DETERMINATION OF APPARENT DENSITY OF CERAMIC TILES USING WATER: VALIDATION OF THE METHOD

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ABSTRACT

The most widely known method for determining the apparent density of ceramic tiles is by immersion in mercury. Mercury is a toxic heavy metal that poses risks to human health and to the environment. In 2017, Brazil ratified the Minamata Convention calling for a total reduction or replacement of mercury use by 2020. To eliminate the use of mercury, a method was developed for industrial purposes. This method uses water as immersive media. However, the new methodology is still considered uncertain due to great variability of the results. The present work compares the methods to determine the apparent density of ceramic tiles using mercury and water, through the validation of results and test variables. The following variables were studied: immersion time, drying and lifetime of the sealant; the effect of dried and fired samples; the effect of deionized, mineral and tap water. To evaluate the influence of the sealant, a $2^2 + 3$ factorial design was used. The F test was used to determine the influence of water quality. For the evaluation of sample conditions, linearity, repeatability and reproducibility (R&R) were analyzed. The best results using water were achieved for tap water, with the samples immersed for 1 s. Drying time up to 25 min does not interfere with the results. According to the R&R analysis, constant operational training is required. Under these recommendations, the method for determination of apparent density using water shows precision, but not accuracy.

1. INTRODUCTION:

The best known and most widespread method for determining the apparent density of both fired and unfired ceramic tiles is by immersion in mercury [1], in addition to other methods such as ultrasound [2] and x-ray absorption [1,3]. Mercury, although present in nature, is a toxic heavy metal that poses risks to human health and the environment. Mercury is a chemical element, which in liquid form evaporates easily and thus can be released into the air, water and soil by natural processes or human action. It is considered one of the most hazardous substances for health and the environment. Exposure to high levels can cause serious effects in humans, causing neurological, cardiac, pulmonary, renal and immunological damage [4,5].

In 2017, Brazil ratified the Minamata Convention on Mercury. This international pact came into force in November, setting strict criteria for eliminating the use of this substance. According to the treaty, by 2020 there should be a total decrease or replacement of mercury use [6].
In view of the need to eliminate mercury use, a new method for determining the apparent density of ceramic tiles has been developed. This new method uses another liquid substance, water. However, the new methodology is still considered doubtful because it shows great variability and different results compared to the methodology using mercury. Given these difficulties in adopting the thrust methodology using water, a comparative study of the methods to evaluate the variability of both will be presented, as well as to establish an analogy between the results of the two measurement methods.

2. MATERIALS AND METHODS:

The most common method to determine the apparent (bulk) density of solid materials is the immersion method, described in ASTM C 373 [7] and ISO 1183-1 [8] standards. A test specimen is weighed in air and then immersed in a liquid and its apparent mass upon immersion is recorded. The density (mass ratio × the density of the liquid) is then calculated. The immersion liquid can be distilled water but, traditionally for ceramic tiles, mercury is used as immersion medium. As mercury has high surface tension, it is suitable to determine the density of porous ceramic tiles (monoporosa, semi-stoneware) because the pores do not fill with it. Using water as immersion medium, some problems arise due to the water surface tension that allows water to enter the ceramic pores. Therefore, the samples must be impregnated with a waterproofing agent before testing.

To evaluate the methods some factors were analyzed:

1) The influence of water quality: deionized, mineral and tap water were evaluated as immersion media. The goal was to determine if the type of water (deionized, mineral and tap water) could influence the results of density. The evaluation was performed through the F test for two samples for variances considering the tap water as a parameter. This kind of assessment analyzes the variance of two data sets (not the averages).

2) The influence of the impermeabilization procedure on the results: the impermeabilizing (waterproof) agent is a mixture of acrylic resin, water and surfactants with adequate wetting for immersion of the samples. The procedure consists of fully immersing the samples in the impermeabilizing (waterproof) agent, keeping the samples immersed for a predetermined time (Table 01), draining the excess impermeabilizing agent for 5 seconds and finally drying the samples at room temperature with forced ventilation according to a predetermined time (Table 01). Therefore, immersion time and drying time were used as factors in the evaluation of the impermeabilization procedure. Table 01 shows the factorial design (2k + 3) that was used for the analysis. A variance analysis (95%) was performed to evaluate the influence of the impermeabilization procedure.

