Experimental investigation on the effect of temperature on thermal conductivity of synthetic rock samples

WANG Zhuo
Chinese Society for Rock Mechanics and Engineering, Beijing 100029, China
Beijing Zhongke Force Blasting Technology Co., LTD, Beijing, 100080, China;
Email: 201455@cumtb.edu.cn

Abstract. The effective thermal conductivity (ETC) plays an important role in many fields such as to solve basic geological problems, rock engineering, and utilization of heat energy; ETC is one of the most important thermo-physical properties of porous media. In this study, experiments on synthetic rock samples with different material mixture ratios under different operating temperatures are conducted to estimate the thermal conductivity property of the rock samples. The experiments were performed on synthetic samples with different ratios of gypsum, fine or medium sand, and water; 21 groups of tests were conducted under room temperature; another five groups of tests were conducted under different temperatures from 20 to 50 °C to assess the effect of temperature on thermal conductivity. According to existing studies and equations, thermal conductivity increases with an increase of sand content and a decrease in temperature. Moreover, based on our experiments, it is easy to identify a singularity on the general changing trend of thermal conductivity for each sample. Following our experimental results, we attempted to observe and interpret this alteration mechanism. According to the heat capacity theory in solid-state physics, this research provides new explanations for the above alteration.

1. Introduction
The effective thermal conductivity (ETC) is one of the most important thermo-physical properties of porous media [1-2]. This parameter is necessary for the analysis of heat transfer [3-4]. It is well known that a general equation for $\lambda(T)$ was set by Sass et al. (1992) [5], which is based on the coupled effect of composition and temperature on thermal conductivity [6-7]. The equation was further verified for other rocks [8-10]. Thermal conductivity is also related to other physical properties of porous rocks such as thermal diffusivity and heat capacity [11-12]. Generally, ETC and other thermo-physical properties of rock materials are affected by various factors such as temperature, pressure, mineralogical composition, porosity, stratification, size and shape of components, and nature of pore fluid. [13-14]. Knowledge of the thermal properties of rocks is required to understand heat transport processes. Although numerous research studies on the effect of temperature on rock thermal conductivity have been conducted recently, data collection in this regard was not intensive
[15-17]. Due to the lack of high-accurate reports on the effect of temperature on thermal conductivity, we conducted six experiments, namely groups 1–6, on rock samples (including igneous rock, sedimentary rock, and metamorphic rock) under different operating temperature range 20℃–50 ℃. Through these experiments, we studied the different effects of temperature on the thermal conductivity of rocks.

2. Methods
2.1 Sample selection

Sample lithology:
Gypsum, sands

Preparation method:
Cut samples using a general cutting machine.

Sample required:
Prior to carrying out measurements, the samples were dried in a vacuum at a temperature of 120℃ for 5–8 h and then cooled slowly to remove water in the samples, which can affect thermal conductivity. The samples were cut into measurement pairs as required. Videlicet, each group of the samples was divided into two identical samples. The natural rock samples must be ground after cutting until a sufficiently smooth surface area is achieved. This is because the samples’ surface contact with the cutting machine must be sufficiently smooth when measured.

2.2 Thermal conductivity measurements

Thermal conductivity was measured from 20℃ to 50℃ (per 5℃) using the “TC-3000 Thermal Conductivity Meter” of XIAXI Electronic Technology Co., LTD., Xi’an, which is based on the transient hot-wire method that has been used in this context for more than ten years.

Commissioning for equipment
To evaluate the precision of measuring equipment, first, standard samples should be tested, which can validate the accuracy of the equipment. Standard samples mainly comprise organic glass, borosilicate glass, and stainless steel. The standard samples shall be tested each time before using the equipment.

Test procedure
(1) Setting instrument. Check the conditions of the test instruments and sensor parameters;
(2) Sensor installation. Cautiously selecting the samples with a smooth surface for testing;
(3) Temperature monitoring. Monitor the temperature of each sample and test when stability is reached;
(4) Measurement parameter settings. Set measurement parameters, including time interval, sampling frequency, sampling mode, acquisition time, and voltage;
(5) Thermal conductivity test. Record the average thermal conductivity for each group.

