

Ultrasonic Determination of Porosity in Homogeneous Ceramic Samples

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Abstract

An ultrasonic method was tested to rapidly determine the porosity in custom made ceramic samples. The samples with porosities between 4 and 33% were of identical composition. The porosity estimates by ultrasonic method were validated against those obtained by helium and air pycnometry as well as with Archimedean method. The ultrasonic measurements can be performed rapidly (less than a minute) but they require a well prepared sample.

Keywords: porosity, ultrasound, shear wave, longitudinal wave, pycnometry

1 Introduction

Porosity is a physical parameter that affects the mechanical, electrical, and thermal properties of rocks, meteorites, construction materials (asphalt, concrete), and many biological materials, e.g. wood. The porosity p of a solid body is defined as the ratio of the total pore volume (V_P) to the bulk volume (V_B):

$$p = V_P / V_B, \quad (1)$$

Pore volume is usually determined as a difference between bulk and grain volume (V_G – the volume of the solid matrix only).

Porosity can be measured in several ways. In petrophysics, the most widely used laboratory methods include Archimedean water immersion method, gas pycnometry, or X-ray microtomography (*Rasilainen et al.*, 1996, *Schön*, 2004 and references therein). Most of these methods are slow, or include sample contamination by the measuring medium (gas, water, mercury etc.). Therefore, novel methods for rapid and non-destructive porosity measurements are required, especially to measure rare or sensitive materials, such as extraterrestrial samples (*Kohout et al.*, 2008). Many physical properties of rocks and minerals depend strongly on porosity. For example, while permeability, elastic constants, and seismic attenuation depend almost linearly on porosity, the density, electric

resistivity, thermal conductivity, and seismic velocities (longitudinal – v_p , shear – v_s) depend inversely on porosity. However, the published “physical property vs. porosity” plots (see review in Schön, 2004 and references therein) reveal considerable scatter. This scatter may be caused by differences in grain size, packing density, structure of the minerals and their bonding, and lithological variation (e.g, quartz content, etc.; Schön, 2004). Recent studies also indicate inverse relationships between seismic (ultrasonic) velocities and porosity of rocks from a Precambrian Outokumpu assemblage (Elbra *et al.*, 2011; Lassila *et al.*, 2010), as well as from meteorite impact structures on crystalline target rocks (Elbra and Pesonen, 2011; Pesonen, 2011).

In order to determine the relation between porosity and ultrasound velocity we carried out experimental measurements on artificially manufactured ceramic samples featuring constant composition and distinct variation in porosity. Porosities were determined with gas pycnometry and Archimedean water immersion method while ultrasonic velocities were obtained from time of flight measurements (TOF). Additionally, the effect of pore filling medium (air vs. water) on ultrasound velocity was tested.

To determine the precision and accuracy of methods relying on ultrasonics, we employed the gas pycnometry and the Archimedean water immersion methods to determine independently porosity of the samples.

2 *Materials and methods*

The ceramic samples were prepared at University of Art and Design Helsinki, Finland. A K69 clay mixture was prepared from commercially available materials: 40% feldspar (FFF K7), 30% kaolin (Grolleg ECC), 20% ball clay (Hyplas 64), and 10% quartz (FFQ). The mixture was prepared to ~ 10 cm diameter cylinders and subsequently fired in a kiln at 1000°C – 1200°C for 6-8hours (Table 1). Generally, an increase in the firing temperature reduces the porosity of the ceramics product. Hence by adjusting the firing temperature it was possible to adjust the porosity from 4% to 33% with identical mineral composition. Cylindrical core samples (2.5 cm diameter) were drilled from the final ceramic products for the measurements. The faces of the cylinders were cut parallel and polished for easy and reliable ultrasonic measurements. Table 1 shows the porosity and grain density of the manufactured samples. Based on nearly constant grain density composition of the samples is similar almost through the whole porosity range. Only at the highest firing temperatures (over 1100°C, porosities below 15%) the grain density starts to slowly decrease indicating possible mineralogical changes or changes in bonding which has taken place during fabrication.

3 *Ultrasound velocity method*

The *TOF* measurements across the ceramic cylinders were done using a through transmission technique (see Lassila *et al.*, 2010). Briefly, the sample was placed between two identical vertically aligned transducers: Karl Deutsch S 24 HB 0.3–1.3 MHz transducers for longitudinal wave (v_p) measurements and custom built 3.5 MHz

(3.2-4.2 MHz -6 dB band width) shear transducers for shear wave (v_s) measurements. A lead weight (1 kg) on the topmost transducer induced a static load to provide better contact between the sample and transducer. A 20 mm long fused quartz delay line between the longitudinal transducer and the sample provided a reference time of flight value. The shear transducers featured internal delay lines, so a reference time of flight could be obtained without a separate delay line.

