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# Volatilization behaviors of diesel oil from the soils

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**Abstract**: The volatilization of diesel oil, Shengli crude oil and 90 # gasoline on glass surface of petri dishes were conducted at the ambient temperature of 25℃. Diesel oil evaporates in a power manner, where the loss of mass is approximately power with time. 90 # gasoline evaporates in a logarithmic with time. Where as the volatilization of Shengli crude oil fit either the logarithmic or power equation after different time, and has similar $R^2$. And the effects of soil type and diesel oil and water content on volatilization behavior in unsaturated soil were studied in this paper. Diesel oil and water content in the soils play a large role in volatilization from soils. Appropriate water helps the wicking action but too much water stops it. The wicking action behaves differently in four different types of soils in the same volatilization experiment of 18% diesel oil content and air-dry condition.

**Keywords**: volatilization; diesel oil; power curve

## Introduction

Contamination from oil spill to the unsaturated zone accidents is likely to occur in the forms of pipeline leaks, train derailments, storage tank ruptures, and transport accidents. The behavior of oil contaminants in the unsaturated zone is difficult to predict related to a number of soil factors, oil properties and environmental conditions that determine the eventual fate of oil contaminants. The oil contaminants undergo with complex activities such as volatilization, adsorption, desorption and degradation processes, in which volatilization is a very important process as there are many volatile hydrocarbons in the petroleum products and pose safety and health threats due to vapor migration into the atmosphere and underground structures such as basements and sewers.

Diesel oil, a middle distillation fraction of crude oil, is one of the major pollutants of soil near gas filling stations. Generally, gasoline is volatile and diesel oil is semi-volatile, so very little empirical data on diesel oil volatilization has been published. But according to the findings of Koenig (Koenig, 2001) the losses of diesel by volatilization were found to be as high as 58% over 360 d, which suggesting that volatilization may be a significant method of contaminant removal that may has been previously underestimated or overlooked in short term studies.

The basis for the oil volatilization in the literature is water evaporation. The evaporation rate of water is a constant with respect to time(Jones, 1992; Brulsaert, 1982). But for multi-component fuel mixtures such as crude oils and petroleum products, the evaporative losses by total weight or volume are not line with time(Merv, 1997; Stiver, 1973). Diesel oil is a mixture of hydrocarbons with a range of physical and chemical properties. Although the kinetics of multi-component volatilization has been studied (Labutin, 1984; Migunov, 1984; Martinez de la Cruz, 1990), the volatilization of multi-component from soils has just recently been studied experimentally (Galin, 1990a; 1990b; Fine, 1993; Jarsjö, 1993; 1994).

The experimental evidences showed that soil type and water content in soil will affect the volatilization process of contaminants(Acher, 1990; Spencer, 1982). Soils such as clays, which exhibit higher porosities and have pore size distributions skewed towards smaller pores, show lower volatilization rates than sand due to increased adsorption. Arthurs(Arthurs, 1995) and Smith(Smith, 1994) found that the immiscible phase itself could rise in soils as the effect of capillary rise. However, most of the volatilization tests are about gasoline and kerosene, and the volatilization study of diesel oil from soils is limited. The effects of soil type, water content, and diesel contaminant on volatilization from soil are discussed in this paper.

## 1 Materials and methods

### 1.1 Materials

The soils used in the present experiments were collected from four different places in Zibo City, China. The properties of the experimental soils are presented in Table 1. Soil sample No. 1 was collected from a clean riverbank, soil sample No.2 was taken from an orchard soil, soil sample No. 3 was obtained from the Qilu Petrochemical Corporation, and soil sample No.4 was sampled from the farm land, and all the soils mentioned above were collected from 20—30 cm below the surface of the respective spots.

After soil samples collection, the soils were air-dried, grounded and sized through a screen with 1 mm openings, and be stored in sealed containers respectively at room temperature.

The diesel oil, Shengli crude oil and 90 # gasoline used in this experiment were taken from Qilu Petrochemical Corporation.

