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TECHNICAL NOTE

# Identification of Primary Mineral Elements and Macroscopic Parameters in Thermal Damage Process of Limestone with Canonical Correlation Analysis

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## 1 Introduction

Under or after high-temperature treatment, the internal structure, mineral composition, and water content of rock will change, which leads to changes in its physical and mechanical properties, and not only potentially affects the stability of the surrounding rock, but also rock engineering projects, such as underground coal gasification (Lawson et al. 2017; Samdani et al. 2017), disposal of nuclear waste with high levels of radioactivity in deep geological repositories (Salama et al. 2015), and stability analysis in rock tunnels after a fire (Lai et al. 2014). Therefore, there is great theoretical and practical significance in examining the damage characteristics and identification methods of damage of rock under high temperature.

To date, there has been much research work done on the thermal damage of rocks (see, e.g., Brotóns et al. 2013; Sun et al. 2016a; Wang et al. 2016; Yao et al. 2016). Ozguven and Ozcelik (2014) studied the effects of thermal damage on the physico-mechanical properties of Turkish natural building stones and provided equations on changes in the physical and mechanical properties (such as the bulk density, porosity, and compressive and tensile strengths) with temperature. Moreover, the rate of change of most of the properties obviously increases at a temperature over 800 °C. Lokajíček et al. et al. (2012) and Sun et al. (2016b) investigated the effect of temperature on the elastic wave velocity of different lithological rocks. Their results showed that the elastic wave velocity of several types of common rocks gradually decreases with increases in heating temperature. Variations in the rock microstructure with temperature have also been investigated with X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and computerized tomography (CT) scanning. The findings show that the microscopic origins of thermal damage are mainly caused by crack development, mineral decomposition or chemical reactions, desiccation, and heat fusion (Chen et al. 2017; Guo et al. 2017). Although the aforementioned research works have provided a solid foundation for further studies, studies that examine the response of rocks to changes in physical and mechanical properties and microscopic parameters, as well as a method that can quickly identify the thermal damage of rocks under high temperatures, are relatively rare and warrant further studies.

In this paper, the effect of temperature on the physical and mechanical properties of limestone as well as the mineral elements composition are studied, and the canonical correlation analysis algorithm is first applied to calculate the relationship and the response characteristics between the macro-parameters and mineral elements composition after treatment at different temperatures, and then determine the primary mineral compositions that affect the thermal damage of the rock and a method that can quickly identify the degree of damage will be provided. The results contribute to studies that examine the relationship between the macro-physical and mechanical properties and mineral elements composition of rock in the thermal damage process, and act

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as a reference in rock engineering studies for detecting thermal damage.

## 2 Experimental Studies

Experiments were carried out on limestone samples to examine the changes in the macro-properties and mineral elements composition at different temperatures. (The samples were subjected to a temperature gradient of room temperature, 100, 200, 300, 400, 500, 600, 700 and 800 °C.) The samples that were tested for their physical and mechanical properties were cut into $\Phi 50 \times 100$ mm cylinders, while the samples that were tested for the mineral elements composition were grinded into a powder that was finer than 200 mesh. The samples had an average bulk density of 2.71 g/cm$^3$ and a primary mineral composition of dolomite and calcite. The samples were subjected to high temperatures prior to testing (heated to the target temperature at a rate of 5 °C/min, then at a constant temperature for 2 h and then cooled down to room temperature at 5 °C/min). The mass of the samples was determined with a high-precision balance. The compressive strength, peak strain, and tensile strength were tested by using a WES-D1000 electro-hydraulic servo universal testing machine with an XL 2101B6 static strain sensor. The P-wave velocity of the samples was measured by using an RS-ST01C integrated digital acoustic sensor. The thermal conductivity was determined by using a hot disk instrument with double-sided sample testing.

