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THERMAL PROPERTIES INVESTIGATION OF ORNAMENTAL STONE WASTE OBTAINED BY PHOTOPYROELECTRIC METHODOLOGY

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Abstract. *The photopyroelectric technique is suitable for study pasty substance of processing stone residues in Cachoeiro de Itapemirim's region, Espírito Santo. Due to the non-destructive character, application in transparent or opaque materials and possibility of sample's thickness or modulation radiating frequency scanning for thermal properties detection. This technique can be configured in several setups. In this work, standard (SPPE) one were used for determination sample's thermal diffusivity, and inverse (IPPE) one, that allows determination sample's thermal effusiveness. By these thermal parameters values, it's possible get the sample's thermal conductivity. The objective of this work is to analyze the different values of thermal diffusivity and effusivity for different kind stones, hard and soft classified, in order to determine thermal parameters, as a thermal conductivity, and to promote an observation of the sensitivity of the technique.*

Keywords: *photothermal techniques, photopyroelectric methodology, thermophysics properties, residues, waste stone.*

1. INTRODUCTION

The industry of ornamental stones in Espírito Santo state is an important economic sector, targeting worldly scale. From January to April 2018, Brazil exports US\$ 302,146,725.00 and the refereed state was responsible by 78.73% of the total amount (SINDIROCHAS, 2018). However, all process since extraction of stone until its benefit processing generates a large amount of residues. This waste stone is disposed on pools, affecting directly the environment, or can be reused. When reused, the waste can be treated and applied as filler in ceramic, cement, clays or other products to civil construction (Piazzarollo, *et al.*, 2016; Alexandre, *et al.*, 2016). For both ends and aiming the lowest effect on the environment as possible, this stone waste should be analyzed and known. An important parameter to be determined is the thermal one.

There are several qualities of stones, like marble and granite. They can be, as classified by own industry sector, like hard or soft accordingly its level hardness. Generally, the hardest one has greater value embedded. These materials are used mainly in civil construction and architecture, but also in urban elements, funeral art and decoration.

In this work the photopyroelectric methodology, a photothermal one, was applied. This technique allows obtaining thermal parameters of pasty samples. These ones were obtained from different granites, hard and soft. The samples were taken in a company that performing granite plate as of cutting process the whole block. It is important note that stone waste of the mentioned process is physically pasty, making the photopyroelectric methodologic suitable in this study (Delgadillo-Holfort, 2004).

The referred technique can be applied in different setups, which allows determine thermal diffusivity (α) and thermal effusivity (e). Knowing theses parameters, the thermal conductivity (k) is determined. Since this waste can either be disposed of in environment or reused, the thermal parameters help to define its better end.

As observed, both the treated material as its residue can be used in building materials. If one has a very changed property than other, a building's thermal comfort calculations may change, for example. Therefore, the photopyroelectric methodology was applied in this study, analyzing different thermal properties to each different sample, making them more known.

2. PHOTOPYROELECTRIC METHODOLOGY

The photopyroelectric methodology (PPE) is based on pyroelectric effect of the sensor. Pyroelectric materials show electric polarization when submitted a temperature variations in media. The polarization induces an electrical charge, carrying with it thermal information of the sample. When the sensor and sample are exposed to a modular radiation (laser light), thermal waves propagate into system.

The pyroelectric response $S(t)$ of the detector due to a periodic temperature variation (frequency f) is given by (Chirtoc and Mihailescu, 1989):

$$S(t) = A(f)\Gamma(f)e^{i2\pi ft} \quad (1)$$

where $A(f)$ is considered as transfer function. It represents the global frequency response of the used electric circuit that converts the oscillating temperature into the ac voltage or ac current signal is the electrical time constant that is synchronously detected by the lock-in analyzer. $\Gamma(f)$ is a dimensionless response factor containing relevant information about the thermal properties and thickness of the different layers, which include sensor and sample of interest. For both PPE configurations, standard and inverse ones, the 1-D heat diffusion is considered in a four or three layers system, constituted by air (g), sample (s), pyroelectric sensor (p) and backing (b).