Accounting relative error

\[
\varepsilon = \frac{|K-K'|}{K} \quad (1)
\]

2.3 Transient hot-wire method theory

The theory of the transient hot-wire method originated from the test of fluid thermal conductivity. The ideal model is to apply a heat source with an infinite length and infinitesimal diameter to an infinite isothermal fluid until the heat source and the fluid are in thermal equilibrium. When a heat source with step constant heat flux is used, the temperature of the heat source and its surrounding fluid rises. We can obtain the coefficient of the thermal conductivity of the fluid based on the temperature increase of the heat source. In the study, Fourier equation was the basic control equation, i.e.
\[ \frac{\partial T}{\partial t} = a \nabla^2 T \]  \hspace{1cm} (2)

where \( T \) denotes temperature; \( t \) denotes time; \( a = \frac{k}{\rho c_p} \) is the thermal diffusion coefficient of a fluid; \( K \) is the thermal conductivity coefficient of a fluid; \( \rho \) and \( c_p \) are the density and specific heat at a constant pressure of a fluid. Finally, we derived the following equations;

\[ \frac{\partial T}{\Delta T_{at} r} = \frac{r_a^2}{4\alpha t} \cdot \frac{1}{\ln(4\alpha t/r_a^2 C)} \]  \hspace{1cm} (3)

Then,

\[ K = \frac{q}{4\pi A} \]  \hspace{1cm} (4)

3. Results

Following the summary and analysis of previous studies on most crystalline rocks, thermal conductivity is a function of temperature:

\[ K(T) = \frac{1}{(A + BT)} \]

\[ A = -(532 \pm 45) \times B + (0.448 \pm 0.014) \]

\[ K(T) = \frac{1}{B \times T - 532 + 0.448} \]  \hspace{1cm} (5)

The above equation can make thermal conductivity a decreasing monotone function of temperature.

3.1 Thermal conductivity on synthetic samples by different proportions

Experiments on gypsum samples prepared with pure plaster using three different mixture ratios under room temperature.

The first batch of specimens was prepared with pure plaster. Samples with three different mixture ratios of water and plaster (0.8:1, 1:1, and 1.2:1) were tested under room temperature. The test results are shown in the following figure below.

Six or more measurements were made for samples with each mixture ratio. The thermal conductivity \( K \) value varies between 0.2 and 0.36. Thermal conductivity decreases significantly with the increase of water content.
Figure 1. Samples with three different mixture ratios of water and plaster

Experiments on gypsum samples prepared with fine sand using six different mixture ratios under room temperature

The second batch of specimens was prepared with plaster and fine sand. Samples with six different mixture ratios of water, plaster, and sand (3:4:2, 6:10:5, 4:10:5, 0.8:1:0.1, 0.8:1:0.2, and 0.8:1:0.3) were tested under room temperature. Consequently, the sand contents of the different mixture ratios were different.

Test results show that the thermal conductivity of the afore-stated specimens with six different mixture ratios under room temperature varies in the range 0.3–0.8. Overall, increasing sand content increases thermal conductivity.

The particle size distributions of the fine sand were 65% sand with a grain size of 0.01 mm, 30% sand with a grain size of 0.1 mm, and 5% sand with a grain size of 0.2 mm.

Figure 2. Six different mixture ratios of water, plaster, and sand

Experiments on gypsum samples prepared with medium sand using six different mixture ratios under room temperature

The mixture ratios (i.e., water, plaster, and sand) of the third batch of samples were the same as that of the second batch. However, the fine sand was replaced by medium sand in this batch. The particle size distributions of the medium sand are 75% sand with a grain size of 0.5 mm, 10% sand with a grain size of 0.4 mm, 3% sand with a grain size of 0.3 mm, and 2% sand with a grain size of 0.2 mm.
Figure 3. Six different medium sand mixture ratios under room temperature

Test results show that the thermal conductivity of the third batch of specimens under room temperature varies from 0.35 to 0.8. Thermal conductivity $K$ significantly increases with an increase in sand content.

