Thermal degradation study of Westerly granite by ultrasonic sounding and mercury porosimetry

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ABSTRACT: Westerly granite (WG) is a well-known rock, believed to be isotropic. We studied WG samples heated between 100°C and 800°C, by ultrasonic sounding (US), mercury intrusion porosimetry (MIP). Thermal treatment studies are important for localities like nuclear waste storages, geothermal projects, rocks and earthquake mechanics. All measurements were done at room temperature. It was found that P and S US wave velocity, amplitude, frequency and elastic modulus decreased more than 60% as a result of thermal rock material disintegration due to the increased temperature treatment. Image analyses showed that there is also a preferred orientation of microcracks regardless of their size and thermal treatment level. MIP showed that the pore size distributions vary with different heating temperatures in depending on the thermal WG treatment.

Keywords: Westerly granite, thermal treatment, ultrasonic sounding, mercury intrusion porosimetry.

1 INTRODUCTION

Granite can be important rock for nuclear waste disposal or in other engineering and industrial applications where the knowledge of granite thermal degradation can be very important due to the changes of original low native porosity/permeability and high integrity. In the past, high temperature treatment has been demonstrated as having a great effect on the mechanical behaviour of some rocks (Lokajíček et al., 2012; Lokajíček et al., 2020, etc.). Increasing temperature mostly causes the changes of pore network of the rock by the formation of new microcracks and enlargement of them. Porosity and pore size distribution is the main factor influencing the associated mechanical properties as strength, elasticity, permeability and ultrasonic wave propagation. There was found that poroelastic properties of hard rocks can be affected by microstructural evolution such as porosity change and micro-cracks growth. High temperatures may induce microcrack formation and propagation and result in elastic properties change of rocks and increase of porosity. To investigate the effect of thermal degradation on granite, slow heating thermal treatments were carried out on WG granite samples in this study. The mechanical properties (e.g. elastic properties, elastic modulus, ultrasonic waves propagation, textural properties pore network, pore surface area and volume etc.), and thermal dependence of all studied parameters were investigated.

2 EXPERIMENTAL

In this study, the thermally induced microcrack in granite are studied by ultrasonic sounding, mercury intrusion porosimetry. To compare directly the ultrasonic and porosimetry results, small cylindrical specimens were used. The same samples were first studied by ultrasonics and by mercury porosimetry. Spherical sample was used for thermal disintegration studies.

2.1 Samples and thermal treatment procedure

Studied material was fine-grained and compact Westerly granite (WG). WG main rock forming minerals are 42,9 - Plagioclase, 24.4 - Orthoclase, 23.8 – Quartz, 5.4 – Biotite (wt%). 36 WG specimens - cylinders diameter 11.5 mm and height 15 mm were prepared for the study. All specimens had the same heating regime with maximum heating temperatures equal to 100 °C, 200 °C, 350 °C, 500 °C, 650 °C and 800 °C. Preheating was performed at a constant heating rate of 0.5 °C/min, then the desired temperature level was maintained constant for 24 h, and afterward the sample was cooled down at a rate of 0.5 °C/min or slower due to the good thermal insulation of the oven. The measured dry density of samples before heating was 2.635 g/cm^3.

2.2 Ultrasonic sounding (US)

Thermal effect on WG material was studied by ultrasonic sounding of small 36 cylindrical specimens. The set of 6 specimens were heated to different temperatures 100 °C, 200 °C, 350 °C, 500 °C, 650 °C and 800 °C and after the cooling they were ultrasonically sounded along the cylinder axis by P- and S-waves by the pairs of Olympus sensors V103, V153 respectively. High voltage electronic pulse generator was Olympus 5072PR and recording unit digital scope Agilent DSO 1024A. During all the experiments, the recorded full ultrasonic waveform was stored, and first onset of P- and S-waves arrival was determined.

2.3 Spherical sample thermal treatment

For the comparable measurements of Westerly granite porosity changes, subjected to thermal treatment, we prepared larger spherical sample diameter 45.55 ± 0.02 mm. WG sphere was step by step thermally heated to 100, 200, 350, 500, 650 and 800 °C. The heating regime was the same as for the small cylinders. After each thermal treatment the sample was weighted and there was determined the mean sphere diameter in three profiles, altogether 30 measurements, from which the volume was calculated.