## 3 Experimental Results

### 3.1 Changes in Physical and Mechanical Properties

The variation of physical and mechanical properties of the sample used in study is given in Fig. 1 and Table 1. Generally, the compressive strength, thermal conductivity, and P-wave velocity gradually decrease, and the peak strain and mass loss ratio increase as the heating temperature is

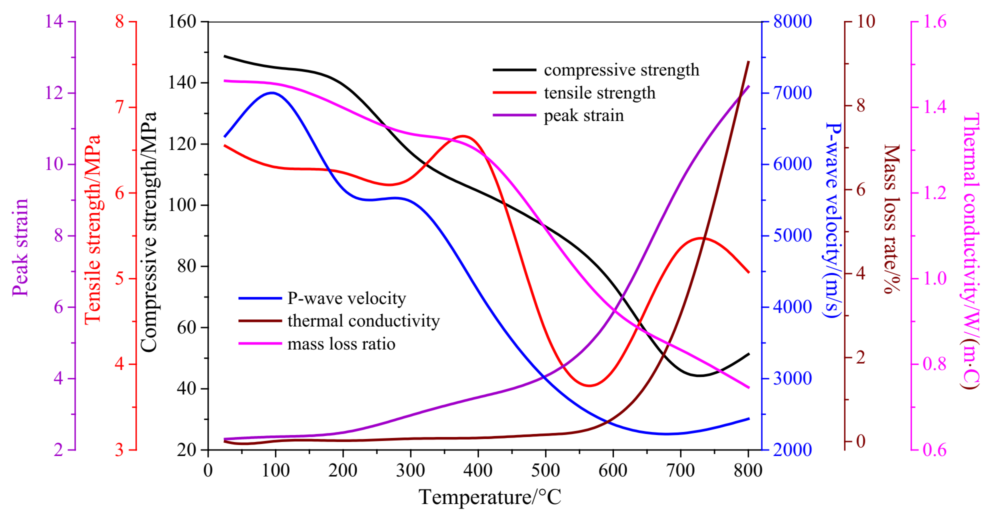


**Fig. 1** Changes in physical and mechanical properties of limestone with temperature

**Table 1** Changes in physical and mechanical properties with temperature

| Temp/°C | Test data | | | | | |
|---|---|---|---|---|---|---|
| | Compressive strength/MPa | Tensile strength/MPa | Peak strain | P-wave velocity/(m/s) | Mass loss rate/% | Thermal conductivity/(W/(m·s)) |
| 25 | 148.63 | 6.97 | 2.31 | 6396.20 | 0.00 | 1.46 |
| 100 | 145.00 | 6.59 | 2.39 | 6994.65 | 0.01 | 1.45 |
| 200 | 139.38 | 6.07 | 2.39 | 5656.38 | 0.02 | 1.40 |
| 300 | 117.24 | 6.06 | 2.99 | 5482.26 | 0.07 | 1.34 |
| 400 | 104.63 | 6.76 | 3.49 | 4229.91 | 0.09 | 1.30 |
| 500 | 92.99 | 4.08 | 3.90 | 2993.40 | 0.16 | 1.12 |
| 600 | 74.02 | 3.43 | 5.33 | 2360.00 | 0.55 | 0.93 |
| 700 | 46.03 | 5.62 | 9.87 | 2230.68 | 3.04 | 0.83 |
| 800 | 51.28 | 4.67 | 12.18 | 2435.83 | 9.03 | 0.75 |

increased. The mass loss rate curve shows minimal changes in the mass of the limestone samples at a temperature under 500 °C, and then the mass loss rate quickly increases due to the decomposition of some of the minerals (such as magnesite, dolomite, and calcium carbonate). This shows that lower temperatures (under 500 °C) have little effects on the primary mineral composition of limestone. From the changes in the compressive strength, peak strength, P-wave velocity, and thermal conductivity with temperature note that the rate of change at lower temperatures is lower, and when the heating temperature reaches a certain higher temperature, the rate of change will rapidly increase. The temperature that corresponds to the inflection point in the plotted compressive strength, peak strain, P-wave velocity, and thermal conductivity is 500, 500, 300, and 400 °C, respectively, which were distribute in 300–500 °C. Therefore, the temperature range from 300 to 500 °C is a critical temperature threshold for changes in the physical and mechanical properties of rock.