Levels	Immersion time (s)	Drying time (min)
-1 and -1	1	5
-1 and +1	1	25
+1 and -1	9	5
+1 and +1	9	25
0 and 0	5	15
0 and 0	5	15
0 and 0	5	15

Table 01. *Factorial design for the impermeabilization procedure*

The accumulation of dust in the impermeabilizing agent was also studied. For this, a dry specimen of monoporosa was disaggregated and added by 10% by weight to the impermeabilizing agent. After this preparation, the contaminated impermeabilizing agent was used for the apparent density test. For the evaluation of the impermeabilizing agent lifetime, the lifetime for 10, 38, 90 and 220 days was tested. All results were analyzed by their statistical variance by the F test for two samples, taking as a standard sample the life span of 10 days.

3) The densification state of the sample: i.e. dry and fired samples, varying the density within the working range found for different processes (drying and firing). Linearity, repeatability and reproducibility (R&R) were evaluated. In this case, two operators performed the R&R validation test, however, one operator was properly trained and one was not. The fired samples were previously subjected to the water absorption test in a porosimeter for saturation. The fired samples were not covered with the impermeabilizing agent. All samples were analyzed by the methodology with mercury thrust to obtain the reference values.

Equation (1) refers to the method for determining apparent density using mercury, equation (2) for the method using water for dry samples and equation (3) for the method using water for fired samples. Dap is the apparent density of the sample (g/cm^3); mdry is the dry mass of the sample (g); mwet is the wet mass of the sample (g); mimmerse is the mass of the sample after immersion (g); dHg is the mercury density (g/cm^3); dH2O is water density (g/cm^3).

$$\text{Dap}\ (g/cm^3) = \left(\frac{m_{dry}}{m_{immerse}}\right) \times d_{Hg} \qquad (1)$$

$$\text{Dap}\ (g/cm^3) = \left(\frac{m_{initial}}{m_{initial} - (m_{final} \times C)}\right) \times d_{H_2O} \qquad (2)$$

$$\text{Dap}\ (g/cm^3) = \left(\frac{m_{dry}}{m_{wet} - m_{immerse}}\right) \times d_{H_2O} \qquad (3)$$

3. RESULTS AND DISCUSSION:

Regarding the water quality assessment, Tables 02 and 03 show the results of the F test for dry samples.

	Tap water	Mineral water
Average (g/cm^3)	1.85	1.85
Variance	$2.35 \cdot 10^{-4}$	$2.32 \cdot 10^{-4}$
Observation	5.00	5.00
gL	4.00	4.00
F	**1.01**	
P(F≤f) one-tailed	0.50	
F one-tailed critic	**6.39**	

Table 02. *F test for tap water × mineral water for dry samples*

	Tap water	Deionized water
Average (g/cm^3)	1.85	1.86
Variance	$2.35 \cdot 10^{-4}$	$3.64 \cdot 10^{-4}$
Observation	5.00	5.00
gL	4.00	4.00
F	**0.65**	
P(F≤f) one-tailed	0.34	
F one-tailed critic	**0.16**	

Table 03. *F test for tap water × deionized water for dry samples*

For dry samples, the mineral water condition does not interfere with the apparent density results (Fvalue < Fcritical). Deionized water, on the other hand, increases the variance of the results, and its use is not recommended (Fvalue > Fcritical). Tables 04 and 05 show the results for the fired samples regarding the influence of the water quality on the apparent density.

	Tap water	Mineral water
Average (g/cm³)	2.32	2.32
Variance	$3.22 \cdot 10^{-5}$	$7.06 \cdot 10^{-6}$
Observation	5.00	5.00
gL	4.00	4.00
F	**4.56**	
P(F≤f) one-tailed	0.09	
F one-tailed critic	**6.39**	

Table 04. *F test for tap water × mineral water for fired samples*

	Tap water	Deionized water
Average (g/cm³)	2.32	2.32
Variance	$3.22 \cdot 10^{-5}$	$1.02 \cdot 10^{-5}$
Observation	5.00	5.00
gL	4.00	4.00
F	**3.16**	
P(F≤f) one-tailed	0.15	
F one-tailed critic	**6.39**	

Table 05. *F test for tap water × deionized water for fired samples*

For fired samples, water quality has no significance in the apparent density ($F_{value} < F_{critical}$) results. Possibly this result is due to the samples being practically saturated with water.

Regarding the effect of the impermeabilizing agent characteristics on apparent density, Figure 01 shows the Pareto graph of the factorial design performed. Figure 02 shows the response surface of the factorial design.

