hydrocarbon
Pc	Capillary pressure
PCB	Polychlorinated biphenyls
PCE	Tetrachloroethylene
ppb	Parts-per-billion
ppm	Parts-per-million
PRB	Permeable reactive barrier
PTFE	Polytetrafluoroethylene
r	radius of capillary tube
r	radius of glass column
s	Aqueous phase
SARA	Saturates, aromatics, resins, asphaltenes
SEE	Steam-enhanced extraction
SVE	Soil vapor extraction
TCE	Trichloroethane
UNEP	United Nations Environment Programme
USGS	United States Geological Survey
UST	Underground storage tanks
UV	Ultraviolet

USWAG	Utility Solid Waste Activities Group
V	Total packed volume
$V_{col}=V_{tot}$	Total volume in soil column
V_{pore}	Pore Volume
VC	Vinyl chloride
VOC	Volatile organic compounds
W_a	Adhesional wetting parameter
w	Solid phase
wt%	Weight percent
ZVI	Zero-valent iron
1D	One-dimensional
1/L	Per unit length
1/T	Per unit time
γ	Interfacial tension
γ^{ns}	Interfacial tension between the NAPL phase and aqueous phase
γ^{ws}	Interfacial tension between the solid phase and aqueous phase
γ^{nw}	Interfacial tension between the NAPL phase and solid phase
ε^{na}	Specific interfacial area between NAPL and aqueous phases
θ	Contact angle
µm	Micrometer
µL	Microliter
ρ_{b_dover}	Bulk density of Dover sand
ρ_{grain}	Density of Dover sand

1. Introduction

1.1 Overview of Groundwater in the United States

Freshwater is essential for human and ecological well-being. Freshwater resources on the global scale are approximately 2.5% of all water. Of this total freshwater resource, an estimated 68.9% is in the form of ice and permanent snow, 30.8% is in the form of groundwater, and less than 0.3% is in the form of surface water (lakes and rivers) [UNEP, 2002]. Thus, groundwater is an important water source for domestic and commercial consumption, agriculture, and industrial sectors. There are an estimated 147,000 public water systems that rely upon groundwater to provide drinking water to as many as 100 million people within the U.S. as of 2003 [EPA, 2006]. A water usage study in the U.S. found that 92% of fresh groundwater withdrawals was used for agricultural irrigation, public supply, and self-supplied industrial uses [Huston et al., 2004]. The remaining groundwater withdrawals were used for livestock, mining, and thermoelectric power [Maupin and Barber, 2005]. The heavy reliance on groundwater as a source of water supply has led to concerns of overproduction, leading to dwindling supplies in some areas, and threats to groundwater quality by organic and inorganic pollutants.

1.2 Sources of Contamination in Groundwater and Surface Water

From a U.S. government report on protecting the nation's groundwater supplies from contamination, the Office of Technology Assessment has categorized the various means of groundwater contamination into six major groups:

- Category I-Sources Designed to Discharge Substances
- Category II-Sources Designed to Store, Treat and/or Dispose of Substances and Discharge Through Unplanned Release
- Category III-Sources Designed to Retain Substances during Transport and Transmission
- Category IV-Sources Discharging Substances as Consequence of Other Planned Activities
- Category V-Sources Providing Conduit or Inducing Discharge Through Altered Flow Patterns
- Category VI-Naturally Occurring Sources whose Discharge is Created and/or Exacerbated by Human Activity

These six groups are a compilation of the pathways in which groundwater can become contaminated from various industries, processes, and operations [OTA, 1984; Barcelona, 1987]. The following sections (1.2.1-1.2.6) provide examples that correspond to each of these contaminant source groups.

1.2.1 Category I-Sources Designed to Discharge Substances

Designed systems that fall within this category include subsurface percolation systems, injection wells, and land application of wastewater, hazardous and non-hazardous wastes. Subsurface percolation systems include the use of septic tanks and cesspools to dispose of wastewaters [Barcelona, 1987]. Examples of non-hazardous wastes used by injection wells include brine disposal and drainage while non-wastes used by injection wells include enhanced recovery and artificial recharge. Land application usage involves disposal of wastewater and sludge after treatment on or below surface of the land [Barcelona, 1987; EPA, 1994]. Groundwater contamination can occur in these designed systems in several ways: faulty well construction in injection wells, overflow or seepage of wastes from septic tanks, and untreated wastewater sprayed or injected into the ground [Barcelona, 1987; OTA, 1984; Yates, 1985; Zaporozec; 1981].

1.2.2 Category II-Sources Designed to Store, Treat and/or Dispose of Substances and Discharge Through Unplanned Release

The types of sources within this category include landfills, open dumps, above and underground storage tanks (UST), impoundments and other related disposal sites [Barcelona, 1987; OTA, 1984]. At several of these sites, the sources can be designed to handle and dispose of hazardous, non-hazardous, or non-wastes. Concerns for groundwater contamination within landfills and open dumps stems from leachate infiltration into the ground. UST pollution in groundwater occurs from corrosion and subsequent leakage of contaminant into the subsurface. Breaches of UST can occur where UST have been installed and operated at locations such as gasoline stations, manufacturing and industrial facilities [Nadim et al., 2000].

1.2.3 Category III-Sources Designed to Retain Substances During Transport and Transmission

Sources within this category are attributed to pipelines and material transport and transfer operations that can affect groundwater quality [Barcelona, 1987]. Common scenarios causing groundwater contamination are leaks or ruptures in pipelines used for sewer, industrial, and petroleum production facilities. The extent of contamination from leaking pipes may not be recognized due to the difficulty in detecting pipeline leaks [Zaporozec, 1981]. Groundwater contamination from material transport and transfer operations occur when there are accidental releases of hazardous materials from several modes of transportation used to move hazardous chemicals. Examples of such incidents include vehicular accidents with tractor-trailer tankers, container vehicles and trucks on roadways, train derailments, spills or leakage from loading and unloading of hazardous materials, and packaging and container failures storing hazardous materials [Marler et al, 2005; Quince and Gardner, 1982].

1.2.4 Category IV-Sources Discharging Substances as Consequence of Other Planned Activities

Sources discharging substances due to planned activities involve the type of processes and applications such as agricultural practices, mining and mine drainage, and urban activities. Groundwater contamination due to agricultural practices includes irrigation practices, pesticide and fertilizer applications, and animal feeding operations [Barcelona, 1987; OTA, 1984]. These agricultural practices affect groundwater quality due to the release of excess nitrogen, phosphorous, pathogens, and other inorganic chemicals [Almarsi and Kaluarachchi, 2004; Bohlke, 2002; Harter et al., 2002]. Mining and mine drainage practices that impact groundwater quality include both surface and underground mine-related activities [Barcelona, 1987]. Groundwater quality issues in mining arise from large quantities of water pumped during operations that cause saltwater intrusion and/or contamination due to oxidized minerals. Other mining operations reported to impact groundwater quality include leachate and runoff from mine waste piles, abandoned excavations later refilled with water used during surface mining, and the use of heavy metals during the coal mining process [Pauwels et al., 2010; Zaporozec, 1981]. Urban activities that act as a source of groundwater contamination include urban runoff, highway desalting, and percolation of atmospheric pollutants [Barcelona, 1987; OTA, 1984].

1.2.5 Category V-Sources Providing Conduit or Inducing Discharge Through Altered Flow Patterns

Sources providing conduit or induced discharge through altered flow patterns include operations and processes utilizing production and monitoring wells, construction for excavations and exploration holes. Typically, impairment of groundwater is not a major issue if construction and operation of these sources are properly maintained and monitored. Well operations include those used for oil and gas, geothermal and water supply [Barcelona, 1987]. Groundwater quality in well operations are compromised due to overpumping, abandoned wells and boreholes, and wells that end up in disrepair after years of operation [Barcelona, 1987; OTA, 1984; Zaporozec, 1981]. These compromised well sites and excavations affects groundwater quality due to pollutants entering the groundwater supply through aquifer interchange, saltwater intrusion, and vertical migration [Barcelona, 1987; Zaporozec, 1981].

1.2.6 Category VI-Naturally Occurring Sources Whose Discharge Created and/or Exacerbated by Human Activity

Sources within this category affect groundwater quality due to discharges made worse by human activities and actions. Natural interactions between groundwater and surface water allow for the introduction of pollutants through infiltration, direct migration, interaquifer exchange, and surface water recharge. In addition, the introduction of salt-water intrusion from pumpage and naturally occurring leaching falls within this category [Barcelona, 1987; OTA, 1984].

1.2.7 Point and Nonpoint Sources of Pollution

Point and nonpoint source pollution classifies the origins of pollutants found in groundwater and surface-water systems. Point source pollution involves contaminant discharge from unique and defined locations such as injection wells or septic tanks. Nonpoint source pollution is contaminant discharges that do not originate from a single source but from several sources and are more diffuse in nature, such as water runoff from farmlands and urban areas [Barcelona, 1987; OTA, 1984]. Groundwater contamination within this category occurs due to groundwater and surface water interactions, non-human effects of leaching, and saltwater intrusion. Due to the various locations in which the origins of pollutants in nonpoint pollution can occur, it is often difficult to trace the contaminants' origins [Barcelona, 1987].

1.3 Groundwater Contamination at Former Manufacturing Gas Plants (FMGPs)

Groundwater quality at FMGP sites continues to be a significant concern in the United States today. Remediation of contaminated groundwater located at FMGP has been an ongoing process over the past three decades. According to an EPA report, a high estimate of 50,000 FMGP sites were constructed and operated in the United States during their existence [EPA, 2004]. Due to the nature of activities and processes performed at FMGP, many types of hazardous wastes were generated and disposal methods have compromised subsurface environments over the course of several decades. In this section, an overview of the origins, types, and productions at FMGPs are discussed, along with the common types of wastes, disposal methods, and threats to ecological and human health these FMGPs pose today.

1.3.1 FMGP Origins

FMGPs were in operation from the 1800's until the mid 1960's, primarily converting coal or oil into natural gas for use in heating stoves, street lamps and homes. The majority of FMGPs were concentrated in the eastern and Midwest cities and towns within the United States; even though there were some plants established in the west [Birak and Miller, 2009; EPA, 2004]. The first FMGP established was located in Baltimore in 1816 [Birak and Miller, 2009]. FMGPs were constructed and located near large metropolitan areas and/or in close proximity to waterways. The volume of wastes and byproducts produced at FMGP sites depended upon the size of the plant, the years the plant was in operation, the type of processes and gas used [USWAG, 1984].

There were several types of FMGPs that were operated based on the nature of product produced. Examples of the types of FMGPs include commercial manufactured gas plant sites, rail yard pintsch oil-gas plants, district gasholders, and kerosene refiners [EPA, 2004]. Commercial manufactured gas plant sites produced and sold gas that was utilized in lighting, heating and cooking applications. Rail yard pintsch oil-gas plants generated illuminated gas for use in rail passenger cars. District gasholders stored and distributed gas from MGP sites to distances beyond areas served by commercial manufactured gas plants, while kerosene refiners produced distilled lamp oil from soft coal [EPA, 2004]. The site ranges of FMGP varied anywhere from 10 to 200 acres. FMGPs were rendered obsolete and replaced by the 1950's as the construction, distribution, and supporting infrastructure for petroleum and natural gas pipelines became more established [USWAG, 1984].

1.3.2 Types of Manufactured Gas Produced

There were three universal types of manufactured gas that were produced: carbureted water gas, oil gas, and coal gas. Carbureted water gas (sometimes referred to as carbureted blue gas) was generated after cracking the oil in the presence of water gas (sometimes referred to as blue gas) and steam. Water gas contained hydrogen and carbon monoxide that was produced from the reaction of steam passed over incandescent coke [Birak and Miller, 2009; USWAG, 1984]. Carbureted water gas was preferred over water gas because of the higher heating value and illuminants [Harkins et al., 1988]. Oil gas was created by heating and cracking of naphtha and petroleum oils. Oil gases contained copious amounts of methane, ethane, hydrogen and light hydrocarbons. Coal gas has two major subsets of production based on the process of carbonization: production from coke oven plants and production from coal gas plants [Birak and Miller, 2009]. The production of coal gas was obtained by heating bituminous coal to high temperatures in a closed vessel [Harkins et al., 1988]. Up until the early 20th century, coal gas was produced from the carbonization of bituminous coal in horizontal, inclined or vertical retorts. Before the 1850's, coal gas was produced from the use of horizontal retorts but towards the late 19th and into the early 20th century, horizontal retorts were replaced with vertical retorts [Birak and Miller, 2009]. In coke oven plants, bituminous coal underwent the process of carbonization in by-product coke ovens that operated at temperatures ranging from 850°C to 900°C to generate high grade coke and coke oven gas [Harkins et al., 1988]. The composition of coal gas from coke oven plants or coal gas plants was similar in composition, containing carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane and nitrogen [USWAG, 1984].

1.3.3 Byproducts and Wastes Generated

The major types of byproducts and wastes generated at FMGPs common to coal, carbureted water and oil gas plants include tars, sludges, spent iron oxide, ash, clinkers and dust. The waste byproducts generated contained major compounds such as VOCs (volatile organic compounds), PAHs (polycyclic aromatic hydrocarbons), heavy metals (such as lead, iron), ferrocyanides, phenolics, and inorganic compounds (such as nitrogen or sulfur) [EPA, 2004; USWAG, 1984]. The composition of tars generated at gas plants was related to the type of gas that was produced. Tars generated from the manufacturing of coal are referred to as coal tars; tars generated from the production of water gas are labeled as water-gas tars; and, tars from the production of oil gas are called oil-gas tars [Birak and Miller, 2009]. Before the late 1800's, the manner of discarding coal tars was through lagoons, pits, and wells on the plant site and nearby bodies of water until technology was developed to refine and reuse the coal tar. By the early 1900's, coal tar was captured and used as a raw product in tar distillation plants. Examples of new chemicals formed during the processing of coal tar include benzene and naphthalene; while further refining of coal tar led to its uses in paint and road tar [EPA, 2004; Luthy et al., 1994; USWAG, 1984]. In carbureted water gas processes, the tars produced were characterized as light carbureted water gas tars (light water gas tars) or heavy carbureted water gas tars (heavy water gas tars). The light carbureted water gas tars were commonly used for the following: fuel for gas plant operations, road tars and paints and coatings.

Heavy carbureted water gas tars and oil gas tars were limited to uses such as fuels and road tar because of the difficulties in breaking the formation of emulsions, high viscosities, and their chemical composition [Birak and Miller, 2009; Harkins et al., 1988; USWAG, 1984].

1.3.4 Tar Classification

The majority of the tars at FMGP sites are classified as DNAPLs, (Dense Nonaqueous Phase Liquids), which are denser than water and possess low water solubility. DNAPLs are a subcategory of NAPLs (Nonaqueous Phase Liquids), which are liquids that are sparingly soluble in water, and since NAPLs do not mix with water, they form a separate phase. Liquids that are less dense than water are termed as LNAPL (Light Nonaqueous Phase Liquids). Tar DNAPLs have not been studied as extensively as tetrachloroethylene (PCE) and trichloroethane (TCE) DNAPLs because of accessibility issues in retrieving tars. In addition, the numerous compounds within the tars make identifying and analyzing all of the components within the tars difficult [Luthy et al., 1994; USWAG, 1984].