Figure 1 shows measured WG sphere parameters as a result of thermal treatment. A - shows the total sphere weight dependence on the temperature. Starting weight of WG sphere after 100 °C heating was 167.7405 g. We can see quasi linear weight decrease. On the contrary the mean value of sphere diameter shown in Figure 1 B shows exponential diameter increase from 45.55 mm to 50.143 mm after 800 °C treatment, what is about 0.6 % of diameter increase. The knowledge of sphere diameter enabled us to calculate its volume. From volume and total weight the total density was calculated - see Figure 1 C. The thermal treatment results in a density drop from 2.633 g/cm^3 to 2.533 g/cm^3. The knowledge of WG volume enables us to recalculate this to porosity increase from 100 °C level. The starting porosity level at 100 °C was determined by (Petružálek et al., 2017) to be 0.86%. This porosity increase with temperature is shown in Figure 1 D. It shows that up to 350 °C there is nearly no increase of the total porosity. But above this temperature there is observed gradual increase of porosity, what can be explained by further material cracking, but also boosted by the effect of α-β transition of quartz at 573°C.

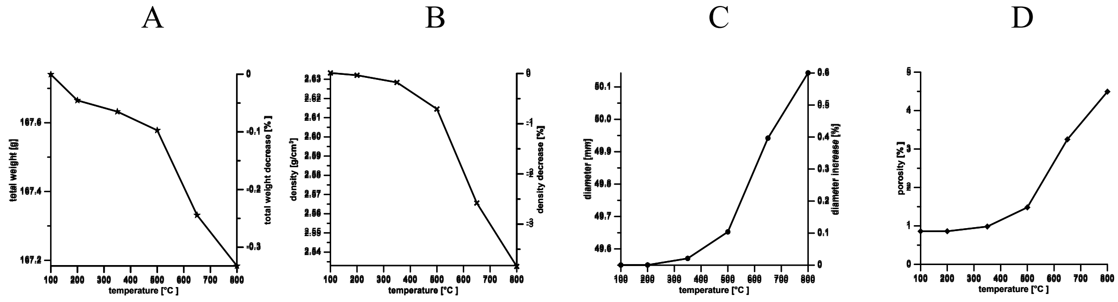

Figure 1. A – total WG weight decrease in thermal treatment range 100 – 800 °C, left axis – in grams, right axis – weight decrease in %; B – WG diameter increase dependence, left axis – in mm, right axis – diameter increase in %; C – WG density decrease, left axis – in grams/cm^3, right axis – density decrease in %; D – WG porosity increase as a result of thermal treatment.

2.4 Mercury intrusion porosimetry (MIP)

MIP was used on thermally treated specimens. Three cylinders subjected to individual heating temperatures between 100°C to 800°C were selected for MIP. MIP was done by means of PASCAL 140 Evo and PASCAL 440 Evo mercury porosimeters (Thermo Fisher Scientific, USA). The pore size distribution is calculated from the impressed volume of mercury at a given pressure according to Washburn's equation (Washburn, 1921).

3 RESULTS

3.1 Ultrasonic measurements

Set of 36 cylindrical samples diameter 11.5 mm and high 15 mm were all dried/heated at 105 °C. After the heating there was measured the exact high of each cylinder to use this value for P- and S-wave velocity calculation. Examples of US waveforms recorded after cylinders thermal treatment are shown in Figure 2. Signal amplitudes are normalized. Left image shows waveforms recorded by P-wave sensors. There are plotted first 30 microseconds of the signal. Red bars at individual signals show determined arrival time of the P-wave first onsets of the signal. This time was used for P-wave velocity calculation. On the contrary, right images shows 60 microseconds of the ultrasonic signals recorded by the pair of S-wave sensors. Blue bars show determined S-wave first arrival onset. With increasing specimen thermal degradation, due to the increasing number of cracks, we can observe later signal time arrival as well as the decreasing of signal frequency content.

