Study of effect of moisture and temperature on thermal and physical properties of limestone using a transient plane source technique

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Abstract. This study investigated the thermophysical properties of limestone in its dry and moist states. A thermal constant analyzer, based on Transient Plane Source (TPS) technique, was used to study the thermophysical properties. Temperature dependence of thermophysical properties of limestone was investigated by elevating the temperature up to 433 K. The chemical and mineral composition of samples were studied using SEM-EDS and XRD analysis. The thermal conductivity of dry and moist limestone showed that in situ measurements are necessary for the precise determination of thermal properties. The variations in thermal properties of limestones as a function of temperature were described by mineral composition and heat transfer mechanism. The thermal conductivity of limestone was measured in the range of 2.586 to 3.054 Wm⁻¹K⁻¹. The thermal diffusivity of samples was ranged from 1.390 to 1.601 mm²s⁻¹ while specific heat capacity of limestone was in the range of 1.847 to 2.066 MJm⁻³K⁻¹. A noticeable change in thermal properties of moist limestone was observed as compared to the dry limestone.

1. Introduction

Porous stones are used in strengthen building structures due to their durability and high compressive strength. Natural stones as building materials are being used for thousands of years in the construction of structures and monuments. High volume of past literature is focused on sustainable energy resources and energy conservation techniques [1, 2]. The most efficient source of energy conservation is the use of thermal insulation to provide thermal comfort inside the buildings. In recent years, heat transfer properties of rocks are widely used to construct underground chambers for nuclear waste dumping, measurement of heat dissipation, determination of the rate of heat loss from earth due to the geothermal gradient, retrieving the history of earth’s evolution, and construction of buildings on permafrost earth’s zone [3, 4]. All these applications need accurate determinations of thermophysical properties of rocks.

In Pakistan, three types of stone are widely used in construction of monument and repairing the historic buildings. These stones include sandstone, limestone and marble. They can easily be cut into different shapes. For this study, limestone was chosen which is a sedimentary rock. The limestone consists of calcium carbonate (calcite) with small amount of magnesium carbonate (dolomite), silica, clay, iron oxide and carbonaceous material. Limestone is also used as raw material for cement [5, 6]. Calcite in limestone is sensitive to temperature and may affect the building environment.

The objective of this study was to investigate the influence of calcite content, moisture and temperature on the thermal properties of limestones. A thermal constant analyzer, based on transient plane source (TPS) method, was used to generate the data on thermal properties of limestone [5]. The
goal of this research was to compare the accuracy of in-situ thermal properties of dry and moist limestone samples with the existing theoretical thermal conductivity models. Furthermore, the temperature dependence of thermal conductivity, thermal diffusivity and specific heat capacity of limestone was measured to get important information about lithology and structure of the limestone.

2. Materials and methods

The limestone samples were collected from a mountain located in the Murree Salt Range of Pakistan. The sampling was done at the height of 566 m to 799 m. From each bulk stone, three samples were cut in cubic blocks of dimensions 2.8 cm$^3$. The surface of all stones was polished with silicon carbide paper. After washing in distilled water, stone samples were dried in a heating oven at 110 °C for least 24 hours. The water absorption, water accessible porosity and bulk density of blocks were determined using Archimedes principle. The following equations were used in these calculations:

$$ WA(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1) $$

$$ Porosity (\%) = \frac{W_{wet} - W_{dry}}{W_{dry} - W_{suspended}} \times 100 \quad (2) $$

$$ Bulk density (g/cm^3) = \frac{W_{dry}}{W_{dry} - W_{suspended}} \quad (3) $$

where $W_{dry}$ is the dry weight of samples after drying at 110°C, $W_{wet}$ is the water-saturated weight of samples after boiling in distilled water for 4 h and cooling to room temperature. In case of building stones, $W_{wet}$ was determined by immersing stones in distilled water for 96 hours. $W_{suspended}$ is the suspended weight of water saturated samples, which was measured using equal arm balance (whose one pan was removed and a wire of equal weight was attached to suspend samples in water). During measurements, it was made sure that the sample does not touch the base or sides of the water container.

The chemical analysis of limestones was carried out through SEM based EDS. Thermal conductivity, thermal diffusivity and specific heat capacity of samples were measured using hot disk thermal constant analyzer based on TPS technique. Schematic design of humidity box attached with TPS setup for measurement of moist limestones is shown in figure 1.