1.3.5 Health and Ecological Concerns from FMGPs

Waste residuals and byproducts from FMGP sites containing tars are a particular concern because of tar DNAPLs penetrating, traversing, and diffusing into soils and groundwater. Tars contain hundreds to thousands of monocyclic and polycyclic aromatic hydrocarbons such as benzene, naphthalene, and phenanthrene that are carcinogenic

[EPA, 2004]. Additional compounds found in coal, carbureted-water gas, and oil gas tars that can affect human health include arsenic, lead, cyanide, and quinoline.

Health related issues at surrounding FMGP sites include indoor and outdoor air quality, and contamination of surface waters located adjacent to gas plants [Wisconsin Public Service Corporation et al., 2007]. From a risk assessment standpoint, human exposures to FMGPs include industrial/commercial construction workers exposed to contaminated soils and vapors. Other humans at risk from exposure near bodies of water down site of FMGPs include recreational boaters, fisherman, waders, swimmers, and water consumers (e.g. drinking, farming, cooking). Human exposure to PAH compounds can occur via inhalation, ingestion of food and water where PAH compounds are present, and contact with the dermis [USWAG, 1984].

Aquatic concerns in groundwater and surface waters impacted by tar DNAPL include bioaccumulation of PAH compounds in fish, invertebrates, and other similar organisms [Exponent, 2007]. The uptake of tar compounds by aquatic species can occur via food sources, sediments or water. Accumulation within aquatic animals is more commonly due to exposure to contaminated waters than food uptake. The degree of PAH absorption in aquatic life is related to whether species exposure is acute or chronic and the concentration and solubility characteristics of PAH compounds [Arfsten et al, 1996; USWAG, 1984]. Studies in the acute exposure to PAH compounds in aquatic species have shown immediate toxic impacts to sensitive organisms while chronic exposure can lead to negative effects in reproduction, species survival, and increased likelihood of cancer. In addition, studies on the effects of low PAH concentration in aquatic environments exposed to UV light have shown increases in cellular damage and carcinogenesis in aquatic species [Arfsten et al, 1996].

Terrestrial ecosystems located on-site or adjacent to FMGP sites are affected by toxicity of PAH compounds leaching into soils and plants. One mechanism of contaminant accumulation is the adsorption of tar compounds by plant roots and leaves. Plants and crops can contain higher levels of PAHs if grown near tar-contaminated sites or due to translocation of PAH compounds to other terrestrial ecosystems [USWAG, 1984]. One crucial indicator of evaluating the toxicity present in soils is studying the response, behavior, and changes of soil microorganisms to acute and chronic exposure to PAH compounds [Kordybach-Maliszewska et al, 2007].

1.4 Overview of Remediation Techniques

Remediation techniques used at groundwater-contaminated sites can be classified into four general types: (1) mobilization-based techniques, (2) mass-transferred techniques, (3) reaction-based techniques, and (4) containment methods. These four general types are briefly described below, along with current considerations in remediation of DNAPL residuals in contaminated groundwater.

1.4.1 Considerations in Remediation of DNAPL Residuals in Contaminated Groundwater

In-situ and ex-situ techniques are applied in continuing efforts to clean up groundwater and soils near FMGP sites containing tar DNAPL residuals. Current methods in remediation at FMGP sites are categorized into one of the following: source-zone removal, source-zone containment, and source-zone treatment [Birak and Miller, 2009, Deuren et al, 2002]. Complications that arise in cleaning up FMGP sites are multiple components within waste materials that interact with the media in various ways, the geographical and topographical characteristics, and the conditions present [EPA, 2004].

DNAPL contamination in the subsurface continues to be a challenge in remediation efforts due to the complexity in DNAPL composition, and the subsurface system being heterogeneous in nature. When DNAPL contamination occurs, the DNAPL enters into the groundwater system by permeating the unsaturated zone via vertical movement to the water table due to gravity, eventually penetrating into the saturated zone [Soga et al., 2004; Wright et al., 2010]. DNAPL presence in the saturated zone in the subsurface, along with interactions from the flows of groundwater and infiltrated surface water forms a source zone of contamination where dissolution of harmful compounds present within the DNAPL results in contaminated groundwater. Within this source zone, DNAPL residuals are partially dissolved in the aqueous phase and can yield configurations due to dissolution fingering [Soga et al., 2004]. Furthermore, the partially dissolved DNAPL residuals form dissolved contaminant plumes downstream from the source zone [Soga et al., 2004]. In determining the quantities and rates of DNAPL migration, several key properties must be considered such as the saturation of the DNAPL, the media in which the DNAPL is navigating, interfacial tension, wettability, density and capillary pressure [OERR and ORD, 1994].

Initial attempts to remediate DNAPL-contaminated systems involved ex-situ treatments such as pump and treat techniques and excavation to treat large quantities of free-phase DNAPL present in groundwater and soils. In some cases, these treatments were not successful due to significant quantities of DNAPL residual formed or already present at multiple sites and DNAPL penetration into the saturated zone [Birak and Miller, 2009; Soga et al., 2004]. Subsequently, several source-zone remediation methods have been developed over the last two decades to treat DNAPL residuals present in subsurface systems. These in-situ remediation methods are classified as primary, secondary, and tertiary source-zone remediation methods.

Primary remediation methods (primary mobilization-based remediation) deal with sites that have DNAPL saturations greater than 3%. In these instances, mobilization of the DNAPL has been used as a means to remove the contaminant as a separate phrase via surfactant, co-solvent, density change and thermal methods [Kavanaugh and Rao, 2003; Miller, 2007; Paterson et al., 1999; Soga et al., 2004; Wright et al., 2010]. Concerns with these methods involve the possibility of remaining contaminant concentrations downstream from the original source zone at levels above EPA drinking water standards. Drinking water standards are difficult to meet with mobilization methods alone because capillary forces typically result in residual DNAPL saturations of a few percent.

Secondary source-zone remediation methods involve efforts to further reduce DNAPL saturation present in less than a few percent [Miller, 2007]. Methods that have been developed in removal of these DNAPL include surfactant and cosolvent flushing. In cases of DNAPLs that are volatile or semi-volatile, techniques such as vapor extraction, air sparaging, or heating the subsurface are utilized [Miller, 2007; Soga et al., 2004].

Tertiary remediating techniques are introduced when primary and secondary remediating techniques are no longer effective. Issues with primary and secondary remediating techniques arise due to mass transfer limitations and economical costs for minute amounts of DNAPL saturation. Examples of technologies used to address minute amounts of DNAPL saturations include bioremediation and reactive barriers [Miller, 2007; Soga et al., 2004].

1.4.2 Mobilization-Based Techniques

Mobilization-based techniques involve processes that aid in the removal of DNAPLs by inducing movement through porous media. Mobilization-based techniques developed include cosolvent and surfactant flushing, density change based processes, and thermal methods. Surfactant and cosolvent flushing increases the removal of DNAPL by augmenting the rate of solubilization and mobilization in DNAPLs due to lowering of interfacial tensions and desorption of sorbed contaminants [Gupta and Mohanty, 2001; Paterson et al., 1999; Rao et al., 1997; Soga et al., 2004; Wright et al., 2010]. Thermal methods involve in-situ treatment of contaminated DNAPL source zones such as steam-enhanced extraction (SEE), thermal conductive heating, and electrical resistive heating (ERH). These thermal method procedures have been considered as means to overcome challenges in DNAPL migration and mass transfer reduction issues within the subsurface [Burghardt and Kueper, 2008; Soga et al., 2004; Wright et al., 2010]. A recent mobilization technique developed is dense-brine technologies where the dense-brine solution causes movement of trapped DNAPLs and control the DNAPL migration in the subsurface system [Hill et al., 2001; Miller et al., 2000; Wright et al., 2010].

1.4.3 Mass-Transfer Techniques

Mass-transfer techniques aim to reduce the concentrations of contaminants present in porous media through enhanced solubilization and/or volatilization of the contaminants in question. Common mass-transfer techniques applied to contaminated DNAPL source zones include the pump and treat methods, air sparging (In-situ Air Sparging-IAS), and soil vapor extraction techniques [Bouwer et al, 1988; Deuren et al, 2002; Murphy, 2006; Plummer et al, 1997]. Pump and treat methods were used in early initiatives in DNAPL source zone remediation by increasing the amount of groundwater flow through the DNAPL source zone in order to enhance DNAPL dissolution. Concerns arose from this method because of the length of time it would take to remove a DNAPL solution and the increased possibility of contaminant concentrations downstream in previously non-contaminated regions [Kavanaugh and Rao, 2003; Soga et al., 2004; Wright et al., 2010]. In addition, cosolvent and surfactant flushes can be categorized as mass-transfer techniques because of their ability to increase rates of dissolution with low DNAPL saturations.

1.4.4 Reaction-Based Techniques

Reaction-based techniques utilize various chemical reactions to convert or transform DNAPL contaminants within subsurface systems. Chemical processes used to alter DNAPL behavior within subsurface systems include in-situ chemical oxidation (ISCO), chemical reduction, and bioremediation [Deuren et al, 2002; Murphy, 2006]. ISCO methods rely on chemical reactions between injected oxidants and the chemical species within DNAPL to make the species inert or less harmful. Common oxidants used in ISCO techniques include potassium and sodium permanganates, hydrogen peroxide, persulfate, and Fenton's reagent [Heiderscheidt et al., 2008; Kavanaugh and Rao, 2003; Soga et al., 2004]. Chemical reduction involves the injection of zero-valent iron (ZVI) to foster mixing between DNAPL components and ZVI to initiate reduction of the halogenated components within the DNAPL. Chemical reduction is commonly used with DNAPL containing halogens [Kavanaugh and Rao, 2003]. Bioremediation techniques utilize the introduction of microorganisms, which consume components within the DNAPL. Microbial degradation of DNAPL species causes the compounds originally present in the DNAPL to be transformed to a set of byproducts, which may be either more or less harmful than the parent compounds. Examples of bioremediation techniques consist of monitored natural attenuation (MNA), in-situ biodegradation (ISB) and enhanced bioremediation. To increase the rates of biodegradation within DNAPL sites, enhancements of oxygen using air sparging and hydrogen peroxide or nitrates are employed [Deuren et al, 2002; Kavanaugh and Rao, 2003].

1.4.5 Containment Methods

Containment methods pertain to the construction and installation of treatment walls or barriers to remediate contaminated porous media. Containment methods can be described either as physical or hydraulic. A type of a physical containment is the permeable reactive barrier (PRB) and a type of a hydraulic containment is the physical barrier or slurry wall. PRBs contain reactive material placed in the reactive barrier to treat the incoming contaminant water via chemical, biological and physical reactions and reduce contaminant concentrations once the groundwater exits the reactive barrier [Deuren et al, 2002; Miller, 2007]. Slurry walls are constructed via excavation vertically aligned trenches and filling the trenches with a mixture of water, soil and bentonite [Deuren et al, 2002].

1.5 Objectives

The overall goal of this work is to advance our understanding of the remediation of contaminated FMGP porous medium systems. The specific objectives of this work are: (1) to review approaches typically used to mobilize DNAPLs, (2) to advance a method for mobilizing tar wastes, (3) to evaluate physicochemical mechanisms that affect DNAPL mobilization, (4) to investigate a mass-transfer-based approach for reducing tar residual from a porous medium system after mobilization, and (5) to characterize the flux of contaminants from a source zone as a function of the extent of treatment.

2. Background

The purpose of this section is to review the current knowledge regarding the remediation of waste materials from FMGP sites. Of particular focus are the physicochemical properties of these complex waste mixtures, which influence greatly the fate and transport of contaminant species originating in these mixtures. Next, considerations for the methods that have been applied to remediate subsurface systems contaminated with non-aqueous phase liquid (NAPL) mixtures. Lastly, a summarization of the challenges and open issues regarding the remediation of FMGP sites and consider the potential of alkaline flushing techniques for DNAPL removal from contaminated FMGP sites.

2.1 Properties and Characteristics of Byproducts and Waste Materials from FMGP Sites

Waste materials generated at FMGP sites were dependent upon the raw materials and processes utilized to produce a specific manufactured gas. There were similar waste materials that were produced regardless of the type of gas manufactured (i.e. tars and ash). Differentiation between waste materials and byproducts were based on whether the materials produced at FMGP sites could be reused, given away, or sold off. Despite byproducts that were reused, given away, or sold, pollution still occurred from byproducts due to spillage, handling, or leakages at or near plant sites [Harkins et al., 1988].

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Waste materials generated at coke oven plants include tar and oil sludges, clinkers, coke, salts of cyanide, ammonia and sulfur, residuals from processes used in sulfur removal, additional sludges (i.e. acid, lime and caustic sludges), and contaminated liquids (i.e. ammonia). Waste materials produced at oil gas plants include remnants of lampblack and free carbon, oxide box wastes, sludges, emulsions, and pitch. Waste products that were generated at water gas plants include sludges (i.e. tar, petroleum) clinkers, lampblack, and coke fines [USWAG, 1984].

Characteristics and properties of the types of tars manufactured were similar, with some exceptions and distinctions between carbureted water gas, oil gas and coal tars. Overall, tars of all types contained copious amounts of compounds (i.e. PAHs, heterocyclic compounds, inorganic compounds), which have been nearly impossible to identify and characterize [Birak and Miller, 2009; Peters and Luthy, 1993]. Most tars are opaque viscous liquids that have considerable amounts of high molecular weight residual materials [Birak and Miller, 2009; USWAG, 1984]. Carbureted water gas tars are characterized as possessing no tar acids and being lighter than coal tars. Depending on the type of carbureting oil used, the oil gas and carbureted water gas tars contained similar properties [USWAG, 1984]. In addition, carbureted water gas and oil-gas tars were inclined to possess more sulfur compounds than coal tar. A distinguishing trait between oil gas tars and carbureted water gas tars were the oil gas tars contained a higher percentage of carbon than the carbureted water gas tars [Harkins et al., 1988]. Coal tar production either at coke oven or coal plants was further classified by the temperatures used during these processes. Coal tars from temperature gradients was referred to as high-temperature or low-temperature coal tars. Key differences between the temperature based coal tars were the low-temperature coal tars possessed a lower density and viscosity [Harkins et al., 1988]. This signified that these low density and viscosity coal tars were more fluid and mobile than the high-temperature coal tars. Key differences between coal tars and carbureted water tars and oil gas tars was coal tars contained higher levels of carbon content, phenolics (tar acids), and inorganic compounds (i.e. nitrogen). Therefore, coal tars possessed higher densities and viscosities than carbureted water tars and oil gas tars [Harkins et al., 1988; USWAG, 1984].

The ability to apply remediation techniques to contaminated subsurface sites is dependent upon the knowledge of the composition and properties of the contaminant in question. Here, difficulty arises because of the complex nature of the tars, the amount of tars present in subsurface systems, the period of time tars have had to become ingrained into the soil and groundwater, and in some cases availability of historical records and data specific to FMGP sites. The following sections describe key characteristics of coal tars that has been analyzed and characterized over the course of several decades.

2.1.1 Organic Compounds in Tars

Past and current analyses of tars have been fractionally compartmentalized into the following components: saturates, aromatics, resins, and asphaltenes. SARA techniques are especially used in the identification of crude oils in the petroleum industry. An analysis of the amount of sulfonation residue present indicates that more than 90% of tars contain some kind of aromatic structure within its composition. Another important component within tars includes the solid residual remaining after distillation at high boiling points called pitch [Birak and Miller, 2009]. Its estimated that the pitch fraction within tars can constitute upward to 70% of the tar mass. Newer analytical techniques have reported compounds within this pitch in tars with upward to 210 rings [Birak and Miller, 2009]. The following sections (2.1.1.1-2.1.1.4) provide brief information on saturates, aromatics, resins and asphaltenes found in coal tars.

