Hindawi
Advances in Civil Engineering
Volume 2018, Article ID 9530813, 11 pages
https://doi.org/10.1155/2018/9530813

Research Article

Thermal Conductivity of Compacted GO-GMZ Bentonite Used as Buffer Material for a High-Level Radioactive Waste Repository

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Received 19 May 2018; Revised 3 July 2018; Accepted 19 July 2018; Published 4 September 2018

Academic Editor: Filippo Ubertini

In China, Gaomiaozi (GMZ) bentonite serves as a feasible buffer material in the high-level radioactive waste (HLW) repository, while its thermal conductivity is seen as a crucial parameter for the safety running of the HLW disposal. Due to the tremendous amount of heat released by such waste, the thermal conductivity of the buffer material is a crucial parameter for the safety running of the high-level radioactive waste disposal. For the purpose of improving its thermal conductivity, this research used the graphene oxide (GO) to modify the pure bentonite and then the nanocarbon-based bentonite (GO-GMZ) was obtained chemically. The thermal conductivity of this modified soil has been measured and investigated under various conditions in this study: the GO content, dry density, and water content. Researches confirm that the thermal conductivity of the modified bentonite is codetermined by the three conditions mentioned above, namely, the value of GO content, dry density, and water content. Besides, the study proposes an improved geometric mean model based on the special condition to predict the thermal conductivity of the compacted specimen; moreover, the calculated values are also compared with the experimental data.

1. Introduction

Burying the high-level radioactive waste (HLW) in a deep geological disposal (800 m–1500 m underground) has been widely accepted as an approach for the permanent disposal of such waste generated from a nuclear reactor. The HLW repositories generally consist of a multibarrier system, in which the natural geological barrier and an engineered barrier system are included. The buffer material, as a pivotal part of the engineered barrier, plays a crucial role in keeping the chronic safety of the HLW repository, from which enough strength for construction and effective intercept for the radionuclide can be drawn [1]. Compacted bentonite has been valued as the feasible buffer material for the HLW repository, due to its excellent properties of swelling and sealing, the low permeability, and high retention capability of radionuclides [2, 3]. In China, a local bentonite named Gaomiaozi (GMZ) has been selected for this aim [4, 5].

As in the deep geological disposal, the buffer material can diffuse decay heat generated from the HLW to the host rock. Literatures show that the ambient temperature could rise to a peak of 90°C [6] and the maximum temperature grades could reach 24°C over a buffer material whose thickness is 35 cm [7]. According to the design criterion [8–10], the highest temperature in the engineered barrier system ought not to exceed 100°C because the smectite may undergo a mineralogical alteration exposed to alkaline/salt pore fluids at high temperature [11–14]. Both compacted bentonite and the host rock will undergo a decrease in the hydraulic, mechanical, and chemical performances because of these kinds of transformation under the high temperature which could threaten the safety of the HLW disposal [13, 15]. Therefore, it is of essence to study the thermal conductivity of the buffer material and to comprehend how it behaves under the given conditions in the disposal.

Over the past few decades, previous researches have been conducted on the thermal conductivity of many kinds of soil, and calculation models were developed to predict its thermal conductivity under different conditions [16–18]. Thermal conductivity is the basic property of a material to conduct heat which depends mainly upon its composition, pore fluid, density, environment temperature, and texture [19]. Coulon et al. [20] have measured this property of 18 smectite clays from 14 deposits, and based on these measurement results, they claimed that the value of the thermal conductivity was jointly influenced by soil parameters such as the water content, the dry density, the microstructure of clay samples, and the mineral composition of the soil as well. A large volume of measured data has been found in the works of Zhu et al. [21] on GMZ bentonite, and the similar conclusion has been drawn. However, the thermal conductivity of bentonite fails to meet the expected value even at high density and water content [22–25]. To improve the thermal performance of bentonite as the buffer material, some admixtures were added physically to modify its property. Using sand as a modifier was first reported in Japan [26]. Moreover, results from further more investigations confirmed that the thermal conductivity of the bentonite-sand mixture will increase as the sand content increases [27–30]. Nevertheless, the increasing degree becomes constant or even decreases with more increasing sand content [25, 31]. Because of the high thermal conductivity of graphite, Pacovsky [32] added graphite to Czech RMN bentonite to increase its thermal conductivity. Michael and Gunter [33] compared the improvement effect of sand to graphite and found that using sand as the only admixture is not enough to achieve suitable thermal conductivity while the addition of 15% graphite can make the thermal conductivity of the barrier approximately equal to that of the clay host rock. Nanocarbon material possesses high specific surface and strong interface effect which exerts extraordinary mechanics and thermal property compared to the macromaterial [34–36]; therefore, the graphene oxide was used as a proper modifier.

In China, a lot of studies about the basic physical and chemical properties, hydromechanical behaviour, and soil water retention characteristics (SWRC) of GMZ bentonite have been extensively researched during the past few years [37–44]. Studies on the thermal conductivity of pure bentonite and bentonite-sand mixture have also been carried out with varied sand content, dry density, and water content [45–47]. However, few researches consider graphite or other materials as a modifier to increase the thermal conductivity of bentonite [48].

In this study, graphene oxide (GO) was added to the GMZ bentonite, and the thermal conductivity of GO-GMZ bentonite was measured using the hot wire method. In this experiment, several factors including GO content, dry density, and water content of the modified soil were considered. At last, an empirical model was introduced to predict the thermal conductivity of compacted GO-GMZ bentonite in advance.

