Feasibility of Remediating Manufactured Gas Plant Tar in Fractured Bedrock

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ABSTRACT

Remediation of residual manufactured gas plant (MGP) tar in fractured bedrock is widely recognized as a challenge, and some lead agencies may require responsible parties to evaluate or implement source-reduction technologies for residual tar. Evaluating and implementing remedies can often be a process of trial and error that can be associated with significant costs and limited effectiveness. To improve this process, a set of metrics was developed as a proof-of-concept approach for evaluating the potential effectiveness of source-reduction technologies for MGP tar in fractured bedrock. The approach can potentially streamline remedy evaluation and allow for a quantitative assessment of technology effectiveness in place of the more typical trial-and-error approach.

The results of this analysis for a range of generic site conditions and MGP tar properties demonstrate that three commonly considered source-reduction technologies—water flooding, surfactant or solvent flushing, and thermal technologies—have limited effectiveness and, in some cases, may be counterproductive.

Keywords

Dense nonaqueous phase liquid (DNAPL)
Fractured bedrock
Manufactured gas plant (MGP) tar
Surfactant and cosolvent flushing
Thermal treatment
Water flooding

EXECUTIVE SUMMARY

Introduction

Remediation of residual manufactured gas plant (MGP) tar in fractured bedrock is widely recognized as a challenge, and some lead agencies may require responsible parties to evaluate or implement source-reduction technologies for residual tar. Evaluating and implementing remedies can often be a process of trial and error that can be associated with significant costs and limited effectiveness. To improve this process, a set of metrics was developed as a proof-of-concept approach for evaluating the potential effectiveness of source-reduction technologies for MGP tar in fractured bedrock. The approach can potentially streamline remedy evaluation and allow for a quantitative assessment of technology effectiveness in place of the more typical trial-and-error approach.

Research Overview

A quantitative framework was developed by identifying dimensionless numbers (or metrics) that characterize the ratio of physicochemical processes that control tar mobility in fractured rock (such as drag forces, capillary forces, and buoyancy). These metrics have been shown to correlate with the magnitude of residual nonaqueous phase liquid saturation in a variety of settings, including in fractured bedrock. Variables that are used to calculate the identified metrics include data that can be readily measured at MGP sites or that are available as tabulated values in the open literature. Relationships are then used to show how the controlling variables (and therefore the metrics) change when a given technology is applied, allowing for an assessment of the extent to which residual tar saturation might be reduced. For example, when water flooding is applied at a site, the primary change that occurs is an increase in the drag force on residual tar, changing the balance between mobilizing and resisting forces that control tar mobility. Based on the magnitude of changes that can be achieved by a given technology, the approach can be used to evaluate the extent to which tar saturation might be reduced. On this basis, the approach can be used to screen potentially relevant technologies for reducing residual tar saturation within a quantitative and physically based framework.

Conclusions

The results of this analysis for a range of generic site conditions and MGP tar properties demonstrate that the following commonly considered source-reduction technologies (water flooding, surfactant or solvent flushing, and thermal technologies) have limited effectiveness and, in some cases, may be counterproductive:

- Water flooding is unlikely to increase residual tar mobility above the point of initial mobilization; therefore, it cannot be considered as a feasible approach to reduce residual tar saturation.
- Flushing solutions that include surfactants, cosolvents, and strong bases (such as sodium hydroxide) have potential to increase tar mobility. However, high concentrations (on the order of 10%) of surfactants or solvents might be required, and the technology may still mobilize only a small fraction of the residual tar. Furthermore, applying surfactants has potentially negative consequences, such as the possibility of changing the tar to a wetting fluid (causing it to stick to fracture walls) or of causing undesirable migration of tar to locations where it might be even more difficult to remediate. Removal of tar through

enhanced solubility in the presence of surfactants could be evaluated in future work. These and other potential complicating factors should be carefully considered to assess whether surfactant flushing would actually be effective at a given site.

- Heating technologies have only negative effects on residual tar mobility in fractured rock. Temperatures that are high enough to destroy the tar or volatilize a significant fraction generally cannot be achieved below the water table. Increasing the temperature changes water and tar properties in ways that reduce tar mobility and also cause bedrock to thermally expand, which causes fractures to close. These combined effects severely reduce tar mobility as temperature increases.

This analysis should be considered as a hypothetical best-case potential for technology effectiveness, because it was assumed that subsurface tar was fully delineated and accessible to the evaluated technologies. When considering application of any technology at an MGP site, additional factors must be considered, such as whether it is possible to accurately locate MGP tar in the subsurface and whether treatment fluids can be effectively delivered to fractures with entrapped tar. For example, for flushing solutions to be effective, the total fracture volume must be flushed with the treatment solution many times to achieve a high degree of removal. In narrow or dead-end fractures, such a high degree of flushing might not be achievable.

These findings are consistent with available research on MGP tar remediation in laboratory experiments. From the idealized, process-based considerations evaluated in this report, none of the available technologies would be clearly beneficial for reducing residual MGP tar saturation in fractured bedrock settings.

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INTRODUCTION

Remediating dense nonaqueous phase liquids (DNAPLs) in bedrock is a challenge at many sites in the US, including manufactured gas plants (MGPs) where MGP tar (MGP byproducts inclusive of coal tar and other types of tar generated by MGP processes) might be present in the subsurface. In consideration of these challenges, EPRI published a technical update in 2014 that qualitatively evaluated remediation technologies potentially applicable to remediating MGP tar in bedrock and compiled a list of sites that have previously dealt with tar in bedrock [1]. The overall findings of that prior analysis were that none of the available technologies were technically appropriate for remediating tar in bedrock and, consistent with that finding, few sites had implemented available technologies for source reduction. Thus, it was concluded that remediation of MGP tar in fractured bedrock was technically impracticable and other methods (e.g., containment and exposure control) are the most appropriate options.

1.1 Objectives and Scope of the Analysis

This report builds upon the qualitative evaluation [1] of the feasibility of remediating MGP tar in bedrock by developing a quantitative framework that can be used up front in the remediation process to screen technologies with respect to their potential effectiveness in remediating residual MGP tar in bedrock via source reduction. The analysis is a proof-of-concept, in that a range of representative technologies are evaluated rather than the entire panoply of potential remediation options. The framework is also developed with respect to key metrics that describe tar mobility, and it is acknowledged that other metrics could potentially be developed to further extend this approach to consider all relevant aspects of tar remediation in bedrock.

The scope of this analysis is limited to the following general classes of remediation technologies (discussed further in Section 2.1), which might be considered for the purposes of remediating residual MGP tar in fractured rock:

- Water flooding
- Surfactant and cosolvent flushing
- Thermal treatment technologies
- An example with a combination of these technologies

These technologies are evaluated in a quantitative framework with respect to the physical and chemical phenomena that affect their suitability for remediating residual MGP tar in fractured rock. The focus is on residual rather than mobile tar, since the former presents a more difficult challenge and likely plays a larger role in terms of long term site management and closure. Moreover, conventional remediation technologies (e.g., passive collection wells) can remove mobile tar to some extent, ultimately leading to the question of how to deal with the residual fraction, which is not amenable to removal by technologies that can address mobile tar. We also do not address some technologies that are more often used as polishing steps in groundwater remediation, such as *in situ* chemical oxidation (ISCO). ISCO and other technologies could be evaluated in the future with similar approaches to those described in this report.