2.1 SPPE configuration

The standard photopyroelectric (SPPE) configuration is performed in a four-layer system for boundary conditions and 1-D thermal wave's propagation. In order to guarantee the superficial absorption of the incident radiation, a thin aluminum foil is used in the gas-sample interface. Besides the opaque sample assumption, it is considered that the thermal waves are completely attenuated on the sensor (thermally thick regime). Then one can write the amplitude and phase of $\Gamma(f)$, respectively, as:

$$|\Gamma(f)| = \frac{2(b_{gp} + 1)}{(b_{gs} + 1)(b_{sp} + 1)} e^{-\frac{L_s}{\mu_s}} \quad (2)$$

$$\varphi(f) = -\frac{L_s}{\mu_s} \quad (3)$$

where $\mu_s = (\alpha_s/\pi f)^{1/2}$ is the sample thermal diffusion length, which depends on its thermal diffusivity α_s and the modulation frequency. L_s is the sample's thickness and the term b_{ij} is the ratio of the thermal effusivities of the adjacent media ($b_{ij} = e_i/e_j$).

From Eq. (2) and Eq. (3), it is clear that both $\ln |\Gamma(f, L_s)|$ and $\varphi(f, L_s)$ present a linear dependence with sample thickness with the same slope, S , equal to the reciprocal of the thermal diffusion length. Thus, such configuration can be used to determine the thermal diffusivity of pasty samples, from both amplitude and phase of the PPE signal, by performing a thickness scan while keeping the modulation frequency fixed (Dadarlat, *et al.*, 2009). The thermal diffusivity is obtained, in this case, by:

$$\alpha_s = \frac{\pi f}{S^2} \quad (4)$$

2.2 IPPE configuration

For the inverse photopyroelectric (IPPE), 1-D diffusion is considered in a three-layer system: air (g), pyroelectric sensor (p) and sample (s). The main modification in this setup is the modulated light beam reaching first the detector, and not the sample like in SPPE. If the radiation is completely absorbed on its surface and the thermal waves are totally attenuated in the gas and sample layers, then the PPE signal become sensitive to the thermal effusivity of the sample.

Assuming the extreme and opposite thermal effusivities of air and sensor, one can find $b_{gp} = 0$ and $R_{gp} = -1$, i. e., constant, where $R_{ij} = (b_{ij} - 1) / (b_{ij} + 1)$. Moreover, if the frequency is high enough to assume that the sensor is thermally

thick ($\mu_p < L_p$), and the pyroelectric signal for the sample is normalized by the empty cell signal, the normalized $\Gamma_n(f)$ can be obtained, and its phase is write as, respectively (Sahraoui, *et al*, 2002):

$$\Gamma_n(f) = 1 - (1 + R_{sp})e^{-\sigma_p L_p} \quad (5)$$

$$\tan \varphi_n = \frac{(1 + R_{sp})\sin(L_p / \mu_p)e^{-L_p / \mu_p}}{1 - (1 + R_{sp})\cos(L_p / \mu_p)e^{-L_p / \mu_p}} \quad (6)$$

where the factor R_{sp} is the reflection coefficient, which carries information about the sample's thermal effusivity.

The normalized phase is an oscillating function, which crosses the abscissa axis when $L_p / \mu_p = n\pi$, with $n = 1, 2, 3, \dots$. Thus, performing a frequency scan, the parameter L_p / μ_p can be obtained from the signal phase and used in equation 5 in order to get R_{sp} . It is possible to choose a frequency range where R_{sp} is constant and consider an average value for that. Knowing the sensor's thermal effusivity, e_p , one can obtain the sample's thermal effusivity, e_s , from:

$$e_s = \frac{(1 + R_{sp})}{(1 - R_{sp})} e_p \quad (7)$$

Note that thermal effusivity is obtained only by signal phase considering the assumed boundary conditions layers system.

2.3 Experimental setup

The experimental arrangement is schematically shown in Fig. 1. Both for SPPE (Fig. 1a) and IPPE (Fig. 1b) setups, the sensor used was a PZT (lead-titanium-zirconate) ceramic, 305 μm thick. The pyroelectric signal was measured by a SR830 lock-in analyzer, using the current mode detection. For both configurations, reference samples (distilled water and ethylene glycol) were measured to improve the data obtained, which according with Dadarlat and Neamtu (2006) and Bindhu, *et al.*, (1998).