2. Materials and Method

2.1. Materials. The GMZ bentonite analysed with the X-ray diffraction in this test is sampled from Gaomiaozi township in Northern China. This light-grey powder consists of several minerals including 75.4% of montmorillonite, 11.7% of quartz, 7.3% of cristobalite, 4.3% of feldspar, 0.5% of calcite, and 0.8% kaolinite [38]. The other basic properties are listed in Table 1 [49].

The graphene oxide (GO) used in the present work is produced by Suzhou Tanfeng Graphene Technology Co., Ltd (Jiangsu Province, China). It is a drab powder material whose monolayer ratio is more than 99%. The structure schematics of graphite and graphene oxide are pictured in Figure 1, and its basic properties are listed in Table 2. Graphene oxide is an important and promising ramification of graphite which is obtained by treating graphite with strong oxidizers and is produced based on the improved Hummers method [50]. It has been proved that graphene oxide is nontoxic and biodegradable among all nanocarbon materials [51].

2.2. Bentonite Modification. In order to obtain GO-GMZ bentonite, firstly the GMZ bentonite was grafted using 3-aminopropyltriethoxysilane (APTES); then, the graft bentonite was modified by using 1-ethyl-3-(dimethylamino) propylcarbodiimide (EDC) and *n*-hydroxysuccinimide (NHS) as an activator. The modification procedure is showed in Figure 2. Quantities of 2.5 g GMZ bentonite, 50 mL APTES, and 200 mL absolute ethanol (with a purity of 99.7%) were poured into a 500 mL round bottom flask with three necks. The mixture was heated in a water bath at 80°C for 2 h. To keep it uniform, the mixture was intensively stirred (400 rad/min) in the process. The product was washed with absolute ethanol for six times and then dried in a vacuum oven at 60°C. The dried mass was pulverized and sieved (200 mm sieve). Quantities of 2 g powder, 2.5 g NHS, 2.5 g EDC, and 20 ml GO solution (10 mg/mL) were poured into a 50 mL beaker and stirred uniformly for 12 h at room temperature. After standing, centrifugation, freeze-drying, and sieving in a 2 mm mesh, the GO-GMZ bentonite was ready to use.

2.3. Specimen Preparation. To obtain the compacted GO-GMZ bentonite at a certain dry density, its powder was compressed statically in a steel mould using a 300 kN electronic universal testing machine (Model CSS-44000, produced by Changchun Research Institute for Mechanical Science) at a steady displacement rate of 0.2 mm/min. Besides, in order to make the dry density of the specimen longitudinal uniformly, the compression process was divided into four steps: (1) 1/3 soil powder of the total mass was compacted to obtain a specimen whose height is 40 mm; (2) the upper surface of the compacted specimen was carefully scratched with a thin steal stick; (3) the next 1/3 soil powder of the total mass was poured and compacted to form another soil segment; and (4) repeat steps 2 and 3 until the height of the compacted soil rises up to its target height

Table 1: Basic properties of GMZ01 bentonite.

Chemical component	SiO_2, Al_2O_3, and H_2O
Specific gravity (mg/m^3)	2.66
Alkaline coefficient	1.14
pH value	8.68–9.86
Liquid limit (%)	276
Plastic limit (%)	37
Plastic index	239
Total specific surface area (m^2/g)	570
Cation exchange capacity (cmol/kg)	77.30
Main exchange cations (cmol/kg)	Na^+ (43.36); 1/2 Ca^{2+} (14.57); 1/2 Mg^{2+} (6.17); K^+ (2.51)

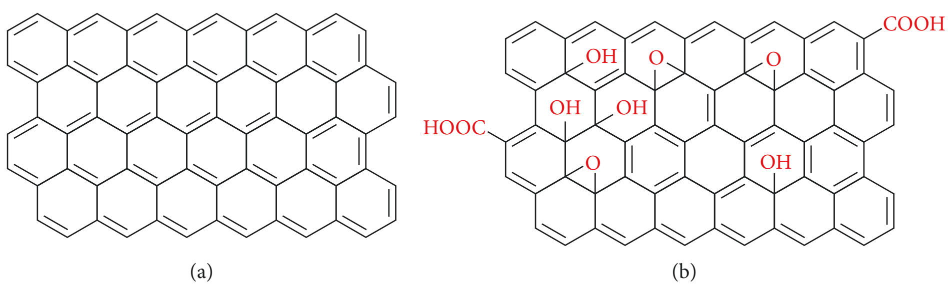

Figure 1: The structure schematic of (a) graphite and (b) graphene oxide.

Table 2: Basic properties of graphene oxide (GO).

Purity (wt.%)	>99
Thickness (nm)	0.6–1.0
Layers	1–2
Particle diameter (μm)	0.5–5
Specific surface area (m^2/g)	1000–1217

(i.e., 120 mm). Once the dry density of bentonite reached the desirable value (1.7 Mg/m^3, 1.8 Mg/m^3, and 1.9 Mg/m^3), the press on bentonite will stop and be kept still for 1 hour to avoid resilience. The sample is 50 mm in diameter and 120 mm high.

2.4. Measurement Method

2.4.1. Apparatus and Test Principle. Usually, two main kinds of laboratory techniques, steady-state methods [52, 53] and unsteady methods [54, 55], are utilized to measure the thermal conductivity of many kinds of materials. In this study, the thermoprobe method, as one of the unsteady methods, is adopted to measure the thermal conductivity of compacted GO-GMZ bentonite using a Decagon Device KD2 PRO thermal analyser (Figure 3). It is composed of a thermal needle probe, a cable, and a controller. Through monitoring heat dissipation of linear heat resource under specific voltage, the thermal conductivity of materials can be calculated and displayed on the controller's screen (ASTM D 5334-00, 2000). After the insertion of the thermoprobe which is 1.28 mm in diameter and 120 mm long into the soil, the thermal conductivity can be obtained by heating the soil and monitoring temperature variation during the heat transfer.