1.2 Summary of Findings

The following key findings summarize the results of the quantitative framework used to evaluate technology effectiveness:

- Water flooding is not promising as an effective technology. The technology is unlikely to increase residual tar mobility above the point of initial mobilization and hence cannot be considered as a feasible approach to reduce residual tar saturation.
- Flushing solutions that include surfactants, cosolvents, and strong bases (i.e., NaOH) have potential to increase tar mobility. Each of these technologies has limited effectiveness when implemented on its own, but recent research suggests that combinations of these technologies could potentially have greater effectiveness [2]. However, very high solvent concentrations (e.g., on the order of 10%) might be required and the magnitude of N_T potentially achievable may still only mobilize a small fraction of the residual tar. Furthermore, there are also potential negative consequences of applying surfactants, such as potentially changing the tar to a wetting fluid (causing it to stick to fracture walls) and undesirable migration of tar to locations where it might be even more difficult to remediate. Removal of tar via enhanced solubility in the presence of surfactants could be evaluated in future work. These and other potential complicating factors would need to be carefully considered to assess whether surfactant flushing would actually be effective at a given site.
- Heating technologies have only negative effects on residual tar mobility in fractured rock. Temperatures high enough to destroy the tar or volatilize a significant fraction generally cannot be achieved below the water table. Increasing the temperature changes water and tar properties in ways that reduce tar mobility and also cause bedrock to thermally expand, which causes fractures to close. These combined effects severely reduce tar mobility as temperature increases.

In the above summary, it was assumed that the bedrock fractures and spatial distribution of tar have been fully characterized and that it is physically possible to access residual tar with the evaluated technologies. Thus, our analysis should be considered as a hypothetical “best-case” potential for technology effectiveness. When considering application of any technology at a real MGP site, additional factors must be considered, such as the ability to accurately locate MGP tar in the subsurface and whether treatment fluids can be effectively delivered to fractures with entrapped tar. For example, in order for flushing solutions to be effective, the total fracture volume must be flushed with the treatment solution many times to achieve a high degree of removal. In narrow or dead-end fractures, such a high degree of flushing might not be achievable.

The findings above are consistent with available research on MGP tar remediation in laboratory experiments. From the idealized process-based considerations evaluated in this report, none of the available technologies would be clearly beneficial for reducing residual MGP tar saturation in fractured bedrock settings.

2

APPROACH FOR SCREENING REMEDIATION TECHNOLOGIES FOR MANUFACTURED GAS PLANT TAR

This section provides an overview of the approach used to select and evaluate potentially relevant technologies for source reduction of MGP tar. First, potentially viable technologies are screened to rule out those that are not applicable to MGP tar and identify the relevant technologies for this evaluation. For example, the composition of MGP tar, which is dominated by semi-volatile compounds, is not amenable to some phase-change technologies that are designed to convert liquid DNAPLs to vapors. Then, the general behavior of MGP tar in fractured-rock aquifers is introduced with two key concepts that are important for the current evaluation—tar wettability and the difference between mobile and residual tar. Lastly, the quantitative approach to evaluating technologies is discussed, including the metrics that can be used to evaluate the potential effectiveness of a given technology. The data required to calculate these metrics can be acquired from tabulated data on MGP tar and fractured-rock aquifers or from site-specific data.

2.1 Classes of Remediation Technologies Evaluated

Remediation technologies that can remove or destroy entrapped tar from fractured-rock aquifers[1] can be divided into the following three categories:

- **Mobilization approaches:** These technologies alter the balance between the mobilizing and retaining forces, with the goal of trying to force residual tar to become mobile;
- **Phase-change approaches:** These technologies are based on changing the physicochemical state of tar, such as enhancing the solubility of tar or changing it from the liquid phase to the gaseous phase; and
- ***In situ* degradation approaches:** These technologies use chemical reactants or microorganisms to destroy the tar in place.

Considering the properties of MGP tar and the limitations of some approaches, not all available technologies are relevant for addressing residual tar in fractured rock. For example, given the high boiling point of some PAH compounds that comprise a large portion of MGP tar, volatilization based technologies are not a viable choice. In addition, *in situ* degradation approaches (e.g., *in situ* chemical oxidation [ISCO]) are generally used as polishing steps after another technology has been implemented. Thus, the use of ISCO to destroy large quantities of residual tar is also unlikely to be viable.

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[1] The same technologies also apply to porous media such as soils and unconsolidated aquifers.

For the purposes of this report, we have identified the following technologies as potentially applicable as tar source-reduction technologies, which are the focus of the remainder of this report:

- **Water flooding:** Involves injection of water to mobilize tar through hydraulic forces. The mobilized tar is removed via extraction wells [1];
- **Surfactant/solvent flushing:** Enhanced tar removal can potentially be achieved by flushing the tar containing zone within an aquifer with chemical additives such as surfactants and solvents. The injected chemicals potentially enhance tar removal by either increasing tar dissolution (solvents) or changing tar-water surface properties (surfactants). The mobilized tar is recovered via an active recovery system [3];
- **Thermal technologies:** Injection of hot water or steam or the placement of heating apparatus (thermal conduction elements or electrical resistance heating) can be used to enhance hydraulic displacement of tar. The efficiency of the hydraulic displacement caused by thermal treatment depends on the thermal changes in organic phase viscosity, interfacial tensions, and wettability conditions [3]. Similar to other mobilization methods, an active recovery system is needed to capture the displaced tar; and
- **The combination of heating and cosolvent flushing:** A combination of different treatment technologies may be implemented at a site to maximize tar removal [1]. As a hypothetical example, the combination of thermal treatment and cosolvent flushing is evaluated. The potential application of this combination has been explored by other researchers, as well (e.g., Kong [4]).

2.2 Overview of Manufactured Gas Plant Tar Behavior in Fractured-Rock Aquifers

MGP tar is generally classified as a DNAPL. DNAPLs are denser-than-water liquids, which do not mix with water and have a limited solubility in water. In cases where they enter a fractured-rock aquifer, DNAPLs tend to sink downward as a separate liquid phase through the surrounding groundwater. Their subsequent migration and physical behavior are governed by the physics of multiphase flow in fractured media [5]. The multiphase flow behavior is substantially more complex than the more common cases of dissolved contaminant migration through groundwater. While a general description of multiphase flow is described in detail elsewhere (e.g., Interstate Technology and Regulatory Council [5]), two key aspects of tar migration that are important for the current analysis are introduced below—i.e., tar wettability and the difference between mobile and residual tar.

When two immiscible fluids (e.g., MGP tar and water) are present in a fracture, the difference between the surface tensions of materials typically results in one of the fluids spreading over the fracture surface and the other filling the space between the fracture walls (see Figure 2-1a). The fluid that spreads over the surface is called the *wetting phase* and the fluid that fills the space between the fracture walls is called the *non-wetting phase* [6]. In cases where tar and water are present in a fracture, tar is often the non-wetting fluid; however, this is not always the case. Interfacial tensions and wettability of tar may change when tar is pushed (i.e., advances or recedes) along a fracture, or when the tar's chemical properties are altered by a change in the groundwater pH or the introduction of surfactants [7]. These chemical changes can cause tar to become the wetting fluid (i.e., stick to the fracture walls) instead of water.

Figure 2-1 schematically illustrates a single fracture with residual tar present in the wetting and non-wetting conditions. This distinction is critical for evaluating remediation options, since tar can potentially be pushed out of fractures under water-wet conditions (if mobilizing forces are large compared to resistive forces) but cannot be pushed under tar-wet conditions.

