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Influence of cyclic freeze-thaw on the mobilization of LNAPL and soluble oil in a porous media

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ABSTRACT

Subsurface behavior of spilled fuel in freezing and frozen porous media including fractured bedrock is not well understood. To simulate a bedrock fracture, a freezing cell consisting of two parallel glass plates filled with glass beads was constructed to study the impact of cyclic freeze–thaw on LNAPL movement. The test procedure involved introduction of LNAPL atop the cell that contained water mixed with fluorescein dye. Freezing progressed from the top down, with observation and measurement of the LNAPL migration using a high-resolution digital camera and time-lapse photography. Both diesel and soluble oil were used for the experiments. Tests with soluble oil involved thorough mixing at 12.5% volume ratio with the fluorescein–water mixture in the freezing cell. The results showed upward mobility of the LNAPL under cyclic freezing and downward progressive expulsion of the soluble oil ahead of the advancing freezing front. The results corroborated literature findings on organic solute expulsion ahead of freezing front, and provided insight into the behavior of trapped LNAPL below the water table when subjected to freeze–thaw conditions. Additionally, micro fissures were observed in the formed ice inside the freezing cell under prolonged freezing. Such micro fissures may provide potential migration pathways for fresh spilled fuel in permafrost environments.

1. Introduction

Understanding the subsurface behavior of spilled fuel in a contaminated site is crucial to its successful remediation. Achieving this requires detailed site characterization and determination of mechanisms aiding its migration and accumulation in the environment. Most spilled fuels (i.e., gasoline and diesel) are subsets of light nonaqueous phase liquids (LNAPLs) because they are less dense than water and mostly immiscible with it. In temperate regions, the behavior of spilled fuel is well documented in the literature. However, in cold regions overlapping permafrost environments, subsurface behavior of spilled fuel is an ongoing research area.

The behavior of petroleum hydrocarbon (PHC) contamination in frozen media is important in discerning its behavior in permafrost environments. Permafrost is often viewed as a barrier to contaminant migration in cold regions, which has often contributed to improper environmental practices involving spilled fuel (Barnes and Chuvlin, 2009). Studies have shown that ice or completely ice-saturated frozen soil without defects have very low permeability in the order of 10^{-15} cm^2, and are mostly impervious. This formed the basis for the development and use of frozen core barriers for contaminant mitigation. A study by Andersand et al. (1996) on such barrier's resistance to ice erosion by liquid contaminant showed that minimization of ice erosion requires full ice saturation and barrier temperature below the freezing point depression of the contaminant. However, in ice-saturated frozen soil, there is a natural propensity for microcracks development, especially at temperatures below freezing (Yershov et al., 1988) because frozen ground is a spatially inhomogeneous system (Frolov, 1982).

Laboratory experiments by Biggar and Neufeld (1996) on vertical migration of diesel into columns of saturated silty-sand subjected to freeze–thaw cycles showed no contamination in the permanently frozen soil layer at depth after eight cycles of freeze–thaw. There was, however diesel contamination in the saturated soil up to the thaw depth. Thus, they postulated that the contaminant movement into the saturated soil was due to migration into fissures induced during freezing. Furthermore, site investigations of fuel migration into permafrost at two different fuel-contaminated sites in the Canadian Arctic by Biggar et al. (1998) found significant contamination below the permafrost table. They postulated that gravity drainage along fissures induced by thermal contraction or gravity drainage via interconnected air voids accounted for this movement. Thus, permafrost may not be an effective barrier to contaminant propagation.

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Laboratory experiment by Chuvilin et al. (2001) on factors affecting oil migration in frozen ground observed components of oil even in wholly ice-saturated soil, corroborating the work of Biggar et al. (1998). Later work by Chuvilin and Miklyaeva (2003) suggested that capillary transfer via micropores might be responsible for the oil penetration. Chuvilin et al. (2001) showed that surface spreadability of oil increased with increasing ice saturation and oil hardening temperature but decreased from sand to clay to ice as a result of increasing wetting angle on the mineral surfaces respectively. Laboratory experiment by Barnes and Wolfe (2008) on the effects of pore-ice on spreadability and penetration of petroleum products in coarse grained soils showed that ice content increased lateral migration of petroleum due to the formation of dead end pores by ice especially in the vadose zone, thereby creating irregular preferential flow paths resulting in deeper contaminant penetration.

The nucleation process that occurs during ice formation is known to cause rejection and concentration of solutes in the unfrozen water (Konrad and Seto, 1991; Tumeo and Davidson, 1993; and Chuvilin et al., 2001). This process is commonly referred to as solute exclusion or rejection in freezing experiments and hydrocarbon exclusion when petroleum products are involved. Barnes and Chuvlin (2009) referred to this process as cryogenic expulsion, and related it to separation of more mobile components from petroleum. In this study, the term “cryogenic expulsion”, is adopted. Different studies have shown that cryogenic expulsion is enhanced at lower freezing rates (Konrad and McCammon, 1990; Konrad and Seto, 1991; Panday and Corapcioglu, 1991), however, the phenomenon has been observed at higher freezing rates (Ershov et al., 1992). In a top-down freezing experiment conducted by Konrad and Seto (1991) on a partially saturated clay sample contaminated with miscible organic solvent (propanol), there was an increase in solvent concentrations in front of advancing freezing front. Other studies conducted in the laboratory corroborated such observation (Chuvilin et al., 2001; Tumeo and Davidson, 1993; Panday and Corapcioglu, 1991). According to Wilson and Mackay (1987), freezing can cause oil to weather, which may lead to increased density and viscosity, thereby enhancing downward pull potential but decreased fluid's mobility. In addition to the concept of cryogenic expulsion, Barnes et al. (2004) proposed the mechanism of physical displacement of mobile LNAPL from pore spaces as water expands.