2.1.1.1 Saturates

Saturates (also called paraffins) are sub-components of saturated hydrocarbons with no ring structure and containing straight or branching chains. Typically saturates do not contain metals, nitrogen, sulfur, or oxygen atoms. Saturated hydrocarbons with one or more rings that contain chains with paraffins are termed as alicyclic hydrocarbons (or naphthenes) [Speight, 1999].

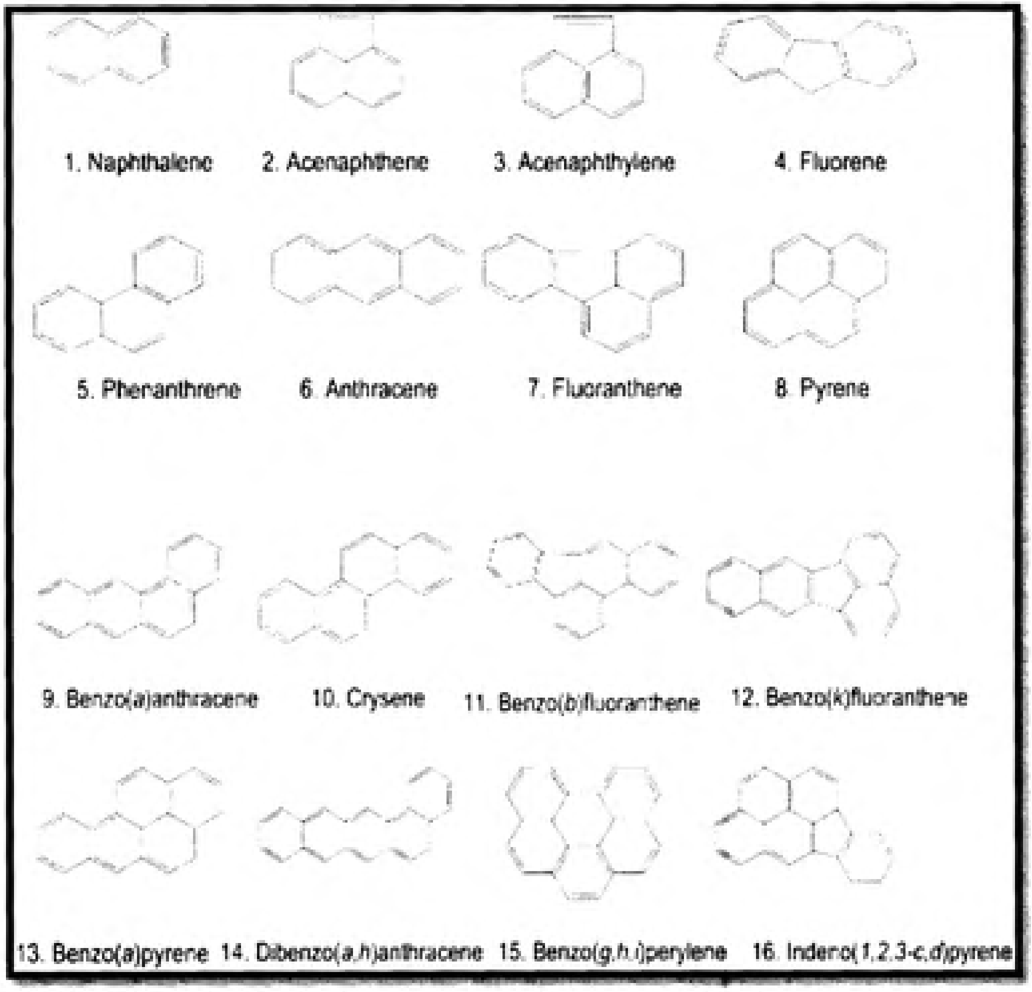
2.1.1.2 Aromatics

Organic compounds that are present in tars in large concentrations include polycyclic aromatic hydrocarbons (PAH); additional organic compounds that are present within coal tars include phenolics, light aromatics, and heterocyclic compounds containing nitrogen, sulfur, and oxygen. PAHs are two or more fused aromatic rings containing carbon and hydrogen atoms [USWAG, 1984]. PAH presence in coal tars is classified and prioritized by the EPA's designation of 16 priority pollutants identified in Table 2.1.1-1 and Figure 2.1.1-1 respectively [Bojes and Pope, 2007; Yan et al., 2004]. Further, priority pollutants identified as organic compounds within tars include monocyclic aromatic hydrocarbons such as benzene, toluene, and ethylbenzene and heterocyclic compounds such as quinoline, acridine, carbazole, thiophenes and furans [Birak and Miller, 2009].

Polycyclic aromatic hydrocarbons*	Structure (# of rings)	Molecular weight (g/mole)	Solubility (mg/L)	Vapor pressure (mm Hg)
Naphthalene	2	128.17	31	8.89E–02
Acenaphthene	3	154.21	3.8	3.75E–03
Acenaphthylene	3	152.20	16.1	2.90E–02
Anthracene	3	178.23	0.045	2.55E–05
Phenanthrene	3	178.23	1.1	6.80E–04
Fluorene	3	166.22	1.9	3.24E–03
Fluoranthene	4	202.26	0.26	8.13E–06
Benzo(a)anthracene	4	228.29	0.011	1.54E–07
Chrysene	4	228.29	0.0015	7.80E–09
Pyrene	4	202.26	0.132	4.25E–06
Benzo(a)pyrene	5	252.32	0.0038	4.89E–09
Benzo(b)fluoranthene	5	252.32	0.0015	8.06E–08
Benzo(k)fluoranthene	5	252.32	0.0008	9.59E–11
Dibenz(a,h)anthracene	6	278.35	0.0005	2.10E–11
Benzo(g,h,i)perylene	6	276.34	0.00026	1.00E–10
Indeno[1,2,3-cd]pyrene	6	276.34	0.062	1.40E–10

* US EPA has classified PAHs in italics as probable human carcinogens (NTP, 2005).

Table 2.1.1-1: US EPA's 16 Priority-Pollutant PAHs and Selected Physical-Chemical Properties [Bojes and Pope, 2007]



1. Naphthalene 2. Acenaphthene 3. Acenaphthylene 4. Fluorene

5. Phenanthrene 6. Anthracene 7. Fluoranthene 8. Pyrene

9. Benzo(*a*)anthracene 10. Crysene 11. Benzo(*b*)fluoranthene 12. Benzo(*k*)fluoranthene

13. Benzo(*a*)pyrene 14. Dibenzo(*a,h*)anthracene 15. Benzo(*g,h,i*)perylene 16. Indeno(*1,2,3-c,d*)pyrene

Figure 2.1.1-1: Chemical Structures of EPA's 16 Priority Pollutant Polycyclic Aromatic Hydrocarbons (PAHs)

2.1.1.3 Resins

Resins (also referred to as polars) are defined as high molecular compounds that can be dissolved in n-pentane and solvents (such as toluene). Resins are insoluble in ethyl acetate [Demirba, 2002]. Resins can be semisolid or solid and very adhesive with the resin content depending on the composition of the tar, how the resins are precipitated out of a system, and the temperature the resins are exposed to within tars [Speight, 1999]. It is hypothesized that resins (along with asphaltenes) affect wettability in petroleum-based systems [Birak and Miller, 2009].

2.1.1.4 Asphaltenes

Asphaltenes are high molecular compounds that contain aromatic compounds with heteroatoms such as nitrogen, oxygen and sulfur and/or aliphatic compounds. Asphaltenes are also defined as materials that are insoluble in n-pentane or can be re-dissolved in toluene. Past analysis of tars from FMGPs show asphaltenes occurring at high concentrations [Birak and Miller, 2009; Speight, 1999; Zheng et al., 2001].

2.1.2 Inorganic Compounds in Tars

Inorganic compounds that have been measured and identified in tars from FMGPs include metals such as arsenic, chromium, and lead; and, non-metals such as cyanide [Birak and Miller, 2009]. Metals identified with the largest concentration in coal tars include arsenic, chromium, and lead. In addition, all types of tar contain some amount of water. Carbureted water gas tars can contain as much as 90% water while coal tars can contain a water content upwards of 5% [Birak and Miller, 2009]. Higher water content present in tars lead to formation of emulsions, which are difficult to separate, reuse, or sell. Coal tars separate fairly easily from water and other condensates present (hence the much lower water content). Water presence was a bigger issue in carbureted water gas and oil gas tars after the type of oil feedstock used was altered during the manufacturing processes of carbureted water and oil gas [Birak and Miller, 2009; Harkins et al, 1988].

2.2 Physicochemical Properties

Considerations for the physicochemical properties of coal tars are determined primarily by the composition of these tars. Characterization of the physicochemical properties of coal tars is based upon the tars' specific gravity, viscosity, wettability, capillary pressure, interfacial tension, and effects from weathering.

2.2.1 Specific Gravity and Viscosity

The specific gravity and viscosity of tars are dependent upon the process in which the tar was produced from (e.g. coal gas, oil gas or water-gas processes). Overall, specific gravity measurements for various coal tars (i.e. retorts, coke ovens) from manufactured gas tars ranged from 1.103-1.249. In addition, specific gravity ranges for carbureted water-gas tars (whether light, heavy, or fuel) were 1.061-1.227; while, specific gravity ranges for oil gas (whether medium, high temperatures or fuel oil) were 1.206-1.334 [Birak and Miller, 2009; Harkins et al, 1988]. Trends indicate the lowest specific gravity occurs in the carbureted water-gas tars and the highest specific gravity measurements occur in the oil-gas tars. The specific gravity for the various tars is functionally dependent on the temperature of the process utilized. Viscosity measurements of coal tars produced from various processes ranged from 2.6×10^2 -1.8×10^4 cP [Birak and Miller, 2009].

2.2.2 Wettability and Contact Angles

Wettability describes the interaction between the liquid phase and a solid phase and is measured as the contact angle between a droplet of liquid in thermal equilibrium on a horizontal surface [Barranco and Dawson, 1999; Zheng et al, 2001]. Wettability is an important property that affects capillary pressure in studies of NAPL contaminants within subsurface systems. Wettability influences the transport of the organic phase [Barranco and Dawson, 1999]. NAPL contaminants can alter the wettability of the solid phase from water to NAPL wet. Water-wet systems are systems in which the water preferentially coats the solid phase, and NAPL-wet systems are systems in which the NAPL phase preferentially wet the solid phase. Wettability is quantified through measurement of the contact angle between the solid phase and the interface between the fluids. When this angle through the water phase is less than 90° the system is classified as water-wet, while, angles passing through the water phase to the interface between the fluids measuring greater than 90° are labeled as oil wet [Birak and Miller, 2009; Wang et al., 1999]. Young's equation is notably used to describe the contact angle, θ, within the system as follows:

$$\gamma^{ns} - \gamma^{ws} = \gamma^{nw} \cos\theta \quad (1)$$

where γ^{ns} is the interfacial tension between the NAPL phase (n) and the aqueous phase (s), γ^{ws} is the interfacial tension between the solid phase (w) and the aqueous phase (s), and γ^{nw} is the interfacial tension between the NAPL phase (n) and the solid phase (w). Contact angle measurements vary due to ranges of pH and the presence of films forming at the NAPL-aqueous phase interface [Birak and Miller, 2009].

2.2.3 Capillary Pressure

Capillary pressure is a fundamental concept in the study of multiphase porous medium systems. The Laplace equation for a simplified capillary tube pore structure is used to describe the relationship of capillary pressure as a function of the interfacial tension, contact angle, and radius of curvature and is given by:

$$P_c = \frac{2\gamma^{nw}\cos\theta}{r} \quad (2)$$

where P_c is the capillary pressure, γ^{nw} is the interfacial tension between the NAPL phase (n) and the solid phase (w) and r is the radius of the capillary tube [Birak and Miller, 2009; Dong et al, 2004; Lord et al, 1997]. The Laplace equation describes the importance of the IFT and contact angle as crucial parameters that affects the capillary nature of the system. For NAPL contaminants such as TCE and PCE, the capillary pressure is influenced primarily by the interfacial tension (IFT), while the effects of contact angle and wettability also influences the capillary pressure in tars [Birak and Miller, 2009]. Another phenomenon that affects the capillary nature of the system include the impact of sorption of a surfactant [Dong et al, 2004; Lord et al., 2000]. This phenomenon on contact angles is characterized by the equation associated with adhesional wetting, given by:

$$W_a = \gamma\frac{ct}{w}(1-\cos\theta) \quad (3)$$

where this equation is a result of the substitution of the Young equation into the general adhesional wetting equation, ct/w is the mineral surface/coal tar IFT, γ is the interfacial tension between the coal tar and water, θ is the contact angle measured between the fluid to fluid interface between the coal tar and the water on a solid surface, and W_a is the adhesional wetting parameter [Birak and Miller, 2009; Dong et al, 2004].

2.2.4 Interfacial Tension (IFT)

Interfacial tension (IFT) changes have been attributed to the presence of asphaltenes in the coal tar [Zheng and Powers, 2003]. Asphaltenes, along with being high molecular compounds, are polar compounds due to the presence of heteroatoms, which cause the surfaces of the asphaltenes to have both acid and base characteristics [Zheng and Powers, 2003; Zheng et al., 2001]. The ranges of IFT measurements between a NAPL and water interface is estimated between 20 to 50 mN/m. Much lower IFT measurements have been observed to occur in the presence of degreasing solvents in the subsurface and coal tars exposed to basic conditions (less than 10 mN/m in degreasing solvents and less than 5 mN/m for coal tars) [Zheng and Powers, 2003]. In experimental studies of the IFT between coal tar and water, within a pH interval of 3.4-9.1, average IFT values were 23.5 mN/m, while at pH values above 9.1, IFT values decreased significantly with a low value of 0.6 mN/m at a pH at 12.6 [Barranco and Dawson, 1999].

2.2.5 Weathering

Weathering of coal tar can have an impact on the tar's composition. Weathering relates to the combination of biological and physiochemical processes such as evaporation, dissolution, microbial degradation, sequestration and photooxidation that can reduce the concentrations of compounds in the systems (e.g. PAHs) [Birak and Miller, 2009]. The impact of weathering causes the reduction and removal of the lower molecular weight PAHs, but little to no change in the higher molecular weight PAHs [Brenner et al., 2002; Wang et al., 1999].

2.3 Mass Transfer Considerations

Mass transfer occurs when NAPL compounds are transferred to the aqueous phase within subsurface systems via solubilization. Mass transfer within a subsurface system is dependent upon the NAPL distribution within the source zones [Soga et al., 2004; Wright et al., 2010]. The following sections briefly describe the key mechanisms in NAPL mass transfers to the aqueous phase follow by limitations present during mass transfer processes.

2.3.1 Equilibrium Characteristics

Raoult's Law is often used to describe the relationship between the aqueous concentrations of a compound at equilibrium to the compound's mole fraction in multi-component mixtures. The relationship is described by the following equation:

$$C_{aq}^{i} = \chi_i \frac{C_{sol}^{i}}{FR_i} \quad (4)$$

where C^{i}_{sol} is the aqueous solubility of the pure component, C^{i}_{aq} is the aqueous concentration of component i in equilibrium with the mixture, and FR_i refers to the solid/liquid fugacity ratio of the component i. The fugacity ratio can be obtained either from studies in the literature or by estimating an equation for the free-energy change between the liquid and solid state [Brown et al, 2005; Peters and Luthy, 1993]. Raoult's Law has been used previously as a predictor for tar NAPL dissolution. Over a period of years as tars degrade, PAHs that are readily soluble will dissolve, leading to an increase in the mole fractions of the less water soluble components within the tars [Birak and Miller, 2009].