2.4.2. Test Procedure. To ensure the smooth insertion of the thermoprobe, a hole sized 1.3 mm in diameter and 120 mm in depth is drilled into the middle of the specimen with a gimlet before testing. To avoid a small gap between the soil and thermoprobe which may influence the heat transfer, a thin layer of thermal grease was smeared on the surface of the thermoprobe. After that, it was inserted into the hole. Figure 3 shows the measuring operation and the KD2 analyser instrument. In the measurement, the controller was first balanced for 30 seconds, and the sample was then heated with the probe for another 30 seconds. The thermal conductivity was computed according to the cooling rate of the probe during the heat transmission. To ensure the accuracy of the experiment data, the testing values of repeated measurements were averaged as the final value.

3. Results and Discussion

3.1. Influence of GO Content on Thermal Conductivity. To figure out the enhancement of thermal conductivity of GO-GMZ bentonite, various GO contents (between 0 and 50% wt.) were used in the process of modification. The test results are illustrated in Figure 4, which shows a clear change of the thermal conductivity with different GO contents. According to the experimental data, the thermal conductivity shows apparent increases with greater dry density of GO content. Generally, the relation between the thermal conductivity and GO content can be formulated as a quadratic function with different dry densities: 1.7 Mg/m^3, 1.8 Mg/m^3, and 1.9 Mg/m^3. As seen from the results, values of thermal conductivity range from 0.864 W/(mK) to 21.662 W/(mK) as GO content increases from 0% to 50% in given conditions. This attributes to the better heat

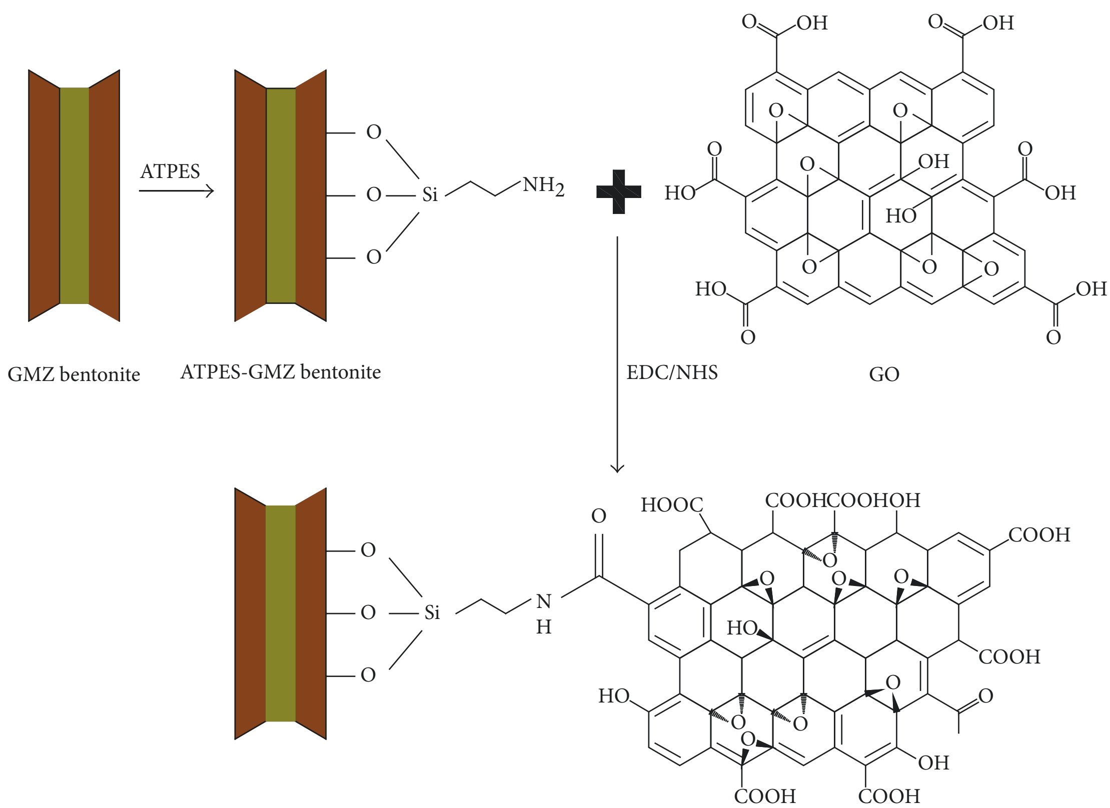

Figure 2: The schematic diagram of preparation of GO-GMZ bentonite.

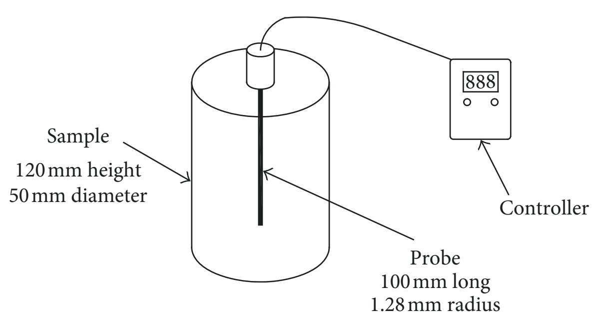

Figure 3: Measurement of thermal conductivity.

