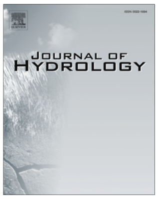
Journal of Hydrology 515 (2014) 281–291

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol



Effect of residual oil saturation on hydrodynamic properties of porous media

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ARTICLE INFO

Article history:
Received 19 October 2013
Received in revised form 19 April 2014
Accepted 29 April 2014
Available online 9 May 2014
This manuscript was handled by Corrado Corradini, Editor-in-Chief, with the assistance of Juan V. Giraldez, Associate Editor

Keywords:
Residual oil saturation
Porous medium
Effective porosity
Permeability
Dispersivity

SUMMARY

To understand the effect of residual oil on hydraulic properties and solute dispersive behavior of porous media, miscible displacement column experiments were conducted using two petroleum products (diesel and engine oil) and a sandy soil. The effective water permeability, effective water-filled porosity, and dispersivity were investigated in two-fluid systems of water and oil as a function of residual oil saturation (ROS). At the end of each experiment, the distribution of ending ROS along the sand column was determined by the method of petroleum ether extraction-ultraviolet spectrophotometry. Darcy's Law was used to determine permeability, while breakthrough curves (BTCs) of a tracer, Cl^-, were used to calibrate effective porosity and dispersivity. The experimental results indicate that the maximum saturated zone residual saturation of diesel and engine oil in this study are 16.0% and 45.7%, respectively. Cl^- is found to have no sorption on the solid matrix. Generated BTCs are sigmoid in shape with no evidence of tailing. The effective porosity of sand is inversely proportional to ROS. For the same level of ROS, the magnitude of reduction in effective porosity by diesel is close to that by engine oil. The relative permeability of sand to water saturation decreases with increasing amount of trapped oil, and the slope of the relative permeability–saturation curve for water is larger at higher water saturations, indicating that oil first occupies larger pores, which have the most contribution to the conductivity of the water. In addition, the reduction rate of relative permeability by diesel is greater than that by engine oil. The dispersivity increases with increasing ROS, suggesting that the blockage of pore spaces by immobile oil globules may enhance local velocity variations and increase the tortuosity of aqueous-phase flow paths.

1. Introduction

With a large demand for oil as an energy source, oil contamination occurs quite often as a result of exploration, production, maintenance, transportation, storage, use and accidental release of oil and petroleum products (Wilson and Jones, 1993; Guerin et al., 2002; He et al., 2008; Tiehm et al., 2008; Liang et al., 2012). Once oil spill penetrates the subsurface, oil contaminants may spread laterally when they encounter the capillary fringe and the water table (Schwille, 1981; Pfannkuch, 1984). Contaminants may also be distributed vertically over the entire range of water table fluctuations (Hunt et al., 1988). The percolation, dissolution, and equilibration of oil contaminants, especially low viscosity and highly soluble oil products, threaten potable groundwater quality (EPA, 2013a). This poses a serious risk to maintain public health and safety. It has been suggested that petroleum hydrocarbons, such as benzene, polycyclic aromatic hydrocarbons (PAHs), and methyl tert-butyl ether (MTBE), which contain toxic and hazardous substances, may lead to carcinogenesis, teratogenesis, and mutagenesis (Nadim et al., 2000; Sadikovic and Rodenhiser, 2006).

In saturated zone, oil is usually not uniformly distributed due to spatial heterogeneity of medium pore size distribution, causing spatial variation in oil saturation (Hunt et al., 1988). This may lead to alteration of hydrodynamic properties of this water–oil two-phase system. During the past several decades, many studies regarding dispersion as well as saturation-relative permeability-capillary pressure relationships during water–oil two-phase flow have been reported (Maini et al., 1986; Wang, 1988; Parker and Lenhard, 1990; Demond et al., 1994; Bekri and Adler, 2002; O'Carroll et al., 2005; Manthey et al., 2008). However, these research results can be applied only to conditions where both fluids are continuous, but not necessarily to conditions where oil contaminants are found at residual saturation.

After oil becomes discontinuous and is immobilized by capillary forces at residual saturation, the volume of residual oil may change as dissolution and natural degradation progress under ambient groundwater flow conditions. To accurately design a remediation

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http://dx.doi.org/10.1016/j.jhydrol.2014.04.067
0022-1694/

system, such as reactive barrier and bioattenuation, it is necessary to understand the effect of variation in residual oil saturation (ROS) on porous-medium properties, including effective porosity, permeability, and the hydrodynamic dispersion coefficient, for studying solute transport. However, only few studies concerning this issue have been conducted so far.

In literature, variation of porous-medium permeability caused by residual oil has been demonstrated (Demond and Roberts, 1993; Puri, 2000; Shin and Das, 2000; Khamehchiyan et al., 2007; Rahman et al., 2010). It has been suggested by previous study that permeability increase monotonically with increasing sand-particle size and decrease with increasing ROS. In other words, these studies further confirm the Kozeny–Carman equation (Bear, 1972, 1979) that permeability is a function of porosity. However, few studies have been undertaken to compare the effect of high (e.g. crude oil and engine oil) and low viscosity (e.g., gasoline and diesel) oils on permeability. High viscosity oils contain some polar fractions (non-hydrocarbon, asphaltene) which do not exist in low viscosity oils. These polar compounds may change the wettability of the porous medium (Crocker and Marchin, 1988), thus affecting the relative water permeability in the water–oil two-phase system.