2.3.2 Rate-Limiting Mass Transfer

The equation used to describe the mass transfer mechanisms from a NAPL to an aqueous phase is given by:

$$\overset{in \rightarrow ia}{M} = \varepsilon^{na} k_{ai} (C_{ei}^{a} - C_{i}^{a}) \quad (5)$$

where k_{ai} is the mass transfer coefficient of the species in the aqueous phase (units: L/T), C^{a}_{i} is the aqueous phase species concentration in the bulk solution (units: M/L^3), $M^{in \rightarrow ia}$ is the mass transfer exchange from the species in the NAPL phase to the species in the aqueous phase (units: M/L^3T), C^a_{ei} is the species concentration of the NAPL present in the aqueous phase at equilibrium (units: M/L^3), and ε^{na} is the specific interfacial areas between the NAPL and aqueous phases (the ratio of the interfacial area between the NAPL and aqueous phases to the total volume of the porous system in question, units: 1/L) [Birak and Miller, 2009; Miller et al., 1990]. Since the specific interfacial areas are usually not known, the mass transfer can be represented as a lumped mass transfer rate coefficient as:

$$K_{ai} = \varepsilon^{na} k_{ai} \quad (6)$$

where K_{ai} is the mass transfer rate coefficient of the species in the aqueous phase (units: 1/T [Birak and Miller, 2009; Miller et al., 1990; Soga et al., 2004] .

In single species NAPLs, several empirical relationships and parameters have been identified in determining the mass transfer rate in porous media. Typically these mass transfer relationships have been characterized through the use of non-dimensional parameters [Birak and Miller, 2009]. In studies of multiple species of NAPLs such as tars, identification and characterization of mass transfer variables are change in composition over long periods of time. Due to the ever-changing nature in the NAPLs composition, crucial parameters such as viscosity and specific gravity can change, complicating mass transfer coefficient characterization efforts. Additional mass transfer complications can occur when equilibrium concentrations of NAPL systems deviate from Raoult's Law and precipitation of certain NAPL soluble molecules occurs [Birak and Miller, 2009].

2.4 Remediation Approaches

Remediation techniques discussed in this section are categorized into the following four methods: mobilization-based, mass-transfer based, reaction based, and containment. Within this categorization, remediation of contaminated groundwater can be applied as in-situ or ex-situ treatments. In-situ techniques involve treatment application within the groundwater while ex-situ techniques entail physical removal, treatment and/or disposal of the contaminant from the groundwater site [Delleur, 2007; Deuren et al, 2002; Simon and Meggyes, 2000]. In-situ and ex-situ techniques applied to contaminated groundwater sites with coal tars include bioremediation, excavation and hauling, thermal techniques, chemical oxidation, and permeable reactive barriers.

2.4.1 Mobilization-Based Remediation Techniques

Mobilization-based techniques involve processes that aid in the removal of DNAPLs by inducing movement of the DNAPL through the porous media without relying upon mass transfer to a different fluid phase. Surfactant flushing and cosolvent flushing can increase the rates of solubilization and/or mobilization of DNAPLs within a subsurface environment. Surfactants used in flushing can be a variety of chemical compounds (i.e. block polymers, sodium dodecyl sulfate) while cosolvents can consist of various alcohols (i.e. ethanol, methanol) [Lowe et al, 1999; Zhou and Rhue, 2000]. In surfactant flushing in which emphasis is on mobilization of the NAPL, an injection of a surfactant chemical solution is made into the subsurface environment with the objective of lowering the interfacial tension between the NAPL compound and water interface to enable NAPL movement [Lowe et al, 1999]. Surfactant flushing techniques originated from applications of surfactants used in enhanced oil recovery processes in the petroleum industry. Cosolvent flushing strategies in mobilization and solubilization are similar to surfactant flushing, with the only difference being that cosolvents do not causing micelles to form when interacting with NAPLs [Lowe et al, 1999].

Thermal methods involve in-situ treatment of contaminated DNAPL source zones such as steam-enhanced extraction (SEE), thermal conductive heating, and electrical resistive heating (ERH). SEE methods remove DNAPLs in contaminated water and vapors in the subsurface with the use of steam heat to the subsurface. SEE methods are used in conjunction with vapor and liquid extractions [Kavanaugh and Rao, 2003]. Typically, steam is produced from a boiler on the surface and is injected into the subsurface. Once injected into the subsurface, the steam traverses several zones in the subsurface and directly heats the groundwater to either vaporize and/or mobilizes compounds in the DNAPLs. The mobilized DNAPLs are then collected into strategically located extraction wells. The extracted fluids are then bought to the surface to remove the contaminant [ITRC, 2004; Kavanaugh and Rao, 2003]. Other similar steam injection techniques within thermal treatment include dynamic underground stripping (DUS) and steam-enhanced recovery processes [ITRC, 2004]. Thermal conductive heating (or in-situ thermal desorption (ISTD)) is a technique that utilizes several vertical or horizontal thermal heaters to warm the soil via conduction up to temperatures of 1400°F-1500°F. Vertical alignments of the heaters are sometimes refer to as thermal walls. Several processes occur to reduce the presence of organic contaminants within the soil such as evaporation, boiling, and oxidation within the vadose zone of the subsurface [ITRC, 2004; Kavanaugh and Rao, 2003]. ERH techniques using vertical electrodes apply a high voltage (as much as 440 volts) of electrical current to the subsurface to spur thermal energy. The types of voltage configuration used in ERH techniques include three and six phase AC and DC voltage. After heating the subsurface to high temperatures, contaminants and contaminated groundwater are either vaporized or captured in extraction wells [Kavanaugh and Rao, 2003].

2.4.2 Mass-Transfer-Based Techniques

Mass-transfer techniques aim to reduce the concentration of contaminants present in porous media through enhanced solubilization and/or volatilization of the contaminants in question. Pump-and-treat methods were used in early initiatives in DNAPL source zone remediation techniques by increasing the amount of groundwater flow through a DNAPL source zone in order to capture the mobile DNAPL and contaminated groundwater and pump to the surface to treat [Mercer et al., 1990]. Typically, are a series of underground injection wells that facilitate groundwater flow throughout the contaminated region causing dissolution of contaminant compounds and removing the contaminated water through a set of extraction wells. Effluent from the extraction wells is then bought to the surface and the groundwater is treated with methods applicable to the contaminant present in the water (e.g. adsorption, precipitation) [Murphy, 2006; Newman, 2008].

Air sparging (or in-situ air sparging (IAS)) is a technique that injects compressed air into a well positioned in groundwater below the water table. The injected air traverses through the groundwater and ultimately discharges into the unsaturated zone leading to

2004; Kavanaugh and Rao, 2003]. ERH techniques using vertical electrodes voltage (as much as 440 volts) of electrical current to the subsurface to spur th energy. The types of voltage configuration used in ERH techniques include thre phase AC and DC voltage. After heating the subsurface to high temperatures, contaminants and contaminated groundwater are either vaporized or captured in extraction wells [Kavanaugh and Rao, 2003].

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Air sparging (or in-situ air sparging (IAS)) is a technique that injects compressed air into a well positioned in groundwater below the water table. The injected air traverses through the groundwater and ultimately discharges into the unsaturated zone leading to the DNAPL removal via volatilization [Plummer et al, 1997]. For further optimal remediation, the IAS method is combined with soil vapor extraction within a contaminated subsurface site. For long-term effectiveness, detailed information must be known about the depth of the contaminants and characteristics of the site geology in question. In addition, caution must be used if the airflow is uneven, because this can indicate the presence of unconstrained dangerous vapors in the groundwater [Deuren et al, 2002].

Surfactant and cosolvent flushing (sometimes referred to as in-situ chemical flushing) are mass-transfer techniques focusing on enhanced solubilization in subsurface systems. Typical surfactant flushing with emphasis on solubilization involves the injection of the surfactant solution into the subsurface environment in which interactions between the surfactant can cause an increase of solubility in components in NAPL compounds by a process called micellar solubilization [ITRC, 2002; Lowe et al, 1999].

2.4.3 Reaction Based Remediation Techniques

Reaction-based techniques utilize various chemical reactions to convert or transform DNAPL contaminants within subsurface systems. The process of chemical oxidation involves subsequent oxidation reactions that occur to transform toxic contaminants into less hazardous materials or more stable and non-reactive species. Several oxidants used in the degradation and chemical destruction of such contaminated agents include ozone, peroxide, permanganate, hydrogen peroxide, hypochlorites and chlorine. Optimum removal of these types of contaminants occurred for unsaturated aliphatic and aromatic compounds [Deuren et al, 2002]. For example, BTEX, phenols, chlorinated ethenes, and polychlorinated biphenyls (PCBs) are most effective in being removed by permanganates [Huling and Pivetz, 2006]. Some oxidants assist in only a partial degradation that contributes to higher rates of microbial degradation when bioremediation is used subsequent to chemical oxidation. When selecting the appropriate oxidants, care must be taking in handling certain types of oxidizers since several are classified as hazardous. A complete understanding of the contaminant in the groundwater is necessary since there are some agents that are resistant and unaffected to the methods of oxidation. Also, additional considerations and research should be done to determine whether any harmful or dangerous side effects occur during the oxidation processes [Deuren et al, 2002].

Bioremediation involves natural processes that aid in reducing the plume and concentration of a contaminant due to actions such as leaching, chemical spills, and dumping. Typically, no engineered processes or controls are utilized during this process [Khan et al, 2004]. Ideal organic compounds that bioremediation have been show to impact include petroleum hydrocarbons, certain chlorinated aromatic and aliphatic compounds, and non-chlorinated solvents. Processes that occur within the subsurface during bioremediation include dilution, volatilization, biodegradation, and sorption to aid in the reduction of the concentration of the contaminant [Deuren et al, 2002]. In some cases, enhanced bioremediation occurs when oxygen is added within reactive barriers to jump-start the aerobic degradation of several compounds classified as monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) [Scherer et al., 2000]. Bioremediation is considered a relatively effective remediation technology because of the lack of need for additional technologies, mediums, or methods. Depending on the deadlines and scope given to clean up a contaminated site, time can become a disadvantage because of rate of degradation of the contaminant in question. Long term, costs can occur because of the requirement of monitoring to determine rates of degradation and potential occurrences of contaminant movement within the subsurface medium [Deuren et al, 2002].

2.4.4 Containment Based Remediation Techniques

Containment methods pertain to the construction and installation of treatment walls or barriers to remediate contaminated porous media. Phytoremediation is a process that utilizes plant and other vegetation to either destroy, stabilized, or transfer contaminants present in subsurface systems. Phytoremediation has also been referred to by alternate names such as green remediation, vegetative remediation, and agroremediation [Pivetz, 2001]. Several types of phytoremediation can be used depending on the target goals of contamination reduction/elimination such as: phyto-accumulation, phyto-degradation, and phyto-stabilization. Phyto-stabilization uses chemicals produced naturally from plants to immobilize and retard contaminant spreading in the subsurface [Deuren et al, 2002]. Hydraulic control is maintained during phytoremediation by the plant and root uptake of the groundwater [Pivetz, 2001]. The use of phytoremediation for hydraulic control can reduce rates of contaminant plume expansion within subsurface systems. Phytoremediation processes have been used to treat a variety of contaminants present in groundwater such as metals, PAHs, crude oils, and pesticides. Some limitations with the use of phytoremediation include mass transfer limitations, the conditions and characteristics of the treatment zone in question, and the impact of plants from exposure to large concentrations of hazardous contaminants in question [Deuren et al, 2002].

Permeable reactive barriers (PRBs) is an in situ method that was developed during the 1990's with the first PRB designed and implemented in Ontario, Canada in 1991. A full-scale funnel and gate PRB was instituted in Sunnyvale, California in 1995 using zero-valent iron (ZVI) to treat not only TCE, but in addition dichloroethene (DCE), vinyl chloride (VC) and chlorinated fluorocarbons (CFCs) [Birke et al, 2003]. Since then, PRBs have quickly risen as a means to treat contaminated groundwater due to its low energy demands and lower costs compared to ex-situ methods. In addition, PRBs have the potential to treat a variety of contaminants, ensuring much more efficient and universal removal of contaminants in groundwater and soil sites. The type of medium required in PRBs is dependent on the type and characteristics of the contaminants present in the groundwater [Simon and Meggyes, 2000]. The common design of PRBs fall under two categories: continuous reactive barrier (or permeable reactive trench) and funnel-and-gate system reactive barriers. The reactive barrier that is needed for treatment of contaminated groundwater will typically depend upon the hydrogeological properties and characteristics of the site, the placement of the barrier, and the type and associated costs of the reactive material used within the barrier [Roehl, 2004]. One limitation of PRBs includes understanding the long-term effectiveness of these barriers to treat contaminated groundwater [Simon and Meggyes, 2000].

2.5 Open Issues with FMGP Remediation

FMGP remediation attempts can be characterized by source-zone removal, containment and treatment with the intentions of decreasing the mass flux from the source zone. Initial attempts in remediation at FMGP sites made use of the pump and treat method, but this method has not been considered an effective remediation technique because of DNAPL residual remaining and low efficiencies of removal at FMGP sites [Birak and Miller, 2009; Soga et al., 2004]. Flushing and dissolution techniques were developed as an alternative to pump-and-treat methods. Since concerns of trapped residual NAPL remain, additional efforts are needed to remove NAPLs after flushing and dissolution techniques are used such as mobilization, chemical and biological treatment. Issues for FMGP remediation with DNAPL compounds include the extent of dissolution and movement of the dissolved phase contaminant, the age of the DNAPL spill, the subsequent contaminant plume formed, the length scale of the source zone and the aqueous phase velocity [Wright et al., 2010]. A recent issue to arise in FMGP remediation is the consideration that the amount of mass flux removed from the source zone is not an effective assessment of the efficiency of a remediation technique, due to the uncertainties in DNAPL distribution in the contaminated groundwater site [Soga et al., 2004]. Techniques developed for high NAPL removal are developed in idealized scenarios within contaminated groundwater through simulations, modeling, and 1D homogeneous, well defined and uniform flow fields [Soga et al., 2004]. In this situation, results do not reflect the actual field conditions due to the heterogeneity and multiphase and multi-components present in subsurface systems [Soga et al., 2004; Wright et al, 2010]. Continuing research and improvement of models that reflect actual conditions and characteristics at DNAPL contaminated sites will be crucial in developing multiple scale remediation techniques and treatments for contaminated groundwater.

2.6 Novel Alkali Flushing Technique

Application of alkaline flushing as a potential mobilization-based technique in FMGP remediation is originally based on principles from the petroleum research in recovering sizeable amounts of residual oil from oil-field reservoirs. The effects of alkaline flushing on crude oils can potentially be applicable to tars because of the similar properties and characteristics shared between crude oils and tars. One such example include the presence of asphaltenes and resins in both crude oils and tars. In addition, tertiary recovery of crude oils have also included the use of cosolvents, surfactants, and polymers. Alkaline flushing has not yet been considered as a method of mobilization for FMGP waste.