## 3.2 Changes in Mineral Elements Composition

Based on the X-ray fluorimetry experiment, the variation characteristics of main mineral elements content in limestone after different temperatures heated are obtained, as shown in Fig. 2 and Table 2. The overall changes are shown by the eight plotted curves, in which there is a significant change in the limestone composition of calcium oxide (CaO), carbon dioxide ($CO_2$) matrix and magnesium oxide (MgO) at temperatures higher than 500 °C, especially at temperatures between 500 and 600 °C. According to rock mineralogy studies, magnesite and dolomite will gradually decompose after exposure to temperatures of 524 and 700 °C respectively, as shown in Eqs. 1 and 2 (Wu et al. 2009). The decomposition characteristics of magnesite and dolomite show that the changes in the mineral elements composition between 500 and 700 °C are caused by the decomposition of magnesite, and the preliminary

**Fig. 2** Changes in primary mineral elements in limestone with temperature

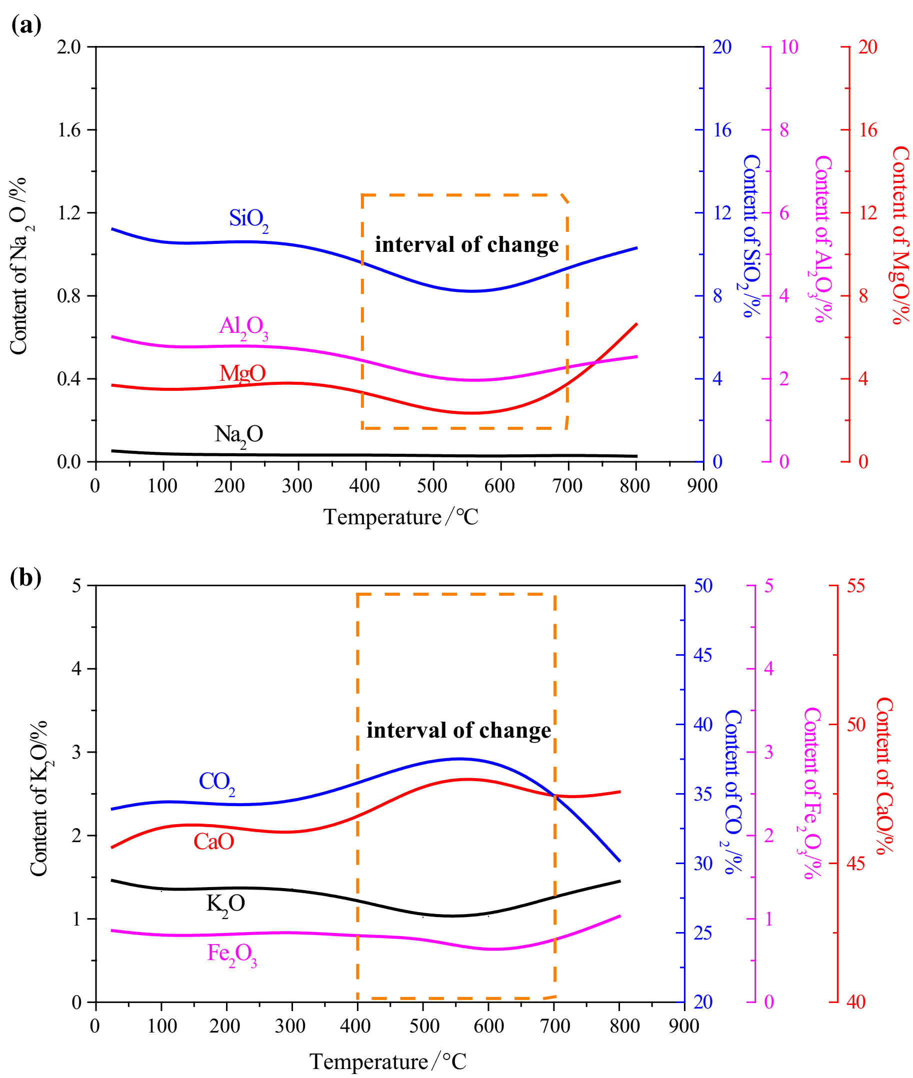

**Table 2** Changes in primary mineral elements in limestone with temperature

| Temp/°C | Content/% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $Fe_2O_3$ | $CO_2$ |
| 25 | 0.05 | 3.69 | 3.01 | 11.21 | 1.46 | 45.58 | 0.86 | 33.91 |
| 100 | 0.04 | 3.41 | 2.72 | 10.4 | 1.33 | 46.46 | 0.79 | 34.62 |
| 200 | 0.03 | 3.62 | 2.81 | 10.66 | 1.38 | 46.35 | 0.81 | 34.12 |
| 300 | 0.03 | 3.92 | 2.76 | 10.55 | 1.36 | 45.96 | 0.85 | 34.33 |
| 400 | 0.03 | 3.37 | 2.45 | 9.60 | 1.23 | 46.57 | 0.79 | 35.74 |
| 500 | 0.03 | 2.37 | 1.97 | 8.22 | 1.02 | 47.93 | 0.78 | 37.45 |
| 600 | 0.03 | 2.23 | 1.93 | 8.11 | 1.03 | 48.16 | 0.58 | 37.74 |
| 700 | 0.03 | 3.48 | 2.31 | 9.42 | 1.27 | 47.23 | 0.72 | 35.30 |
| 800 | 0.03 | 6.62 | 2.53 | 10.3 | 1.45 | 47.57 | 1.03 | 30.19 |

decomposition of dolomite causes changes in the mineral elements composition at 700–800 °C.

$$MgCO_3 \rightarrow MgO + CO_2 \uparrow \quad (1)$$

$$nCaMg(CO_3)_2 \rightarrow (n-1)MgO + MgCO_3 \cdot nCaCO_3 + (n-1)CO_2 \uparrow \quad (2)$$

## 4 Calculated Results and Analysis

Based on the experimental data presented above, the composition of the mineral elements at different temperatures in the limestone samples are taken as the independent variables, and the designation of each variable is shown in Table 3. The physical and mechanical properties of the limestone samples after treatment with different temperatures are the dependent variables, and the designation of each variable is shown in Table 4. The calculation of the canonical correlation of these two groups of variables was carried out by running the Canonical Correlation.sps macro in IBM SPSS Statistics V22, and the main results are shown in Table 5. The *U* and *V* in Table 5 represent the typical variables of the macroscopic physical and mechanical properties and micro-mineral elements composition, and their expressions are the linear combinations of two sets of parameters, as shown in Eq. 1.