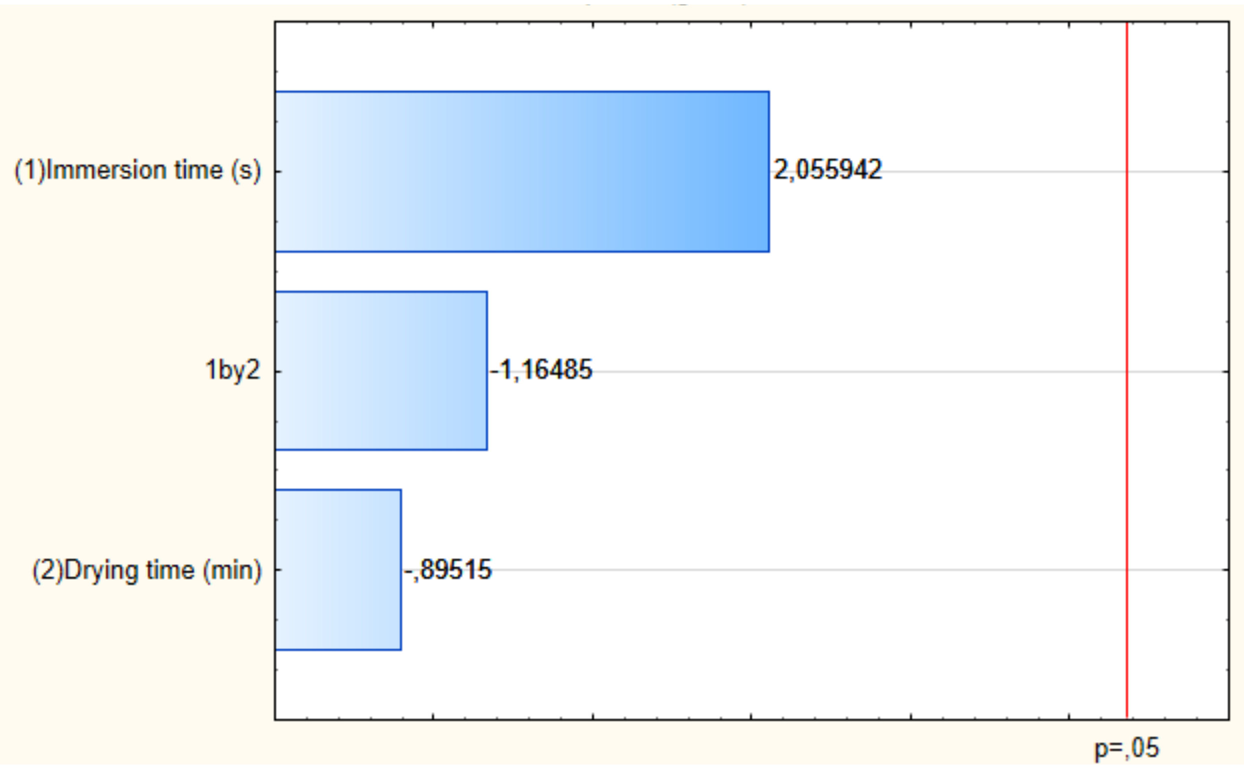

Figure 01. *Pareto graph for the immersion time and drying time as a function of the impermeabilizing agent*

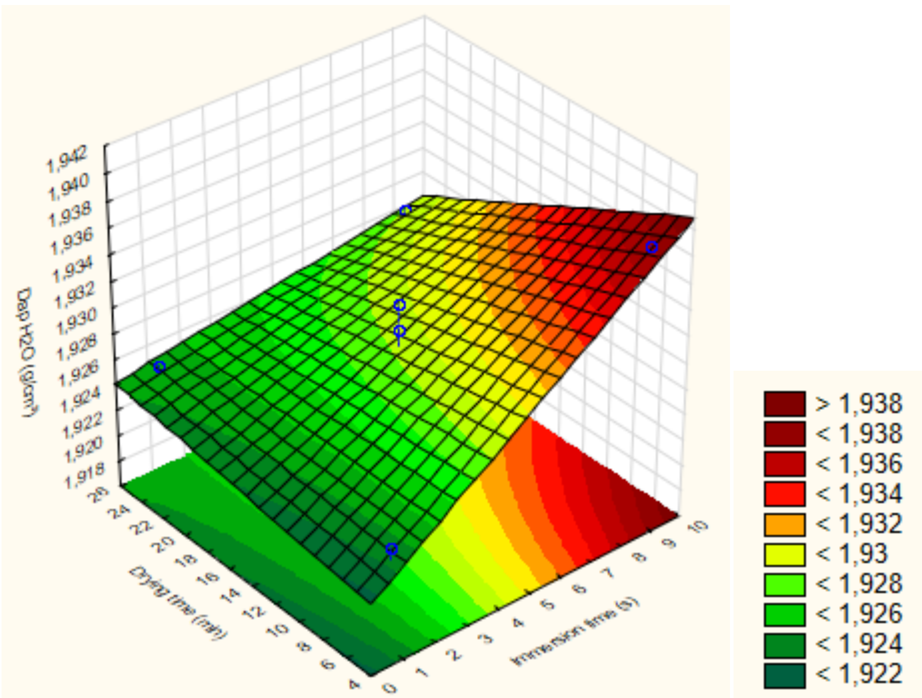

Figure 02. *Response surface for immersion time and drying time as a function of the impermeabilizing agent*

Figure 01 shows that neither the immersion time nor the drying time has significance in the apparent density result at 95% confidence ($p_{value} > 0.05$). Nevertheless, the response surface and the Pareto graph indicate that the immersion time is the most critical factor.