2.6.1 Alkaline Flooding

The use of alkaline solutions has been applied in the petroleum industry in efforts to maximize optimal oil recovery (referred to as EOR-enhanced oil recovery). Enhanced oil recovery is a term used to describe techniques that can aid in recovering residual oil after primary and secondary methods (i.e. water flooding) have been employed in oil fields [Cambridge et al, 1986; Sayyouh and Al-Blehed, 1993]. There are three major techniques in EOR that are used in oil recovery: chemical methods such as alkaline flooding or micellar-polymer flooding, miscible displacement, and thermal recovery.

Alkaline flooding is utilized to overcome the difficulties in oil recovery in the field such as: reactions within the reservoir rock, poor mobility control, inability to sustain low IFT, and other events [Cambridge et al, 1986]. Advantages of using alkaline in EOR efforts is the cost benefit and availability of alkaline solutions to use in the field compared to other techniques used (e.g. surfactant flooding) [Cambridge et al, 1986]. Some issues in the use of alkaline flooding on a large-scale range from alkali loss stemming from silica dissolution, clay transformation, various ion-exchange reactions, and the composition of the crude oil itself [Cambridge et al, 1986; Nasr-El-Din et al, 1992].

2.6.2 Alkaline Flooding Characteristics

The method of alkaline flooding is ideally suited for acidic crude oils and it's success is attributed to causing the lowering of the IFT in crude oil-water interfaces. Acidic components identified within crude oils included asphaltenes and resins [Babu et al, 1984]. Initial observations on the lowering of the IFT were a function of the pH of the aqueous phase, along with the concentrations, chemical properties, and composition of the crude oil [Jang et al, 1982]. Jang et al. attributed the lowering of the IFT to the formation of soap molecules by the interactions of the alkali and the acids within the crude oil. Alkaline solutions of NaOH and Na_2CO_3 are commonly used in caustic flooding of crude oil fields [Dong et al, 2009]. IFT variations within oil fields are due to the types of crude oil, how much salinity is present in the oil reservoir, and the alkalinity of floodwater [Chiwetelu et al, 1990]. For simple alkaline flooding, four mechanisms have been proposed to occur: emulsification and entrainement, wettability reversal from water-wet to oil-wet, wettability reversal from oil-wet to water-wet, and emulsification and entrapment [Islam and Chakma, 1991]. Emulsification and entrainement involve the crude oil being emulsified by the displacing water solution and carried along by the flowing of alkaline solution. Wettability reversal from water-wet to oil-wet pertains to the changes of wettability in the rocks that causes favorable conditions of permeability leading to increased oil recovery [Islam and Chakma, 1991]. The wettability reversal from oil-wet to water-wet is obtained during the simultaneous occurrence of a lowered IFT and the presence of viscous water in the crude oil emulsion. This simultaneous occurrence during wettability reversal from oil-wet to water-wet yields low residual oil saturation. Emulsification and entrapment yields an increase in sweep efficiency due to the suspended crude oil droplets blocking small pore throats [Islam and Chakma, 1991]. Alkaline flooding in recovery of heavy oils has been found to be better suited to thin reservoirs than heavy oil in thick reservoirs. This is due to major problems in fingering and channeling that occur during heavy oil displacement. To counteract the effects of fingering, along with other issues in heavy oil reservoirs (i.e. high salinity, mineral surfaces), several techniques have been developed such as the use of plugging agents, in-situ air oxidation, alcohol-assisted alkaline flooding, surfactants and polymers [Cambridge et al, 1986; Dahami et al, 1988; Islam and Chakma, 1991; Liu et al, 2007].

2.6.3 Cosurfacants, Surfactants, and Additional Aids in Enhancing Alkaline Flushing

Due to problems that arise from the sole use of alkaline solutions, several scientists have engaged in adding surfactants, polymers, and other materials to enhance oil recovery and minimize alkaline losses within crude oil. Examples of methods and surfactants include the use of sodium dodecyl benzene sulfonate, calcium lignin sulfonate (at 0.5% concentrations), a combination of sodium hydroxide and sodium carbonate, an alkaline/surfactant/polymer (such as the combination of sodium hydroxide, Neodol 25-3S(a commercial alcohol ethoxysulfate), and partially hydrolyzed polyacrylamide) [Jennings et al, 1974; Liu et al, 2007; Nasr-El-Din, 1992]. In these experiments, authors have shown that the combination of a surfactant and an alkaline solution increases the enhancement and recovery percentage of the sample crude oil in sand pack flood tests. Alcohol-assisted alkaline flooding has also been employed as a means to increase oil recovery efficiency. The condition that warranted such improvement was the changes to emulsion characteristics. In one experiment, addition of alcohol yielded a decrease in emulsion viscosity, which led to an improvement in oil bank stability. The higher the molecular weights of the alcohols in question (i.e. from methanol to butanol), the higher the trend in oil recovery while decreasing trends of oil recovery were observed in the less water soluble pentanol isomers. Decreasing trends in oil recovery were noted to occur when there were elevated interfacial shear viscosities (IFSV) and IFT in the presence of alcohol additives [Dahami et al, 1988]. In alkaline flooding tests, attempts at in-situ surfactants formation within the heavy oils using a water based surfactant solution yielded sodium hydroxide optimum concentrations at 0.05% at 25°C with an incremental oil recovery rate of 42.4% [Liu et al, 2007; Ma et al, 2007; Ma, 2005]. At increasing temperatures, a decrease in oil recovery was recorded at a similar NaOH concentration (7.3% oil recovery rate at 65°C). This was attributed to increasing temperature causing an increase in the IFT, hence lowering the oil recovery rates.

3. Materials and Methods

In this section, the materials and methods utilized in a lab study on alkaline flushing in a tar-saturated column are discussed. The materials and methods used in this soil column experiment were developed from previous column experiments and initial batch tests. The soil column used in this laboratory study is referred to here on out as Dover (D4) column.

3.1 Materials

3.1.1 Soil Properties

The soil used for the column experiment is a sieved fraction #35-#25 (500 μm-710 μm sieve diameter) originally obtained from the Dover National Test Site in Dover, Delaware. The Dover National Test Site has a water table aquifer named the Columbia formation, which sits over the clay formation labeled as the Calvert Formation. Qualitative properties of the Dover Sand include fine to medium sands with some clay and silt present. The density of the Dover sand was 2.65 g/cm^3 and the vertically averaged hydraulic conductivity measured at the Dover site was 3×10^{-3} cm/sec [Wright et al., 2010].

3.1.2 Tar Properties

The coal tar primarily used for the column experiments was a tar sample from a FMGP in Baltimore, Maryland. The percent of asphaltenes for this sample was 17.7%, with a specific gravity of 1.069, a dynamic viscosity of 103 cP, and a water content of 3038 ppm. The percentage of acid to base extractable mass measured for this tar was the following: acid: 0.23%, base 0.08%, and acid/base ratio: 2.875.

The composition of the tar is shown in Table 3.1.2-1. The five compounds with the highest concentration present within the tar were the following: naphthalene (93.48 mg/g), 2-methylnaphthalene (33.00 mg/g), 1-methylnaphthalene (23.91 mg/g), phenanthrene (22.83 mg/g), and pyrene (11.99 mg/g). In addition, detectable compounds present in Sample 6A include acenaphthene (11.69 mg/g), fluoranthene (9.98 mg/g), and fluorene (8.99 mg/g).

Adjusted	*6A*
Compound	Concentration (mg/g)
Benzene	0.48
Toluene	1.38
Ethylbenzene	1.65
m/p-xylene	2.98
Styrene	ND
o-xylene	1.50
1,3,5-trimethylbenzene	0.96
Phenol	ND
1,2,4-trimethylbenzene	2.96
1,2,3-trimethylbenzene	1.44
Indane	3.91
Indene	3.01
o-cresol	ND
m/p-cresol	ND
Naphthalene	93.48
Benzo(b)thiophene	4.10
Quinoline	ND
2-methylnaphthalene	33.00
1-methylnaphthalene	23.91
Biphenyl	4.67
2-ethylnaphthalene	4.38
Acenaphthylene	1.75
Acenaphthene	11.69
Dibenzofuran	4.04
Fluorene	8.99
Dibenzothiophene	3.65
Phenanthrene	22.83
Anthracene	6.07
Carbazole	1.44
Fluoranthene	9.98
Pyrene	11.99
Benzo(a)anthracene	4.36
Triphenylene/chrysene	4.81
Benzo(b)fluoranthene	2.90
Benzo(k)fluoranthene	2.76

Benzo(a)pyrene	3.37	
Indeno(1,2,3-CD)pyrene	1.66	
Dibenz(a,h)anthracene	0.72	
Benzo(ghi)perylene	1.75	
Concentration Summation (mg/g)		288.58
ND-not detectable		

Table 3.1.2-1: Tar Composition

3.1.3 Alkaline Solution Properties

Materials used to prepare the alkaline solution was solid sodium hydroxide (formula weight: 40 g/mol) (NaOH) pellets by Fisher Scientific: s318~100 and deionized water with Cas#: 1310-73-2/497-19-8 with an assay of 99.8%.

3.1.4 Ethanol Properties

Alcohol flushing was conducted with ethanol (ethyl alcohol absolute) and deionized water. The ethanol solution was 70% by volume when prepared. The ethanol (formula weight: 48 g/mol) (C_2H_6O) had an assay of 99.5% ACS with a Cas#: 64-17-5.

3.1.5 Apparatuses

All fluids pumped into the Dover 4 (D4) soil column utilized a Harvard Apparatus PHD4400 programmable syringe pump, along with a Hamilton 50-mL gastight syringe and a 30-mL BD Luer-Lok tip syringe. All pH measurements were performed using an Orion Research expendable ionAnalyzer EA 940. All density measurements were performed utilizing the DMA 48 density/specific gravity/concentration meter. Camera and software used for qualitative observations of the soil column was the Nikon D90 camera and Nikon Camera Control Pro, v.2.7.1. Analyses of all the samples collected were performed using the following analytical equipment and software: Hewlett Packard Series II Plus Gas Chromatograph with a Flame Ionization Detector (FID) and

ChemStation A.10.02 [1757] software and Waters HPLC Plus and Empower Pro Software.

3.2 Soil Column Preparation and Methods

3.2.1 Dover 4 (D4) Soil Column Experiment Overview

After several column trials, a protocol was established for the flushing stages as followed for the Dover (D4) column aligned vertically:

- Stage 1-Carbon Dioxide Pumped in an Upward Direction
- Stage 2-Buffered Water in an Upward Direction
- Stage 3-Tar Pumped in an Upward Direction
- Stage 4-Buffered Water in a Downward Direction
- Stage 5-Alkali Solution in a Downward Direction
- Stage 6-Buffered Water in a Downward Direction
- Stage 7-Alcohol Solution in a Downward Direction
- Stage 8-Buffered Water in a Downward Direction

See Figure 3.2.2-1 for an illustration of the flushing stages for the column.

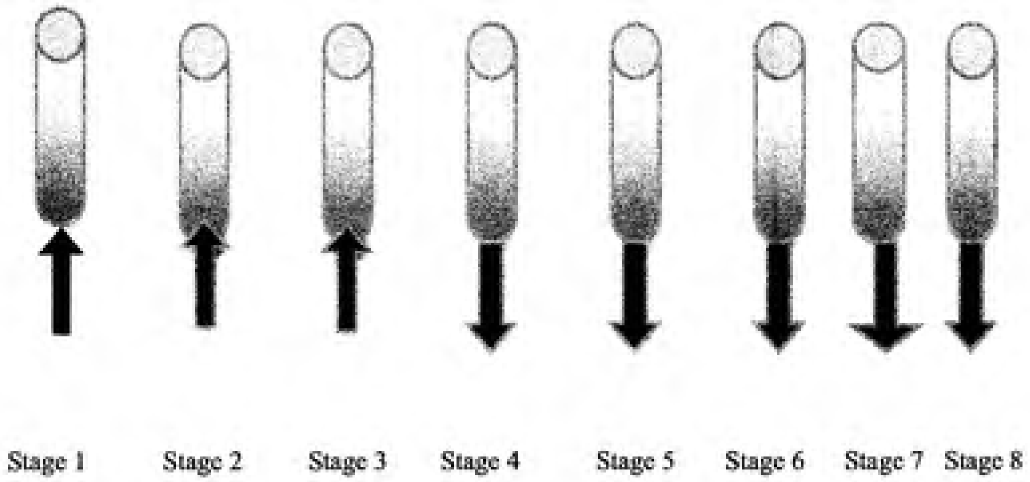

Figure 3.2.1-1: Column Flushing Illustration

Three triplicate 10-mL water effluent samples were taken at the tail end of the water flushing stages in the column. The water effluent collections occurred at Stage 4 after initial coal tar was pumped into the column, at Stage 6 after the alkaline solution was pumped down into the column, and at Stage 8 after the alcohol flushing was pumped down into the column. The water effluent collections were later prepped for analysis on the HPLC (see Section 3.3.1-HPLC Analytical Methods). All of the 10-mL vials used to collect water effluent were cleaned, pretreated (with: methylene chloride ($MeCl_2$), acetone, and acetonitrile (ACN)), and dried in an air vacuum. The 40-mL centrifuge tubes used to collect effluent at all stages of the Dover (D4) column flushing experiments were cleaned and pretreated in the following order: 15 minute soak in a caustic sodium hydroxide bath, 15 minute soak in a deionized water bath, 15 minute soak in a methanol bath and dried in an air vacuum.

A detailed method was developed in order to account for the coal tar entering and leaving the column from Stage 3, tar residual in tubing connected in and out of the column, and centrifuge tubes used to collect excess tar and tar residual. Extraction methods and analytical equipment used for analysis of column effluents for tar concentrations are described in Section 3.3.2.

3.2.2 Soil Column Assembly

The column used for the D4 column experiments was a glass column with a diameter of 2.5 cm and a height of 24 cm. One end of the column was fitted with a stainless steel plunger, and the column was filled with the Dover sand. After the Dover sand was filled in the column, the other open end of the column was fitted with a second stainless steel plunger. The Dover sand was packed tightly using an air vibrator for approximately 10 minutes. The mass of the Dover sand added to the column was 76.31g. Measurements for the Teflon tubing used during the initial stages of column flushing were 21.7-cm for the top tubing and 21.4-cm for the bottom tubing. The diameter of the Teflon tubing used for the column was 0.16002-cm. The packed column height was 10.3-cm. Figure 3.2.2-1 shows the assembled column before stage 1 of the column flushing was started.