Table 1. Sample firing temperature (T), bulk (D_B) and grain (D_G) density, porosity (p) determined by Archimedeian method (average of three individual measurements, samples F2 G1 and G2 average of two individual measurements), air and helium pycnometry, longitudinal (v_p) and shear (v_s) wave ultrasound velocities measured for oven dried and water saturated samples. Bulk density was calculated from sample mass and geometrically determined volume. Grain density was calculated from sample mass and grain volume determined by helium pycnometer.

Sample	T (°C)	He. pyc. DG (kg/m ³)	Geom. DB (kg/m ³)	Arch. p (%)	Air pyc. p (%)	He pyc. p (%)	Saturated		Oven dry	
							v_p (m/s)	v_s (m/s)	v_p (m/s)	v_s (m/s)
A1	1000	2635	1698	32	39	35.6	1898	1026	1781	1107
A2	1000	2637	1712	32	39	35.1	1542	1072	1512	1152
G1	1030	2625	1694	33	36	35.5	1399	1198	1412	1257
G2	1030	2633	1705	33	38	35.2	1477	1188	1476	1296
B1	1070	2621	1735	31	38	33.8	1769	1366	1753	1503
B2	1070	2621	1738	31	36	33.7	1790	1392	1825	1493
E1	1100	2608	1696	29	32	35.0	2514	1603	2302	1731
C1	1130	2579	2055	16	19	20.3	3503	2413	3484	2510
C2	1130	2572	2050	15	20	20.3	3424	2428	3437	2466
F2	1170	2453	2259	4	6	7.9	4935	3246	4800	3196

A pulser/receiver (Olympus 5072 PR) was used to excite the transducers. The pulse generator settings are listed in Table 2. Coupling gel (Ultragel II) between the transmitting transducer and the delay line improved the acoustic coupling. Using gel on the samples would block the pores and cause sample contamination and misleading results. An oscilloscope (Lecroy 9310) collected the received ultrasonic waveforms which were saved to a computer using LabVIEW. For the longitudinal and shear waveforms averaging of 300 and 500 times were used, respectively.

The samples were dried in an oven at 1001°C for 2 hours. After drying they were measured with both longitudinal and shear mode transducers, respectively.

To saturate the pore space, the samples were soaked in water for 12 hours under reduced pressure using a water flow pump. After water saturation, the samples were measured again using the same procedure as in the oven-dry case. The sample surfaces were gently swiped with a paper towel to remove excess water from the surface.

Table 2. Settings for pulse generator (Olympus 5072 PR).

Measurement type	Longitudinal	Shear
Gain [dB]	20 & 0*	30
Energy	3	3 & 2*
Damping	2	3
100 Hz PRF		
*Measurements with saturated samples		

Ultrasonic v_p and v_s velocities were determined from the measured longitudinal and shear wave propagation mode *TOF* values. The *TOF* for each signal was determined from a point above the noise level prior to the first arrival, which is approximately 2% of the maximum intensity of the signal. Provided that the signal shape after travelling through the sample is similar to the shape of the launched signal this time coordinate corresponds to the arrival of the fastest traveled wave. *TOF* values through the delay lines were subtracted from the measured values to get the *TOF* values through the sample. The measurement was repeated four times and the average value was used as result. The thickness of the sample was measured with a Vernier caliper from four different locations. The uncertainty of the velocity estimate was calculated from the standard errors of *TOF* and thickness using the error propagation law and is presented in Fig. 1.

4 Gas pycnometry method

In a gas pycnometry an “ideal” gas (e.g. helium, air) is used to measure grain volume as it penetrates into the open pores of the samples. (e.g. *Kuoppamäki et al.*, 1996; *Kuoppamäki*, 1997). The porosity p was determined using independently determined bulk volume V_B using equation (1).

A Notari air pycnometer ($\sim 0.1 \text{ cm}^3$ resolution) and Quantachrome Ultrapyc 1000 Helium Pycnometer ($\sim 0.01 \text{ cm}^3$ resolution) were used to estimate V_G whereas V_B was calculated from the geometric shape of the sample. The geometric measurements were done using a micrometer and performed ten times per sample with an accuracy of 0.05 cm^3 .

5 Archimedean immersion method

For the measurements we used an Ohaus Scout Pro SPU402 digital balance with 10 mg resolution. Prior the measurements, the samples were dried in an oven at 110°C for 12 h. We weighted the samples first with free pore space and then with their pore space saturated with water (e.g. *Kivekäs*, 1993). To saturate the pore space the samples were soaked in water for 12 h under reduced pressure using a water flow pump. The samples were weighted first in air and then suspended in water. The porosity p was determined as:

$$p = (m_{SA} - m_{FA}) / (m_{SA} - m_{SL}), \quad (2)$$

where m_{SA} is the mass of sample in air with water saturated pore space, m_{FA} is the mass of sample in air with free pore space, and m_{SL} is the mass of sample suspended in water with water saturated pore space.