**Table 1 Characteristics of the soils used in the experiments**

| Analysis | Soil sample | | | |
|---|---|---|---|---|
| | No.1 | No.2 | No.3 | No.4 |
| Particle size analysis | | | | |
| Sand, % | 33.3 | 65.6 | 5.1 | 44.2 |
| Silt, % | 61.2 | 29.7 | 74.4 | 50.5 |
| Clay, % | 5.5 | 4.7 | 20.5 | 5.3 |
| Bulk density, kg/m | 1595 | 1648 | 1461 | 1772 |
| Moisture content | 18.2 | 13.2 | 24.6 | 15.2 |
| Organic matter(by weight) | 0.6 | 1.3 | 0.1 | 2.8 |
| Air-dried water content, g water/g dry soil | 2.1 | 1.8 | 7.5 | 3.3 |

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### 1.2 Experimental procedures

#### 1.2.1 Oils ( crude oil, diesel oil and gasoline ) volatilization from the glass surface of petri dishes

The comparisons of volatilization capabilities of Shengli crude oil, diesel oil and 90 # gasoline were conducted on the standard 13 mm diameter(ID) petri dishes respectively. The volatilization was conducted directly from the glass surface of the dishes at an ambient temperature of 25℃. The volatilization rate was measured by weight loss using an electronic balance, which is capable of measurements to 0.0001 g. The tarred petri dishes are loaded with a measured amount of oils respectively. The height of the lip of the glass above the oil is 1 mm. Volatilization data were measured periodically.

#### 1.2.2 Diesel oil volatilization from the soil columns

The diesel oil volatilizations from the soil columns at different water and oil contents for four different soils were conducted and the soils were sterilized to eliminate the action of microorganisms. The 35 mm in ID and 20 cm in length PVC columns are used. The column was marked into five parts along the side. After the desired duration, the column was divided into five segments destructively according to the marks along the side of the soil column, and then the middle part of each segment was analyzed for oil content.

Seven experimental conditions were tested, as presented in Table 2.

**Table 2 Experimental conditions**

| Soil number | Diesel content, % (dry weight) | Water content, % (dry weight) | Experiment condition code |
|---|---|---|---|
| No.1 | 18 | 2 | 18D-2W (No.1) |
| No.2 | 18 | 2 | 18D-2W (No.2) |
| No.2 | 4 | 2 | 4D-2W (No.2) |
| No.2 | 4 | 10 | 4D-10W (No.2) |
| No.2 | 4 | 20 | 4D-20W (No.2) |
| No.3 | 18 | 7.5 | 18D-7.5W (No.3) |
| No.4 | 18 | 2 | 18D-2W (No.4) |

For each experimental condition, seven columns of different oil and water content were set up, after 0, 24, 96, 192, 288, 432 and 624 h test, the columns were destructively sampled and the middle parts of each segment was analyzed for oil content. In order to establish initial oil contents after the losses in column preparation, the zero hour columns were set up for each experimental conditions.

The 5-lift method is used for all experiments in order to eliminate poor initial distribution of diesel oil and water in the soils. For each experiment, five equal lifts of soil were first shaken with the appropriate amount of water, then the appropriate diesel oil was added respectively, and then the five lifts of soil were mixed thoroughly. At the end, the soils were added to the column with the desired bulk density.

### 1.3 Analytical procedure

For the volatilization experiments on the glass surfaces of petri dishes, the volatilization rate was recorded according to the weight loss using an electronic balance. In the volatilization experiments on soil columns, each column was destructively sampled and analyzed after the desired duration, and the diesel oil content was determined by infrared spectrometry described as follows. Three to four grams of soil sample were taken from the middle of each segment of a soil column and placed into a 50 ml borosilicate vial with a Teflon™-lined septum. And then, anhydrous sodium sulphate was added as a drying agent in a 1:3 ratio of soil sample to anhydrous sodium sulphate to the vial, and the soil drying agent mixture was mixed until the soil sample had been sufficiently dispersed. Then 20 ml of carbon tetrachloride ($CCl_4$) was added to the vial and mixed for 20 min with a wrist-action shaker to partition the diesel oil into the solvent phase. The soil-solvent mixture was then transferred into the semi-auto extractor; another 20 ml $CCl_4$ was added to the vial to rinse the remainder in the vial and also transferred into the same semi-auto extractor. The total mixture is mixed thoroughly, and then allowed to settle for 0.5 h. The fraction of separated solvent was removed from the semi-auto extractor for analysis by infrared spectrometry.