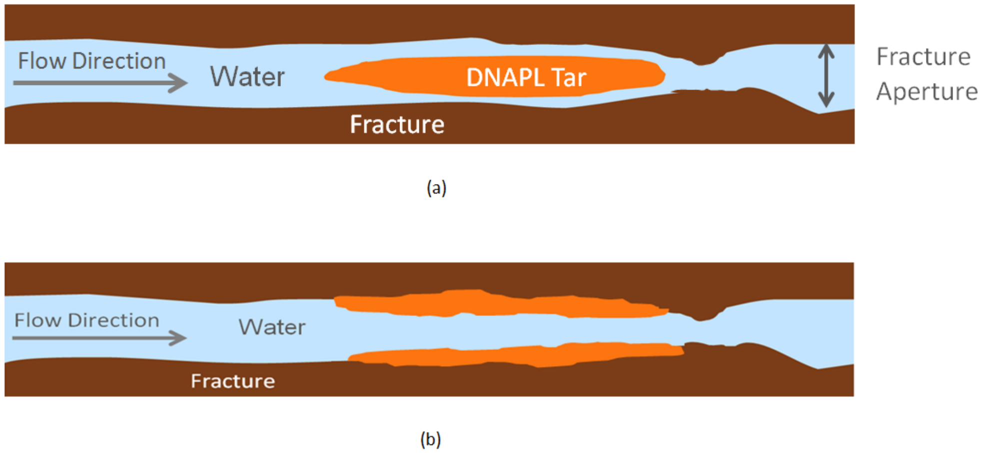

Figure 2-1
Tar and water concurrently present in a single fracture when (a) water is the wetting fluid and (b) tar is the wetting fluid

Tar can be present in fractures as either a mobile or residual form. *Mobile tar* refers to cases where the tar readily migrates under natural (e.g., gravity) or applied (e.g., active or passive extraction wells) pressure gradients, sometimes referred to as *free-flowing tar*. Under free-flowing conditions, tar is mobile and a conventional DNAPL recovery system can potentially reduce tar saturation. After free-flowing tar has been removed, however, the tar breaks into discontinuous pools or globules surrounded by water. In this case, the discontinuous tar pools/globules do not flow and are entrapped in the fracture network. The entrapped tar, also known as *residual tar*, is not generally recoverable by gravity drainage or conventional pumping approaches. Further, the residual saturation of MGP tar in porous or fractured media can be as high as 20% to 30% of void spaces in the media [8, 9]. Thus, even if mobile tar is removed, there may still be a substantial amount of tar present in the residual form.

2.3 Approach for Evaluating Technologies for Removing MGP Tar from Fractured-Rock Aquifers

Technologies have been developed to remove DNAPLs (such as MGP tar) from aquifers, although there is already recognition that these technologies have limited effectiveness, especially in fractured-rock aquifers [1, 3]. A prior EPRI study determined that available source-reduction technologies are unlikely to be effective for residual MGP tar in fracture rock, based on prior experience at MGP sites and a qualitative evaluation of available technologies [1]. Although that qualitative evaluation of technologies suggested major limitations, few of the identified source-reduction technologies had been implemented at MGP sites with tar in fractured bedrock. Thus, there is a question as to whether there are technologies that have not been tried at an MGP site that could potentially be effective. In this report we address this question using a quantitative analysis to evaluate how the application of different remediation technologies affects the mobility of MGP tar. To accomplish this goal, we use a dimensionless number analysis, which is a problem solving technique that first identifies the governing processes of a physicochemical phenomenon, and then uses ratios of these governing processes to determine how changes to the aquifer/tar will alter the mobility of MGP tar. This section discusses those governing processes and the dimensionless numbers (or scoring metrics) that are used to evaluate the identified technologies.

The mobility of entrapped tar in a fracture depends on the magnitude and direction of all forces acting on the tar. Figure 2-2 schematically shows an entrapped tar globule in a pore/fracture.

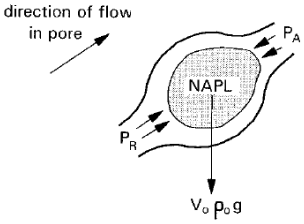

Figure 2-2
Schematic diagram showing forces acting on a single, entrapped dense nonaqueous phase liquid pool

The following forces control the potential mobility of residual MGP tar:

- **Buoyant force:** Controls the tendency of tar to float or sink, a function of the difference between the densities of water and MGP tar (depends on temperature and tar composition).
- **Viscous force:** A function of the friction between the flowing water and immobile tar that pushes the entrapped tar in the direction of the flowing water. The magnitude of the viscous force depends on the velocity and viscosity of the flowing water.
- **Capillary force:** A surface force related to the interfacial tension between water, tar, and the fracture walls. This is a resistive force that prevents tar from moving and depends on temperature, tar composition, and fracture aperture (i.e., distance between fracture walls).

Calculating the ratios of these controlling forces leads to a set of dimensionless numbers that can be used as metrics for evaluating tar mobility in fractured rock.

2.3.1 Metrics for Evaluation Mobilization Technologies

In this section, three dimensionless numbers are described as the primary metrics for evaluating tar mobility in fractured rock:

- **The capillary number (NCa)**: The ratio of the viscous mobilizing force to the capillary resistive force.
- **The bond number (NB)**: The ratio of the buoyant force to the capillary resistive force.
- **The trapping number (NT)**: The combination of NCa and NB, which captures the combined effects of viscous, buoyant, and capillary forces.

The capillary number is defined as follows [10]:

$$\boldsymbol{N_{Ca}} = \frac{\boldsymbol{\rho_w g k k_{rw} i}}{\boldsymbol{\sigma_{ow} cos\theta}} \qquad \textbf{Eq. 2-1}$$

Where:

ρ_w is the density of water $[ML^{-3}]$.

g is the gravitational constant $[LT^{-2}]$.

k is the intrinsic permeability of the medium $[L^2]$.

k_{rw} is the relative permeability to water $[-]$.

i is the hydraulic gradient across the fracture $[-]$.

σ_{ow} is the interfacial tension between the tar and water $[MT^{-2}]$.

θ is the tar-water contact angle $[-]$.

The bond number is defined as follows [10]:

$$\boldsymbol{N_B} = \frac{\boldsymbol{\Delta\rho g k k_{rw}}}{\boldsymbol{\sigma_{ow} cos\theta}} \qquad \textbf{Eq. 2-2}$$

Where $\Delta\rho$ is the difference between the densities of tar and water.

Pennell et al. [10] combined N_{Ca} and N_B to create the total trapping number, N_T. They showed that in a vertical flow system (e.g., vertical fracture) the total trapping number is equal to the absolute value of the sum of the capillary and bond numbers [10]:

$$\boldsymbol{N_T} = |\boldsymbol{N_{Ca}} + \boldsymbol{N_B}| \qquad \textbf{Eq. 2-3}$$

Since N_T captures the three forces that govern tar mobility, it can be used to evaluate the potential effectiveness of remediation technologies aimed at enhancing tar mobility. For example, the surfactant flushing technology reduces the interfacial tension between tar and water, thereby reducing the capillary force and allowing the tar to be displaced more easily. Temperature change is another factor that can affect tar mobility. Sleep and Ma [11] studied the thermal variation of organic fluid properties to evaluate the possibility of thermal remediation of entrapped PCE in porous media. They showed that viscosities, interfacial tensions, and PCE–water contact angles decreased with increasing subsurface temperature. These observations are specific to the tested organic DNAPL, and the same thermal variation may result in different observations for a different DNAPL, such as tar.

The analysis of the aforementioned dimensionless numbers can be used to quantitatively describe these impacts on tar mobilization. For example, Pennell et al. [10] used surfactant flushing in laboratory experiments to mobilize entrapped PCE–DNAPL pools in a porous medium. They reported that PCE displacement started at $N_T = 1 \times 10^{-5}$, and the complete displacement was achieved at $N_T > 1 \times 10^{-3}$. Kong [4] and Hauswirth et al. [9] conducted similar experiments for mobilization of MGP tar using surfactant flushing. Both studies showed that tar saturation decreases with increasing trapping number. However, tar unlike PCE, did not show a threshold value for near complete removal. Even at very high values of N_T, residual tar saturation remained as high as 15% to 20%. Thus, the following analysis will assess the ability of remediation technologies to bring tar above the initial mobilization threshold (i.e., N_T in the range of 10^{-5} to 10^{-4}), however the lowest residual tar saturations my still be high (e.g., 15% to 20%) even if large values of N_T could be achieved by a given technology.