The measurements were cross-checked in two laboratories (Solid Earth geophysics laboratory of the University of Helsinki and at the Petrophysics Laboratory of the Geological Survey of Finland) with a repeatability within $\pm 1\%$.

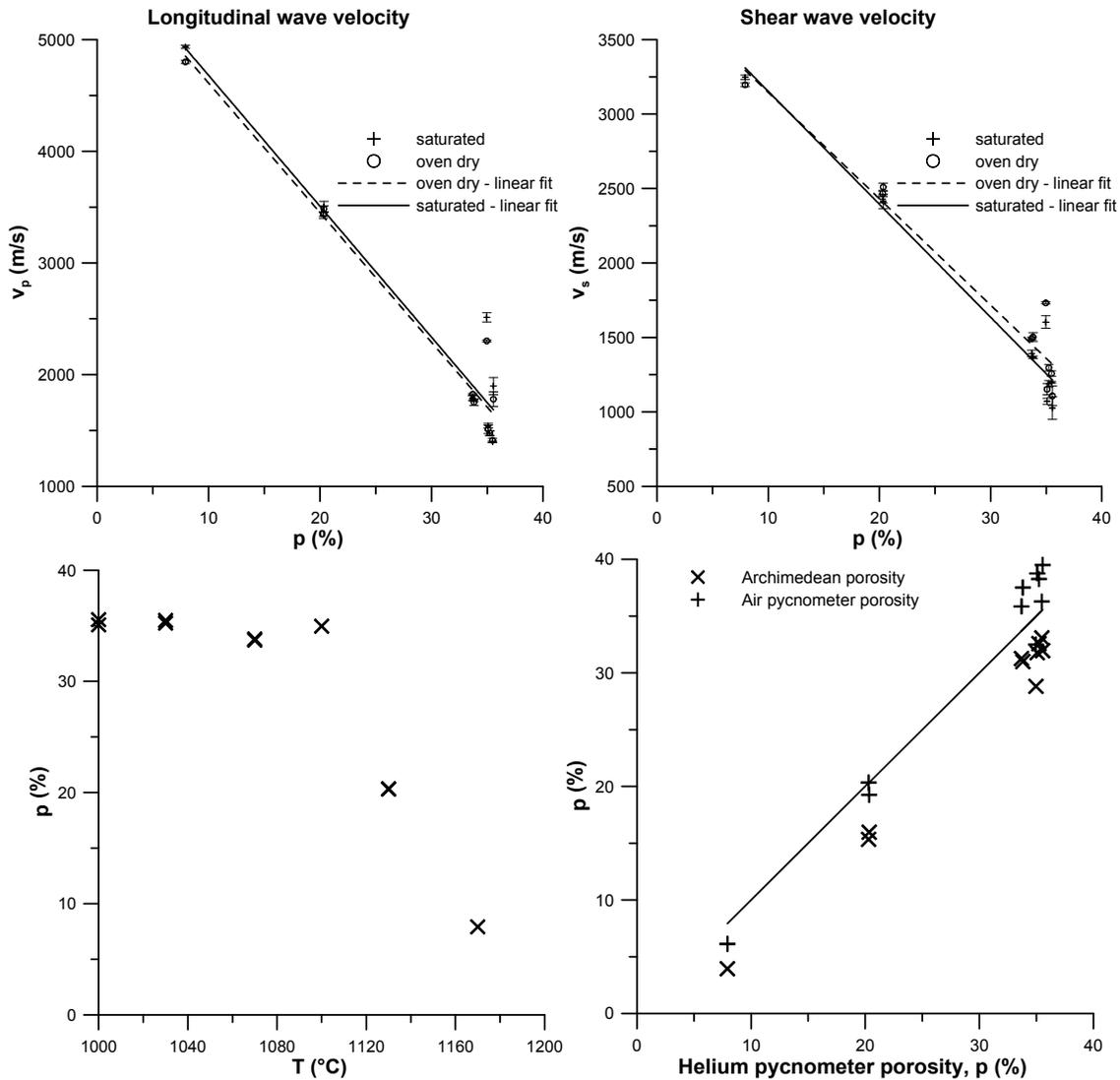


Fig. 1. Correlation between longitudinal v_p (upper left) and shear v_s (upper right) ultrasound velocity with errorbars and porosity derived from helium gas pycnometry for oven-dry and water saturated ceramic samples. The error in porosity determined by helium pycnometry is within the data symbol size. Lower-left figure shows relation between baking temperature of ceramic material and its measured porosity by helium gas pycnometry. Lower right figure shows comparison of the porosity measured by Archimedean method and Air pycnometer to the porosity measured by helium gas pycnometry. The line indicates 1:1 dependence.