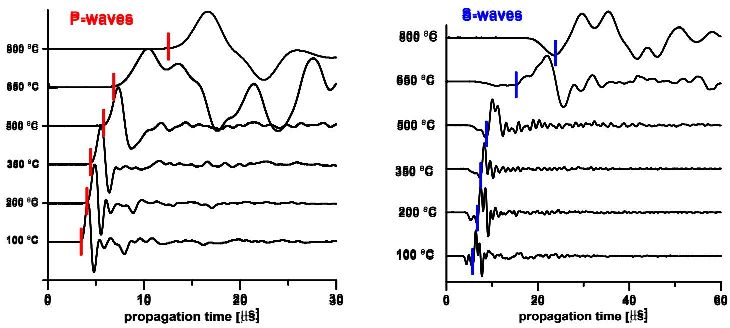

Figure 2. Left- First 30 microseconds of ultrasonic signals recorded by the pair of P-wave sensors. Right - First 60 microseconds of ultrasonic signals recorded by the pair of S-wave sensors. Waveforms are shown for the specimens heated to temperatures from 100 °C up to 800 °C.

Figure 3A - there are shown mean velocities determined for all the 6 cylinders subjected to given thermal treatment level. Red color shows P-wave velocity data. By blue color there are plotted S-wave velocities. Black bars denote the range of determined velocities from 6 samples. The initiation and growth of pores in rock material are accompanied by the weakened passing of ultrasonic waves through the rock. The figure shows the v_P and v_S wave velocities decrease due to the WG thermal degradation.

A B

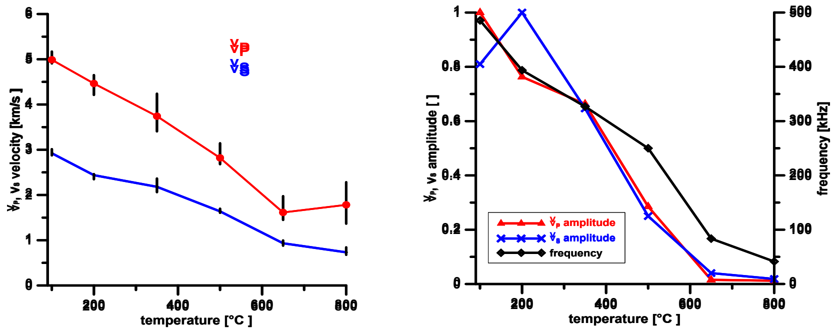

Figure 3. A – P and S wave velocities, B – P and S wave first onset amplitude (normalized) and frequency of P-wave first arrival.

The P-wave velocity drops by 64% (from 4.99 km/s to 1.78 km/s), while the S-wave velocity decreases by 74% when heated from 100°C to 800°C. Both P- and S-wave velocities show their highest drop, 38% and 44% respectively, in the range 500°C-600°C which may be attributed to the $\alpha\beta$ quartz phase transition as also reported by other researchers for ganitic rocks in general and Westerly granite in particular.

Figure 3 B – shows the dependence of P and S- wave first onset amplitude. Red color denotes the amplitude decay of P-wave arrival. Blue color mark amplitude decay of S-wave arrival. Due to the different sensitivity of P and S sensor pairs, amplitude values are normalized to maximum value. There is seen that with the higher heating temperature due to the increasing material disintegration, there is increasing attenuation of ultrasonic signal. This is documented not only by the drop of P and S-wave amplitudes, but also by the decay of frequency content of the recorded US signals.

3.2 Mercury intrusion porosimetry (MIP)

The mercury porosimetry provide information of the total porous system of materials with exception of micropores. The main obtained parameters are the pore size distributions, porosity (P), bulk density (ρ_{Hg}), volume and surface of mesopores and macropores (V and S) and permeability (Per).

The pore size distributions were different for all samples in dependence of the heating temperature. Figure 4 shows pore size distribution of mesopores and macropores obtained by the Hg porosimetry; Samples exposed to temperatures at and above 500 °C are on the Y2 axis.

4 DISCUSSION

4.1 Elastic modulus

Figure 5 shows dynamic Young's - E, shear - μ, and bulk moduli - K decrease with heating temperature calculated from P and S wave velocities. Poisson's ratio is almost constant at lower temperatures up to 500°C but it increases at higher temperatures.

