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Effects of Diesel Concentration on the Thermal Conductivity, Specific Heat Capacity and Thermal Diffusivity of Diesel-Contaminated Soil

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Abstract: High energy consumption is a serious issue associated with in situ thermal desorption (TD) remediation of sites contaminated by petroleum hydrocarbons (PHs). The knowledge on the thermophysical properties of contaminated soil can help predict accurately the transient temperature distribution in a remediation site, for the purpose of energy conservation. However, such data are rarely reported for PH-contaminated soil. In this study, by taking diesel as a representative example for PHs, soil samples with constant dry bulk density but different diesel mass concentrations ranging from 0% to 20% were prepared, and the variations of their thermal conductivity, specific heat capacity and thermal diffusivity were measured and analyzed over a wide temperature range between 0°C and 120°C. It was found that the effect of diesel concentration on the thermal conductivity of soil is negligible when it is below 1%. When diesel concentration is below 10%, the thermal conductivity of soil increases with raising the temperature. However, when diesel concentration becomes above 10%, the change of the thermal conductivity of soil with temperature exhibits the opposite trend. This is mainly due to the competition between soil minerals and diesel, because the thermal conductivity of minerals increases with temperature, whereas the thermal conductivity of diesel decreases with temperature. The analysis results showed that, compared with temperature, the diesel concentration has more significant effects on soil thermal conductivity. Regardless of the diesel concentration, with the increase of temperature, the specific heat capacity of soil increases, while the thermal diffusivity of soil decreases. In addition, the results of a control experiment exhibited that the relative differences of the thermal conductivity of the soil samples containing the same concentration of both diesel and a pure alkane are all below 10%, indicating that the results obtained with diesel in this study can be extended to the family of PHs. A theoretical prediction model was proposed based on cubic fractal and thermal resistance analysis, which confirmed that diesel concentration does have a significant effect on soil thermal

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conductivity. For the sake of practical applications, a regression model with the diesel concentration as a primary parameter was also proposed.

Keywords: contaminated soil; diesel concentration; thermal conductivity; specific heat capacity; thermal diffusivity; thermal desorption; fractal model

1. Introduction

Soil is an important part of the earth's surface system, as well as the material basis of human survival, production and development. However, the increasingly serious issue of soil contamination has raised global concern [1, 2]. The leakage of PHs is prevailing during exploitation, transportation, storage and utilization of petroleum [3], and soil contaminated by PHs is becoming prominent because global economic activities are strongly related to petroleum-based energy sources in recent decades [4]. PHs refer to the mixtures of alkanes, cyclanes, arenes and a small amount of other organic matters, such as organic acids, phenol and ketone [5], which have relatively low volatility and high hydrophobicity, and are easily adsorbed in soil for a long time [6]. The PHs adsorbed in soil will pose a serious threat to the surrounding ecological environment and human health if they are not remediated in time [7].

Thermal desorption (TD) remediation technology has been widely applied to various organic contaminated sites because of its advantages of high removal rate, rapid remediation and wide applicability [8]. It volatilizes, separates and centrally treats organic contaminants by heating the soil [9]. At present, the heating temperature of TD can reach 500°C–600°C [10], which exceeds the boiling point of most components in PHs, making it applicable for remediating PH-contaminated sites. However, heating soil requires massive device construction and energy consumption, so the cost of TD is very high, especially for in situ remediation scenarios.

The existing studies on TD have mainly been focused on various aspects, including the changes in soil ecological properties after the remediation [11–14], the removal efficiency of contaminants [1, 7, 15], as well as its combination with other remediation technologies, such as bioremediation [16, 17] and chemical oxidation [8]. However, little attention has been paid to reducing energy consumption during the TD remediation process. In view of the growing global concern about carbon emissions and the carbon neutrality goal proposed by governments of many countries, it will become increasingly significant to reduce the energy consumption of TD towards a sustainable future. In the practical TD remediation project, only by accurately knowing the thermophysical properties of the contaminated soil and the influence of contaminant migration and phase change on the site temperature distribution, can we effectively guide the reasonable layout of heating wells and immediate adjustment of the heating power, with the

Nomenclature

a	Thermal diffusivity/m^2·s^{-1}	d,a	Diesel-air mixture
c_p	Specific heat capacity/kJ·(kg·°C)$^{-1}$	dry	Dry soil
k	Thermal conductivity/W·(m·°C)$^{-1}$	s	Solid phase in soil
L	Side length/m	I	Fractal part of a soil unit
m	Mass/kg	I1	Fractal part of a soil unit
n	Porosity/%	I2	Fractal part of a soil unit
R	Thermal resistance/m^2·K·W^{-1}	I3	Fractal part of a soil unit
V	Volume/m^3	II	Fractal part of a soil unit
Greek letters		**Abbreviations**	
θ	Mass fraction	DSC	Differential scanning calorimeter
ρ	Density/kg·m^{-3}	PHs	petroleum hydrocarbons
φ	Volume fraction	RMSV	Ratio of mean square value
Subscripts		SEM	Scanning electron microscope
a	Air	TD	Thermal desorption
d	Diesel		

purpose of reducing total energy consumption. It is in the context of TD that the knowledge on thermophysical properties (i.e., thermal conductivity, specific heat capacity and thermal diffusivity) of contaminated soil are crucial.

There have been numerous studies on the various influencing factors of soil thermophysical properties, including the stable inherent factors which determine soil classification, such as mineral composition and particle size distribution, as well as the changeable extrinsic factors, such as moisture content, saturation, porosity, dry bulk density and temperature. Mineral composition, especially the mass fraction of quartz, is one of the decisive parameters in the classical normalized model of soil thermal conductivity established by Johansen [18], because quartz is in general the most abundant mineral in soil and has high thermal conductivity. Some improved models and subsequent studies [19–22] have also recognized the prominent role of quartz content. For the extrinsic factors, moisture content and saturation, which are directly related to water, are considered having the most significant effects on soil thermophysical properties, followed by porosity and dry bulk density, while temperature has relatively less significant effects [22–25].

However, the referential studies on the influence of contaminate concentration on soil thermophysical properties are scarce. Malyshev et al. [26] analyzed the thermal conductivity and volumetric specific heat capacity of sandy soil contaminated in two scenarios of oil pollution. In the first scenario, the oil product was introduced into wet soil, while in the second scenario, dry soil was contaminated by the oil product and was then moistened with water. These two scenarios were considered as multi-component dispersion systems with varying degrees of contamination and humidity. The theoretical calculations showed that the thermal conductivity of the sandy soil increases under the first scenario and decreases under the second, while the change of the volumetric specific heat capacity is proportional only to the amount of oil pollution, which is not dependent on the way by which the oil was introduced. The experimental results were consistent with the theoretical calculations. Besides, the temperature dependence of the two thermophysical properties of sandy soil when polluted by oil was determined. However, the temperature range involved in this study was only between −35°C and 20°C, so the corresponding conclusions have great limitations when applied in the practical TD remediation project where much higher heating temperatures are expected.