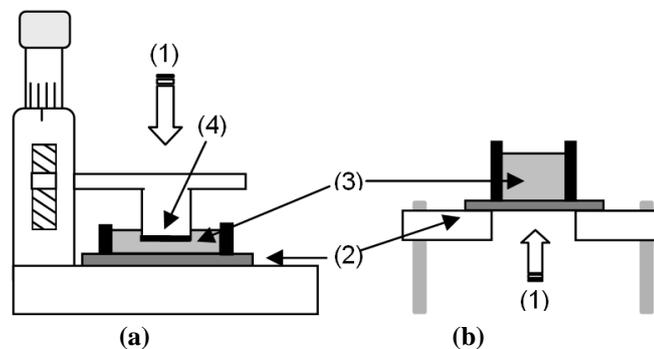


Figure 1. Schematic diagrams for (a) SPPE and (b) IPPE configurations, where the numbers indicating: (1) modulated laser beam, (2) pyroelectric sensors, (3) sample, (4) aluminum foil.

For the SPPE configuration the samples were held by a copper cylinder, glued to the sensor with silicone. An aluminum foil (30 μm thick) provides both superficial absorption and sample's thickness control, by means of an attached manual micrometer. The radiation source was a 300 mW diode laser, electronically modulated. Measurements were performed at a fixed frequency (3 Hz), scanning the sample's thickness from 400 μm to 200 μm , with a 40 μm step.

For the IPPE, the sensor was a black-inked surface to absorb the laser beam. The sample is held as in SPPE, but in this case having around 5 mm thickness, securely fulfilling the sample's thermally thick condition. The radiation source was a 10 mW diode laser, also electronically modulated. The frequency range used was 1 to 30 Hz, 10% step.

3. RESULTS AND DISCUSSIONS

The first set of measurements was conducted by means of the SPPE configuration in order to evaluate the thermal diffusivity. The data obtained for each thickness' sample and recorded during 2 minutes, as shown in Fig. 2.

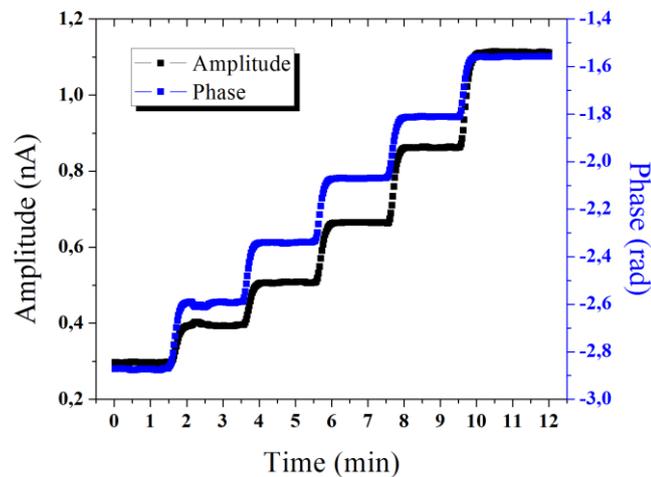


Figure 2. Data acquisition by sample's thickness scans on SPPE measurements.

The Fig. 3 displays the natural logarithm of the amplitude and phase of the pyroelectric signal average from each thickness, every 2 min as presented above on Fig. 2. The signal presented good stability and both fits for the amplitude and phase are in excellent agreement with those predicted by Eq. (2) and Eq. (3).