![Figure 1. Schematic of humidity box attached with TPS setup.](image)

3. Results and discussion

The results on physical properties, chemical and mineral composition and thermal properties of the limestone samples are discussed in this section.
3.1. Physical properties
Physical characterization of limestone samples is shown in Table 1. WA (%) of samples was found in a range of 0.8 to 1.4 and porosity (%) varied from 2.1% to 3.5%. Porosity (%) decreases with elevation from the baseline. The density of limestone also followed an increasing trend with elevation from the baseline. Overall, density increased from 2.62 g.cm$^{-3}$ to 2.69 g.cm$^{-3}$. Figure 2 shows graphically the porosity at different positions above the baseline [7-9]. The trend in figure 2 satisfies a linear fit of the equation of $6.68 - 0.0061x$ and $R^2$ was determined as 0.91.

The compressive strength of limestones lied between 36 to 60.3 MPa and it is noticeable that the compressive strength of limestone decreased by 40% with moving from 566 m to 799 m above the baseline.

Table 1. Thermal properties of limestone samples.

| Sample | Thermal conductivity (Wm$^{-1}$K$^{-1}$) | Thermal diffusivity (mm$^2$s$^{-1}$) | Specific heat capacity (MJm$^{-3}$K$^{-1}$) |
|--------|----------------------------------------|-------------------------------------|------------------------------------------|
| CC-1   | 2.586 ± 0.01                           | 1.390 ± 0.09                        | 1.865 ± 0.01                             |
| CC-2   | 2.860 ± 0.07                           | 1.579 ± 0.11                        | 1.847 ± 0.04                             |
| CC-3   | 2.903 ± 0.08                           | 1.402 ± 0.03                        | 2.066 ± 0.03                             |
| CC-4   | 3.054 ± 0.03                           | 1.601 ± 0.05                        | 2.029 ± 0.09                             |

Figure 2. Variation in porosity (%) due to elevation from baseline.

3.2. Physical properties
EDS analysis was carried out on three data points for each limestone sample and the test data listed in Table 2 shows the average value of weight (%) with a standard deviation of each chemical element. The major elements were C, O, Ca. Some wt.% of Na, Mg, Al, Si, and K was also seen in the samples. Fe was found in CC-2, CC-3, and CC-4 samples while Cl was found in CC-1, CC-2, and CC-3 samples. EDS analysis confirmed that the major mineral phase in limestone is CaCO$_3$ (calcite).
Table 2. SEM-EDS results of limestone samples.

| Elements | CC-1 Weight (%) | CC-2 Weight (%) | CC-3 Weight (%) | CC-4 Weight (%) | Chemical compound Standards |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------------------|
| C K      | 12.60 ± 6.55    | 27.02 ± 3.76    | 21.01 ± 6.84    | 21.80 ± 1.25    | CaCO$_3$ 1-Jun-99           |
| O K      | 39.73 ± 8.49    | 55.05 ± 1.28    | 47.60 ± 0.66    | 47.80 ± 3.40    | SiO$_2$ 1-Jun-99            |
| Na K     | 0.41 ± 0.49     | 0.22 ± 0.12     | 0.30 ± 0.25     | 0.28 ± 0.12     | Albite 1-Jun-99             |
| Mg K     | 0.19 ± 0.09     | 3.18 ± 3.56     | 0.18 ± 0.25     | 0.34 ± 0.23     | MgO 1-Jun-99                |
| Al K     | 0.20 ± 0.14     | 0.21 ± 0.05     | 0.19 ± 0.23     | 0.15 ± 0.04     | Al$_2$O$_3$ 1-Jun-99        |
| Si K     | 0.08 ± 0.07     | 1.68 ± 2.59     | 1.07 ± 0.01     | 0.19 ± 0.01     | SiO$_2$ 1-Jun-99            |
| Cl K     | 0.39 ± 0.39     | 0.09 ± 0.05     | 0.23 ± 0.13     | -               |                             |
| K K      | 0.11±0.02       | 0.04 ± 0.04     | 0.27 ± 0.18     | 0.12 ± 0.01     | MAD-10 Feldspar 1-Jun-99    |
| Ca K     | 46.29 ± 14.58   | 12.30 ± 1.30    | 28.90 ± 7.88    | 29.02 ± 2.45    | Wollastonite 1-Jun-99       |
| Fe K     | -               | 0.21 ± 0.01     | 0.25 ± 0.31     | 0.30 ± 0.22     | Fe 1-Jun-99                 |