In view of the lack of important thermophysical property data of PH-contaminated soil in existing literature, as well as the knowledge on the influence of PH concentration on these properties, in-house measurements on the thermal conductivity, specific heat capacity and thermal diffusivity of artificially contaminated soil by diesel with various concentrations were carried out in this work. Diesel was used to represent the family of PHs. The soil samples were taken from a PH-contaminated site in Gansu Province, China. The particle size distribution and mineral composition of the soil samples were characterized. After a TD treatment at 400°C to remove the original contaminants, artificially contaminated soil samples with various diesel concentrations (by mass fraction) up to 20% were prepared. Considering that diesel is a mixture of various PHs, soil samples containing the same concentration of pure alkanes were also prepared as the control group. The thermal conductivity and thermal diffusivity of the samples were measured by a KD2 Pro analyzer based on the thermal probe method, while the specific heat capacity was measured by a differential scanning calorimeter (DSC). According to the experimental results, the effects of diesel concentration on soil thermophysical properties were analyzed, and the prediction models for the thermophysical properties of diesel contaminated soil were proposed which will be useful for the application and optimization of TD remediation of PH-contaminated soils.

2. Materials and Methods

2.1 Soil sampling, characterization and thermal desorption

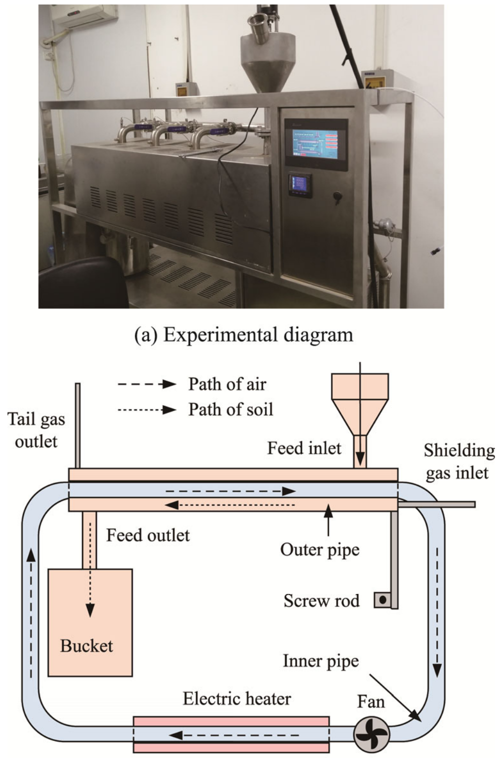
Soil samples (depth, 0.5–9.5 m) were taken from 3 sampling points in an in situ remediation site contaminated mainly by PHs (C_6–C_{40}) in Gansu Province, China. The density of solid particles in soil is 2700 kg/cm^3; the dry bulk density of soil is 1400 kg/cm^3, and the porosity is 0.481. A preliminary site investigation showed that the contaminants in this site are mainly concentrated in the silt and silty sand layers with an average depth of 0.5–9.5 m. The mass concentrations of C_6–C_9 and C_{10}–C_{40} at each sampling point were characterized by purge and trap/gas chromatography method [27] and gas chromatography method [28], respectively. As shown in Table 1, the distribution of PHs in this remediation site is uneven, and the concentration of total PHs (C_6–C_{40}) at a certain point (#1, 5.0 m) is close to 7% (converted into mass percentage).

After sampling, the particle size distribution and the mineral composition of the soil samples were characterized. To classify the soil samples by texture, the particle size distribution was characterized by the sieving method and the densitometer method [29]. The type and the mass fraction of various minerals were characterized by the X-ray diffraction method, which is used to obtain the diffraction pattern of soil samples by X-ray, followed by a comparison of the diffraction characteristics, such as peak type, peak intensity and D-value, with the standard mineral types, to judge the mineral types and corresponding content in the samples [30].

Table 1 Concentration of PHs at each sampling point of the remediation site

Sampling point	Depth/ m	Concentration of (C_6–C_9)/mg·kg^{-1}	Concentration of (C_{10}–C_{40})/mg·kg^{-1}
#1	5.0	56 000	13 800
	9.5	1720	2820
#2	5.0	7050	3350
	9.5	35 000	6540
#3	5.0	26 200	2700
	9.5	23 000	4650

The soil taken from the remediation site may contain some other contaminants, such as halogenated hydrocarbons and pesticides. In addition, the concentration distribution of the original contaminants is extremely uneven, which may interfere with the analysis of experimental results. In order to control variables and eliminate the potential interference from other contaminants, it is necessary to remove all the original contaminants in the soil to obtain "clean" blank samples, and then introduce the target contaminant to the blank samples and mix them up to make the target contaminant evenly distributed. A previous study [31] on a compound contaminated site found that the main organic contaminants in soil, including PHs (C_6–C_{20}), benzene series and halogenated hydrocarbons, can be removed through a TD treatment at 350°C. Such treatment caused a slight increase of the average particle size, but did not change the mineral composition. The significance analysis of the experimental results showed that when other parameters such as dry bulk density, moisture content and temperature are the same, the thermal conductivity of the soil samples has no significant change compared with that before the TD treatment, which also indicates that it is feasible and meaningful to study the thermophysical properties of soil samples after the TD treatment. In view of that the boiling points of some soil contaminants in this study are slightly higher than 350°C, a TD treatment at 400°C was conducted on the soil by a lab-scale TD apparatus to remove all the original contaminants. As shown in Fig. 1, the soil was sent into the outer pipe through the feed inlet, and was slowly transported to the feed outlet under the traction of the screw rod. Sufficient heat exchange occurred between the soil in the outer pipe and the heated air flowing in the opposite direction in the inner pipe to remove all the contaminants. A sampling inspection after the TD treatment showed that the concentrations of the original contaminants in the soil have been lower than the detection limits (6 mg/kg for PHs and 0.02–0.5 mg/kg for other volatile organic compounds) of the instrument.