2.3.2 Metrics for Evaluating Solubilization Technologies

Solubility enhancement is another mechanism by which the surfactant and cosolvent flushing can help remove MGP tar. Surfactants are molecules where one part is attracted to water and another part is attracted to hydrophobic substances (e.g., tar). Since the surfactant is attracted to both water and tar, surfactants can pull tar molecules into aqueous solution. When the surfactant concentration in water exceeds a limit known as the *critical micelle concentration (CMC)*, surfactant molecules begin to assemble and form spherical micelles with a hydrophobic core at the center. Essentially, the portion of the surfactant molecules that are attracted to water assemble to form an outer spherical shell, with tar trapped in the inner core of the sphere where the hydrophobic parts of the surfactant molecules are pointed (see Figure 2-3). This hydrophobic core accommodates organic constituents of MGP tar and dramatically increases their apparent solubility. A measure of the effectiveness of a particular surfactant in solubilizing a given compound is the molar solubilization ratio (MSR) which is the slope of the curve that shows the increase in apparent tar solubility as a function of the surfactant concentration [12]:

$$\boldsymbol{MSR} = \frac{\mathbf{S_{surf} - S_0}}{\mathbf{C_{surf} - CMC}} \qquad \textbf{Eq. 2-4}$$

Where:

$\mathrm{C}_{\mathrm{surf}}$ is a given surfactant concentration higher than CMC.

S_0 is the apparent solubility of an organic compound at CMC or the initial solubility.

$\mathrm{S}_{\mathrm{surf}}$ is the initial solubility of the organic compound at $\mathrm{C}_{\mathrm{surf}}$.

Figure 2-3 illustrates the relationship between the solubility, CMC, and MSR.

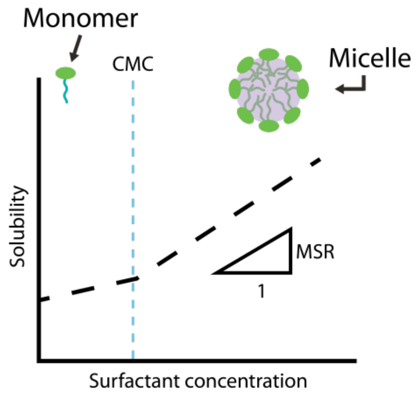

Figure 2-3
Change in apparent solubility with change in surfactant concentration

CMC is a characteristic of the surfactant and is constant for all tar constituents (i.e., above some critical surfactant concentration, micelles will always form). Apparent tar solubility, however, varies for different constituents that compose MGP tar. Since the MSR depends on both apparent tar solubility and the CMC, solubility of different constituents that compose MGP tar are enhanced to different degrees by a given surfactant. To investigate the enhanced solubility of coal tar components, Hauswirth and Miller [2] studied the effects of different surfactant combinations on tar solubility. Figure 2-4 shows the MSR values of 15 PAH components commonly found in tar when a 0.5% TX100 solution (a type of surfactant) is used to enhance solubility. The figure shows that MSR has an inverse relationship to PAH molecular mass, meaning that the overall solubility of lighter PAHs is higher even in the presence of surfactants (as is the case for PAH solubility in water).

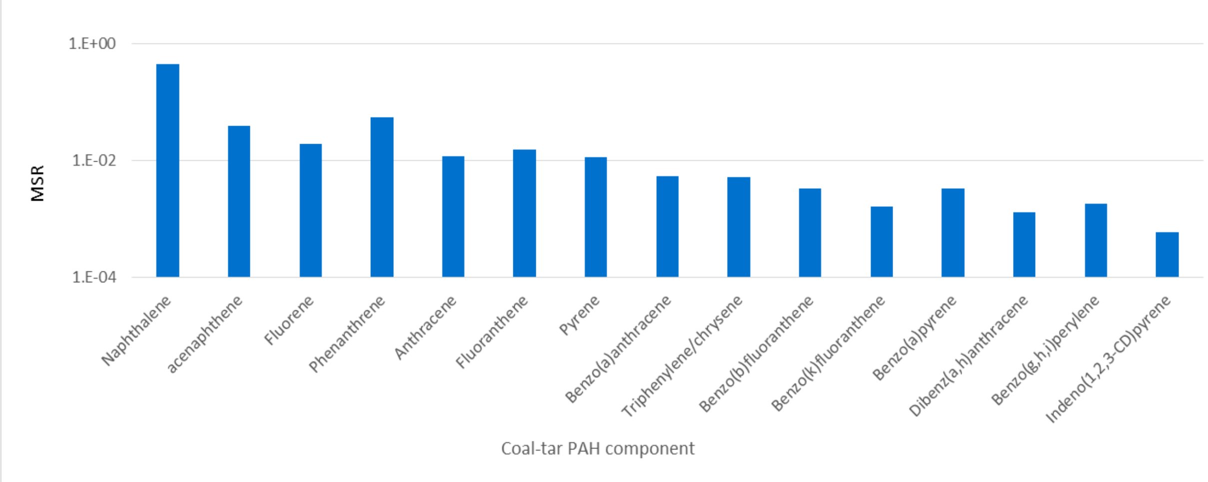

Figure 2-4
Molar solubilization ratio of tar components in 0.5% TX100 solution
Data from Hauswirth and Miller [2]

Although the overall solubility of heavier PAHs is lower than lighter ones (even in the presence of surfactants), the solubility of heavier PAHs is increased most by surfactants. For example, Figure 2-5 shows the solubility of PAHs in water (blue dots and blue line) and in a surfactant solution (green dots and green line). The vertical distance between the two lines characterizes how much the surfactant enhances solubility. The largest solubility enhancement is on the right side of the plot, where the heaviest PAHs are plotted. Thus, the application of surfactants causes the largest solubility increase for heavy PAHs, but the lighter PAHs still have higher overall solubility. The differing solubilities across the range of PAHs will cause fractionation of the tar and hence, may affect tar’s physical properties. These compositional changes are not evaluated here, but could be considered in future work.

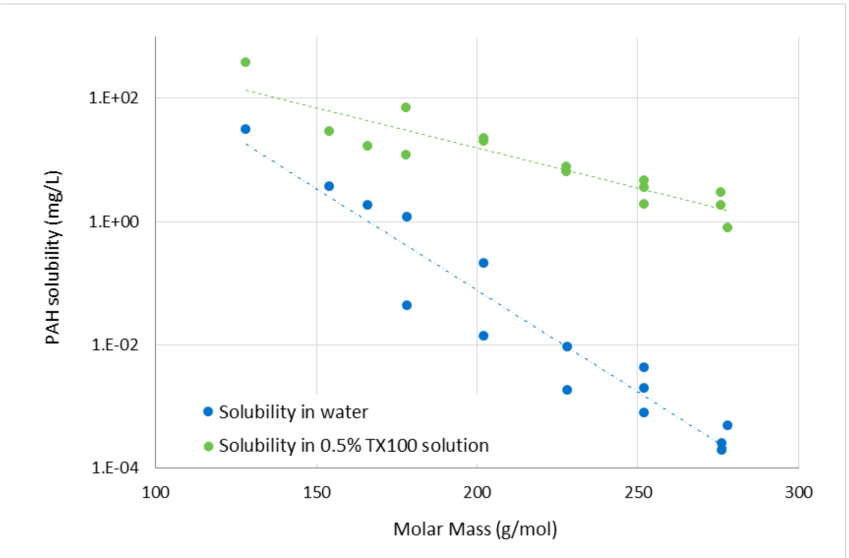

Figure 2-5
Solubility of tar components in pure water and in 0.5% TX100 surfactant solution
Data from Hauswirth and Miller [2]

2.4 Screening System and Data Requirement

The dimensionless numbers presented in Equations 2-1 through 2-3 quantitatively describe the effectiveness of remediation technologies that operate *via* mobilization mechanism. Equation 2-4 presents a dimensionless number that describes the effectiveness of enhanced solubilization approaches. When feasibility of a remediation strategy is under investigation, the potential of the strategy for mobilization or solubilization of entrapped tar in fractured bedrock may be judged by comparing the maximum N_T or MSR that the technology can achieve. A set of site-specific parameters that describes the characteristics of fluids and fractured bedrock and a set of design parameters that describe the remediation technology are required to evaluate the dimensionless numbers. Table 2-1 presents a list of data requirements for feasibility assessment of relevant remediation technologies. Typical values can be found in the literature for some listed parameters, while others might require site-specific measurements. Implementation of this screening system is demonstrated by examples in Section 4, focused on potential enhancement of tar mobility.