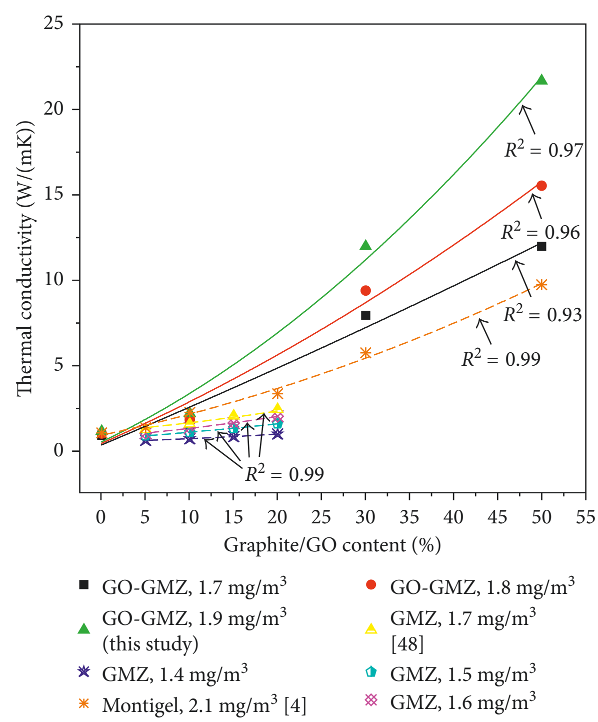

Figure 4: The thermal conductivity and graphite/GO content in the present study (ω = 10%) and available data in published literatures.

conduction behaviour of GO whose thermal conductivity is 129 W/(mK), much higher than that value of the pure bentonite. The thermal conductivity-GO content quadratic relationship at different dry densities can be expressed as follows:

$$\begin{aligned}
\lambda &= 0.38E-3\times\omega_{\mathrm{GO}}^2 + 0.23\times\omega_{\mathrm{GO}} + 0.29 \quad \text{for} \\
&\qquad \rho_{\mathrm{d}} = 1.7\ \mathrm{Mg/m^3}\left(R^2 = 0.93\right), \\
\lambda &= 1.57E-3\times\omega_{\mathrm{GO}}^2 + 0.23\times\omega_{\mathrm{GO}} + 0.39 \quad \text{for} \\
&\qquad \rho_{\mathrm{d}} = 1.8\ \mathrm{Mg/m^3}\left(R^2 = 0.96\right), \\
\lambda &= 3.60E-3\times\omega_{\mathrm{GO}}^2 + 0.16\times g + 1.42 \quad \text{for} \\
&\qquad \rho_{\mathrm{d}} = 1.9\ \mathrm{Mg/m^3}\left(R^2 = 0.97\right),
\end{aligned} \tag{1}$$

where λ is the thermal conductivity (W/(mK)), ω_{GO} is the GO content of the specimens, ρ_{d} represents the dry density of compacted GO-GMZ bentonite (Mg/m^3), and R^2 is the correlation coefficient. As can be seen from the equations, the second-order coefficient for each equation increases with the increase of dry density which maybe because of the increasing contact area between the bentonite and GO particles.

Though the measured data in this study are insufficient enough to draw a perfect relationship between several parameters, the work had been done in literatures and the good fitting result provides convincing evidence for the conclusion. Some researchers use graphite to improve the thermal conductivity of bentonite physically, and similar patterns can be found in Czech RMN bentonite [32], Montigel bentonite [33], and GMZ bentonite [48]. Numbers of experiment results of this study and other literatures have been illustrated in Figure 4. This figure shows the values of GO and graphite content range from 0% to 50%, while values of the dry density of different compacted bentonites range from 1.4 Mg/m^3 to 1.9 Mg/m^3 in different researches. After comparison, the thermal conductivity of bentonite-graphite mixture can range from 0.56 W/(mK) to 9.7 W/(mK) under different experiment conditions which is obviously lower than that of GO-GMZ bentonite. Probable reasons for this situation might be that (1) the thermal conductivity of GO nanoplatelets is higher than the bulk of graphite because of its single-layer structure [35, 56] and the increase in the interlayer coupling because of covalent interactions provided by the oxygen atoms and (2) the bentonite used in this study has been changed chemically with GO, leading to a better heat conduction behaviour. However, the relationship between the thermal conductivity of the mixture and the graphite content agrees with the modified bentonite: the higher the graphite content, the higher the value of thermal conductivity for the bentonite-graphite mixture. This maybe because the thermal conductivity of graphite is more than 10 times than that of pure bentonite [48]. Moreover, the thermal conductivity-graphite content shows similar quadratic trend for reported bentonite with GO-GMZ bentonite in this study for each dry density.