(a) Experimental diagram

(b) Schematic diagram

Fig. 1 Lab-scale TD apparatus

2.2 Experimental conditions, apparatus and processes

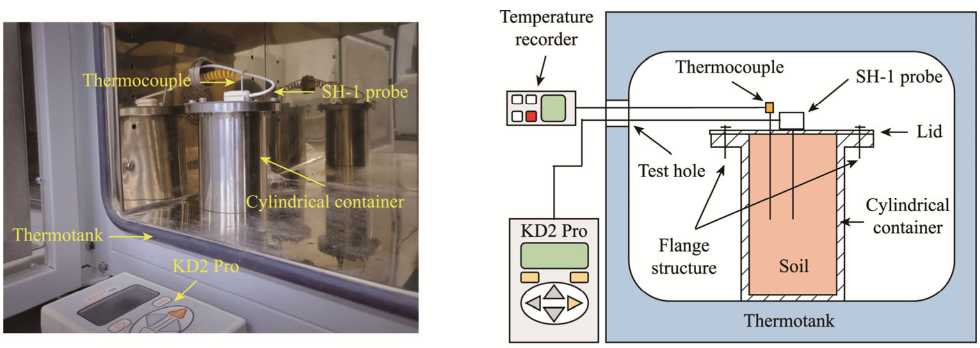
The moisture content of the soil was 0 after the TD treatment. The dry bulk density of each soil sample was controlled to (1400±30) kg/m^3, which was based on the situation of the soil in the sampling site. The target contaminant artificially introduced to the blank soil samples was the Chinese national standard 0# diesel purchased from a petrol station of Sinopec Group. Its hexadecane rating is over 45, and the mass ratio of alkanes, cyclanes and arenes is about 9:2:2. According to Table 1, the PH concentration of the soil in the sampling area is on the order of 4000–70 000 mg/kg, which is 0.4%–7% when converted to mass ratio. Considering the limited sampling points in the preliminary investigation, 7% is not necessarily the upper limit of PH concentration in this remediation site. To make the results have both scientific value and engineering significance, the diesel concentration of soil samples in this study was controlled to 0%, 1%, 2%, 3%, 5%, 10% and 20% (mass ratio), respectively. The particle size distribution and the mineral composition of these artificially contaminated samples were characterized to compare with the samples before the TD treatment. In addition, although the thermophysical properties of different PHs are similar [32], it is doubtful whether the experimental results obtained with diesel (a mixture of multiple alkanes) can be regarded as a representative of the family of PHs. In view of this, three samples respectively containing 3% n-octane (n-C_8H_{18}), 5% n-decane (n-$C_{10}H_{22}$) and 10% n-hexadecane (n-$C_{16}H_{34}$) (mass ratio) were prepared for comparison with the samples containing diesel mentioned above. The artificially contaminated soil samples were prepared in the following steps. (1) A certain mass of blank soil sample after thermal desorption was placed in a low-speed blender with a sealed top cover, and the cover was equipped with a small hole which could be opened and closed for pipette insertion. (2) The top cover was tightened and the small hole was opened, and then a certain mass of contaminations (diesel or alkanes) was dropped in through the pipette. (3) The soil sample and the contaminations were stirred evenly by the blender. Note that adopting a mixer with a sealed cover was intended to prevent contamination volatilization and moisture exchange during the stirring process. Besides, the drop-wise addition of contaminations and the stirring process could be carried out simultaneously.

After sample preparation, the thermophysical properties of the soil samples were measured by two methods for mutual verification. Specifically, thermal conductivity and thermal diffusivity were measured by a KD2 Pro analyzer, while specific heat capacity was measured by a DSC. The relationship between thermal conductivity k, specific heat capacity c_p, thermal diffusivity a, and bulk density ρ is shown in Eq. (1), where the product (ρc_p) is called volumetric specific heat capacity.

$$a = \frac{k}{\rho c_p} \tag{1}$$

The principle of DSC is to measure the relationship between the heat flux and temperature of a reference sample (α-Al_2O_3) as well as the test sample under identical heating condition, and then to calculate the specific heat capacity of the test sample based on the known value of the reference sample. More details of its principle were shown in the reference [33]. The DSC used in this study features a ±0.1°C temperature precision and a ±1% calorimetry precision. A small amount of the test sample (soil) and the reference sample were respectively sealed in a crucible with an inner volume of about 20 mm^3 for heating. The heating rate was 5°C/min from 0°C to 120°C, and the protective gas was nitrogen with a flow rate of 50 mL/min.

The following focuses on the experimental apparatus for measuring thermal conductivity and thermal diffusivity. As shown in Fig. 2, the experimental apparatus mainly comprises a specially made stainless-steel cylindrical container, a thermotank, a copper-constantan thermocouple connected to a temperature recorder, and an SH-1 stainless-steel probe matching with a KD2 Pro thermophysical properties analyzer. The cylindrical container was used to hold the soil, which has an inner diameter of 75 mm, an inner height of 120 mm, and a wall thickness of 5 mm. The container was equipped with a lid with position holes for probe insertion. The hole for the SH-1 probe is at the center of the circle, and the hole for the thermocouple is 20 mm away from the center. The thermotank with a manageable temperature range from –20°C to 200°C was used to control the temperature of the soil. The thermocouple with a length of 60 mm connected to a temperature recorder was vertically and fully inserted into the soil. The KD2 Pro thermophysical properties analyzer is based on the thermal probe technique of the transient measurement method, which can effectively minimize the effect of moisture migration on the temperature distribution of the test sample [34]. The principle of the thermal probe technique is detailed in the reference [35].



(a) Experimental diagram (b) Schematic diagram

Fig. 2 Experimental apparatus for thermophysical properties of soil samples

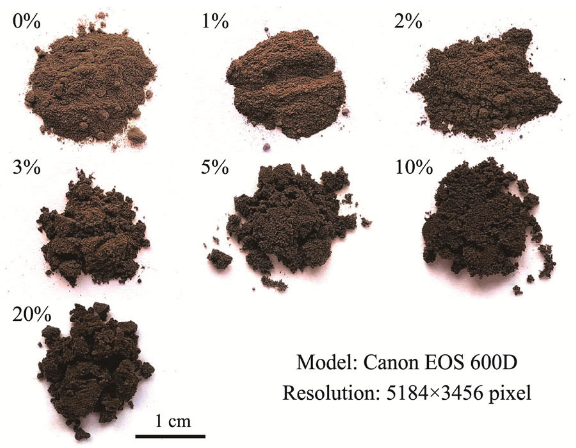
The SH-1 probe with a length of 30 mm and a diameter of 1.3 mm is suitable for porous materials, which features a thermal conductivity measuring range of 0.02–2 W/(m·°C) and a corresponding accuracy of ±10%, as well as a thermal diffusivity measuring range of 1×10^{-7}–1×10^{-6} m^2/s and a corresponding accuracy of ±10%. Note that the SH-1 probe should be fully contacted with the soil sample since the thermal conductivity is calculated based on the temperature rise with time during the measurement. In this sense, the calculation of soil thermal conductivity and thermal diffusivity should have taken the effects of probe length into consideration. However, as shown in Fig. 2, there is a stainless-steel plate above the soil container as the lid, causing a gap between the upper end of the probe and surface of the sample. The thickness of the lid is 0.6 mm, only 2% of the length of the SH-1 probe. Compared to the systematic error (±10%), the measurement error caused by the stainless-steel plate can be ignored. When the temperature is relatively high, diesel volatilization is intensified, and moisture exchange is potential between the soil sample and its surroundings. These may cause a greater error compare to the systematic error. Therefore, it is necessary to adopt the stainless-steel plate as the lid to seal the cylindrical container.