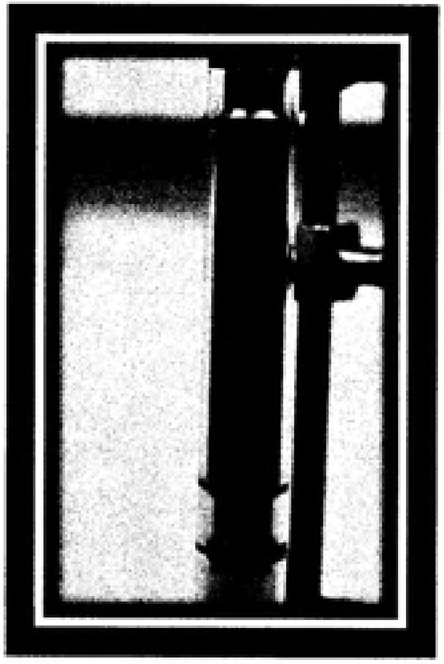

Figure 3.2.2-1: Dover (D4) Column Pre-Flushing

The total packed volume of the soil column was calculated as followed:

$$V = \pi * r^2 h = \pi * (1.25cm)^2 * (10.3cm) = 50.6cm^3 \quad (1)$$

where r is the radius of the glass column (units: L) and h is the height of the sand inside the glass column. The total packed volume of the soil column was used to determine the pore volume of the Dover 4 (D4) column in a series of equations (equations 2-5):

$$\rho_{b\_dover} = \frac{m_{sand}}{V_{col}} = \frac{m_{sand}}{V_{tot}} = \frac{76.3g}{50.6cm^3} = 1.51 \, {}^{g}\!/_{cm^3} \quad (2)$$

$$\rho_{b\_dover} = \frac{m_{sand}}{V_{col}} = \frac{m_{sand}}{V_{tot}} = \frac{76.31g}{50.560cm^3} = 1.50\, g/cm^3 \;(3)$$

$$\frac{V_{pore}}{V_{tot}} = 1 - 0.56955 = 0.430 \;(4)$$

$$V_{pore} = V_{tot} = 50.560cm^3 * 0.43045 = 21.7cm^3 \;(5)$$

where in equation (2), ρ_{b_dover} is the bulk density of the Dover sand, m_{sand} is the mass of the sand added to the column, V_{col}=V_{tot} is the total volume in the soil column. In equation (3), ρ_{grain} is the density of the Dover sand, and in equation (4), V_{pore} is the pore volume.

3.2.3 CO_2 Flushing-Stage 1

After the D4 column was completely packed and settled, CO_2 was flushed into the column to eliminate any air still present within the system. The soil column was flushed for approximately one hour at a rate of 30 ml/min. The CO_2 was orientated to pump upward into the column from the bottom of the column with effluent exiting from the top of the column tubing. To verify whether the air was being pushed out of the column by the CO_2, at one of the end valves connected to the column, the valve was left open in a small beaker filled with deionized water and one would observe air bubbles appearing within the water. Once there was a reduction of air bubbles observed into the beaker, the CO_2 pumping was ended. The column was then prepped to enter into Stage 2 of flushing.

3.2.4 Water Flushing-Stage 2

The water flushed through the D4 column was a 100mM phosphate buffered water prepared as follows: 0.6 g of monosodium phosphate, 1.5 g of disodium phosphate and deionized water was combined to prepare a 100mL solution phosphate. The pH of the 100mL solution buffered phosphate water was adjusted using sodium hydroxide and hydrochloric acid to a pH of 7.22. The phosphate buffered water stock solution was then diluted to a 10:1 ratio of buffered water to deionized water to be used for the Dover (D4) column. The total volume of buffered water pumped was 226-mL over the course of 72 hours. The pH of the water effluent collected from the D4 soil column was 7.37. After the completion of the water flushing, the column was prepped for the tar saturation stage.

3.2.5 Tar Saturation Flushing-Stage 3

A 30-mL BD Luer-Lok tip syringe was filled with the sample tar. The syringe was weighed at three junctions: initially when the syringe was empty, when the tar filled the syringe, and after the tar was pumped into the D4 soil column. The mass of the empty tip syringe was 19.2g, the mass of the syringe filled with tar was 50.1g and the mass of the syringe after the coal tar was pumped into the Dover column was 21.9g. The diameter of the 30-mL BD Luer-Lok Tip Syringe was 20.0-mm and the coal tar filled the tip syringe to the 29-mL mark. The coal tar was pumped into the soil column at a rate of $1.0 mL/hr$ for 25-mL over the course of 24 hours. After tar was pumped into the column, the column was flipped upside down and tubing filled with tar was replaced and reweighed. Tar effluent was collected in the treated 40-mL centrifuge tubes labeled as

TE#1-D4 and TE#2-D4. Pre- and post-effluent masses of TE#1-D4 collected were 37.2g and 54.8g respectively. Pre and post effluent masses of TE#2-D4 collected were 34.7g and 59.9g respectively. Figure 3.2.5-1 shows the end stage of the tar flushing of the Dover (D4) column. The dark area in the column is visual evidence of the saturation of the tar. Note that some regions of non-uniform saturation can be observed, for example at the bottom of the column. However, the majority of the column appeared to be a high and relatively uniform saturation of tar. Methods were not used to quantify the distribution of fluids in the pore space.

After the target tar injection volume into the column was completed, the column was prepped for Stage 4.

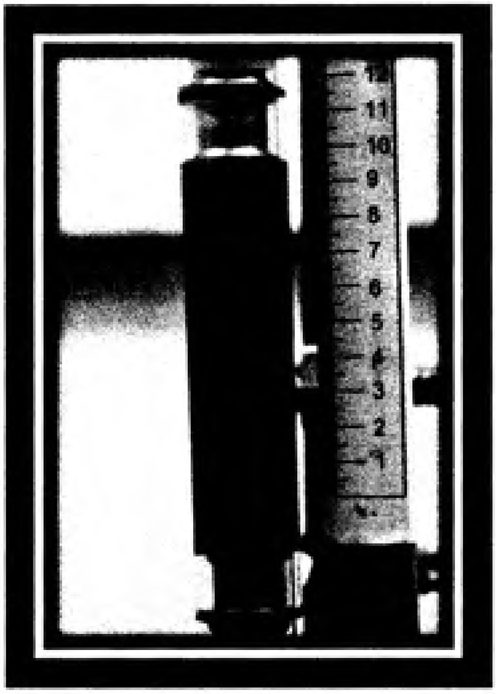

Figure 3.2.5-1: End Stage of Tar Flushing

3.2.6 Post-Tar Water Flushing-Stage 4

The 30-mL BD Luer-Lok tip syringe was replaced with the previously used Hamilton 50-mL gastight syringe and refilled with buffered water. The total volume of buffered water pumped into D4 soil column was 310-mL. The effluent exiting from the bottom end of the column was collected in pretreated 40-mL centrifuge tubes labeled as WF#1-D4 through WF#11-D4. After the buffered water was pumped into the D4 column, the Teflon tubing used during the coal tar and post-tar water flush was replaced with cleaned tubing for the water effluent collection and alkaline flushing stages. Three-10-mL vials were used to collect 15 mL of total effluent for HPLC analysis (5 mL of effluent per vial). The protocol of how the effluent was collected was as followed: 5-mL of acetonitrile, 4-µL of internal standard (I.S.), and 5-mL of effluent from the column was included in each sample. Each of the 10-mL vials was weighed at four junctions during the effluent sampling, when the vials were empty after pretreatment, after 5-mL of acetonitrile was added, after 4-µL of internal standard (I.S.) was added, and after 5mL of column effluent was collected. The samples were then labeled, wrapped in aluminum foil, and stored in a room maintained at 4°C. Figure 3.2.6 shows the tail end of the post-tar water flushing for the column before the alkaline flushing stage started. Visually, the column didn't change significantly during this water flushing stage.

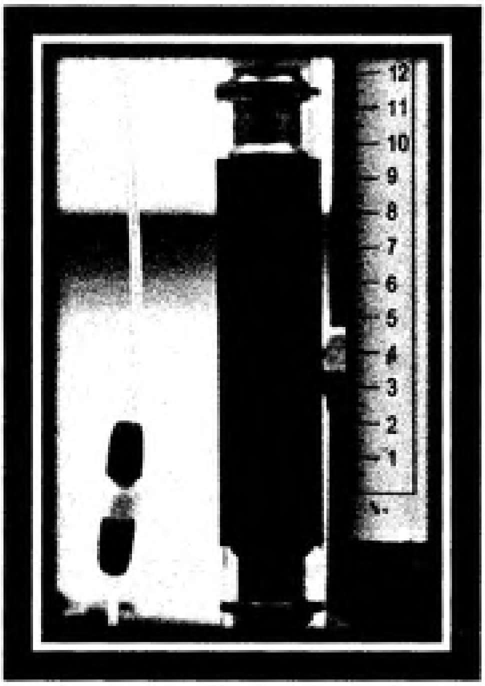

Figure 3.2.6-1: End Stage of Post-Tar Water Flushing

3.2.7 Alkaline Flushing-Stage 5

A 0.35% concentration of a NaOH solution was prepared by the addition of 1.12 g of NaOH pellets and 200 g of deionized water in a 500-mL flask. The mass, the pH and density of the final NaOH solution are shown in Table 3.2.8-1. A total of 200-mL of this alkaline solution was pumped into the Dover (D4) column using the gastight syringe pump. The effluent was collected in pretreated 40-mL centrifuge tubes labeled as D4-AlkaliF1 through D4-AlkaliF15. After the alkaline flushing was completed, the Dover (D4) column was prepped for Stage 6.

Date Batch Prepared	NaOH Concentration	pH	Density (g/cm^3)	Mass of NaOH pellets (g)
6/14/2010 Batch	0.35%±0.025	12.94±0.03	1.00±0.05	1.12±0.08

Table 3.2.8-1: Prepared Alkaline Solution Characteristics

3.2.8 Post-Alkaline Water Flushing-Stage 6

A second water flush was performed on the Dover (D4) soil column with the effluent collected in pretreated 40-mL centrifuge tubes labeled as PAW1-D4 through PAW7-D4. The total volume of water pumped at this stage was 230mL. After the 230 mL of buffered water was pumped, the Teflon tubing was replaced and three pretreated 10-mL vials were used to collect 15-mL of total effluent. The effluent samples were then labeled, wrapped in aluminum foil, and stored in a room maintained at 4°C. After the water effluent was collected for HPLC analysis, the Dover (D4) column was prepped for Stage 7.

3.2.9 Alcohol Flushing-Stage 7

A 70% by volume solution of ethanol and deionized water was prepared in a 1000-mL volumetric flask. After the ethanol-water solution was prepared, a total of 300 mL of ethanol solution was pumped into the column using a gastight syringe and the effluent was collected in pretreated 40-mL centrifuge tubes labeled as D4-AFE#1 through D4-AFE#18. After the effluent samples were collected, the Dover (D4) column was prepped for the final stage of flushing.

3.2.10 Post-Alcohol Water Flushing-Stage 8

A third water flush was performed on the Dover (D4) column after the ethanol flushing stage. A total of 110-mL of buffered water was pumped into the column using a gastight syringe, and the effluent samples were collected in pretreated 40-mL centrifuge tubes labeled as D4-PEWF#1 through D4-PEWF#7. After the column effluent was collected, a final set of three pretreated10-mL vials were used to collect 15 mL of total effluent from the Dover (D4) column for HPLC analysis. The effluent samples were then labeled, wrapped in aluminum foil, and stored in a room maintained at 4°C. After the final stage was completed, the column was disassembled and the remaining soil was extracted from the column and subsequently analyzed to determine the remaining PAH compounds present in the soil. Soil analysis from the Dover (D4) column was performed as followed: soil was extracted from the column and partitioned into four zones equidistant, within one zone; the soil was separated into three centrifuge tubes. Methylene chloride was used to extract residual PAH compounds and the extract collected per centrifuge tube per soil zone was analyzed on the GC for a total of 12 soil extraction samples.

3.2.11 Dover (D4) Column Flushing Summary

Table 3.2.11 summarizes the total volume of fluids pumped at each stage and equivalent pore volumes.

Flushing Stage	Flushing Stage Name	Fluid Pumped	Total Volume Flushed (mL)	Pore Volume (cm^3)
1	Carbon Dioxide	CO_2	N/A	N/A
2	Water Flushing	Buffered Water	226	10.40
3	Tar Flushing	Tar Sample	25.0	1.15
4	Post Tar Water Flushing	Buffered Water	310	14.2
5	Alkaline Flushing	NaOH and buffered water solution	200	9.20
6	Post Alkaline Water Flushing	Buffered Water	230	10.6
7	Ethanol Flushing	70% ethanol by volume	300	13.4
8	Post Ethanol Water Flushing	Buffered Water	110	5.06

Table 3.2.11-1: Dover (D4) Column Flushing Summary

3.3 Analytical Methods

To determine PAH concentrations throughout several stages of the column flushing, sample effluents were collected and analyzed using HPLC and GC methods. The following sections describe these methods.

3.3.1 HPLC Sample Preparation and Analytical Methods

3.3.1.1 Sample Preparation for Analysis

Three 5-mL effluent samples were collected into10-mL vials previously pretreated. A set of 5 calibrations of PAH stock solution ranging from 1.6 ppb-1000ppb, plus two additional calibrations for a 25 mg/L and 5 mg/L naphthalene solution were prepared and analyzed on the HPLC. The internal standard used for the analysis was anthracene-deuterium solution (AD10). All samples were prepared for the HPLC by filtering using a 0.2-µm Polytetrafluoroethylene (PTFE) Filter into 4.0 mL amber vials with a Teflon septum. The samples in the amber vials were analyzed by automatic injection by the HPLC.

3.3.1.2 HPLC Analysis

The column used in the HPLC was a Thermo HYPERSIL green PAH column 100-mm in length and 4.6-mm in diameter. The particle size was 3-um diameter. Table 3.3.1.2-1 summarizes the detected wavelengths for the emission and excitation of the 16 PAH compounds.

Time	Excitation Wavelength (nm)	Emission Wavelength (nm)	PAH Compounds Detected	
0-9.99	270	323	Naphthalene, Acenaphthene, Fluorene	
10.0-13.0	246	383	Phenanthrene, ad10 (HPLC std), Anthracene	
13.01-14.0	282	456	Fluoranthene	
14.01-15.39	336	398	Pyrene	
15.40-20.99	270	390	Benzo (a) Anthracene, Chrysene	
21.0-29.69	300	420	Benzo (b) Fluoranthene, Benzo (k) Fluoranthene, Benzo (a) Pyrene, Dibenz (a, h) Perylene, Benzo (g, h, i) Perylene,	
29.70-34.99	300	500	Indeno (1,2,3 cd) Pyrene	
35.00-45.00	270	323	N/A	

Table 3.3.1.2-1: Detected Wavelengths for the 16 PAH Compounds

3.3.1.3 HPLC Calibration

The PAH calibration curves calculated yielded a linear result. The r-square values for all of the compounds within the stock solution compounds were greater than 99%. The subsequent plot of the calibration curves yield a linear fit with none of the stock compounds deviating from the linear curve. The relative areas of the samples were quantified using the internal standard.

3.3.2 GC Analytical Methods

3.3.2.1 Sample Preparation for Analysis

Effluent samples collected in the pretreated 40-mL centrifuge tubes during the tar, post-tar water flush, alkaline, and post-alkaline column flushes were prepared for GC analysis as follows: a maximum of four 5-mL extractions were performed using methylene chloride. Depending upon the amount of tar extracted, 1-mL of the tar extraction was added to a 10-mL volumetric flask for dilution. A predetermined volume of internal standard for the GC was added to the dilution samples and bought to level with methylene chloride. Small samples of the final dilutions with GC samples were added to 1.5-mL amber vials, capped and analyzed. In addition, triplicates of the sample tar were extracted, diluted and prepared for GC analysis. Ethanol and post-ethanol effluents collected into the pretreated 40-mL centrifuge tubes were extracted for tar and ethanol residue as follow: 80 µL of internal standard injected directly to the effluent samples, 3-mL of methylene chloride, and 10-mL of deionized water. The centrifuge tubes were manually shaken vigorously for approximately 5 minutes. Subsequently, a maximum of three 3-mL extractions were performed and added directly to a 10-mL volumetric flask. The 10-mL flask was then bought to 10 mL using methylene chloride. For the sample extractions taken during the ethanol and post-ethanol flushes, the internal standard allowed for correction for partial extraction.