Regarding the impermeabilizing layer, the following aspects were observed: The impermeabilizing layer does not increase the amplitude of the weight of the samples. When the immersion time was increased, there was no significant increase in the impermeabilizing layer (2% increase). When the drying time of the impermeabilizing agent is increased, there is a slight decrease in sample weight (0.2% of the total weight). Therefore, these data support the results shown by the Pareto chart.

Table 06 shows the F test to evaluate the interference of dirt present in the impermeabilizing agent.

	Clean	Dirt
Average (g/cm³)	1.86	1.85
Variance	$6.94 \cdot 10^{-4}$	$2.35 \cdot 10^{-4}$
Observation	5.00	5.00
gL	4.00	4.00
F	**2.95**	
P(F≤f) one-tailed	1.60E-01	
F one-tailed critic	**6.39**	

Table 06. *F test for the interference of dirt on the impermeabilizing agent*

Table 06 shows that the $F_{value} < F_{critical}$, that is, there was no increase in the variance of the results due to the dirt present in the impermeabilizing agent. The dirt (remains of the sample paste in powder form) is denser than water and therefore is deposited at the bottom of the storage container and not at the surface of the sample to be impermeabilized.

Tables 07, 08 and 09 show the results of the F test for different impermeabilizing agent lifetimes.

	10 days	38 days
Average (g/cm³)	1.92	1.92
Variance	$3.00 \cdot 10^{-5}$	$1.79 \cdot 10^{-5}$
Observation	4.00	4.00
gL	3.00	3.00
F	**1.68**	
P(F≤f) one-tailed	0.34	
F one-tailed critic	**9.28**	

Table 07. *F test for 10 days × 38 days of impermeabilizing agent life*

	10 days	38 days
Average (g/cm³)	1.92	1.93
Variance	0.00	0.00
Observation	4.00	4.00
gL	3.00	3.00
F	**3.83**	
P(F≤f) one-tailed	0.15	
F one-tailed critic	**9.28**	

Table 08. *F test for 10 days × 90 days of impermeabilizing agent life*

	10 days	220 days
Average (g/cm³)	1.92	1.92
Variance	$3.00 \cdot 10^{-5}$	$5.26 \cdot 10^{-6}$
Observation	4.00	4.00
gL	3.00	3.00
F	**5.71**	
P(F≤f) one-tailed	0.09	
F one-tailed critic	**9.28**	

Table 09. *F test for 10 days × 220 days of impermeabilizing agent life*

As the time after impermeabilization increases, the value of F also increases. That is, the variability of the data increases as the sealant ages. Therefore, the supplier's recommendation for the expiration time of 90 days for the impermeabilizing agent should be followed. It is noteworthy that in all situations, the life of the impermeabilizing agent was not significant in the final result of apparent density ($F_{value} < F_{critical}$), i.e. the variance is similar.

Figure 03 shows the analysis of linearity for dry samples for an apparent density range from 1.85 to 1.95 g/cm³ comparing the use of water and mercury.

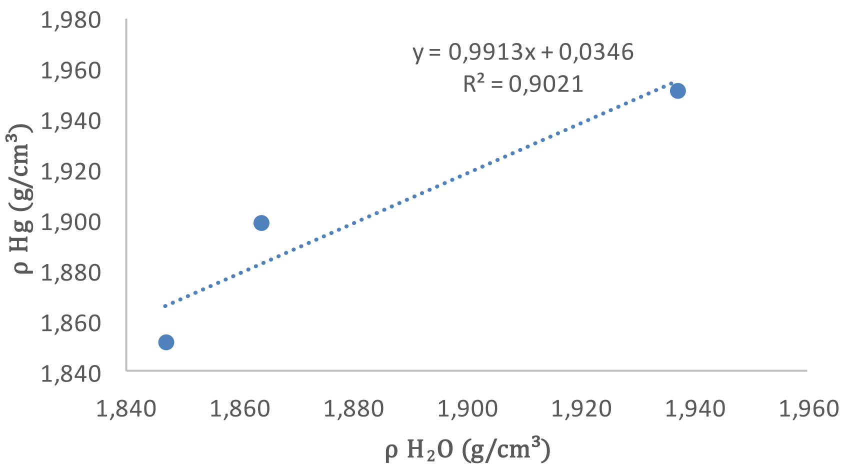

Figure 03. *Linear regression for apparent density ranging from 1.85 to 1.95 g/cm³ comparing the use of water and mercury for dry samples*

The method using water to determine the apparent density of dry samples shows satisfactory linearity, with a correlation (determination) coefficient of 0.9021, high for ceramic materials.