The thermal conductivity and thermal diffusivity of the soil samples were measured in the following steps. (1) A certain quality of soil sample was added into the cylindrical container and was compacted to a dry bulk density of 1400 kg/m^3. (2) The lid was connected to the cylindrical container through the flange structure. (3) The SH-1 probe and the thermocouple were both inserted vertically and fully into the soil sample. (4) Waterproof adhesive was used to seal the apparatus gaps to avoid diesel volatilization and moisture exchange, and also fix up the SH-1 probe and the thermocouple. (5) The cylindrical container was placed in the thermotank, and the target temperature was set. The measurement was supposed to be carried out after the temperature of the soil sample measured by the thermocouple had been stable near the target temperature for about 1 h. (6) For the SH-1 probe, the single measurement time was 2 min, and the interval between two adjacent measurements was supposed to be over 15 min to ensure probe cooling, for the purpose of reducing errors. Besides, errors were also minimized by measuring repeatedly and eliminating bad values.

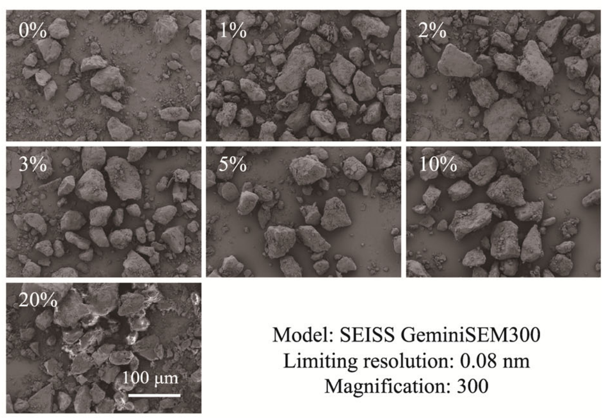
3. Results and Discussion

The soil structure was characterized by camera and scanning electron microscope (SEM) at different scales. As shown in Fig. 3(a), with the increase of diesel concentration, the color of soil gradually deepens brown to black, and soil particles are more likely to agglomerate under the action of the introduced liquid phase. When the concentration of diesel exceeds 10%, diesel can be separated by gently pressing the soil. When the diesel concentration reaches 20%, diesel can be seen evidently without pressing the soil. As shown in Fig. 3(b), there are no obvious differences in particle size distribution of each sample under the SEM. On the macro level, soil particles may agglomerate due to the action of diesel, but on the micro level, they are still independent particles.

As shown in Fig. 4, there are negligible differences among the particle size distribution and mineral composition of the samples. Specifically, each sample is mainly composed of silt (0.002–0.02 mm), and the total proportion of clay (<0.002 mm) and sand (0.02–2 mm) is below 15%, which is consistent with the results characterized by SEM. The soil samples are all classified



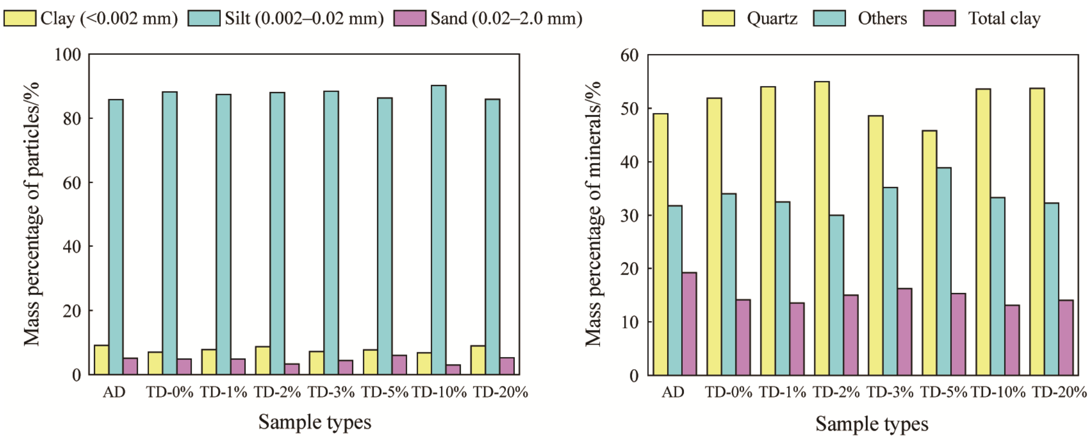
(a) Macrostructure by camera



(b) Microstructure by SEM

Fig. 3 Structural characterization of soil samples as "silt" according to the soil texture triangle [36] proposed by the United States Department of Agriculture. Besides, quartz accounts for about 50% in each sample. These confirm that both the TD treatment at 40°C and the introduction of diesel will not have a significant impact on the intrinsic properties of the soil, that is, the impact of small differences in particle size distribution and mineral composition on the results of soil thermophysical properties can be ignored in this study.

The thermophysical properties of each soil sample were measured by KD2 Pro at 10°C interval in the temperature range of 0–120°C, and five times repeated measurements were conducted at each temperature. Fig. 5(a) and Fig. 5(b) are the curves of soil thermal conductivity varying with temperature and diesel concentration. As shown in Fig. 5(a), the diesel concentration of 10% is the turning point, at which soil thermal conductivity hardly changes with temperature. When the diesel concentration is below 10%, the thermal conductivity of soil increases slightly with the increase of temperature. When the diesel concentration is over 10%, the thermal conductivity of soil decreases slightly with the increase of temperature. Overall, the change of soil thermal conductivity with temperature is not obvious regardless of diesel concentration. When the temperature varies from 0°C to 120°C, the relative difference between the maximum and minimum thermal conductivity of each soil sample is below 20%. However, at the same temperature, the thermal conductivity of soil samples with different diesel concentrations varies greatly. For example, the thermal conductivity of the soil sample containing 10% and 20% diesel at 20°C is about 0.4 W/(m·°C) and 0.6 W/(m·°C), which are 2 and 3 times of the thermal conductivity of the soil sample containing 0% diesel, respectively. The correlation coefficient between temperature and soil thermal conductivity is 0.057, while that between diesel concentration and soil thermal conductivity is 0.982. Therefore, compared with temperature, diesel concentration has a greater impact on soil thermal conductivity. Note that in Fig. 5(b), the change of thermal conductivity with diesel concentration can be roughly divided into two stages. In the first stage,