Experiments on gypsum samples prepared with mixed sand (fine and medium sand) using six different mixture ratios under room temperature

The last batch of specimens was prepared with plaster and an aggregate mixture of fine and medium sand. Samples of six different mixture ratios of water, plaster, and sand were tested under room temperature. The range of the obtained thermal conductivity value is 0.34–0.72. The relationship between thermal conductivity and sand content completely follows a monotonically increasing trend.

Thermal conductivity (W/m*K)

Figure 4. Six different medium sand mixture ratios under room temperature
3.2 Temperature dependence of the thermal conductivity of specimen prepared with plaster and medium sand

Specimen prepared with pure plaster

First, the thermal conductivity of the specimens made with pure plaster was measured under seven different temperatures (20 °C, 25 °C, 30 °C, 35 °C, 37 °C, 40 °C, and 50 °C). The thermal conductivity of the remaining four batches of specimens was also measured under the same temperatures. The first batch of specimens was made by the mixture of water and plaster at a ratio of 0:8:1. The test results are shown in the following figure. Thermal conductivity K within the range 0.33–0.36 decreases significantly with the increase in temperature. An abnormal point for thermal conductivity is observed at 37 °C. For the first batch, thermal conductivity shows a noticeable but moderate fluctuation with a change in temperature.

![Pure gypsum](image)

**Figure 5.** Pure plaster under different temperature

For the second batch, specimens with a mixture ratio of water, plaster, and medium sand 0.8:1:0.1 were tested. The test results are shown in the following figure. Thermal conductivity K ranges between 0.35 and 0.4 and shows an obvious descending trend with an increase in temperature. Thermal conductivity also shows a considerable fluctuation with a convex point at 37 °C.
Figure 6. Specimens with a mixture ratio of water, plaster and medium sand 0:8:1:0.1

The third batch of specimens was prepared by a mixture of water, plaster, and medium sand at a ratio of 0.8:1:0.2. The test results are shown in the following figure. Thermal conductivity $K$ ranges between 0.35 and 0.42 and decreases remarkably with an increase in temperature. The fluctuation of thermal conductivity is very remarkable with the singular value appearing at the same temperature level 37 °C.

Figure 7. Specimens with a mixture ratio of water, plaster, and medium sand 0:8:1:0.2

Specimens with a mixture ratio of water, plaster, and medium sand 0:8:1:0.3

Specimens made by the mixture of water, plaster, and medium sand at a ratio of 0.8:1:0.3 were tested in the fourth batch. The test results are shown in the following figure. Thermal conductivity $K$ varies between 0.42 and 0.52. The following trends are observed: a) an
increase in temperature decreases thermal conductivity; b) significant fluctuation of thermal conductivity with a change in temperature; c) irregular value at 37 °C.

Figure 8. Specimens with a mixture ratio of water, plaster, and medium sand (0:8:1:0.3)

Specimens with a mixture ratio of water, plaster and medium sand (0:8:1:0.5)

For the last batch, sand content was increased further with a mixture of water, plaster, and medium sand at a ratio of 0.8:1:0.5. The test results are shown in the following figure. Thermal conductivity K was observed in a higher range from 0.49 to 0.56. Although a noticeable fluctuation is observed, thermal conductivity still follows a considerable descending trend when there is an increase in temperature. The abnormal point at 37 °C is observed in this batch as in the previous tests.

Figure 9. Specimens with a mixture ratio of water, plaster, and medium sand (0:8:1:0.5)

4. Discussion

According to the theory of thermodynamics, thermal conductivity can be calculated as
\[ K = C \nu l \]  \hspace{1cm} (6)

Where \( C \) is the specific heat per volume; \( \nu \) is the average velocity of particles; \( l \) is the average free path of particles.

We can consider solids as a thermal system composed of phonons. To calculate thermal conductivity, we can use \( C, \nu, \) and \( l \) as the specific heat, average velocity, and average free path of phonons, respectively. Average velocity, which is almost independent of temperature, can be considered as a constant. Hence, we can focus on the specific heat and average free path.