3.3.2.2 GC Methods

The column used in the GC was an Equity-5 Fused Silica Capillary Column (dimensions: 30-m by 0.25-mm with a film thickness of 0.5-μm). The initial temperature was 40°C for two minutes. The detector temperature was 310°C, while the inlet temperature was at 300°C. The temperature of the oven increased at a rate of 4.0°C/min with final temperature reached at 310°C for a period of seven minutes. No splitless injection occurred during sampling and the carrier gas was helium.

3.3.2.3 GC Calibration

The internal standard used for the GC was prepared from a compound stock solution of PAH compounds. Six calibration standards ranging in concentrations from 0.3 mg/L to 100 mg/L were prepared and run on the GC. The r-square values of the compounds in the stock solution were 99.5% and higher for the compounds analyzed. The linear response was achieved for the compounds in the stock compounds by plotting the log concentration versus log area for several key compounds. The relative areas of the samples (from tar flush through post-alkaline water flushes) were quantified using the internal standard.

3.4 pH Measurement Calibrations

The pH for the tar, post-tar water, alkaline, and post-alkaline water flushes (stages 3-6) effluents were measured. Two sets of calibrations were performed on the pH meter. For the tar and post-tar water flush effluents, the pH meter was calibrated using three buffers at pHs of 4, 7, and 10 respectively. The calibration of these three buffers yielded a slope of 99.5%. For all alkaline and post-alkaline water samples, the pH meter was recalibrated using three buffers at pHs of 7, 10, and 13 respectively. The calibration of this set of buffers yielded a slope of 99.2%.

4. Results and Discussion

4.1 Overview

In this section, the effectiveness of alkaline-flushing for the remediation of residual coal tar contamination will be evaluated through qualitative and quantitative measures of an experiment performed as detailed in Section 3. In Section 4.2, several column snapshots are highlighted demonstrating the transformations of the Dover (D4) Column during all eight of the flushing stages. In sections 4.3 and 4.4, tabular and graphical results are provided showing the changes in the PAH compounds within the coal tar at several flushing stages. The HPLC analysis provides a tabular output of the concentrations of the 15 PAH compounds detected in the triplicate water effluent samples. The GC analysis focused on three compounds (naphthalene, benzo(a)pyrene, and phenanthrene) to track concentration and mass in the changes. These three compounds were primarily selected because of their designation by the EPA as apart of the 16 PAH Priority Pollutants.

4.2 Dover 4 Tar Saturation and Reduction

Figures 4.2-1 through 4.2-4 shows the progression of the tar within the column during the various flushing stages. Proceeding from left to right the first row of images shows the column state after the tar flush, post-tar water flush, and initial alkaline flushing stages, respectively. Figure 4.2-2 and Figure 4.2-3 shows the tar propagation throughout the duration of the alkaline flushing. Figure 4.2-4 shows the Dover (D4) column after the post-alkaline flushing, ethanol flushing and post-ethanol water flushing stages, respectively. Qualitatively, one observes a tar line moving through the column and a subsequent reduction of the tar in the column by the last picture in Figure 4.2-3. The definitive tar line movement can be observed in Figure 4.2-2 and 4.2-3, corresponding to the various stages of the alkaline flushing of the column.

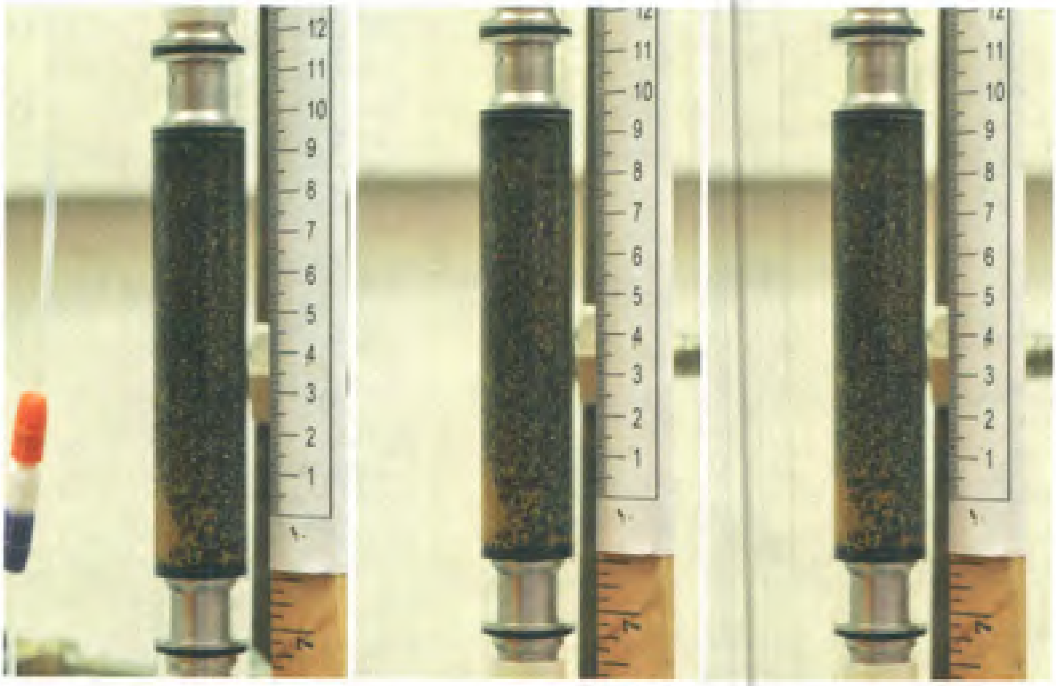

Figure 4.2-1: Pre-Alkaline Flushing of Dover (D4) Column

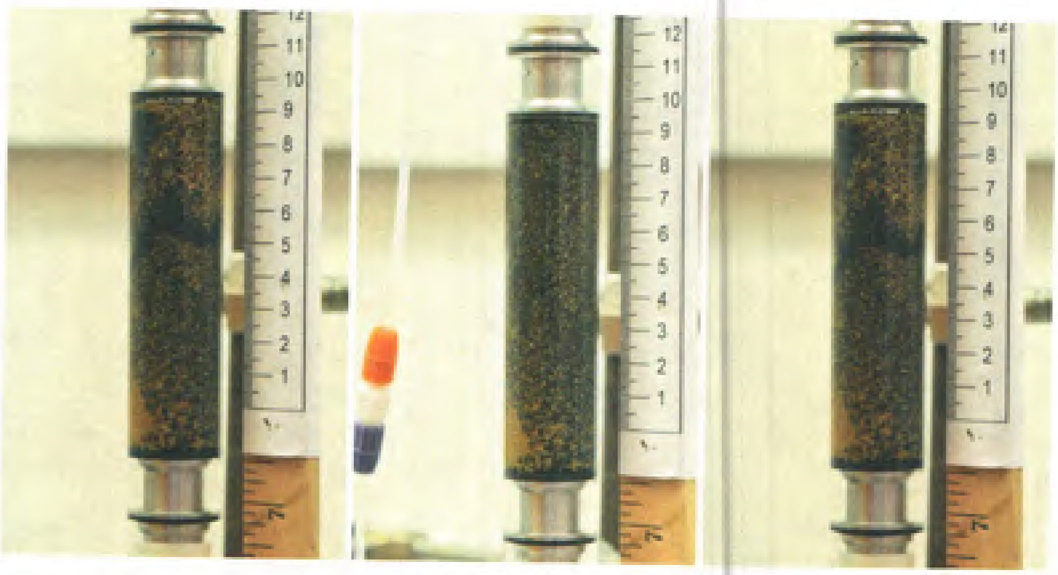

Figure 4.2-2: Alkaline Flushing of Dover (D4) Column

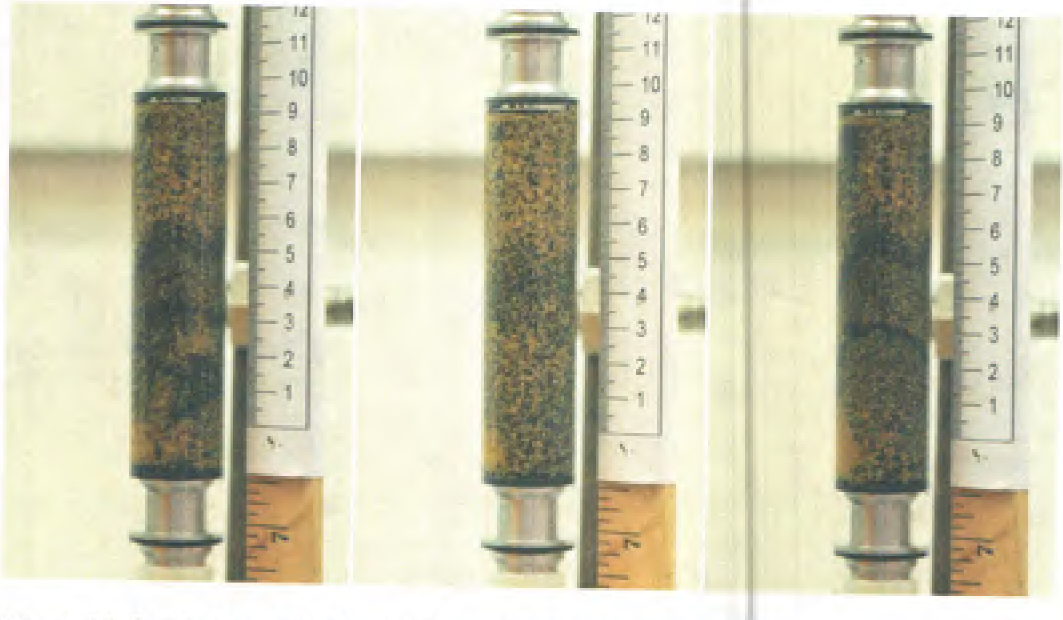

Figure 4.2-3: Alkaline Flushing of Dover (D4) Column-End Stages

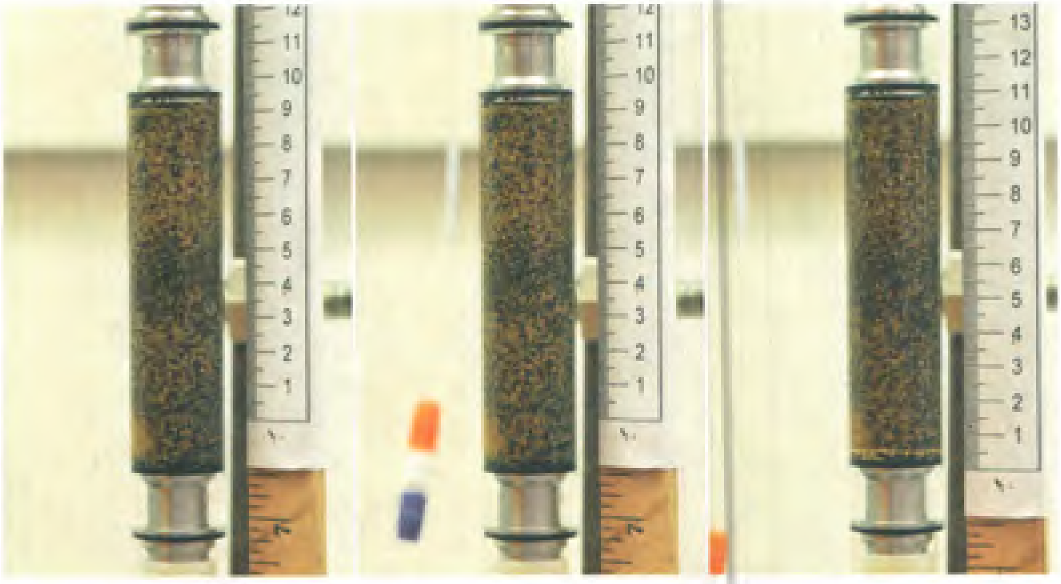

Figure 4.2-4: Post Alkaline Flushing of Dover (D4) Column

4.3 HPLC Results

Tables 4.3-1 through 4.3-3 summarize all concentration data determined for the triplicate water effluents sampled at three particular stages of the column flushing. The PAH compound(s) with the highest concentration after the post tar water flush was naphthalene, acenaphthene, benzo(b)fluoranthene, and indeno(1,2,3 cd) pyrene. Tracking concentration changes with these four compounds for the rest of the triplicates show a moderate decrease in concentration in the last set of triplicates for the post-ethanol water flushing. The concentrations of the four compounds after the post water alkaline flushing did not show any consistent trends. This could have been due to changes in the nature of the complex mixture source.

	PAH Compound	D4-PTWF4: PAH Concentration (mg/mL)	D4-PTWF5: PAH Concentration (mg/mL)	D4-PTWF6: PAH Concentration (mg/mL)
1	Naphthalene	1.52E-02	1.40E-02	1.51E-02
2	Acenaphthene	2.23E-04	2.04E-04	3.02E-04
3	Fluorene	1.37E-04	1.23E-04	1.90E-04
4	Phenanthrene	1.44E-04	1.22E-04	1.42E-04
5	Anthracene	2.92E-05	2.43E-05	2.93E-05
6	Fluoranthene	1.13E-05	9.64E-06	1.25E-05
7	Pyrene	1.26E-05	7.63E-06	9.62E-06
8	Benzo(a) anthracene	8.12E-07	1.27E-06	6.32E-07
9	Chrysene	1.01E-06	1.00E-06	4.49E-07
10	Benzo(b) fluoranthene	3.16E-06	3.83E-04	3.02E-04
11	Benzo(k)fluoranthene	3.75E-07	4.07E-07	4.43E-08
12	Benzo(a)pyrene	6.62E-07	5.49E-07	2.03E-06
13	Dibenz(a,h) anthracene	1.55E-06	2.33E-06	1.76E-06
14	Benzo(g,h,i) perylene	6.13E-07	5.09E-07	1.31E-06
15	Indeno(1,2,3 cd)pyrene	6.49E-05	8.39E-05	5.25E-05

Table 4.3-1: Post Tar Water Flushing PAH Concentrations

	PAH Compound	D4-PAF1: PAH Concentration (mg/mL)	D4-PAF2: PAH Concentration (mg/mL)	D4-PAF3: PAH Concentration (mg/mL)
1	Naphthalene	1.37E-02	1.50E-02	1.38E-02
2	Acenaphthene	2.21E-04	3.08E-04	2.76E-04
3	Fluorene	1.41E-04	1.63E-04	1.78E-04
4	Phenanthrene	1.86E-04	1.56E-04	1.41E-04
5	Anthracene	3.40E-05	3.31E-05	2.96E-05
6	Fluoranthene	3.17E-05	4.61E-05	5.16E-05
7	Pyrene	3.03E-05	1.58E-05	1.35E-05
8	Benzo(a) anthracene	6.33E-06	2.55E-06	2.76E-06
9	Chrysene	6.07E-06	1.80E-06	2.20E-06
10	Benzo(b) fluoranthene	4.74E-06	9.23E-07	9.91E-07
11	Benzo(k)fluoranthene	2.43E-06	8.18E-07	8.16E-07
12	Benzo(a)pyrene	4.67E-06	1.83E-06	1.90E-06
13	Dibenz(a,h) anthracene	1.40E-06	1.60E-06	1.67E-06
14	Benzo(g,h,i) perylene	2.81E-06	1.75E-06	1.68E-06
15	Indeno(1,2,3 cd)pyrene	3.05E-06	1.66E-06	2.11E-06

Table 4.3-2: Post-Alkaline Water Flushing PAH Concentrations

	PAH Compound	D4-PEF1: PAH Concentration (mg/mL)	D4-PEF2: PAH Concentration (mg/mL)	D4-PEF3: PAH Concentration (mg/mL)
1	Naphthalene	8.49E-04	5.94E-04	4.35E-04
2	Acenaphthene	6.09E-05	5.22E-05	4.45E-05
3	Fluorene	5.05E-05	4.28E-05	3.60E-05
4	Phenanthrene	1.09E-04	8.19E-05	6.81E-05
5	Anthracene	3.12E-05	2.49E-05	2.12E-05
6	Fluoranthene	4.18E-05	2.66E-05	2.19E-05
7	Pyrene	4.08E-05	2.51E-05	2.06E-05
8	Benzo(a) anthracene	1.33E-05	6.08E-06	4.54E-06
9	Chrysene	1.36E-05	9.36E-06	4.04E-06
10	Benzo(b) fluoranthene	8.92E-06	3.77E-06	2.19E-06
11	Benzo(k)fluoranthene	4.43E-06	2.15E-06	1.29E-06
12	Benzo(a)pyrene	9.10E-06	4.94E-06	2.93E-06
13	Dibenz(a,h) anthracene	3.11E-06	1.63E-06	1.62E-06
14	Benzo(g,h,i) perylene	5.50E-06	3.25E-06	1.23E-06
15	Indeno(1,2,3 cd)pyrene	5.01E-06	4.13E-06	2.29E-06

Table 4.3-3: Post-Ethanol Water Flushing PAH Concentrations

4.4 GC Results

4.4.1 Tar Saturation Changes in the Dover (D4) Column

Figure 4.4.1-1 shows the tar saturation reduction within the Dover (D4) column. The starting tar saturation within the column was 74%. The column saturation was reduced to 36% by the end of post-tar water flushing stage. The alkaline flushing stage reduced the tar saturation remaining in the Dover (D4) column from 36% to 19%. The end Dover (D4) saturation after the post-alkaline water flush was 18.3%. This signifies that the alkaline flushing removed approximately 50% of the tar mass from the column.