Table 2-1
Data requirements for remediation technologies

Category	**Required Parameters**	**Typical Value Used in Presented Simulations**	**Reference**
General Data Requirements			
Tar characteristics	Specific gravity Viscosity	1.061-1.334 10^2-10^5 (cP)	Birak and Miller [13]
Water characteristics	Density Viscosity	0.998 (g/mL) at 20°C 1.0016 (cP) at 20°C	U.S. Dept. of Commerce [14]
Tar-water characteristics	IFT between water and NAPL Contact angle	20-25 (dynes/cm) 20 (°)	Birak and Miller [13] Barranco and Dawson [15]
Bedrock properties	Permeability Fracture spacing and aperture	$k = b^2/12$ where b is the fracture aperture	Bear [6]
Bedrock-tar characteristics	Relative permeability function	Brooks and Corey model, model parameter $\lambda = 2.5$	Brooks and Corey [16] λ for fractured bedrock from Chown et al. [17]
Technology-Specific Data Requirements			
Water flooding	Flushing hydraulic gradient	0-1.0	
Surfactant/ cosolvent flushing	Flushing hydraulic gradient Initial tar saturation Effect of surfactant/cosolvent on IFT and contact angle Surfactant CMC Applied surfactant concentration	0.5 20% See Section 4.2	
Thermal treatment	Applied hydraulic gradient Ambient water temperature Applied temperature increase Impact of temperature change on IFT and contact angle Fracture stiffness constant Bedrock elastic modulus Linear thermal expansion coefficient Mineral dissolution constant Residual fracture aperture Maximum fracture aperture Fracture spacing	0.5 10°C 10°C to 100°C See Section 4.3 0.1 (MPa^{-1}) 1e10 (Pa) 1.5e-5 (K^{-1}) 1.4 (-) 5e-6 (m) 5e-5 (m) 1.0 (m)	Min et al. [18]

3

CHARACTERISTICS OF MANUFACTURED GAS PLANT TAR

MGP tars were generated as byproducts during the production of gas. Liquid tar was produced by condensation from gas as it cooled while passing through various conditioning and purification processes. The following is a brief review of chemical and physical properties of MGP tar. A more detailed discussion can be found in Birak and Miller [13].

MGP tars are complex mixtures of more than 10,000 organic and inorganic compounds [13]. The genesis of the tar and the degree of weathering determine composition of the tars found in the subsurface environment. Generally, the main constituents of tars are PAHs and VOCs. Naphthalene is the most abundant compound in fresh tar and also in most weathered MGP tar samples. Weathering generally changes the composition of tars in favor of compounds with a higher molecular weight. Tars also contain a number of inorganic compounds, including trace metals and cyanide.

Viscosity and specific gravity of MGP tars are positively correlated and are sensitive to changes in temperature. Figure 3-1 illustrates the correlation between specific gravity and viscosity of 17 historical tar samples at 15.5°C [13], showing that these properties are generally proportional to each other for a range of tars.

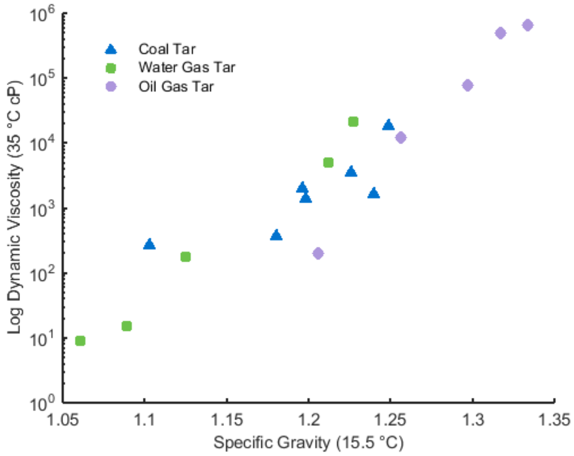

Figure 3-1
Relationship between tar velocity and specific gravity
Data from Birak and Miller [13]

The interfacial tension between MGP tar and water (IFT) is generally considered lower than other DNAPLs and varies between 20 and 25 dynes per centimeter at neutral and acid pH, but decreases to much lower values at higher pH [13]. One important difference between tar and chlorinated solvent DNAPLs, such as PCE, is that tar has a potential for wettability alteration from water-wet to tar-wet conditions. This wettability alteration depends on the pH of groundwater and on whether one is looking at the leading or trailing edge of a tar pool/globule.

For example, the leading edge of tar globules can sometimes be under water-wet conditions, whereas the trailing tail of the same globule can be under tar-wet conditions (i.e., stick to the fracture wall) [9]. This complex wetting behavior, even within a given tar globule, likely contributes to observations of generally low tar recovery from active remediation systems. When the tar sticks to fracture walls, it is unlikely that mobilization technologies can move the tar at all. Other experiments have also shown that the groundwater pH affects tar wettability, with low-pH conditions favoring tar-wet conditions (i.e., tar sticks to fracture walls) and high-pH favoring water-wet conditions [15].

4

SCREENING EVALUATION OF REMEDIATION TECHNOLOGIES

In this section, the previously described metrics are used to quantitatively evaluate the feasibility of selected technologies. The primary metric discussed is the trapping number (N_T). As it was discussed in Section 2.3, multiple researchers have reported that the initial mobilization of MGP tar potentially starts when N_T is in the range of 10^{-5} to 10^{-4}. Initial mobilization is not a condition where significant tar removal occurs, but rather is the threshold where the tar just begins to move. In order for a technology to begin to be effective, the value of N_T must rise to values substantially above the initial mobilization threshold. For some other types of DNAPL (e.g., PCE), the amount of mobilization increases with N_T (once above the initial mobilization threshold), and there is eventually a value of N_T where near complete removal occurs [10]. However, experiments have shown that complete removal of MGP tar does not occur, even at very high values of N_T. This more complicated behavior of MGP tar is likely related to its more complex wettability behavior. Thus, although plots of N_T for the selected technologies in this section can give an indication of whether tar can begin to be mobilized, complete removal of MGP tar should never be expected as an achievable end point.

4.1 Water Flooding

Water flooding is a mobilization approach that uses injection wells to force water through fractured bedrock to displace the entrapped tar. Recovery wells are placed downgradient to collect injected water and potentially mobilized tar. We used the values reported in Table 2-1 to estimate the range of N_T that could be achieved in typical bedrock fractures at a hypothetical MGP site with entrapped tar. In this simulation, the initial tar saturation is assumed to be 20%. Figure 4-1 shows that the trapping number changed between 10^{-5} to 10^{-4} but was not able to rise above the initial mobilization threshold. Thus, the water flooding technology is not capable of mobilizing entrapped tar and should not be considered as a viable option for residual tar source reduction.