(a) Soil texture (b) Mineral composition

Fig. 4 Characterization results of soil samples (AD: air-dried samples; TD-*x*%: thermal desorption treated samples containing *x*% diesel; Others: including orthoclase, plagioclase, calcite, dolomite and hornblende)

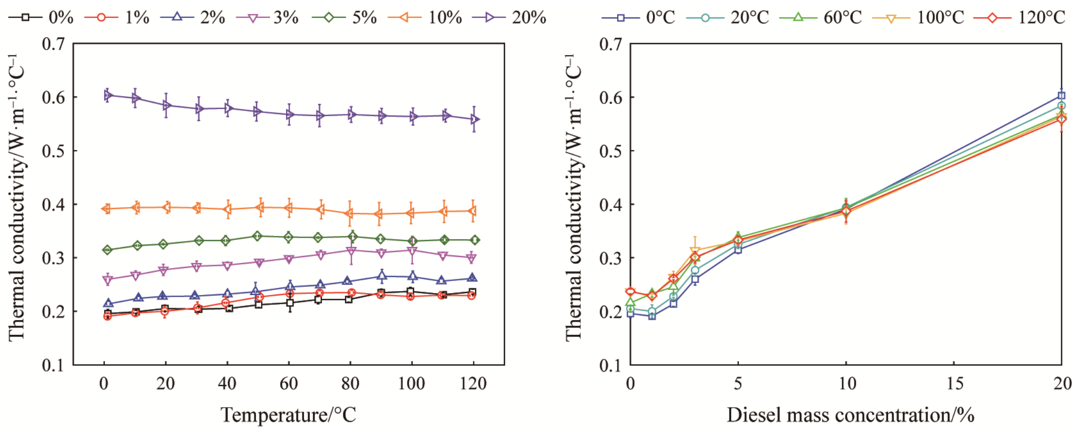


Fig. 5 Effects of temperature and diesel concentration on thermal conductivity of soil samples

when the diesel concentration is below 1%, the soil thermal conductivity hardly changes. While in the second stage, when the diesel concentration exceeds 1%, the soil thermal conductivity gradually increases with the increase of diesel concentration. In addition, the ratio of the mean square value (RMSV) of the thermal conductivity of the soil containing 0% diesel to that containing 1% diesel is 0.219, which is below the critical value 4.260 under the corresponding significance level (α=0.05), indicating that there are no significant differences between them. However, the RMSV of the thermal conductivity of the soil containing 1% diesel to that containing 2% diesel is 12.980, which is over 4.260, indicating that there are already some significant differences between them. To sum up, in the practical TD remediation project, when the diesel concentration is below 1%, the effects of diesel on soil thermal conductivity are ignorable.

Soil is a typical porous medium, which is composed of the solid phase (mainly minerals), as well as the liquid phase and gas phase existing in the pores among the solid particles. The average thermal conductivity of the soil solid is nearly 3 W/(m·°C) [22]. However, the thermal conductivity of the gas phase (air) is only about 0.027 W/(m·°C), which extremely increases the contact thermal resistance among the solid particles, resulting in the thermal conductivity (more accurately, the effective thermal conductivity) of dry soil is generally about 0.2 W/(m·°C), such as the sample with 0% diesel in Fig. 5. The temperature dependence of thermal conductivity of diesel was measured in this study, and then compared with that of n-C_8H_{18} [37], n-$C_{10}H_{22}$ [37] and 10% n-$C_{16}H_{34}$ [38] in the existing studies. As shown in Fig. 6, the thermal conductivity of pure alkanes and diesel decreases with the increase of temperature, and the difference between them is limited. Note that the thermal conductivity of the diesel is 5–6 times that of air at room temperature. The introduced diesel replaces air and occupies a partial of the soil pores, making the soil particles combine more closely. Therefore, the thermal conductivity of soil gradually increases with the introduction of diesel. The effects of the solid phase and the liquid phase on the temperature dependence of the soil thermal conductivity are competitive. The solid particles in the soil are nonmental materials, whose heat conduction mainly depends on lattice vibration as the carrier. The higher the temperature is, the stronger the lattice vibration is, and the more conducive to heat transfer. However, PHs are usually liquid, whose heat conduction mainly depends on the irregular motion of molecules. The higher the temperature is, the more energy loss caused by irregular motion of molecules, and the less conducive to heat transfer. Due to the opposite temperature dependence of solid particles in soil and diesel, there exists a turning point, at which soil thermal conductivity is almost the same at different temperatures. The soil sample containing 10% diesel is right near or at the turning point. In addition, as the results of the contrast experiment shown in Fig. 7, when other factors are identical, the thermal conductivity differences of the soil containing diesel and pure alkanes with the same concentration are limited, for the relative deviations are all less than 10%. Therefore, the experimental results obtained with diesel in this study can be regarded as a representative of the family of PHs.

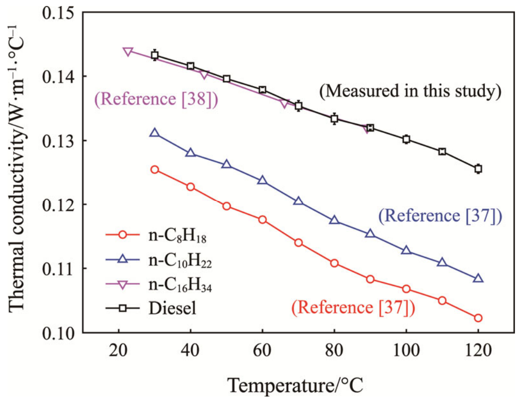


Fig. 6 Temperature dependence of thermal conductivity of diesel and pure alkanes

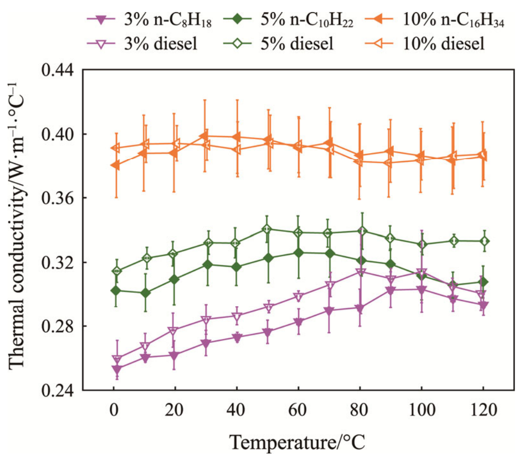


Fig. 7 Comparison of thermal conductivity of soil contaminated by diesel and pure alkanes