3.2. Influence of Dry Density on Thermal Conductivity. Measured values of thermal conductivity for highly compacted GO-GMZ bentonite with different dry densities (1.7 Mg/m^3, 1.8 Mg/m^3, and 1.9 Mg/m^3) are presented in Figure 5. As shown, the effect of dry density can be plotted as a linear function when the GO content equals to 0%, 10%, 30%, and 50%, respectively. For the specimen with GO content of 0% (i.e., pure GMZ bentonite), the value of thermal conductivity increases from 0.86 W/(mK) to 1.10 W/(mK) with the increase of dry density. While for the specimen whose GO content is 50%, its thermal conductivity increases from 11.94 W/(mK) to 21.66 W/(mK) when water content equals to 10%. This phenomenon can be explained as the increasing contact area between the same and different particles (i.e., GO-GMZ bentonite and water particles) with the increase of dry density, leading to a better performance of heat transmission, namely, the thermal conductivity. The specific linear fitting functions and the calculated correlation coefficients of thermal conductivity-dry density are as follows:

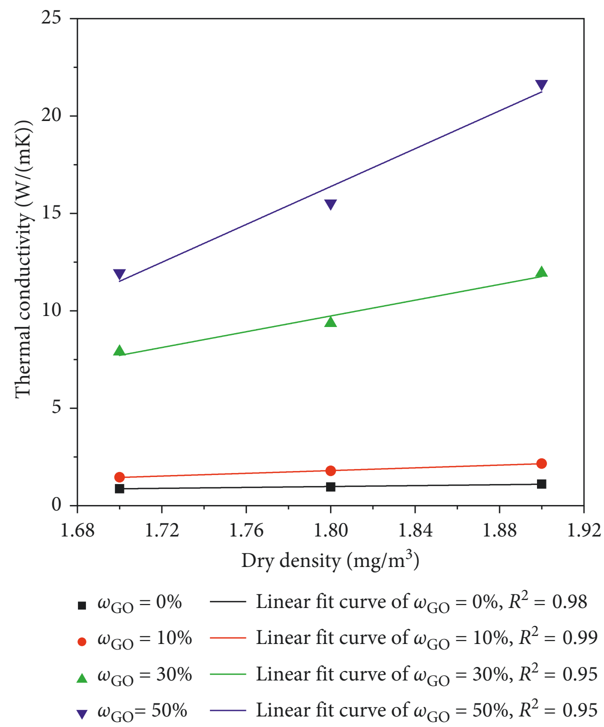

Figure 5: The thermal conductivity and dry density.

$$\begin{aligned}
\lambda &= 1.16\rho_d - 1.11 \quad \text{for} \quad \omega_{GO} = 0\% \ \left(R^2 = 0.98\right),\\
\lambda &= 3.52\rho_d - 4.5 \quad \text{for} \quad \omega_{GO} = 10\% \ \left(R^2 = 0.99\right),\\
\lambda &= 20.24\rho_d - 26.70 \quad \text{for} \quad \omega_{GO} = 30\% \ \left(R^2 = 0.95\right),\\
\lambda &= 48.61\rho_d - 71.12 \quad \text{for} \quad \omega_{GO} = 50\% \ \left(R^2 = 0.95\right),
\end{aligned} \tag{2}$$

where the meaning of λ, ω_{GO}, and R^2 in this equation are the same with (1). According to the equations above, the thermal conductivity of GO-GMZ bentonite has a good linear relationship with its dry density when the water content keeps invariable. This is due to the increase of the contact area between the particles [57].

Figure 5 also shows that the slope coefficient has a greater value at higher GO content. This means that the influence degree of dry density is greater when GO content is higher. This probably attributes to much higher thermal conductivity of graphene oxide than pure bentonite. Previous studies have confirmed that, for various bentonites, a linearity exists in thermal conductivity-dry density relationship, which includes MX-80 [58, 59], Kunigel [60], FEBEX [61], GMZ [46] and Kyeongju bentonite [62]. This relationship has also been found in the bentonite-sand mixture [46, 47]. A comparison of this study with those of the results in literatures has been illustrated in Figure 6. As shown, the dry density for different bentonites and bentonite-sand mixtures ranged from 1.5 Mg/m^3 to 1.9 Mg/m^3 and the water content from 0% to 17.4%. At these experimental conditions, the thermal conductivity of various pure bentonites is in a range of 0.30 W/(mK) to 1. 34 W/(mK). In addition, its value for the bentonite-sand mixture ranges from 0.89 W/(mK) to 1.33 W/(mK) when the sand content ranges from 10% to

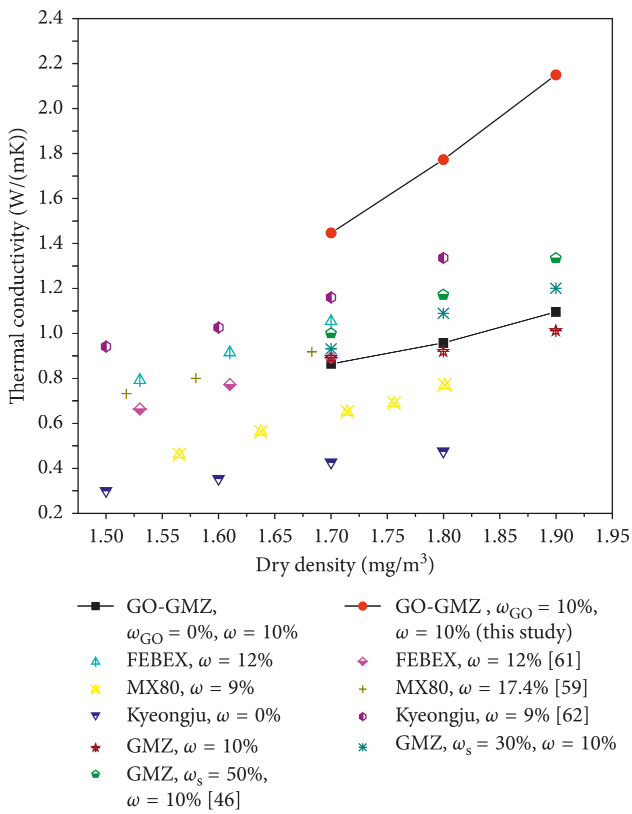

Figure 6: Comparison of the thermal conductivity and dry density in the present study with available data in published literatures.