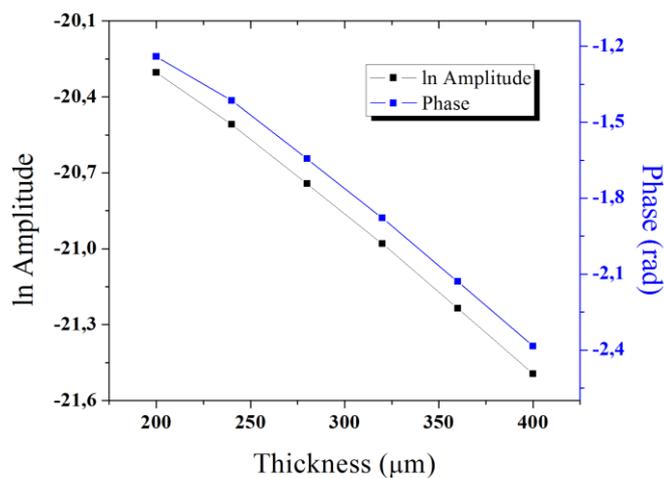


Figure 3. Natural logarithm of amplitude and phase of PPE signal in SPPE configuration represents the soft sample data.

From these fits, the thermal diffusivity was determined, whose values were found are shown in Tab. 1. For each sample, several replica measurements were carried out, allowing checking the good reproducibility of the experiment and determining as average value for thermal diffusivity by theses repetition, not from the data fit. Then, the statistical error considering such repetition is around 15%, value slightly above that found by literature (Dadarlat and Neamtu, 2006, Bindhu, *et al.*, 1998). A possible reason for this increase in error is the sample heterogeneity.

The thermal effusivity determination depends on a reference material with a known thermal effusivity. In this study distilled water was chosen, assuming an average value of $e = (1595 \pm 20) \text{ W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. The normalized phase is plotted as a function of the modulation frequency, scanned in the 1 to 30 Hz as shown in Fig. 4.

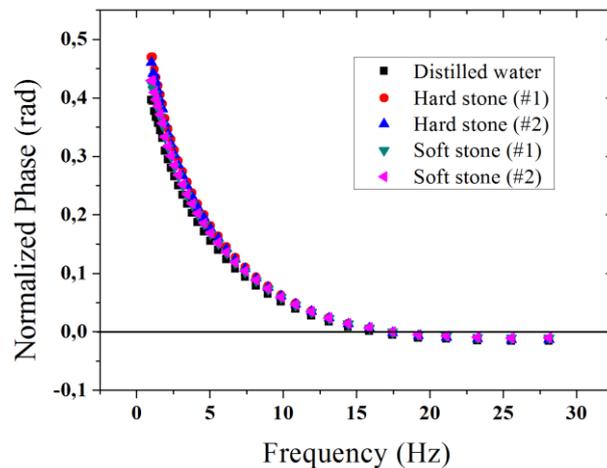


Figure 4. Normalized phase of the IPPE signal as a function of frequency for reference and interest samples.

It is possible to observe that all curves cross the abscissa axis at the same frequency, since it depends only on the properties of the sensor. Thus, by using the thickness of the detector, its thermal diffusivity is obtained. Such a value was used to calculate R_{sp} in Eq. (6).

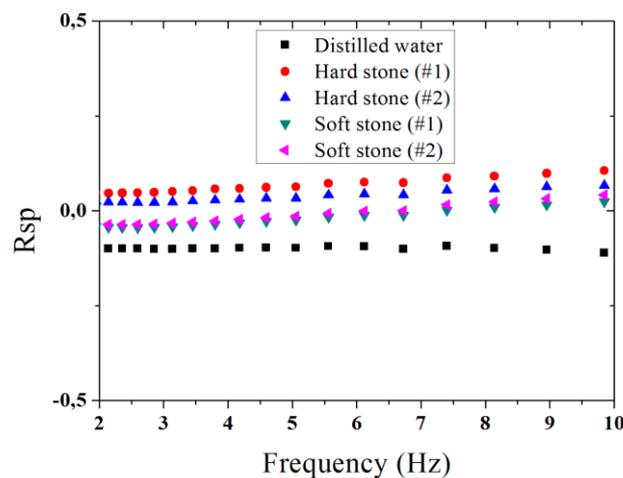


Figure 5. Frequency range with R_{sp} to all samples approximately constant.

Employing distilled water as a reference sample, the thermal effusivity could be obtained for the sensor and subsequently for the other samples (Tab. 1), by means of Eq. (7).