## 2 Results and discussion

### 2.1 The relationship between different oil volatilization rate and time

In order to compare the different oil volatilization rates of diesel oil, Shengli crude oil and 90 # gasoline were used to determine the different volatilization rate with time. The best fit of relationship between volatilization rate and time was done on the basis of the simplest equation fitting with the highest $R^2$. According to this rule, the fitting equation to the Shengli crude oil, 90 # gasoline and diesel oil is presented in Fig.1—3 respectively. The dispersed dots designate the experimental data and the lines are the trendlines. The volatilization of Shengli crude oil fits a logarithmic curve with the $R^2$ of 0.9662(Fig.1a), while fits a power curve with the $R^2$ of 0.9826(Fig.1b). Fig.2 shows that the 90 # gasoline volatilization as a logarithm relationship with time likes many other oils mentioned elsewhere (Merv, 1997). Fig.3a and Fig.3b clearly show that the volatilization of diesel oil fit with a power curve ( $R^2$ = 0.9952) better than the logarithmic curve( $R^2$ = 0.8762). Diesel oil is a semi-volatile petroleum product and its behavior of volatilization differs from other crude oil and petroleum products.

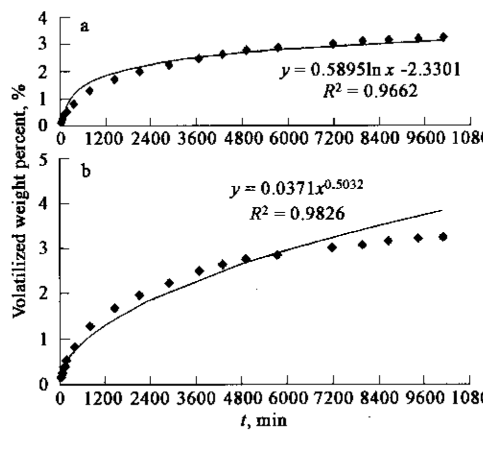


Fig.1 Logarithmic curve fit to Shengli crude oil volatilization data ( a ); exponential curve fit to Shengli crude oil volatilization data(b)

In conclusion, the short-term volatilization of 90 # gasoline fit with the logarithmic curve, and the volatilization data of diesel oil fit best with the power equation. While

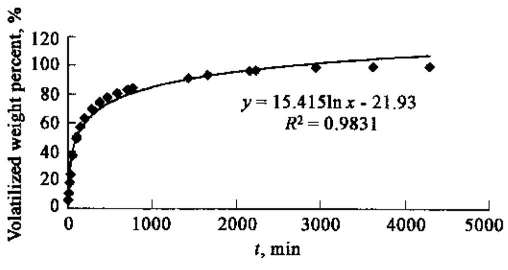


Fig.2 Logarithmic curve fit to 90 # gasoline volatilization data

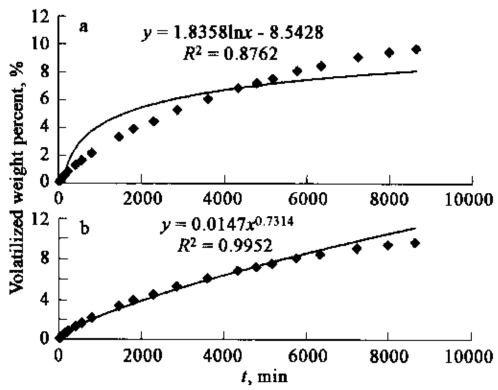


Fig.3 Logarithmic curve fit to diesel oil volatilization data (a); exponential curve fit to diesel oil volatilization data(b)

Shengli crude oil fit either logarithmic or power equation, which is determined by the volatilization time during the short-term volatilization experiment test, it fit with power equation better before 2100 min of volatilization and with logarithmic curve after 2100 min.