6 Results

Figure 1 shows correlations between ultrasound velocities and porosity in the samples. It also shows the inter-method correlations. Table 1 summarizes the main results of this paper. We see that the longitudinal as well as shear wave velocities decrease with increasing porosity. Comparing other porosity methods employed the gas pycnometry yielded higher porosity values than the water immersion method. For some samples air pycnometry yields slightly higher porosity values than the helium pycnometry. However, our air pycnometer is less precise and hence its porosity estimates feature higher uncertainty.

7 Discussion

This study aimed at (1) finding an empirical relation between the v_p and v_s velocities and porosity in compositionally similar ceramic samples and (2) determining whether this relation depends on the medium filling the pore space. Previous studies on the effect of porosity on v_p and v_s (Ermankov *et al.*, 1989; Han *et al.*, 1986; Simmons *et al.*, 1975, Elbra and Pesonen, 2011) show a general trend of decreasing v_p and v_s with increasing porosity. Our results are consistent with those studies and reveal an almost linear trend between v_p , v_s and sample porosity (Table 1 and Fig. 1). The linear fit parameters are listed in Table 3. The porosity values measured with the helium pycnometer are taken as reference values and are shown in Fig. 1 since helium pycnometer is more precise (absolute error $\pm 1\%$ resulting from volume uncertainty of $\sim 0.01 \text{ cm}^3$) than the air pycnometer or Archimedean porosity method. Moreover, compared to Archimedean water immersion method, gas pycnometry probes a larger pore volume due to the fact that, compared to water, helium and air (mostly nitrogen), both being small molecular gases, penetrate the pore space more effectively and reach smaller pores. However, both Archimedean water immersion method and gas pycnometry can detect interconnected pores only.

Table 3. Linear fit parameters to ultrasound speed vs. porosity data.

Measurement setup	Linear fit equation	RMS
Shear wave, oven-dried sample	$p = -71.43 * v + 3860$	0.9431
Shear wave, water saturated sample	$p = -75.85 * v + 3911$	0.9601
Longitudinal wave, oven dried sample	$p = -117.2 * v + 5850$	0.9318
Longitudinal wave, water saturated sample	$p = -116.0 * v + 5770$	0.9558

The general trend that ultrasonic velocity decreases as a function of increasing porosity is explained by the influence of the pore or fracture filling material on the sound velocity. The filling material usually features lower sound velocity and elastic constants than the matrix material (Schön, 2004, p. 159). There is also a slight increase in v_p for water saturated samples compared to the oven dried samples which is consistent with

previous measurements (King, 1984) and theoretical work (Kuster and Toksöz, 1974). This can be explained by the fact that v_p in water is higher (closer to the value in solids) than v_p in air which means that water saturated pores increases the overall v_p of the sample. In contrast to this v_s shows an opposite trend. The reason for this is not well understood.

However, the relation between the porosity and v_p or v_s , when the porosity exceeds 33%, is not necessarily linear. One would guess that for extremely large porosities v_p should approach the velocities of the pore filling medium (here air or water) This is different for longitudinal and shear waves because longitudinal waves do propagate through fluids and gas whereas shear waves do not. Such an approach forms the basis of the “time-average equation” derived by Wyllie *et al.* (1956) for sediments and was later empirically confirmed by Raymer *et al.* (1980) for consolidated rocks.

Based on our results the longitudinal wave method appears to be more suitable for the porosity measurements than the shear method. One would expect opposite result due to the fact that the shear waves do not propagate through fluids and hence the velocities are independent of the pore filling medium while the longitudinal wave velocities show larger dependence on the pore saturating medium. However, the exact arrival of the shear wave is not always easy to determine since it can be influenced by shear- longitudinal-shear wave conversions on sample and pore space boundaries. Such converted waves are slightly faster and always arrive prior to the shear wave obstructing the arrival time of the “true” shear wave.

8 Conclusions

The ultrasonic method to determine porosity of solid samples shows promise in the 4-33% porosity region and after proper calibration with other materials or rocks of interest it should be possible to use it for porosity determinations. The measurement is rapid and does not use any media to infiltrate the pore space, thus, not causing unwanted sample contamination. Proper coupling of the ultrasound wave into the sample is essential and the presence of two flat parallel surfaces and a load to improve coupling is advantageous. Based on our results, the longitudinal wave arrival time can be determined more precisely and, thus, this method is more suitable compared to shear waves.

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