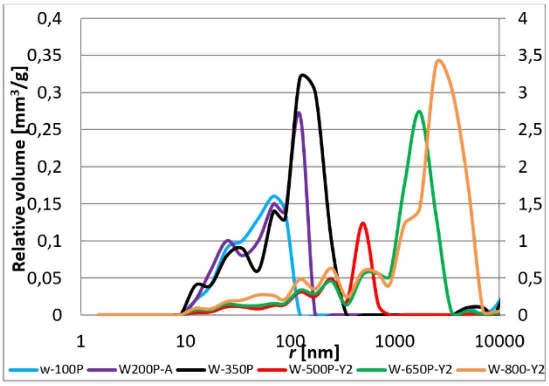

Figure 4. Pore size distribution of mesopores and macropores obtained by the Hg porosimetry; Samples exposed to temperatures at and above 500 °C are on the Y2 axis; X-axis up to 10 µm.

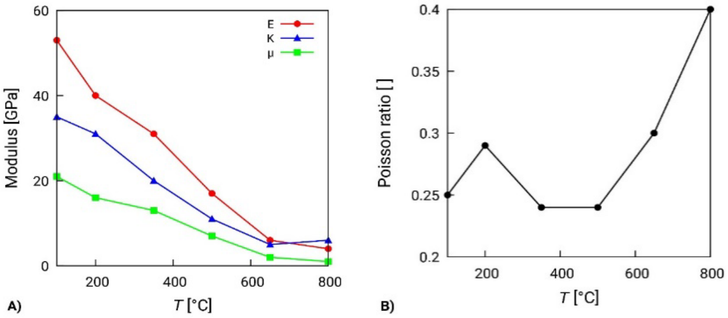

Figure 5. Moduli – A) Elastic dynamic moduli, B) Poisson ratio.

4.2 MIP

A partial positive correlation with the coefficient of determination $R^2 = 0.9693$ was found between P (porosity) and T (temperature), see Figure 6. The content of macropores and coarse pores is affected the higher temperature exposition. Large micropores are also present in the 2-50 nm group, which is also positively influenced by the temperature. The porosity is in a clear dependence with the US parameters across all temperatures.

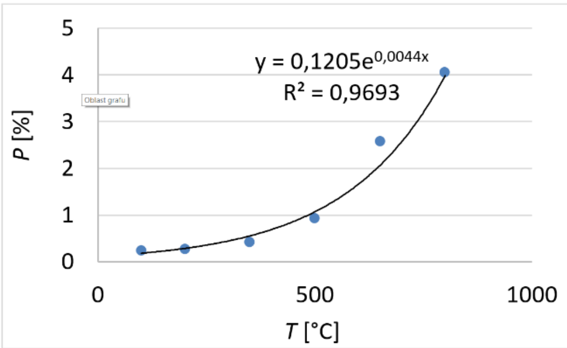

Figure 6. Exponential dependence of the porosity (P) on the heating temperature of samples.

5 CONCLUSION

The raw parameters and the alteration during heating process of the granite, its composition, porosimetry and mechanical properties must be ascertained to understand thermal alteration mechanisms in granite. The use of mercury intrusion porosimetry to study the development of cracks in Westerly granite lent insight into the objective variation in the petrophysical parameters of these materials alters at temperatures from 100 °C to 800 °C.

Mercury intrusion porosimetry revealed numbers of different pore sizes, fissures or cracks. Textural analyses revealed significant material characteristics such as pore size, pore volume and surface of pores which are decisive for the application of these materials. The high content of pores 2 – 50 nm increases the adsorption efficiency for water and pollutant molecules, contrary, the high content of macropores and coarse pores is suitable especially for permeation of water and gases. Studied raw samples and samples heated at temperatures under 350 °C had the low porosity.

Ultrasonic wave properties such as wave velocity, amplitude and signals frequency corroborated the state of thermal damage and enlarging of pores. Microscopic observation made valuable information about the behavior and thermal alteration of minerals in WG. Intergranular and mainly intragranular microcracks with irregular shapes were found.

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