### 4.1 Specific heat

According to Debye theory of specific heat capacity, lattice specific heat is proportional to \( T^3 \) in low temperature, while it is constant in high temperature, i.e.,

\[ C \sim \frac{12 \pi^4}{5} Nk \left( \frac{T}{\Theta} \right)^3 \]

\[ \text{Low temperature} \]

\[ \text{High temperature} \]

\[ C = 3Nk \]  \hspace{1cm} (7)

Where \( N \) is the number of unit cells, \( k \) is Boltzmann constant, \( T \) is temperature, and \( \Theta \) is Debye temperature.

For sufficient low temperatures, the above-mentioned law holds well with the experiments. In this regard, only acoustic phonons with low frequency, which could be considered as elastic waves, can be excited. This is consistent with the approximation we have taken in the calculation of specific heat. Moreover, at high temperatures, all the acoustic phonons are excited. Hence, specific heat is a constant in high temperature due to the energy equipartition theorem.

### 4.2 Average free path

According to the theory of thermodynamics, the free path of phonons, which has significant correlations with temperature, can be defined as the distance of two successive collisions between phonons. Solids can be affected by the following factors below,

1. Collisions between phonons;
2. Collisions between phonons and impurities;
3. Collisions between phonons and boundaries of solids.

First, the collisions between phonons are due to harmonic effects. When ionic cores deviate from equilibrium positions in a larger distance, harmonic coupling occurs, resulting in a phonon-phonon interaction. In high temperatures, ionic cores vibrate dramatically as temperature increases. This leads to the dependence on the temperature of collisions between phonons. In this regard, the free path is inverse proportional to temperature, which is consistent with most of our experiments. Consequently, the following can be understood: the number of excited phonons is proportional to high temperatures, and for a definite phonon, its collision frequency is proportional to the number of phonons it can collide with. Therefore, we can conclude as \( l \sim \frac{1}{T^3} \).

Impurities can also lead to the scattering of phonons due to their destruction of crystal periodicity. A substitutional defect of different mass, for example, can lead to the scattering of phonons. The greater the quality differences, the stronger the scattering, but the shorter the free path.

At low temperatures, only a few phonons, which have wave-length longer than the scale of ionic cores and impurities, can be excited. Hence, phonon-phonon collisions and phonon-defect interactions can be neglected. In this regard, boundary collision is predominant. This mechanism works at low temperatures since the wave-length of excited phonons can be comparable with boundaries. In this condition, the free path, which is independent of temperature, has the same order of magnitude.

### 4.3 Thermal conductivity
Following the above analysis, thermal conductivity is proportional to temperature raised to the power of three at low temperatures. Moreover, at high temperatures, it is inversely proportional to temperature. However, thermal conductivity can also become singular because of the scattering of impurities.

4.4 Final analysis
Following the above figures and derivation, the following can be concluded: thermal conductivity decreases as temperature increases, but a convex point occurs at some particular temperatures according to the above analysis at high temperatures. The convex point can be attributed to the scattering of impurities.

5. Conclusions
We studied the effect of temperature on the thermal conductivity of different rock samples and reported that there is an obvious convex or singular point in the interval of 25°C–37°C for each sample. However, this does not conform to the general rule, i.e. thermal conductivity decreases as temperature increases. This research provides a reasonable explanation for the singular point based on the theory of specific heat in solid states physics. Following the experiments conducted on the specimens with six different mixture ratios under room temperature, the following statements can be made. a) For specimens with a mixture of fine sand and medium sand, a concave point appears when the sand content is between 5% and 10%. Thermal conductivity does not monotonically increase with an increase in sand content. b) Another concave point exists for specimens with a fine sand content range of 14.29%–23.81%. c) The thermal conductivity of the specimens with the mixed sand follows a monotonically increasing trend with the increase of sand content as usually assumed. Experimental results for the specimens with different ratios show that the molecular weight of the component with the largest ratio is greater than that of impurities. It is assumed that thermal conductivity mainly depends on the scattering between different phonons before the singular temperature; subsequently, the scattering between phonons and impurities will play a role in this regard.

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