50% and the dry density increases from 1.7 Mg/m^3 to 1.9 Mg/m^3. This is because the thermal conductivity of sand is higher than that of bentonite. However, the maximum thermal conductivity of compacted GO-GMZ bentonite is 21.66 W/(mK). Apparently, this value is much higher than that of bentonite-sand mixture. This maybe due to the better heat conduction behaviour of GO (129 W/(mK) than quartz sand (7.7 W/(mK)) [63]. In general, the thermal conductivity-dry density relationship for various bentonites has a similar trend with GO bentonite. The denser the compacted soil specimen, the higher the thermal conductivity value of bentonites. This is due to the increase of the interacting area between bentonite particles with increase in dry density. Nevertheless, the increasing rates are somewhat different for different bentonites, and this probably attributes to the differences in their mineralogical composition, texture, and water content [62, 64].

3.3. Influence of Water Content on Thermal Conductivity. The effect of water content on thermal conductivity is illustrated in Figure 7. As shown, the thermal conductivity and water content have a clear linear relationship with increasing water content when water content increases from 0% to 10% and GO content equals to 0%, 10%, 30%, and 50%, respectively. The minimum value of thermal conductivity is 0.37 W/(mK), and the maximum value is 15.52 W/(mK). This increase can be explained that the air in the void has been replaced by the water whose thermal

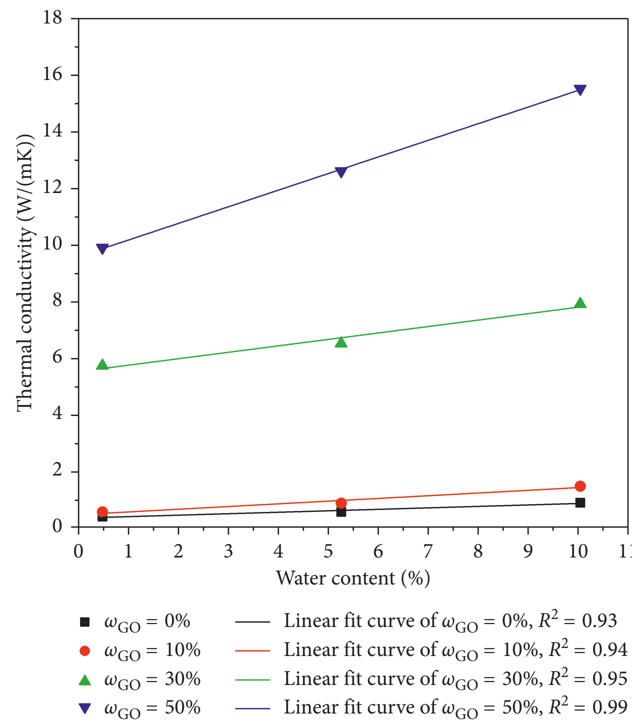

Figure 7: The thermal conductivity and water content.

conductivity is higher than air, leading to an additional increase of the thermal conductivity. The linear relationship can be expressed as follows:

$$\begin{aligned}
\lambda &= 0.05\omega + 0.34 \quad \text{for} \quad \omega_{GO} = 0\% \left(R^2 = 0.93\right),\\
\lambda &= 0.09\omega + 0.48 \quad \text{for} \quad \omega_{GO} = 10\% \left(R^2 = 0.94\right),\\
\lambda &= 0.22\omega + 5.61 \quad \text{for} \quad \omega_{GO} = 30\% \left(R^2 = 0.95\right),\\
\lambda &= 0.56\omega + 9.85 \quad \text{for} \quad \omega_{GO} = 50\% \left(R^2 = 0.99\right),
\end{aligned} \tag{3}$$

where ω is the water content. According to the equations above, the thermal conductivity of GO-GMZ bentonite has a good linear relationship with its water content. However, Lee et al. [62] reported that the thermal conductivity-water content relationship will become nonlinear when the water content is beyond 12%. Several studies used the sigmoidal-type equation to express this nonlinear relationship [61]:

$$\lambda = \frac{\lambda_0 - \lambda_s}{1 + \exp\left(\left(S_r - S_a\right)/A\right)} + \lambda_s, \tag{4}$$

where λ_0 represents the value of λ when $S_r = 0$, λ_s represents that value when $S_r = 1$ (i.e., the specimen is saturated), S_a is the corresponding saturation degree when the thermal conductivity of the specimen equals to the average of the two extreme values, and while A functions as an empirical parameter, S_a is the corresponding saturation degree when the thermal conductivity of the specimen equals to the average of the two extreme value. In the equation above, the saturation degree (S_r) can be calculated by water content (ω), dry density (ρ_d), and water density (ρ_w) as follows:

$$S_r = \omega \cdot \frac{\rho_d}{\rho_w}. \quad (5)$$

Figure 8 plots the fitting curves of thermal conductivity and saturation degree. The parameter values are best fitted and listed in Table 3. Theoretically, the fitted values of λ_0 should be equal to the experimental values when saturation of the samples is 0. However, the fitted values are slightly higher when the GO content is equal or greater than 10%. This maybe due to the inhomogeneous distribution of the material (i.e., GO-GMZ bentonite), leading to a decrease in its thermal conductivity [65].