$$\begin{cases} U_i = a_{i1}x_1 + a_{i2}x_2 + \cdots + a_{i8}x_8 \\ V_i = b_{i1}y_1 + b_{i2}y_2 + \cdots + b_{i6}y_6 \end{cases}, \quad (1)$$

where $U_i$ and $V_i$ are the typical variables of Group I, and a and b are the correlation coefficients.

Table 5 shows the six calculated canonical correlation groups of variables. In each canonical correlation group, the coefficient represents the degree of correlation, and the maximum coefficient is the representative factor of the variable group. It can be seen from the first pair of canonical correlation variables that the variables with the largest coefficients in $U_1$ and $V_1$ are $x_8$ and $y_4$, which also shows that the composition of the $CO_2$ matrix ($x_8$) has the greatest influence on the mineral composition of the limestone under different high temperatures, and the P-wave velocity ($y_4$) is the most ideal parameter for assessing rock thermal damage in macro-physical and mechanical properties. The representative parameters of the independent variables of the remaining five pairs of canonical correlation variables are the composition of the $CO_2$ matrix ($x_8$), potassium oxide ($K_2O$) ($x_5$), $K_2O$ ($x_5$), $K_2O$ ($x_5$), and $CO_2$ matrix ($x_8$), and the representative parameters of the dependent variables are the P-wave velocity ($y_4$), thermal conductivity ($y_6$), thermal conductivity ($y_6$), thermal conductivity ($y_6$), compressive strength ($y_1$), and compressive strength ($y_1$).

The comprehensive results obtained by the canonical correlation analysis show that the macroscopic parameters that can best reflect the degree of thermal damage in limestone is the P-wave velocity, followed by thermal conductivity and compressive strength. This finding is consistent with the experimental results in Zhang et al. (2016). In the mineral

**Table 3** Independent variables

| Compound | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $Fe_2O_3$ | $CO_2$ |
|---|---|---|---|---|---|---|---|---|
| Designation | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | $x_6$ | $x_7$ | $x_8$ |

**Table 4** Dependent variables

| Dependent variable | Compressive strength | Tensile strength | Peak strain | P-wave velocity | Mass loss rate | Thermal conductivity |
|---|---|---|---|---|---|---|
| Designation | $y_1$ | $y_2$ | $y_3$ | $y_4$ | $y_5$ | $y_6$ |