Thermal conductivity is a thermophysical parameter used to characterize the heat transfer rate, while another thermophysical parameter, thermal diffusivity, is used to characterize the temperature transfer rate. The greater the thermal diffusivity of the material, the shorter the time for the temperature field of the material to change from non-uniform distribution to uniform distribution. The TD treatment is a dynamic heat transfer process, and the practical project may pay much attention to the temperature distribution of each remediation point, not only the heat flux provided by the heating wells. Thus, thermal diffusivity is also important in application. The change of soil thermal diffusivity with different diesel concentrations and temperature is shown in Fig. 8. It is obvious that the soil thermal diffusivity decreases with the increase of temperature, and the thermal diffusivity of the soil sample with high diesel concentration changed greatly, which can explain the phenomenon that the higher the temperature is, the lower the temperature rising rate is in the practical applications. On the one hand, with the increase of temperature, the temperature difference between the heating wells and the soil decreases gradually. On the other hand, the soil thermal diffusivity decreases with the increase of temperature. The decrease of temperature difference and thermal diffusivity will both reduce the temperature transfer rate, and the soil temperature will rise more slowly. In the practical TD remediation project, it is necessary to consider the diminishing marginal effect of soil temperature rise, and timely adjust the heating power to reduce energy consumption.

The relationship among thermal conductivity, thermal diffusivity, specific heat capacity and bulk density has been given in Eq. (1). The KD2 Pro analyzer calculates the specific heat capacity based on the measurement results of the thermal conductivity and the thermal diffusivity, as well as the bulk density of the sample. The DSC measures the specific heat capacity of the sample directly and accurately. Therefore, a comparison of the specific heat capacity indirectly measured by KD2 Pro with that directly measured by DSC was carried out. As shown in Fig. 9, the relative deviations between the specific heat capacity measured by KD2 Pro and DSC are mostly less than 10%, which indicates that the measurements are accurate and the conclusions obtained are reliable. In addition, the specific heat capacity of the soil samples increases with the increase of temperature,

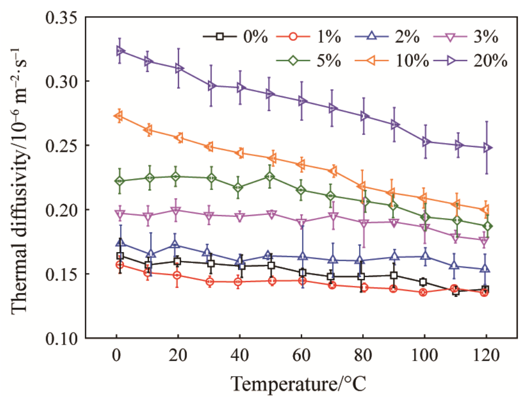


Fig. 8 Effects of diesel concentration on thermal diffusivity of soil samples at different temperatures

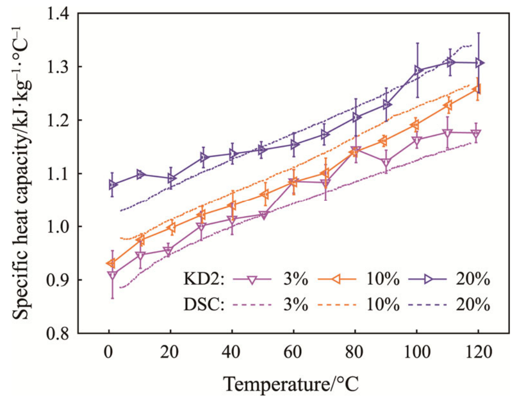


Fig. 9 Effects of diesel concentration on specific heat capacity of soil samples at different temperatures

which is consistent with the experimental results of diesel-contaminated soil below 0°C by Malyshev et al. [26].

4. Prediction Models

4.1 Theoretical model

Fractal theory has been widely used in the studies of porous material. Based on Sierpinski carpet and inspired by some existing studies [26, 39–41], a three-dimensional fractal model of the effective thermal conductivity of diesel-contaminated soil was proposed in this study. As shown in Fig. 10(a), soil was assumed to be a homogeneous medium, and was divided into continuous distributed cubic units with the same side length L. Solid particles in soil were assumed to be cubes with the same side length L_s, and were distributed in the center of each soil unit. The rest part of the soil units were soil pores full of diesel-air mixture. Due to the homogeneity assumption mentioned above, the effective thermal conductivity of soil is equal to that of each soil unit, and the latter can be calculated by the thermal resistance analysis.

As shown in Fig. 10(b), a heat flow q passed through a soil unit along the Z-axis of the three-dimensional coordinate system. Based on the isotropic characteristics of soil and ignored thermal convection and thermal radiation, the heat conduction in a soil unit was simplified as steady-state heat conduction of flat-wall in one-dimension. Derived from Fourier's law of heat conduction, the thermal resistance of the flat-wall is equal to the quotient of the thickness and the thermal conductivity of the wall. Specifically, the thickness of the wall is the distance that the heat flow passed through the wall. Thus, the thermal resistance of the soil unit R was expressed by Eq. (2).

$$R = L/k \tag{2}$$

where L and k are the thickness along Z-axis and the effective thermal conductivity of the soil unit, respectively. Note that k is the parameter of the final calculation.

As shown in the left part of Fig. 10(c), a soil unit was divided into three parts. The part in the middle features a thermal resistance of R_{I}, while the two parts on sides were taken as an ensemble and features a thermal resistance of R_{II}. Thus, R was composed of R_{I} and R_{II} in parallel, and the relationship among the three was expressed by Eq. (3).

$$R=\frac{R_{\mathrm{I}}R_{\mathrm{II}}}{R_{\mathrm{I}}+R_{\mathrm{II}}} \tag{3}$$

As shown in the right part of Fig. 10(c), R_{I} was composed of three thermal resistances, namely R_{I1} and R_{I2} were connected in series and then connected in parallel with R_{I3}. The equivalent electrical circuit of the thermal resistance model of the soil unit was shown in Fig. 10(d). Thus, R_{I} was expressed by Eq. (4).

$$R_{\mathrm{I}}=\frac{\left(R_{\mathrm{I1}}+R_{\mathrm{I2}}\right)R_{\mathrm{I3}}}{R_{\mathrm{I1}}+R_{\mathrm{I2}}+R_{\mathrm{I3}}} \tag{4}$$

Similar to R, the calculation of R_{II}, R_{I1}, R_{I2}, and R_{I3} were based on the theory of steady-state heat conduction of flat-wall in one-dimension mentioned above, and they were expressed by Eqs. (5)–(8), respectively.