Table 10 shows the results of the R&R analysis, where the contribution of the operators and the sample itself can be observed in the final apparent density, by method.

Contribution Table	Mercury	Water
Operators	0	0
Samples	**100**	**100**
Repeatability and reproducibility	$1.53 \cdot 10^{-25}$	$3.30 \cdot 10^{-27}$
Total	100	100

Table 10. *Contribution table of repeatability and reproducibility (R&R) for dry samples*

According to Table 10, for both immersion methods, the apparent density depends exclusively on the sample and not on the operators. That is, both methods show repeatability and reproducibility. Figure 04 shows the linearity analysis for fired samples. The apparent density method using water shows high linearity with R^2 equal to 1.

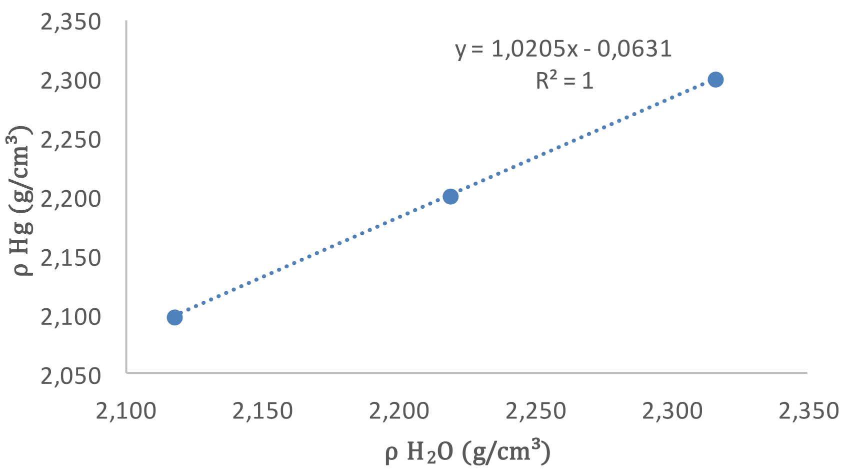

Figure 04. *Linear regression for apparent density ranging from 2.10 to 2.30 g/cm³ comparing the use of water and mercury for fired samples*

Table 11 shows the contribution of the operators and the sample in the final result of apparent density, by method, for fired samples.

Contribution Table	Mercury	Water
Operators	0	**24.18**
Samples	100	75.82
Repeatability and reproducibility	$2.34 \cdot 10^{-25}$	24.18
Total	100	100

Table 11. *Contribution table of repeatability and reproducibility (R&R) for fired samples*

For the apparent density method using water there is an operator contribution of 24.18% on the final density result. Realizing the interference of the operator in the result, it is necessary to keep the operators trained regarding the method, as possibly variations in the way of drying the sample with the damp cloth after water absorption affect the final result.

4. CONCLUSIONS:

Based on the results of this work and the statistical analyses, the following recommendations can be made for the apparent density determination test by buoyancy in water: it is recommended to use tap water for the test; the immersion time in the impermeabilizing agent must be 1 s; up to 25 min drying time in the impermeabilizing agent does not interfere with the results; the impermeabilizing agent must be used within its validity; although dirt does not significantly affect the results, it is recommended to change the impermeabilizing agent and clean the storage container to avoid dirt; the environment where the density equipment is found must be kept at a controlled temperature (25 °C).

According to the R&R analysis, the need for operator training is evident, as the statistical analysis shows the interference of the operator when one of the operators was not properly trained.

For embossed samples, the surface with the largest support area should be placed in contact with the support rod. Placing the embossed surface down affects the immersed weight value (less than actual value).

For samples with water absorption very close to 0.0%, the apparent density test with water can be performed without prior water absorption. In cases where the water absorption of the product is unknown or the water absorption is not null, water absorption should be performed in the porosimeter (under vacuum) and the equation where the water absorption of the product is considered should be used.

In conclusion, maintaining these precautions, the current method for determining apparent density using water has precision but not accuracy.

5. REFERENCES:

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