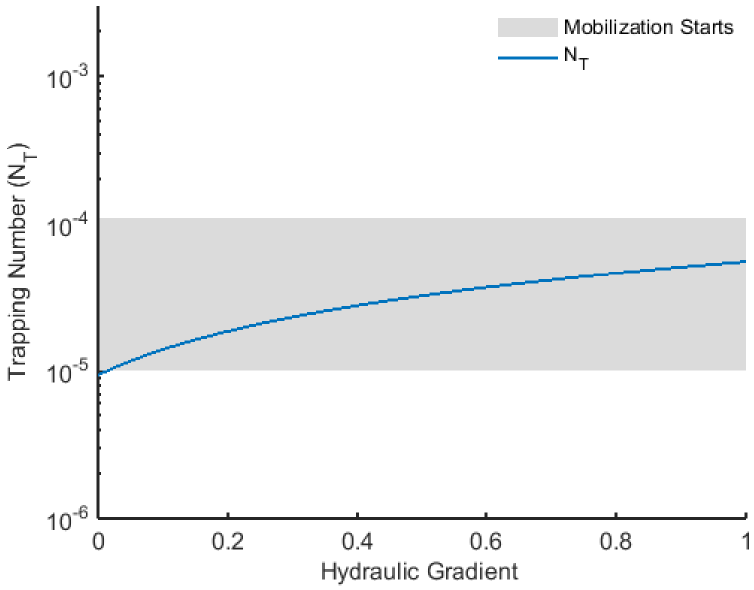

Figure 4-1
Effect of water flooding on the total trapping number

Surfactant flushing reduces the interfacial tension (IFT) between tar and water, thereby enhancing tar mobility.[2] Surfactant-enhanced mobility of MGP tar has been confirmed in laboratory experiments of flow through sand-packed columns, where tar saturation decreases as the value of N_T increases (due to the change in IFT upon adding surfactants). However, the same experiments also showed that complete tar removal did not occur, even at very high values of N_T (see Figure 4-2; Kong [4]; Hauswirth et al.[9]). At most, tar saturation could be reduced to about 15% to 20%, depending on which surfactant was applied (see Figure 4-2).

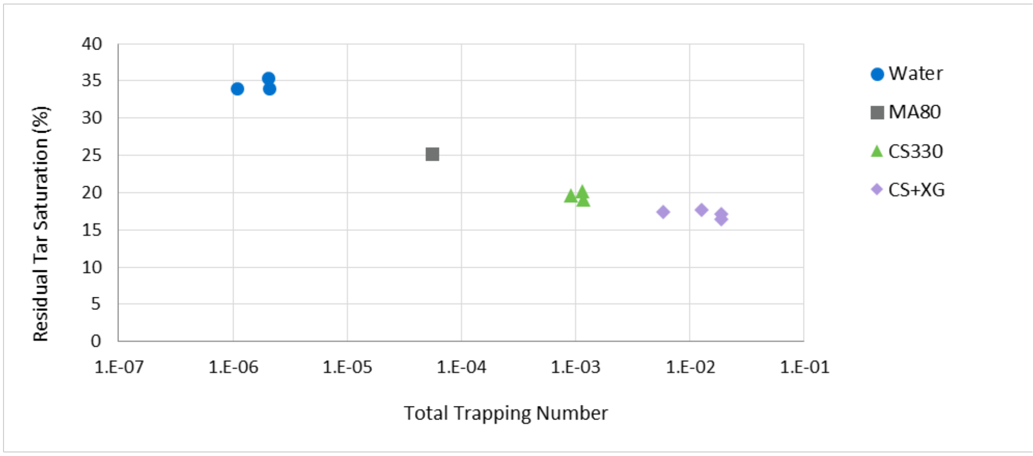

Figure 4-2
Relationship between residual tar saturation in column experiments and total trapping number
Data from Kong [4]

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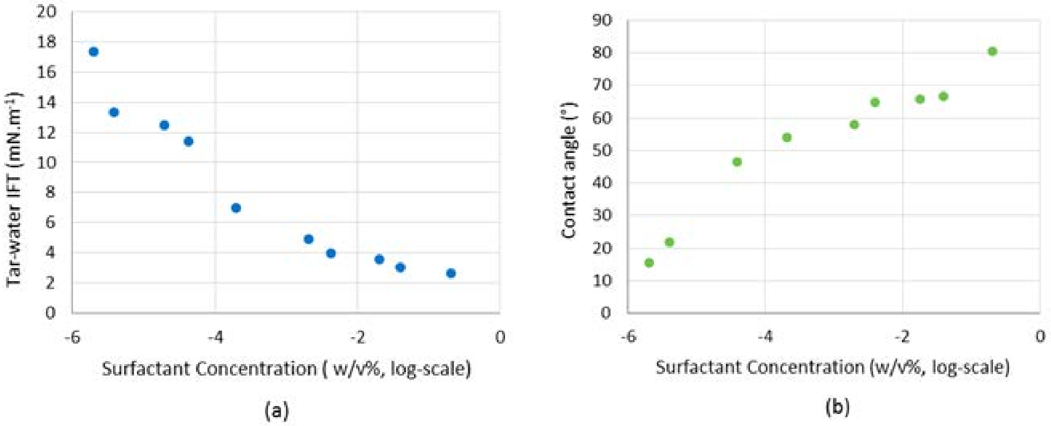
[2] Surfactants can also increase tar solubility; however, enhanced solubilization is not evaluated in this report.

To estimate the effectiveness of surfactant flushing, the value of N_T can be calculated directly from the changes to the properties of entrapped tar upon introduction of a surfactant solution. For example, the tar-water IFT and the contact angle are variables used to calculate N_T, and the changes to IFT and contact angle have been determined previously for selected tar samples and surfactants (e.g., Dong et al. [8]). Figure 4-3 illustrates how the IFT and contact angle change when a poloxamine surfactant[3] is introduced at a range of concentrations. Figure 4-3 shows that, for this specific surfactant and tar combination, the IFT decreases and the contact angle increases at higher surfactant concentration. These changes both cause the total trapping number to increase (see Equations 2-1 through 2-3).



(a)

(b)

Figure 4-3
Relationship between T90R4 poloxamine surfactant concentration and (a) tar-water interfacial tension and (b) contact angle
Data from batch experiments conducted by Dong et al. [8]

In Figure 4-4, the net change in N_T is plotted, taking into account the combined effects of reduced IFT and increased contact angle (from Figure 4-3) associated with surfactant addition. All other variables used to calculate N_T are from Table 2-1. The values of N_T in Figure 4-4 range up to 10^{-3}, however, in comparison to the data in Figure 4-2, the magnitude of N_T may still allow about 15% to 20% of residual tar saturation.

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[3] Poloxamine surfactants are tetrafunctional block copolymeric compounds, which contain four poly(ethylene oxide)-block-poly(propylene oxide) chains joined to a central ethylene diamine moiety via the nitrogen atoms [8].

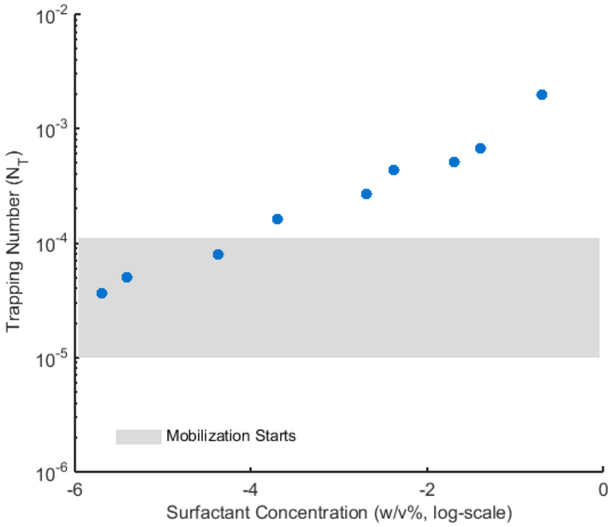


Figure 4-4
Effect of T90R4 poloxamine surfactant concentration on the total trapping number

Since the initial assumed saturation was 20% in this hypothetical example, the relatively large values of N_T potentially achievable with surfactants still might not be adequate to reduce tar saturation substantially (i.e., in the hypothetical example, tar saturation might be reduced by 0-5% from an initial value of 20%). Moreover, extremely high surfactant concentrations (i.e., on the order of 10% w/v) would be needed to achieve $N_T > 10^{-3}$, drawing into question whether such high additive concentrations are practical at a real site. Furthermore, higher N_T values are associated with higher tar mobility only if water remains the wetting phase. Hauswirth et al. [9] and Dong et al. [8] showed that adding surfactants can cause wettability alteration (i.e., tar changing to become a partially wetting fluid). Hugaboom and Powers [7] conducted similar tar mobilization experiments under water-wet and tar-wet conditions and showed that the efficiency of flushing technologies for mobilization of tar was significantly lower under tar-wet conditions. Thus, in addition to considering N_T in evaluations of surfactant-enhanced tar mobility, potential changes to wettability must also be considered, especially since some surfactants can change the subsurface to become tar-wet—a condition which would negate any potential benefits achieved by increasing N_T.