**Table 5** Canonical correlation groups of variables in limestone

| Group | Canonical correlation groups of variables |
|---|---|
| ① | $U_1 = 7.356x_1 + 949.828x_2 + 20.545x_3 + 1149.645x_4 + 61.314x_5 + 675.974x_6 + 103.831x_7 + 1697.818x_8$<br>$V_1 = -0.435y_1 - 1.255y_2 - 1.082y_3 + 1.936y_4 + 0.137y_5 - 1.594y_6$ |
| ② | $U_2 = 0.797x_1 + 20.205x_2 + 11.948x_3 + 5.080x_4 - 0.591x_5 + 9.106x_6 - 0.9301x_7 + 26.495x_8$<br>$V_2 = 0.679y_1 + 5.514y_2 - 17.425y_3 + 4.024y_4 + 4.620y_5 - 20.922y_6$ |
| ③ | $U_3 = -0.020x_1 - 1.042x_2 - 2.853x_3 - 2.293x_4 + 3.436x_5 - 1.228x_6 - 0.205x_7 - 1.464x_8$<br>$V_3 = 0.054y_1 + 0.454y_2 - 0.240y_3 - 0.003y_4 + 0.012y_5 - 1.560y_6$ |
| ④ | $U_4 = -0.086x_1 - 1.264x_2 - 1.456x_3 - 1.928x_4 + 3.285x_5 - 0.859x_6 - 0.252x_7 + 0.222x_8$<br>$V_4 = 1.215y_1 + 0.773y_2 + 0.250y_3 - 0.016y_4 - 2.075y_5 - 3.068y_6$ |
| ⑤ | $U_5 = 0.308x_1 - 2.647x_2 + 0.887x_3 - 1.991x_4 + 3.958x_5 + 1.826x_6 - 0.015x_7 - 0.860x_8$<br>$V_5 = 6.201y_1 + 0.561y_2 + 3.673y_3 - 0.386y_4 - 2.420y_5 - 4.499y_6$ |
| ⑥ | $U_6 = -0.157x_1 - 73.896x_2 - 45.277x_3 - 29.935x_4 - 23.698x_5 - 54.951x_6 - 10.192x_7 - 133.690x_8$<br>$V_6 = -5.703y_1 - 1.706y_2 + 2.491y_3 + 4.176y_4 - 1.184y_5 + 4.454y_6$ |

elements composition, the canonical correlation analysis results show that the mineral element with the most effect on the microscopic properties of limestone is the composition of the $CO_2$ matrix, followed by $K_2O$.

## 5 Conclusions

This technical note presents equations on the changes in the macroscopic physical and mechanical properties and mineral elements composition of limestone after heated at different temperatures and has applied a canonical correlation analysis to study the relationship between the macro and micro parameters. Moreover, the influence of different mineral elements on the thermal damage of rock and the response of the rocks to changes in the macroscopic properties are studied. The main conclusions are as follows.

1. With increases in the heating temperature, the P-wave velocity, compressive strength and thermal conductivity of the limestone gradually decrease, and the peak strain and mass loss rate gradually increase. The variation of these parameters with temperature has a critical value which ranges from 300 to 500 °C, and the rate of change will significantly increase once this critical temperature threshold is reached or exceeded.
2. In the studied temperature range, temperatures over 400 °C have an obvious effect on the mineral elements composition, which is mainly caused by the decomposition of magnesite and dolomite. The variations in the mineral elements composition at temperatures between 500 and 700 and 700 and 800 °C are mainly caused by the decomposition of magnesite and dolomite, respectively.
3. The canonical correlation analysis algorithm is applied to calculate the relationship between the macro-physical and mechanical properties and micro-mineral elements composition of limestone after treatment at different temperatures (up to 800 °C). It is found that the P-wave velocity is an important parameter for detection of thermal damage in rock, and the changes in the $CO_2$ matrix is the primary factor that affects the microscopic origins of thermal damage in limestone.

For rock engineering in high-temperature environments, a quick and noninvasive method of detecting thermal damage can be realized by conducting a wave velocity test, and when the rock mass has damage that reaches the critical value, monitoring should be increased or appropriate measures taken to repair the damage so as to avoid the risk of disasters.

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