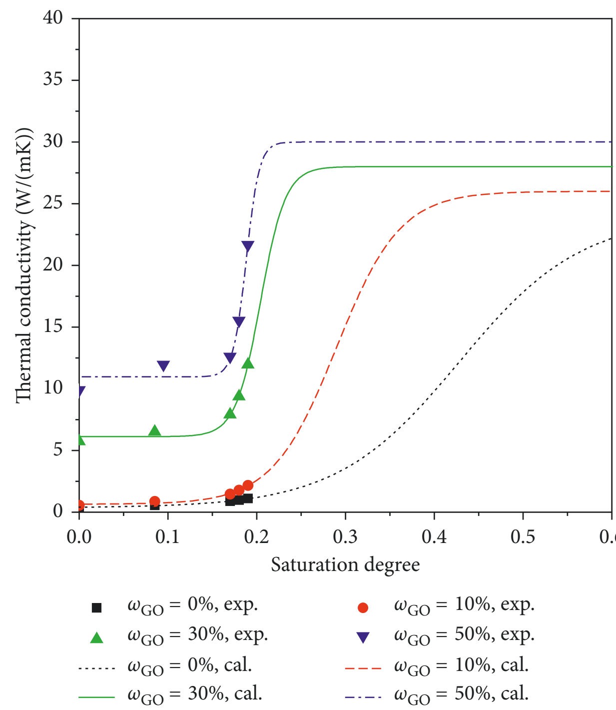

Figure 8: The thermal conductivity and the saturation degree.

Table 3: Fitting values of the parameters in (4).

GO content (%)	Coefficients of fitting				
	λ_0 (W/(mK))	λ_s (W/(mK))	S_a	A	R^2
0	0.034	24	0.428	0.069	0.97
10	0.627	26	0.290	0.036	0.93
30	6.106	28	0.204	0.014	0.95
50	10.954	30	0.188	0.007	0.90

3.4. Model of Thermal Conductivity for GO-GMZ Bentonite. In the HLW repository, the heat transfer behaviour of highly compacted bentonite can influence the process of decay heat from the high-level radioactive to the host rock greatly. Some additives will be added to improve its thermal property due to its low thermal conductivity. Because of the inflowing groundwater coming from the host rock, the buffer material will become saturated gradually. In addition, its dry density also will change when the confining pressure changes. These processes can change its thermal property which will influence the safety of HLW disposal. Therefore, the prediction of thermal conductivity of bentonite is an important part of study for the buffer material. Numerous predicting models of thermal conductivity have been proposed in the past several decades. Among them, empirical models [66–68] and geometric mean model are widely used [16, 62, 69]. Empirical models can be adopted to build up the relationship of the thermal conductivity between various types of soils and their dry density and water content. However, none of them take into account mass additives into the soil. The geometric mean model was firstly presented by Woodside and Messmer [69]. Then, it was improved and successfully used by Lee et al. [62]. Based on the volumetric composition of sample-forming minerals, the geometric mean model can be presented as follows:

$$\lambda = \prod_j^n \lambda_j^{\phi_j} \text{ with } \sum_j^n \phi_j = 1, \quad (6)$$

where $\prod$ represents the product of $\lambda_j^{\phi_j}$. λ_j and ϕ_j are the thermal conductivity of each component and its volumetric proportion, respectively. Obviously, the sum of the volumetric proportion for each component equals to 1. j refers to the jth component, and there are n kinds of components in total.

According to the geometric mean model mentioned above, the present study proposes a new model to predict the thermal conductivity considering the influence of GO. The following prediction model is based on several assumptions: (1) bentonite is homogeneous; (2) GO disperses homogeneously in the soil; and (3) the voids in the compacted soil are full of air at first when the degree of saturation equals to 0, and it has been replaced by water with the increasing water content. To take all components into account, (6) can be rewritten as

$$\begin{gathered}
\lambda = \lambda_b^{\phi_b} \lambda_{GO}^{\phi_{GO}} \lambda_\omega^{\phi_\omega} \lambda_a^{\phi_a} \text{ with } \lambda_b + \lambda_{GO} + \lambda_\omega + \lambda_a = 1, \\
\phi_b = \frac{\rho_d (1 - \omega_{GO})}{\rho_b}, \\
\phi_{GO} = \omega_{GO} \left(\frac{\rho_d}{\rho_{GO}} \right), \\
\phi_w = (1 - \phi_b - \phi_{GO}) S_r, \\
\phi_a = (1 - \phi_b - \phi_{GO})(1 - S_r),
\end{gathered} \quad (7)$$

where $\lambda_b, \lambda_{GO}, \lambda_\omega,$ and λ_a present the thermal conductivity of bentonite, GO, water, and air, respectively, while $\phi_b, \phi_{GO}, \phi_\omega,$ and ϕ_a are the volumetric proportions for bentonite, GO, water, and air, respectively; ρ_d is its dry density; ρ_b and ρ_{GO} are the particle densities of bentonite and graphene oxide, respectively; and S_r is the saturation degree of compacted specimens. Each component of the compacted material would not have homogeneous distribution and its influence on the thermal conductivity is different. In consideration of all these facts, (7) can be modified and expressed as follows:

$$\lambda = \lambda_{b}^{\left(n\rho_{d}\left(1-\omega_{GO}\right)/\rho_{b}\right)}\lambda_{GO}^{\left(p\omega_{GO}\rho_{d}/\rho_{GO}\right)} \cdot \left[\lambda_{\omega}^{S_{r}}\lambda_{a}^{\left(1-S_{r}\right)}\right]^{q\left[1-\left(\left(\rho_{d}\left(1-\omega_{GO}\right)/\rho_{b}\right)-\left(\omega_{GO}\rho_{d}/\rho_{GO}\right)\right)\right]}, \tag{8}$$