3.3. Thermal properties

Table 3 shows the thermal properties of dry limestone samples at ambient temperature and pressure. The thermal conductivity of limestone samples was observed in the range of 2.586 to 3.054 Wm$^{-1}$K$^{-1}$. The porosity (%) and water absorption was decreased with an increase in height from baseline and density. However, the mineral composition remained unchanged by revealing that the thermal properties of the same type of stone characteristically dependent on physical properties [8, 9]. The thermal diffusivity of samples was ranged from 1.390 to 1.601 mm$^2$s$^{-1}$ whereas specific heat capacity of limestone samples was in the range of 1.406 to 1.598 MJm$^{-3}$K$^{-1}$.

In rocks, porosity is generally very low and consequently, thermal properties primarily depend upon rock forming mineralogical constituents. Therefore, an increase in porosity can relate with an increase in pore fillings and as a result, the apparent density of limestone samples decreases (Table 1).

Table 3. Thermal properties of limestone samples.

| Sample | Thermal conductivity (Wm$^{-1}$K$^{-1}$) | Thermal diffusivity (mm$^2$s$^{-1}$) | Specific heat capacity (MJm$^{-3}$K$^{-1}$) |
|--------|----------------------------------------|-------------------------------------|------------------------------------------|
| CC-1   | 2.586 ± 0.01                          | 1.390 ± 0.09                        | 1.865 ± 0.01                             |
| CC-2   | 2.860 ± 0.07                          | 1.579 ± 0.11                        | 1.847 ± 0.04                             |
| CC-3   | 2.903 ± 0.08                          | 1.402 ± 0.03                        | 2.066 ± 0.03                             |
| CC-4   | 3.054 ± 0.03                          | 1.601 ± 0.05                        | 2.029 ± 0.09                             |

The thermal properties of water-saturated limestone samples are shown in table 4. In moist state, the thermal conductivity of limestone remained in the range of 2.984 to 3.153 Wm$^{-1}$K$^{-1}$, thermal diffusivity in the range of 2.079 to 2.289 mm$^2$s$^{-1}$ and specific heat capacity of 1.406 to 1.598 MJm$^{-3}$K$^{-1}$. It is quite understandable that thermal conductivity of water-saturated sample is quite high: 30 times higher than
the thermal conductivity of air [6]. The % increase in thermal conductivity of moist limestone however decreases with a decrease in porosity of limestone. The highest increase in thermal conductivity was 15.4% for moist CC-1 and the lowest increase in thermal conductivity was 8.5% for CC-3 and 8.7% for CC-4.

Table 4. Thermal properties of water saturated limestone samples.

| Sample | Thermal conductivity Wm⁻¹K⁻¹ | % increase from dry state | Thermal diffusivity mm²s⁻¹ | % increase from dry state | Specific heat capacity MJm⁻³K⁻¹ | % decrease from dry state |
|--------|-------------------------------|--------------------------|---------------------------|---------------------------|---------------------------------|--------------------------|
| CC-1   | 2.984 ± 0.02                  | 15.4                     | 2.090 ± 0.11              | 49.9                      | 1.431 ± 0.06                    | 23.3                     |
| CC-2   | 3.153 ± 0.22                  | 10.2                     | 2.079 ± 0.14              | 31.6                      | 1.598 ± 0.17                    | 13.5                     |
| CC-3   | 3.149 ± 0.05                  | 8.5                      | 2.255 ± 0.20              | 60.8                      | 1.406 ± 0.11                    | 31.9                     |
| CC-4   | 3.321 ± 0.06                  | 8.7                      | 2.289 ± 0.24              | 43.0                      | 1.465 ± 0.14                    | 27.8                     |

4. Conclusion
In this paper, four limestone samples were taken from a mountain at different heights from the baseline (566-799 m). The samples were characterized for their thermophysical properties under ambient conditions. The chemical and mineral composition of samples was measured by SEM-EDS analysis, which confirmed that the major composition of samples was calcite. The thermal conductivity of samples was measured about 2.586 to 3.054 Wm⁻¹K⁻¹. The thermal diffusivity of samples was ranged from 1.390 to 1.601 mm²s⁻¹ while specific heat capacity of limestone samples was in the range of 1.847 to 2.066 MJm⁻³K⁻¹. A noticeable change in thermal properties of moist limestone was observed as compared to the dry limestone.

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