At the commencement of freezing in the winter period, the groundwater table is often low due to decreased water infiltration. Fluctuations of the groundwater table have been shown to enhance LNAPL entrapment and remobilization in the formation (Lenhard et al., 1993: Catalan and Dullien, 1995; and Dobson et al., 2007), and numerical models were developed by Aral and Liao (2002) to mimic this behavior. Dobson et al. (2007) further showed that water table fluctuation enhances biodegradation and dissolution of LNAPL components, and increases its migration down-gradient. Ryan and Dhir (1993) performed laboratory column tests using glass bead packs of various sizes to investigate the effect of particle diameter on LNAPL entrapment due to a slowly rising water table. The results showed enhanced LNAPL entrapment for pre-wetted particles but insignificant effect for particle sizes less than 710 μm with an average residual saturation of 11%. Larger particles significantly reduced residual saturation.

Iwakun et al. (2008b) correlated measured LNAPL thickness in a monitoring well (MW) at a fuel contaminated site in Canadian North with both the groundwater elevation and the thermal profile at monitoring well at the site. The study showed a significant inverse correlation of the LNAPL thickness with both the thermal profile and the groundwater elevation. Furthermore, increased LNAPL accumulation in the MW in early winter corresponded to decreased groundwater elevation and vice-versa in early spring when the groundwater table was elevated. There was no significant recharge of LNAPL in the MWs following a product recovery test in the winter (Iwakun and Biggar, 2007), inferring the mechanisms enhancing LNAPL accumulation at the site are not continuous. Further investigations at the site showed that LNAPL contamination is generally limited to the upper seven meters of the subsurface, which consists of 0–4.6 m of overburden soil underlain by fractured bedrock (Iwakun et al., 2010). From the site characterization efforts at the site, Iwakun et al. (2008b) suggested that freezing-induced capillary drainage, gravity drainage due to groundwater table fluctuation, and freezing induced processes are mechanisms controlling LNAPL migration and accumulation in MWs at the site. Thus, this study was designed to complement their previous field work and evaluate the hypothesis that freezing induced displacement may play a secondary role in mobilizing contaminant at the site.

Consequent to discussions above, a freezing cell made of two parallel glass plates representing a fracture was constructed to evaluate the influence of freezing-induced displacement and freeze–thaw cycles on LNAPL mobility, and the effect of freezing on soluble oil in the formation. The method used in this study was a modification of those used by various authors to investigate pore-scale behavior of contaminant in freezing porous media (Niven and Singh, 2008; Barnes and Wolfe, 2008; and Arenson and Sego, 2006).

2. Methodology

Equipment and materials used for this experimental study include: process control equipment (RTD regulator; range ±199.9oC, MODEL 4201APC2-T, omega), two glycol baths (LAUDA BRINKMANN, ecoline RE 120), a digital camera (Canon SLR 1000D), two computers, and freezing cell. Others are Agilent data acquisition unit, diesel, soluble oil, fluorescein, two fluorescent light tube-units, an air bag heater, a water bath, insulated enclosures, RTD probes, copper freezing plates, and weights.

2.1. Freezing cell

The freezing cell is constructed from Perspex glass as shown in Fig. 1. It consists of sealed parallel glass plates interspaced at 1 mm (1000 μm) to mimic a fracture. The initial intent was to roughen the internal surfaces of the glasses but this would have impaired visibility to view the behavior, so glass beads were placed within the fracture instead. The objective of placing beads within the freezing cell is to enable entrapment of LNAPL within the water column.

The emplacement of the beads was done by first setting the required fracture width at both ends of the parallel glass plates and sealing the sides with silicone-laminated glass and the base with a porous filter. The beads were cleaned with hydrofluoric acid before placement into the created aperture. It should be noted that the beads were not of uniform size and shapes. Thus, during placement, some beads were stuck and had to be pushed down using thin wire gauze. Non-uniformity of the bead's geometry led to slight overlapping of some beads within the cell. Porous filter-glass was used between the RTD ports and the beaded filled-annulus of the cell to enable direct contact between the RTD and fluid within the cell.

The dimensions of the freezing cell are shown in Fig. 1. Five RTD probes were fitted to one of the edges of the cell to monitor the thermal profile during the test. A control valve with pressure relief cork was fitted to the base of the cell. The control valve was used to moderate water filling while the pressure relief cork was used to prevent cracking of the apparatus due to volume change of ice. The tube connecting the control valve to the cell was made of expandable rubber to accommodate for displaced water during top-down freezing.

The top of the cell was uncovered, but had an emplaced aluminum mesh with 0.5 mm openings to prevent the beads from falling and to enhance heat dissipation. The apparatus was checked for leaks prior to testing and the RTD probes were calibrated before attachment to the cell using silicone glue.

The cell was insulated as shown in Fig. 1 prior to the testing. The insulation consisted of foam with a glass window as shown in Fig. 1.