4.3 Effect of Heating

Heating is sometimes used to reduce the viscosity of free-flowing NAPL to allow it to flow more readily into collection wells. In settings with residual tar, the effects of heating are more complicated, since the application of heat changes the properties of fluids (water and tar) and the solid matrix and shifts the equilibrium between the retaining and mobilizing forces (i.e., as embodied in the value of N_T). Some coal tars have been studied with respect to how their properties change upon heating [4], and this data is used to evaluate temperature-dependent changes to tar properties. Figure 4-5 shows how fluid densities (for both coal tar and water), IFT, and contact angle changed as temperature increased from 22°C to 50°C. Since tar's surface properties are pH-dependent, the measured data in Figure 4-5 are shown for pH values of 4.7, 7, and 10. Most natural groundwaters have pH closer to 7, with the pH values of 4.7 and 10 representing less common or extreme conditions.

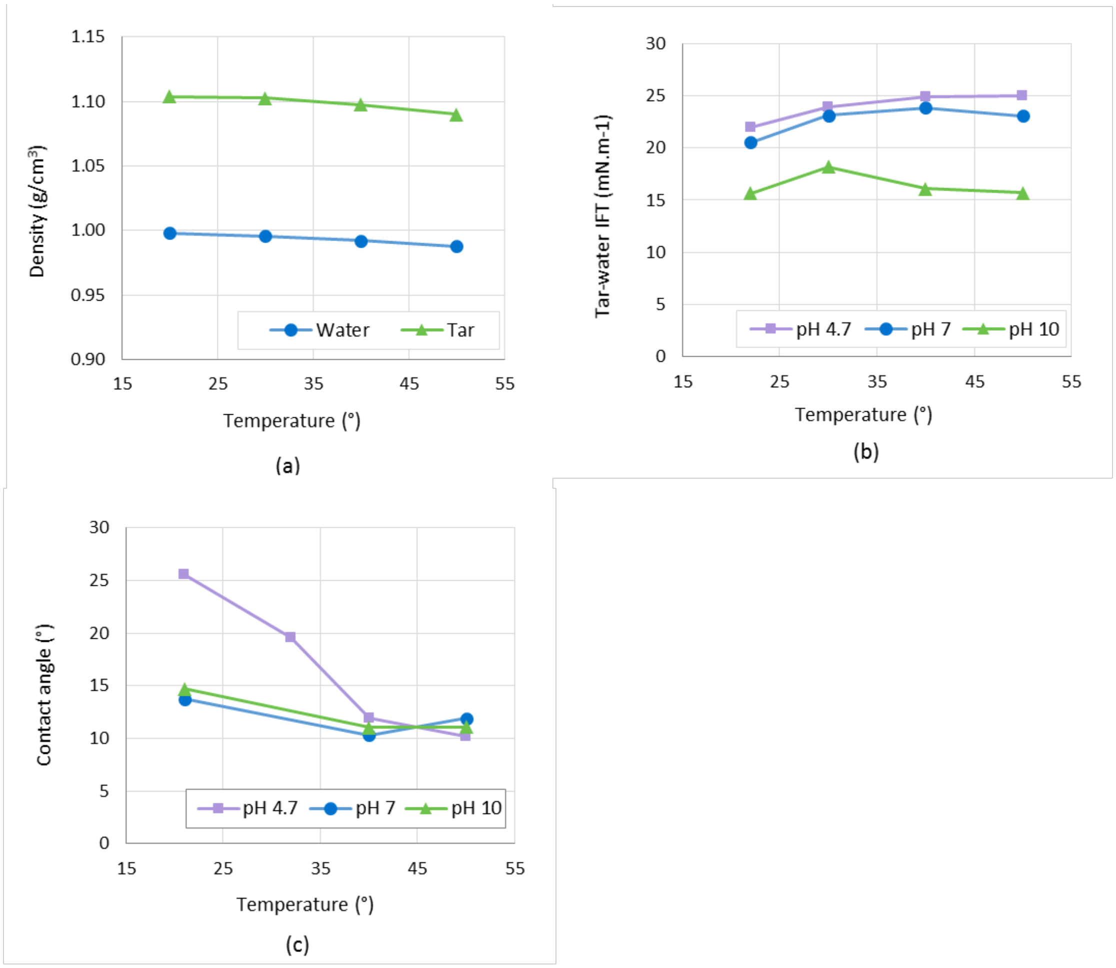


Figure 4-5
Relationship between fluid properties and temperature: (a) tar and water densities, (b) tar-water interfacial tension, and (c) tar-water contact angle
Data from Kong [4]

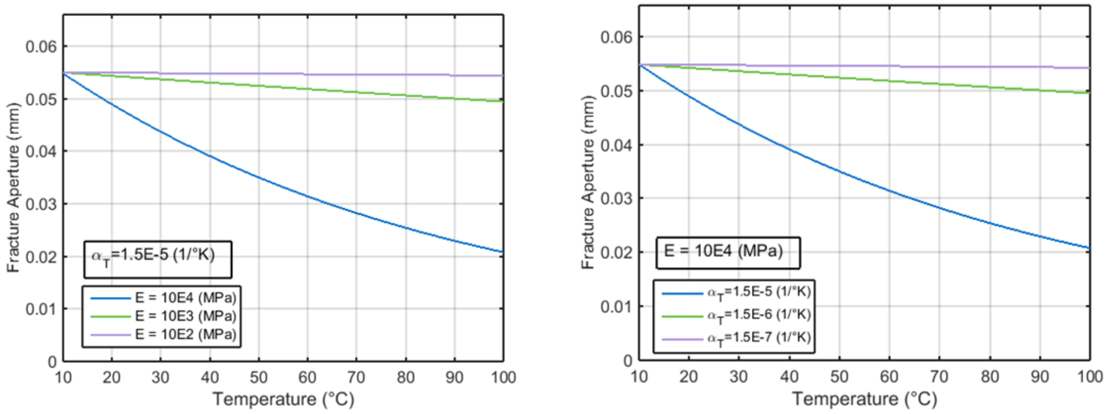
The following interpretation of Figure 4-5 describes how the altered fluid properties at elevated temperature affect tar's mobility:

- The densities of water and tar change almost identically with increasing temperature, which provides little or no change in tar mobility;
- The tar-water IFT remains constant or even slightly increases as temperature increases, which has no effect on tar mobility (or slightly reduces mobility); and
- The contact angle decreases, which reduces tar mobility.

Thus, upon heating, the properties of water and tar change only slightly, with competing effects on the magnitude of N_T (i.e., some property changes would cause N_T to increase while others would cause it to decrease).

An additional aspect of heating that must be considered in fractured bedrock settings is the change in the bedrock permeability. The trapping number is directly related to the permeability of bedrock, which is in turn related to bedrock fracture apertures. When rock is heated, it thermally expands, causing a net volume expansion in the subsurface. This increased volume must be accommodated by compressing the rock and clamping down on fractures (i.e., partially closing fractures). As fractures close (and hence fracture permeability decreases), the mobility of tar also decreases. This effect can be included in calculations of N_T, since N_T is directly related to the permeability of bedrock.