$$R_{\mathrm{II}}=\frac{L}{k_{\mathrm{d,a}}} \tag{5}$$

$$R_{\mathrm{I1}}=\frac{L_{\mathrm{s}}}{k_{\mathrm{s}}} \tag{6}$$

$$R_{\mathrm{I2}}=\frac{L-L_{\mathrm{s}}}{k_{\mathrm{d,a}}} \tag{7}$$

$$R_{\mathrm{I3}}=\frac{L}{k_{\mathrm{d,a}}} \tag{8}$$

where k_{s} and $k_{\mathrm{d,a}}$ are the thermal conductivity of solid particle and diesel-air mixture, respectively. The expression of $k_{\mathrm{d,a}}$ shown in Eq. (9) was taken from the reference [26].

$$k_{\mathrm{d,a}}=k_{\mathrm{a}}\left(1-\frac{\varphi_{\mathrm{d}}}{\frac{k_{\mathrm{a}}}{k_{\mathrm{a}}-k_{\mathrm{d}}}+\frac{1-\varphi_{\mathrm{d}}}{3}}\right) \tag{9}$$

where k_{d} and k_{a} are the thermal conductivity of diesel and air, respectively, and φ_{d} is the volume fraction of diesel in diesel-air mixture, which was expressed by Eq. (10) .

$$\varphi_{\mathrm{d}}=\frac{V_{\mathrm{d}}}{V_{\mathrm{d,a}}}=\frac{V_{\mathrm{d}}}{V_{\mathrm{d}}+V_{\mathrm{a}}} \tag{10}$$

where V_{d}, V_{a}, and $V_{\mathrm{d,a}}$ are the volume of diesel, air and diesel-air mixture in a soil unit. Additional remarks, diesel and air are not miscible. Then, based on the well-known conversion relationship among soil physical parameters, as well as the basic geometric relationship, we can derive Eqs. (11)–(14) .

$$\frac{V_{\mathrm{d,a}}}{V_{\mathrm{d,a}}+V_{\mathrm{s}}}=n=\frac{\rho_{\mathrm{s}}-\rho_{\mathrm{dry}}}{\rho_{\mathrm{s}}} \tag{11}$$

$$V_{\mathrm{s}}=L_{\mathrm{s}}^{3}=\frac{m_{\mathrm{s}}}{\rho_{\mathrm{s}}} \tag{12}$$

$$V_{\mathrm{d}}=\frac{m_{\mathrm{d}}}{\rho_{\mathrm{d}}} \tag{13}$$

$$\theta_{\mathrm{d}}=\frac{m_{\mathrm{d}}}{m_{\mathrm{d}}+m_{\mathrm{s}}} \tag{14}$$

where V_{s} is the volume of the solid particle in a soil unit; n is soil porosity; ρ_{s} is the density of solid particles; ρ_{dry} is the dry bulk density of soil; θ_{d} is the mass fraction of diesel, namely diesel concentration; and m_{d} and m_{s} are the mass of diesel and the solid particle in a soil unit, respectively.

The effective thermal conductivity of the soil unit k can be solved by combining Eqs. (2)–(14) . The density of the solid particles in soil ρ_{s} is 2650 kg/m^3 in this study. As mentioned above, the dry bulk density ρ_{dry} of each sample is controlled to 1400 kg/m^3. The density of 0# diesel ρ_{s} is 835 kg/m^3. At room temperature (20°C), the thermal conductivity of soil solid particle k_{s}, diesel k_{d}, and air k_{a} are about 3.5 W/(m·°C), 0.145 W/(m·°C) and 0.027 W/(m·°C), respectively. The values of θ_{d} are 0%, 1%, 2%, 3%, 5%, 10%, and 20%.

The comparison of the values calculated by the cubic fractal model and the experimental data of the thermal conductivity of soil samples at 20°C is shown in Fig. 11. The model successfully reflected the fact that the thermal conductivity of diesel-contaminated soil increases with the increase of diesel concentration. However, the increase trend of thermal conductivity with temperature calculated by the model was not completely consistent with the experimental data. Specifically, the slope of the experimental data is approximately linear, while that of the values calculated by the model gradually increases. Similar to the prediction model of thermal conductivity of wet soil summarized by Gemant [39], the cubic fractal model in this study is also an idealized model with some limitations. In fact, the solid particles of soil are not ideal cubes of uniform size. Besides, diesel is not uniformly attached to the surface of soil particles, and some droplets may also be dispersed in the air. In addition, diesel may not be mixed with the air in soil completely, for part of them may be adsorbed inside the solid particles. Therefore, the fractal model has relatively high accuracy only in a certain range. Nevertheless, this model proved theoretically that diesel concentration does have an important effect on the thermal conductivity of diesel-contaminated soil.