## 2.2 The effects of soil type, water and oil content on diesel oil volatilization

During the volatilization of oil from soil, the oil and water content and soil types play very important functions. In this paper, the impact of diesel oil and water content on the volatilization rate from soil columns were discussed, and the results are presented in a series of graphs as follows.

Due to the shorter distance to atmosphere, the oil in surface soil evaporates easily. Which can be identified by the results of 4D-2W No. 2 soil case (Fig. 4), the diesel oil concentration near the surface is consistently the lowest in the soil column. But for the case of 18D-2W No. 2 soil condition, the surface diesel oil concentration is always higher than the average oil concentration in the column due to high diesel content (Fig. 6) as there is sufficient diesel present for volatilization, this phenomenon was due to the connectivity of the capillary and chemical action in the soil, and it is called the wicking phenomenon. At the low diesel

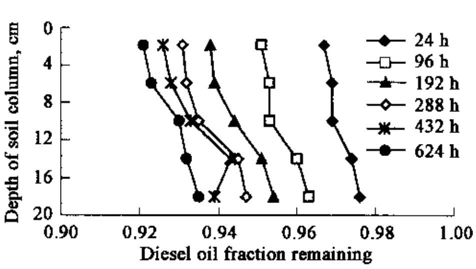


Fig.4 Diesel oil fraction remaining in 4D-2W for soil No.2

oil condition, diesel oil distributes in soil pores disconnectedly, as a result, the chemical conductivity is poor. This behavior was also represent in other three soils with high diesel oil content conditions(Fig.5, 7 and 8).