The extent of fracture closure in response to heating depends on several factors, including the thermal expansion coefficient and elastic modulus of the rock. Equations for calculating fracture closure upon heating have been developed previously, and the approach of Min et al. [18] was adopted for the purposes of this report. Figure 4-6a shows examples of how the fracture aperture changes as temperature increases. In Figure 4-6a, three lines are plotted for three different elastic moduli while holding all other variables constant; in Figure 4-6b, three lines are plotted for three different thermal expansion coefficients while holding all other variables constant. To summarize these plots, the extent of fracture closure upon heating is greatest in rocks with high elastic modulus (i.e., stiff rocks) and high thermal expansion coefficients.



(a) (b)

Figure 4-6
Thermal closure of fractures: (a) sensitivity to elastic modulus and (b) sensitivity to thermal expansion constant

Figure 4-7 combines the effects of thermal changes to fluid and bedrock properties and demonstrates how N_T changes over a temperature range of 10°C to 100°C (i.e., a plausible range of heating below the water table). Since hydraulic conductivity of fractured bedrock also depends on the water saturation (S_w) in bedrock, N_T values in Figure 4-7 are calculated at two water saturations—80% and 95% (corresponding to residual tar saturation of 5% to 20%). Figure 4-7 reveals that N_T decreases about one order of magnitude when temperature increases from 10°C to 100°C, making the residual tar much less mobile—the opposite direction of change that would be desired from any remediation technology. Overall, the effects of heating have only negative consequences on residual tar mobility in fractured-rock aquifers and this technology should generally be avoided in these settings.

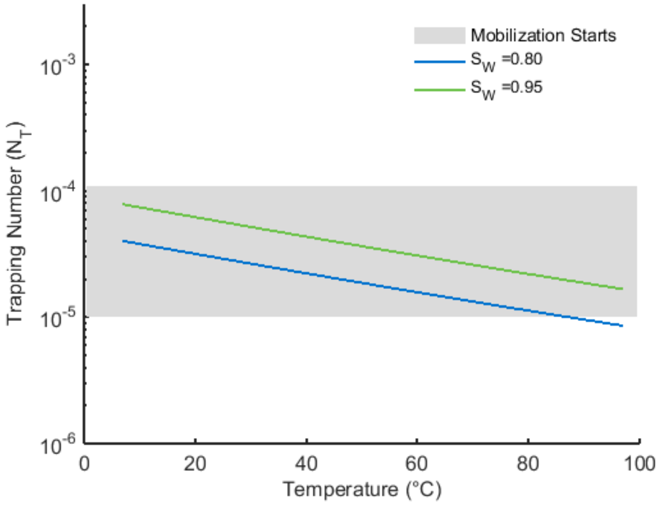


Figure 4-7
Effect of heating on total trapping number

4.4 Example of Combined Technologies: Heating and Cosolvent Flushing

The combined application of two technologies, hot water and cosolvent flushing, is a method suggested in the literature for mobilizing NAPL in porous media (e.g., Aydin et al. [19]). In the last two sections we investigated the tar mobilization potential of these technologies separately. In order to investigate the combined effect, the thermal variation of tar-water surface properties in the presence of cosolvents was required. To the best of our knowledge such data are not available in the literature for any tar-surfactant combination. Therefore, as an analog and simplifying assumption, the IFT measurements reported by Hauswirth et al. [9] in a coal tar-water-NaOH system at 20°C were used and it was assumed that tar-water IFT does not change when temperature increases from 10°C to 100°C. The contact angle of 20° was also held constant for the considered range of temperature increase. These assumptions are expected to have only a minor effect in this analysis, since these properties cause only slight changes to N_T over the temperature range considered (see Figure 4-5).

Figure 4-8 shows the combined effect of heating and cosolvent flushing in changing N_T. The figure suggests implementation of a cosolvent flushing technology alone would be more effective than combining it with heating, due to the negative effects of heating via thermal closure of fractures. As discussed in the prior section, heating has only negative effects on residual tar mobility and these negative effects are large enough to counteract any enhancements to tar mobility potentially achieved by other technologies combined therewith.

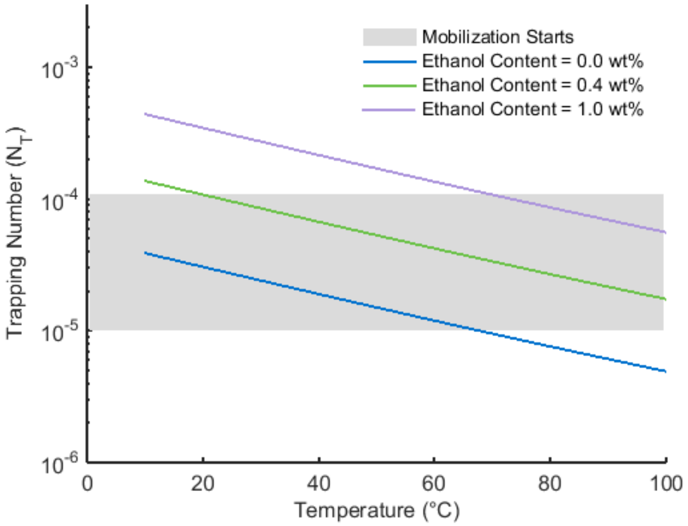


Figure 4-8
Effect of combined application of heating and cosolvent flushing

5

CONCLUSIONS

The preceding analysis presented a general framework that combines the chemical and physical properties that control tar mobility in fractured rock to evaluate the potential effectiveness of remediation technologies up front in the remediation process. The framework can reveal strengths and weaknesses of available technologies, as well as provide a basis for assessing how combinations of technologies might perform. The following key findings summarize the results of the quantitative framework used to evaluate selected technologies:

- Water flooding is not promising as an effective technology. The technology is unlikely to increase residual tar mobility above the point of initial mobilization and hence cannot be considered as a feasible approach to reduce residual tar saturation.
- Flushing solutions that include surfactants, cosolvents, and strong bases (i.e., NaOH) have potential to increase tar mobility. Each of these technologies has limited effectiveness when implemented on its own, but recent research suggests that combinations of these technologies could potentially have greater effectiveness [2]. However, very high solvent concentrations (e.g., on the order of 10%) might be required and the magnitude of N_T potentially achievable may still only mobilize a small fraction of the residual tar. Furthermore, there are also potential negative consequences of applying surfactants, such as potentially changing the tar to a wetting fluid (causing it to stick to fracture walls) and undesirable migration of tar to locations where it might be even more difficult to remediate. Removal of tar via enhanced solubility in the presence of surfactants could be evaluated in future work. These and other potential complicating factors would need to be carefully considered to assess whether surfactant flushing would actually be effective at a given site.
- Heating technologies have only negative effects on residual tar mobility in fractured rock. Temperatures high enough to destroy the tar or volatilize a significant fraction generally cannot be achieved below the water table. Increasing the temperature changes water and tar properties in ways that reduce tar mobility and also cause bedrock to thermally expand, which causes fractures to close. These combined effects severely reduce tar mobility as temperature increases.

In the above summary, it was assumed that the bedrock fractures and spatial distribution of tar have been fully characterized and that it is physically possible to access residual tar with the evaluated technologies. Thus, our analysis should be considered as a hypothetical “best-case” potential for technology effectiveness. When considering application of any technology at a real MGP site, additional factors must be considered, such as the ability to accurately locate MGP tar in the subsurface and whether treatment fluids can be effectively delivered to fractures with entrapped tar. For example, in order for flushing solutions to be effective, the total fracture volume must be flushed with the treatment solution many times to achieve a high degree of removal. In narrow or dead-end fractures, such a high degree of flushing might not be achievable.

The findings above are consistent with available research on MGP tar remediation in laboratory experiments. From the idealized process-based considerations evaluated in this report, none of the available technologies would be clearly beneficial for reducing residual MGP tar saturation in fractured bedrock settings.

6

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