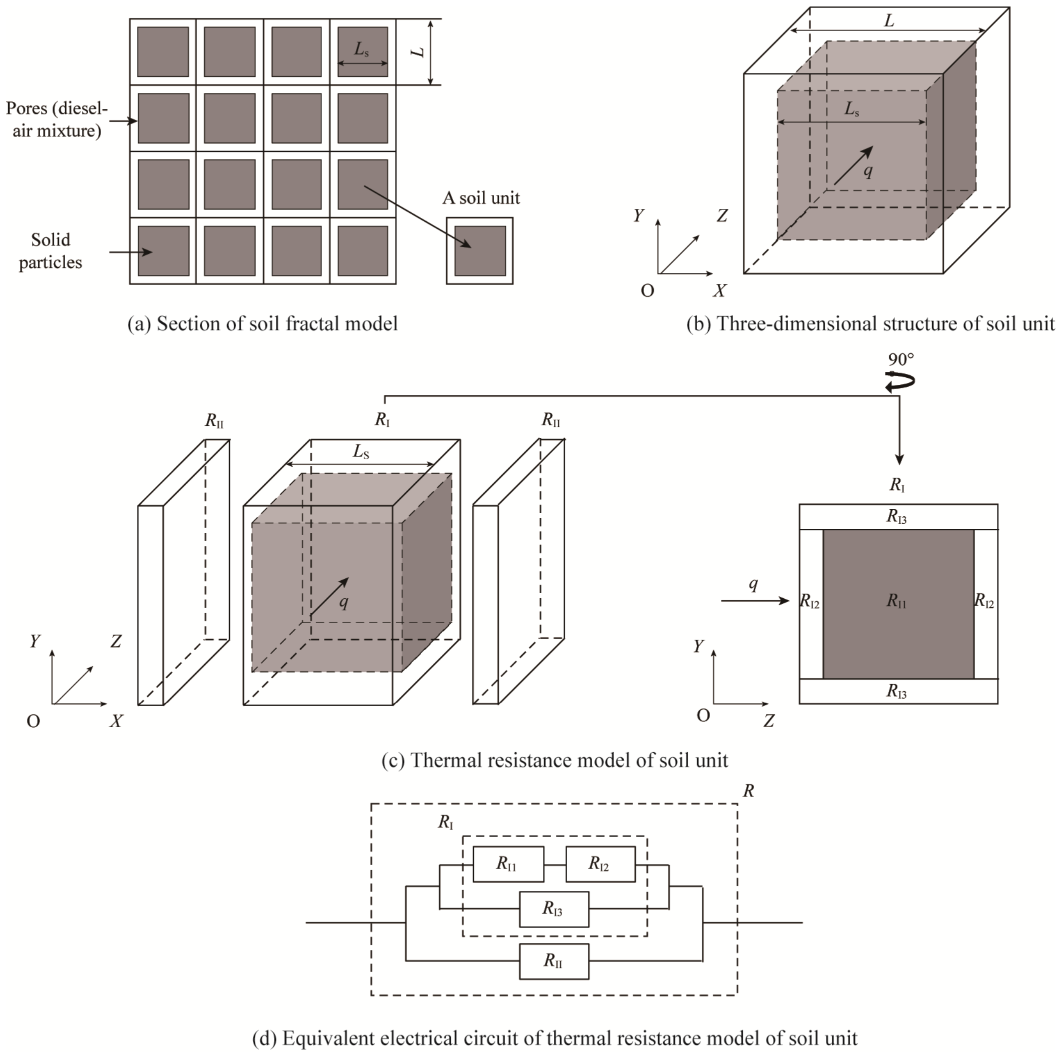


Fig. 10 Fractal model based on cubic soil unit and thermal resistance model of soil units

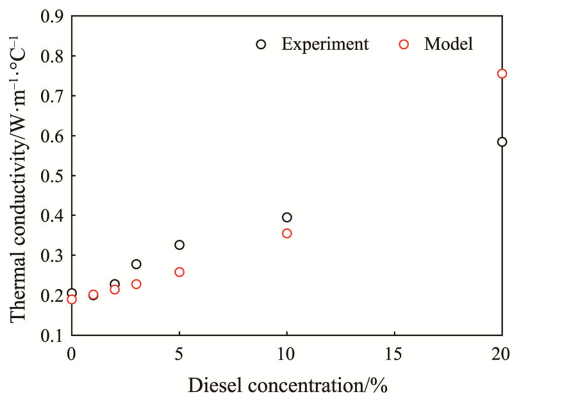


Fig. 11 Comparison of fractal model and experimental data at 20°C

4.2 Regression model

Compared to the relatively complex fractal model, a statistical analysis model may be relatively weak in theory but convenient to use in practical applications. Considering that the effect of temperature on soil thermal conductivity is not significant, diesel concentration θ_d was taken as the only independent variable, and soil thermal conductivity k was taken as the dependent variable in the statistical analysis model. The experimental data of the thermal conductivity of the soil samples with 0%–10% diesel were taken as the training group, while that of the soil sample with 20% diesel were taken as the validation group. As shown in Fig. 12, the model of a simple linear regression expressed by Eq. (15) is in good agreement with the validation group, whose coefficient of determination is 0.8786. Therefore, it is unnecessary to adopt some other complex statistical analysis models. When the types of other soil are similar to the soil in this study, the prediction of the thermal conductivity of diesel-contaminated soil by this linear regression model can meet the accuracy requirements of practical TD remediation.

$$k = 1.8452\theta_d + 0.2179 \quad (15)$$

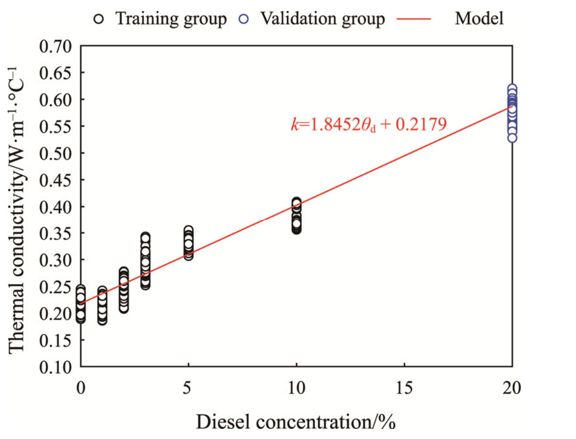


Fig. 12 Comparison of regression model and experimental data

5. Conclusions

In this study, the thermal conductivity, specific heat capacity and thermal diffusivity of diesel-contaminated soil were investigated at 0–120°C through a KD2 Pro analyzer based on the thermal probe method and a DSC, and the modified models were proposed to predict the thermophysical properties of contaminated soil for practical applications.

The soil utilized in this study was taken from a PH-contaminated site, and its original contaminations were removed through a lab-scale TD apparatus at 400°C to control variables and eliminate interferences. Then the diesel was introduced into the soil to prepare samples with the same dry bulk density but with different diesel concentration. The characterization results showed that neither the TD treatment at 400°C nor the introduction of diesel changed the particle size distribution and the mineral composition of soil.

It was found that with the increase of temperature, the thermal conductivity of soil increases when diesel concentration is below 10%, while that decreases when diesel concentration is over 10%, which is mainly due to the inverse temperature dependence of the thermal conductivity of soil minerals and diesel. Compared with temperature, diesel concentration has more significant effects on the thermal conductivity of soil. When diesel concentration is below 1%, the change of thermal conductivity caused by the difference of diesel concentration is ignorable. In addition, a control experiment found that the temperature dependence of the thermal conductivity of diesel and pure alkanes are quite similar, and the relative differences of the thermal conductivity of soil containing the same concentration of diesel and pure alkanes are below 10%, indicating that the variation of the thermal conductivity of soil caused by diesel can be extended to the family of PHs. Regardless of diesel concentration, with the increase of temperature, the specific heat capacity of soil increases, while the thermal diffusivity of soil decreases. Moreover, the relative differences between the specific heat capacity directly measured by DSC and indirectly measured by KD2 Pro are below 10%, indicating that the experimental data obtained in this study are accurate and reliable.

Based on cubic fractal and thermal resistance analysis, a theoretical model of the thermal conductivity of diesel-contaminated soil was proposed, which also proved that soil thermal conductivity increases significantly with the increase of diesel concentration. A regression model with diesel concentration as the independent variable and soil thermal conductivity as the dependent, whose coefficient of determination is 0.8786, was also summarized for practical applications.

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Conflict of Interest

FAN Liwu is an editorial board member for Journal of Thermal Science and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

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