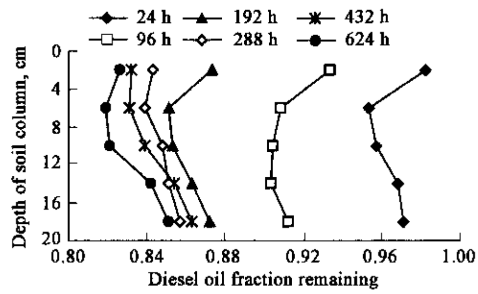


Fig.5 Diesel oil fraction remaining in 18D-2W for soil No.1

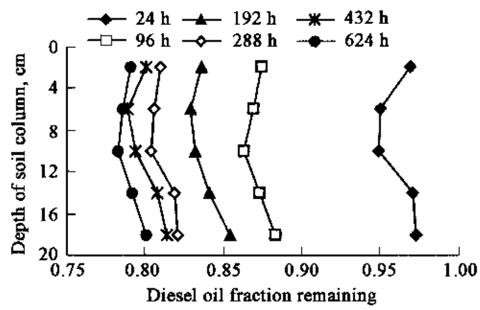


Fig.6 Diesel oil fraction remaining in 18D-2W for soil No.2

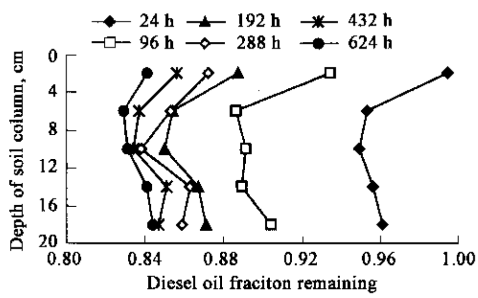


Fig.7 Diesel oil fraction remaining in 18D-7.5W for soil No.3

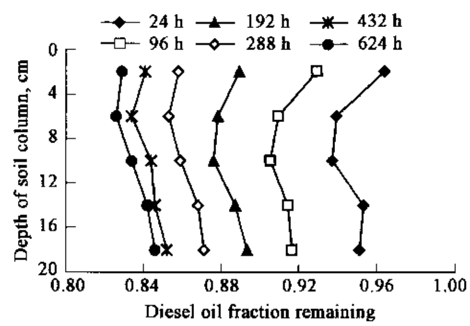


Fig.8 Diesel oil fraction remaining in 18D-2W for soil No.4

Fig. 9 shows the effect of different water content conditions at low oil content condition for No.2 soil during the diesel oil volatilization experiment. The water content increases from air-dry condition(4D-2W) to 4D-10W and to the high water content condition(4D-20W). When the water content increased from the air-dry condition to a high water condition(4D-10W), there was a considerable increase of capillary action, and the diesel oil concentration at the surface of the soil was higher than the average soil column values. But when the water content reaches the higher level of 4D-20W conditions, the capillary action sharply declines. Therefore, the wicking phenomenon is a non-linear function of water content during diesel oil volatilization, while appropriate water helps the process too much water stops it. The water occupies the smaller soil pores in the soil preferentially. Therefore, the diesel oil has to occupy the larger soil pores after spike into the soil because the diesel oil cannot displace the water from the soil. After the diesel occupies the relatively larger soil pores, the wicking action will be promoted as a result of better chemical conductivity. But when the soil pores are too large, it will restrain the capillary action. So the proper water content that helps the capillary action is very important, too low water content will enhance the adsorption of oil to the soil surface while restrain the volatilization to the air, at the same time too high water content will restrain the volatilization of oil from soil due to its occupy the most soil pores.

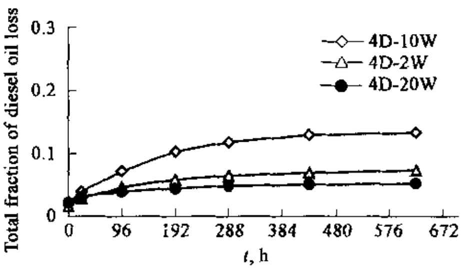


Fig. 9 The effect of water content on diesel oil volatilization (No.2 soil)

In order to evaluate the effect of soil type on diesel oil volatilization, the experiments for four different soils of 18% diesel oil content under air-dry conditions were conducted at an ambient temperature of 25℃. Fig. 10 suggests that there is a similar loss of diesel oil at the end of the volatilization experiment for four different soils, and No. 2 soil has a slightly higher loss while No.3 has a lower loss than the other two soils. However, there is a big difference of wicking action among four different soils. The No.3 soil is the finest soil, in which the soil pores are smaller than the other three soils. As a result, the wicking action lasts to 432 h after the volatilization experiment for No.3 soil while the other three soils just lasted 96 h(Fig.5—8).

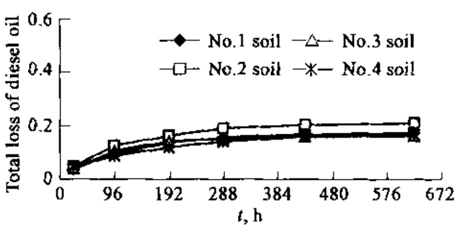


Fig.10 Total fraction of diesel oil lost on four soils (18% diesel at air-dry conditions)

## 3 Conclusions

Diesel oil is an important petroleum product. Therefore, it is very important to study the fate of diesel oil in the environment. The studies of volatilization of diesel oil in this paper can draw some conclusions.

The diesel oil used in this paper evaporates in a power manner, where the loss of mass approximately power with time. And the power equation is $Y = cX^e$, where $Y$ is the percent of the diesel oil volatilized, $c$ is the empirical constant, $X$ is the volatilizing time(min) and $e$ is the power exponent. The correlate fitting equation for diesel oil in this volatilization test was: $Y = 0.0147X^{0.7314}$, and $R^2$ is 0.9952. 90 # gasoline evaporates as a logarithmic with time. While Shengli crude oil fit either the logarithmic or power equation, which was determined by the volatilization time during the short-term volatilization experiment test.

The initial diesel oil content in the soil plays a large role in volatilization behavior. Water impacts the wicking movement of diesel oil in soils; while appropriate water helps the process too much water stops it. Therefore, the appropriate water content can help to pull the oil contaminants to the surface of the soil.

The soil type plays a very important role in diesel oil volatilization from soil. The No.2 soil was a sandy loam and helped the volatilization. While the No.3 soil was the finest soil and showed a lower volatilize rate, and wicking action lasted to 432 h since the beginning of the volatilization experiment.

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