where n, p, and q are the influence factors which take into account the different influence degrees for various components. The values of λ_{GO}, λ_{ω}, and λ_{a} are 129 W/(mK), 0.059 W/(mK), and 0.024 W/(mK) at 20°C, respectively. However, the mineral composition of the compacted specimen may differ from each other because of uneven sampling, leading to a varying value of λ_{b}. Therefore, its value is determined with other parameters including n, p, and q with the multivariate regression analysis method. After regression, the modified model and the fitted values of parameters are presented as follows:

$$\lambda = 2.094^{\left(n\rho_{d}\left(1-\omega_{GO}\right)/\rho_{b}\right)}129^{\left(p\omega_{GO}\rho_{d}/\rho_{GO}\right)} \cdot \left[0.59^{S_{r}}0.024^{1-S_{r}}\right]^{q\left(1-\left(\rho_{d}\left(1-\omega_{GO}\right)/\rho_{b}\right)-\left(\omega_{GO}\rho_{d}/\rho_{GO}\right)\right)}, \tag{9}$$

$$n = 1.195, p = 1.195, q = 0.663.$$

The correlation coefficient of (8) is 0.97. Values of n and p are higher than 1, respectively, while the value of q is lower than 1, which indicate that the bentonite and GO present stronger influence to the thermal conductivity than water and air does.

The comparison of measured values and calculated thermal conductivity using the proposed constitutive model above is plotted in Figure 9. As shown in the figure, when the GO content is higher than 10%, the calculated values are approximately equal to the experimental value. This means that this modified model is proper to predict the thermal conductivity of GO-GMZ bentonite when the GO content is higher than 10%. However, the calculated values are apparently higher than the measured values when the GO content is lower than 10%. Considering such fact, there may cause a misleading in the thermal conductivity prediction when the additive's content is low. Therefore, the practical application of the calculated thermal conductivity using the proposed constitutive model needs more consideration. In general, the modified geometric mean model proposed in this research can be adopted as a constitutive model to predict the thermal conductivity of the GO-GMZ bentonite, which has been considered as the feasible buffer material for an HLW repository in China.

Bentonite will undergo thermal, chemical, and mechanical effects when used in the HLW repository. Therefore, the durability of GO-GMZ bentonite is of concern. Generally, the structure of GO is stable chemically when there is no photocatalyst or peroxidase and its decomposition temperature is found to be above 100°C [70–72]. Some chemical bonds such as the amido bond form in this process, and they are stable thermally and chemically [73]. In addition, the size of the particles used and obtained in the modified process is too small (i.e., nanosized or even smaller) to be influenced by the mechanical pressure. Therefore, the structure of GO-GMZ will stay durable under swelling pressure or other mechanical forces.

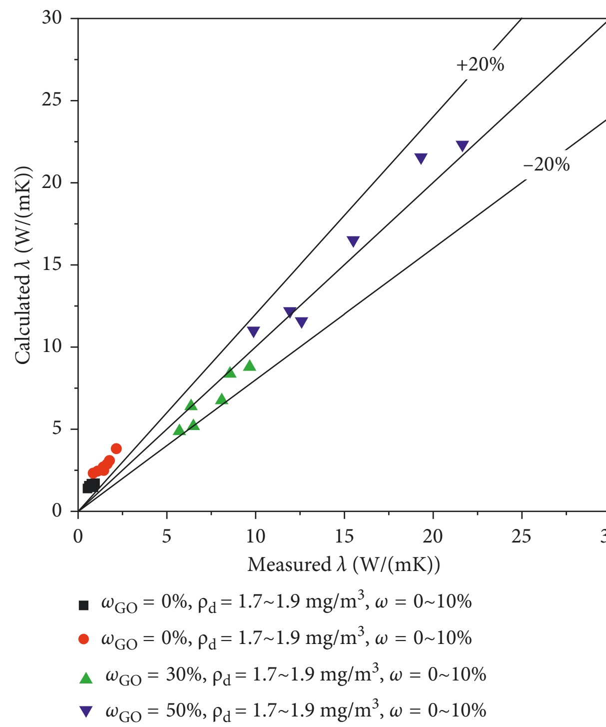

FIGURE 9: Comparison between the calculated values and experimental results of the thermal conductivity for GO-GMZ bentonite.

4. Conclusions

This research measures the thermal conductivity of highly compacted GO-GMZ bentonite under different conditions like graphene oxide content, dry density, and water content with the thermoprobe method. The thermal conductivity of GO-GMZ bentonite increases evidently as values of GO content, dry density, and water content are fortified. The functional relationship between the thermal conductivity and GO content is quadratic. However, thermal conductivity-dry density relationship or thermal conductivity-water content relationship is linear within a certain range. Moreover, a modified geometric mean model is also proposed in the present study to predict the thermal conductivity of GO-GMZ bentonite. The comparison between experimental data and calculated values implies that this model is appropriate for such buffer material when the GO content exceeds beyond a certain range. Therefore, this proposed model can be applied to predict the thermal conductivity of the GO-GMZ bentonite as a constitutive model for a HLW repository in China. In addition, hydraulic conductivity is another crucial parameter for its safe application which will be studied in the further work.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (41422207 and 41772279), China Atomic Energy Authority ([2011]1051), and Fundamental Research Funds for the Central Universities.

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