In order to characterize the effect of residual NAPL on longitudinal dispersion in porous media, Miller et al. (1990) performed tracer tests on columns packed with glass beads and toluene at various levels of residual saturation. The experimental result showed that there was no significant difference in longitudinal dispersivities among the runs performed with different residual saturations. However, this conclusion does not necessarily apply to the real aquifer medium, because both the particle size range and the shape of the glass beads used in this study are quite different from those of ordinary aquifer medium. In three other studies, increased longitudinal dispersivities induced by residual NAPL were observed (Pennell et al., 1993, 1994; Rogers and Logan, 2000). However, the mechanism behind this phenomenon remains unclear. In addition, these studies only measured longitudinal dispersivities in the presence and absence of residual NAPL. The subject about dispersivity as a function of ROS has not been thorough studied. To obtain parameter values for groundwater transport modeling, including effective porosity, hydraulic conductivity and dispersivity, Lundy et al. (2009) performed two dipole tracer tests in a heterogeneous alluvial aquifer LNAPL smear zone with an average ROS of approximately 6.5%. They argued that reduced parameter values are expected when LNAPL shares the void space with groundwater. However, these site-specific parameter values may not contribute much to the understanding concerning the quantitative behavior of porous-medium hydrodynamic properties as a function of oil saturation at levels of ROS.

As stated above, the mechanisms of hydrodynamic-property changes by ROS in porous media are not completely understood. To keep the pace with the increasing need for site remediation of oil-contaminated aquifers, it is necessary to gain quantitative insights into the effect of ROS on hydrodynamic properties. In this study, we conducted experiments of solute transport in sand columns contaminated with diesel and engine oil at various residual oil saturations and calibrated hydrodynamic parameters accordingly. Finally, physical processes of residual-oil impact on hydrodynamic properties are discussed.

2. Materials and methods

2.1. Soil sample

Sandy soil (hereinafter referred to as sand) sampled from the Zihe river basin in Shandong, China, was used as a porous medium in the experiments described below. The sand sample was air-dried and sieved according to the Specification of Soil Test (Ministry of Water Resources, 1999a) to determine particle size distribution. Besides, the sand was also characterized for organic matter content and particle density. Organic matter content was determined using the wet digestion technique (Institute of Soil Science, 1978), and particle density was measured with the pycnometer method (Ministry of Water Resources, 1999b).

2.2. Petroleum products

No. 0 diesel (hereinafter referred to as diesel) and CD15W/40 diesel engine oil (hereinafter referred to as engine oil) provided by Sinopec Qilu Company Ltd., were used in the experiments. Oil properties at 20 °C, including density, viscosity, interfacial tension for air–oil and oil–water, were measured with a commercial densimeter (SY-05, Zhongya, China), a rotational viscometer (VT-04F, RION, Japan), and a ring method (ASTM, 1993), respectively.

2.3. Miscible displacement experiments

Miscible displacement experiments were conducted in a 30 cm long cylindrical plexiglass column with an inner diameter of 5 cm. The column was equipped with a constant head device and a water supply bottle to achieve steady state flow conditions (Fig. 1). All of the experiments were run in up-flow mode, with the column in a vertical position.

The mass of air-dried sand used for packing the column remained constant for each experimental run, and the sand bulk density in all runs was maintained at 1.60 g/cm^3. Before packing, dry sand was first poured into a separate container. A predetermined volume of oil, based on the targeted residual saturation, was then added to the sand from a glass syringe. The sand was thoroughly stirred in order to achieve uniform distribution of residual oil within it (Miller et al., 1990; Parker et al., 1991). Clean column was packed uniformly using oil–sand mixture as quickly as possible. During the mixing and packing processes, care was undertaken to minimize volatilization losses. The top of the column was covered to prevent further volatilization, while tiny holes in the cover allowed air pressure to remain atmospheric. Once packed, the column was saturated from the bottom very slowly with de-aired, distilled water to minimize trapped air, and then flooded with 3 pore volumes of the same water to leach soluble salts and displace mobile oil within the packed bed. Next, a calcium

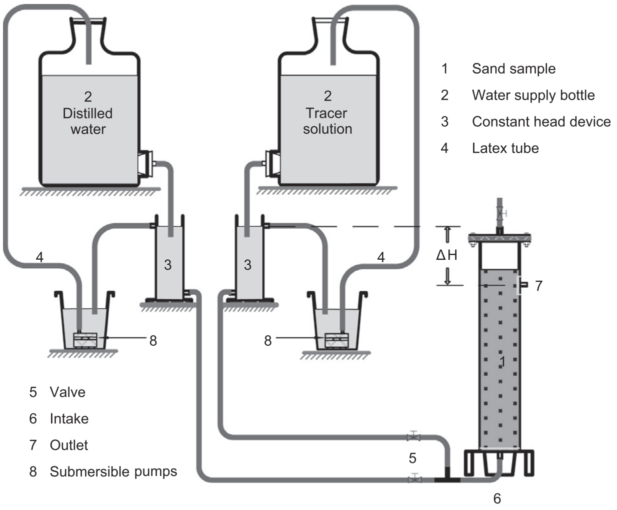

Fig. 1. General setup for miscible displacement experiments.