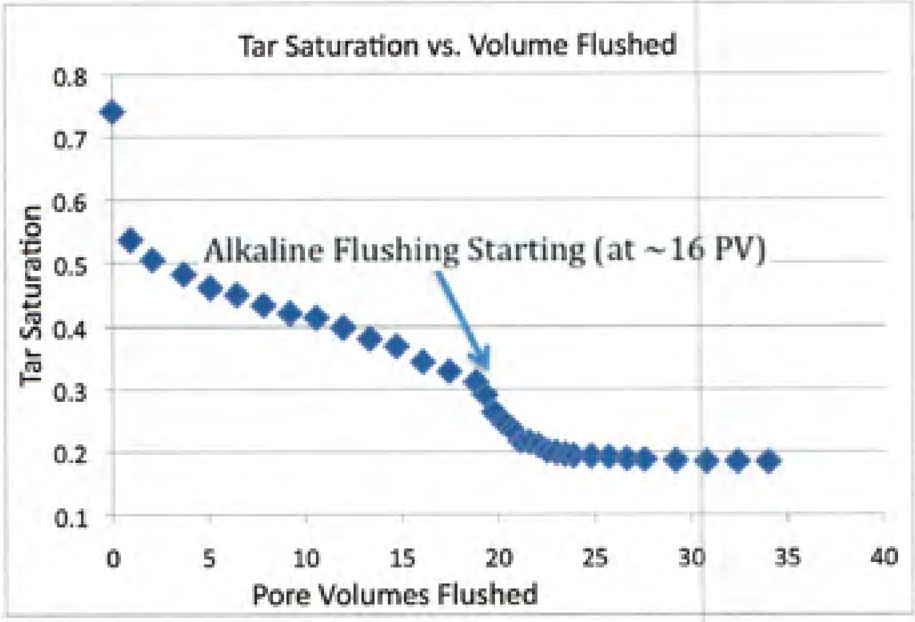

Figure 4.4.1-1: Tar Saturation vs. Volume Flushed

4.4.2 Residual Mass of Selected PAH Compounds

Figure 4.4.2-1 shows four selected PAH compounds (naphthalene, phenanthrene, benzo(a)pyrene, and pyrene through several stages of the Dover (D4) column flushing. The fractional removal of benzo(a)pyrene and naphthalene mass during the alkaline flushing stage was 0.42 (42%) and 0.56(56%) respectively. The fractional removal of phenanthrene and pyrene during the alkaline flushing stage was 0.79 (79%) and 0.73 (73%) respectively. The reduction in the remaining PAH compounds in the Dover (D4) column shows similar mass reductions. This is a good indication of the potential of alkaline flushing in tar reduction. The additional reduction of the residual PAH compounds during the ethanol flushing were inconsistent for several compounds. This was likely due to the small amounts of tar observed to exit the column by the ethanol flushing stage. In addition, the increase in error of the ethanol samples were due to several issues such as the difficulty in separating the ethanol, tar, and water effluents in methylene extractions for GC analysis. From preliminary analysis of several compounds, it appeared that the use of ethanol flushing might not have increased PAH compounds exiting the column. Since higher percentages were observed to occur during the alkaline flushing, a better focus on using optimum alkaline solutions and/or surfactants might yield higher reductions in PAH compounds from a tar saturated column.

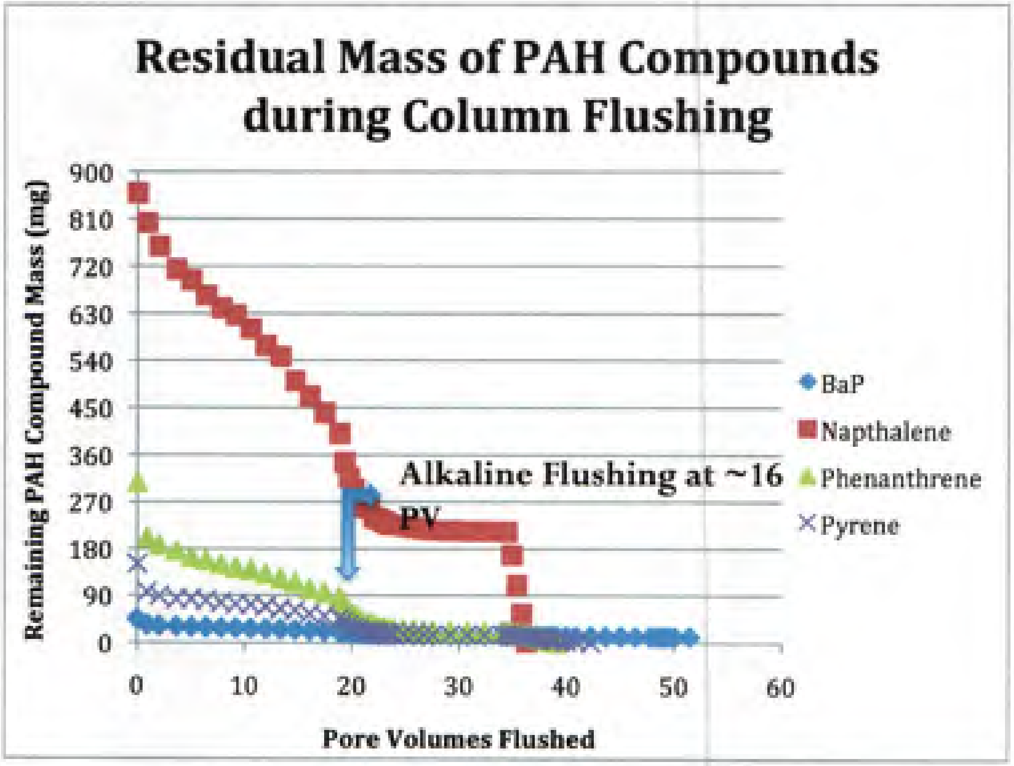

Figure 4.4.2-1: Selective PAH Compound Mass Residual Per Flushing

4.5 IFT and pH Alkaline Data

4.5.1 IFT Data

The interfacial tensions measured for several concentrations of NaOH are shown in Figure 4.5.1-1. The lowest IFT obtained should correlate to the optimal NaOH concentration needed to achieve desired tar mobilization.

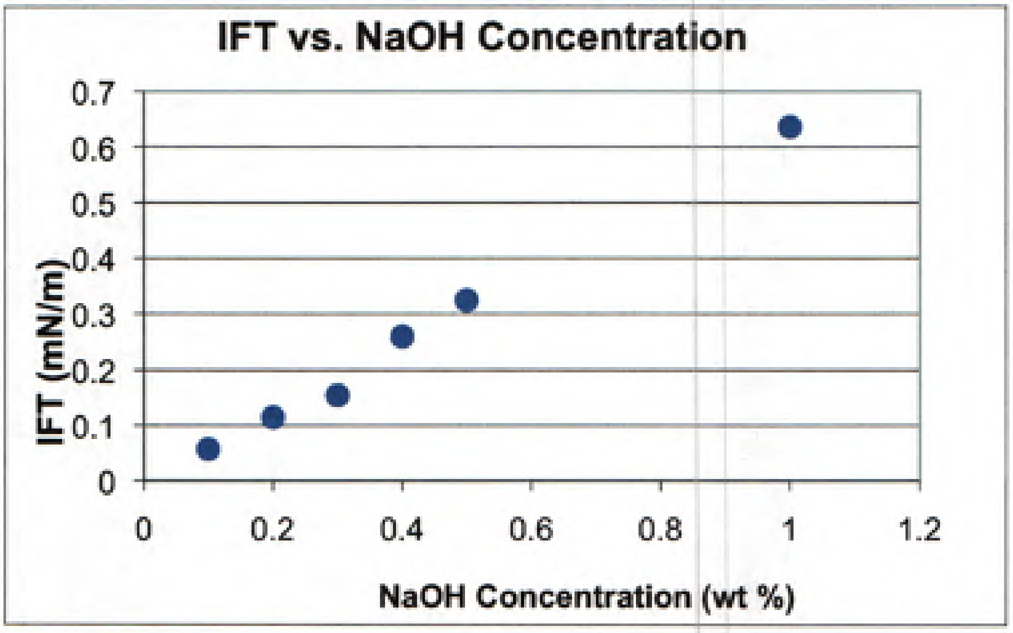

Figure 4.5.1-1: IFT vs. NaOH Concentration

4.5.2 pH Alkaline Data

Figure 4.5.2-1 shows the pHs for the tar, post-tar water, alkaline and post-alkaline water flushes as a function of the amount of pore volumes flushed into the column. The sample effluents prior to the alkaline wash had pH values near the 7.0 thresholds. A sudden spike in pH occurs with the first alkaline sample effluent. The highest pH measured in the alkaline effluent samples was 12.84.

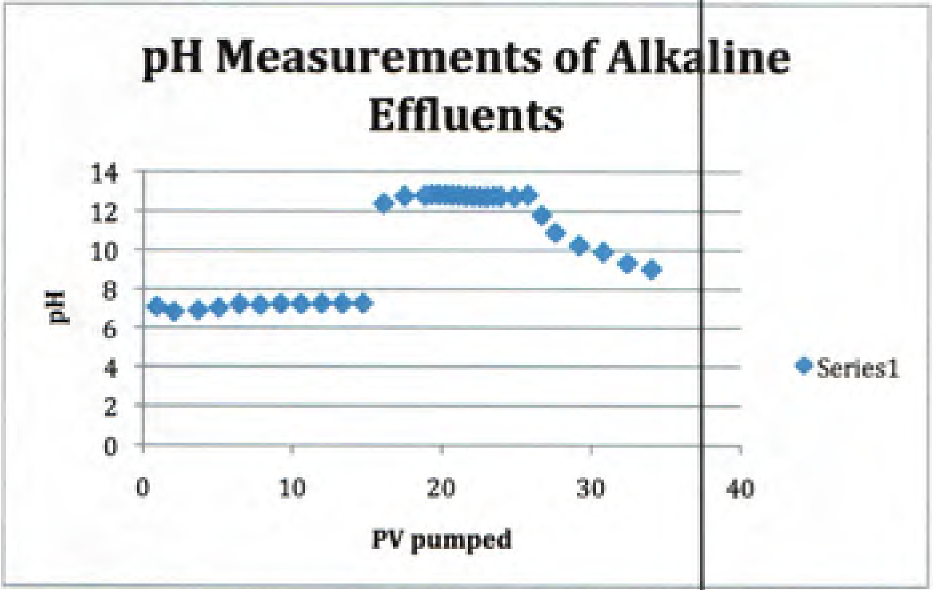

Figure 4.5.2-1: pH Measurements of Alkaline Effluents

4.6 Soil Extraction Data

Table 4.6-1 shows preliminary findings of the remaining concentrations in the extracted soil from the Dover (D4) column. The sum of the total mass of PAH compounds remaining in the extracted soil was 83.7mg. The initial mass of PAH compounds present in the Dover (D4) was 3.94g. The low presence of the total mass of PAH compounds in the extracted soil shows promising results of the effectiveness in alkaline flushing in remediating coal tar contaminated soils.

Dover 4(D4) Column	
Compound	Total Mass (mg)
Indane	0.69
Indene	5.12
Naphthalene	0.51
Benzo(b)thiophene	0.66
2-Methylnaphthalene	0.98
1-Methylnapthalene	0.51
Biphenyl	0.86
2-Ethylnaphthalene	0.51
Acenaphthylene	4.75
Acenaphthene	0.88
Dibenzofuran	0.19
Fluorene	0.85
Dibenzothiophene	0.89
Phenanthrene	4.93
Anthracene	3.26
Carbazole	0.22
Fluoranthene	7.52
Pyrene	10.76
Benzo(a)anthracene	7.06
Triphenylene/chrysene	6.72
Benzo(b)fluoranthene	5.71
Benzo(k)fluoranthene	5.08
Benzo(a)pyrene	6.46

Indeno(1,2,3-CD)pyrene	4.33
Dibenz(a,h)anthracene	1.14
Benzo(ghi)perylene	3.09

Table 4.6-1: Dover (D4) Extracted Soil Concentrations

5. Conclusions

5.1 Summary, Implications, and Future Work

Based on the preliminary findings with the Dover (D4) column, alkaline flushing has the potential to be a promising technique in continuing efforts to remediate tar contaminated subsurface sites. The initial tar saturation of the column was 74% and end saturation up to the post alkaline water flushing stage was ~18%. Decreasing concentrations and presence of several key priority pollutant PAH compounds were demonstrated qualitatively and quantitatively. Further reductions of several PAH compounds seem to occur with the additional ethanol flushing.

Further column tests will be conducted to attempt to replicate results obtained from the Dover (D4) column. Additional column test runs will be conducted to observe what types of effects occur between the interactions of the Dover sand and glass column with prepared alkaline solutions. These additional column runs are necessary in determining how the altering of the pH of various alkaline solutions prepared prior, during, and after pumped into the column. Once a better understanding of the alkaline flushing effects on the sand and glass column are verified, additional experiments will be conducted into the ranges of lower and higher concentrations that would be compatible in solution with surfactants, cosurfactants and polymer floods to further reduce tar residual within several glass columns through IFT experiments.

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