Besides considering several points for the R_{sp} determination, measurements were repeated for all samples in order to confirm the experimental errors (around 3%). The results are in close agreement with those reported in the literature (Dadarlat and Neamtu, 2006, Bindhu, *et al.*, 1998). For this configuration, since the parameter analyzes the heat at interface between layers, the heterogeneity of the sample before considerable now no longer interferes so much.

Then, by getting both thermal diffusivity and effusivity, the thermal conductivity can be calculated by:

$$k = e\sqrt{\alpha} \quad (8)$$

The final results are shown in Tab. 1. These results show that the value of the thermal conductivity of the sample from hard material tends to be greater than soft one. The result is according to the properties previously determined by the photopyroelectric methodology, where both presented higher values for the hard material compared to the soft one. Another observation can be made relating the sample's thermal parameters with distilled water. Once the cutting process involves a lot of amount of water, the stone dusty from benefit stays on suspension in water, forming the pasty mixture.

Table 1. Thermal parameters values results for samples from both soft and hard stones.

Material	Thermal diffusivity ($\times 10^{-7} \text{ m}^2/\text{s}$)	Thermal effusivity ($\text{W}\cdot\text{s}^{1/2}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$)	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
Distilled Water (reference) ⁽¹⁾	1.45 ± 0.02	1595 ± 20	0.61 ± 0.02
Ethylene Glycol (reference)	0.92 ± 0.01	$810^{(1)}$	0.24 ± 0.02
Soft stone sample	1.7 ± 0.3	1661 ± 13	0.68 ± 0.05
Hard stone sample	2.4 ± 0.1	1959 ± 67	0.96 ± 0.05

(1) Taken and compared from Dadarlat, 2009.

4. CONCLUSIONS

This work has presented the thermal analyzes for different samples from diverse ornamental stone waste using PPE methodology. The analysis consisted on three steps basically: determination of thermal diffusivity, then measurements to determination of thermal effusivity and, finally, obtaining the thermal conductivity of each sample. As previously explained, distinct configuration of the technique allows the determination of one thermal parameter, except the thermal conductivity, which was determined by means Eq. (8).

The results for reference samples (distilled water and ethylene glycol) are in agreement with literature values. The measures with interest materials showed a thermal properties tendency to be higher on waste from hard stone than to soft one. Besides, the preliminary results for interest materials shown that PPE methodology has a good sensitivity and reproducibility. It was observed the values convergence besides the tendency of different values of thermal property as a function of the composition of each sample analyzed (soft and hard ones).

Therefore, it can be concluded that the technique used in this work proved to be efficient. In addition, the study of such materials is of great value for the region, since the determination of the thermal parameters makes the applicability of these materials more effective.

5. REFERENCES

- Alexandre, J., et al., "Influence of Weather Exposure on Dimensional Changes in Clay Ceramics Incorporated with Granite Residue", *Materials Science Forum*, Vol. 869, pp. 131-135, 2016.
- Chirtoc, M., Mihăilescu, G., *Phys. Rev. B*, 40, 9606 (1989).
- Dardalat, D., Neamtu, C., *Meas. Sci. Technol.* 17, 3250 (2006)
- Dadarlat, D., Nematu, C., Streza, M., Socaciu, C., Bele, C., Dulf, F., *Eur. J. Lipid Sci. Technol.* 111, 148 (2009).
- Delgadillo-Holfort, I., Pereira, J. R., Guimarães, A.O., da Silva, E.C., *Int. J. Thermophys.* 25, 587 (2004).
- Piazzarollo, C. B., et al., "Factorial Design for 32 Experimental Planning of Clay Ceramic Incorporated with Ornamental Stone Waste", *Materials Science Forum*, Vol. 869, pp. 127-130, 2016.
- Sahraoui, A. H., Longuemart, S., Dadarlat, D., Delencos, S., Kolinsky, C., Buisine, M., *Rev. Sci. Instrum.* 73, 2766 (2002).
- SINDIROCHAS. *Exportação de Rochas: Informativo mensal*. 23 May 2018
<<http://www.sindirochas.com/downloads/relatorios/exportacoes-de-rochas-abril-2018.pdf>>.

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