STATISTICAL ANALYSIS OF DEGRADATION DATA OF RED CERAMIC PIECES INCORPORATED WITH ORNAMENTAL ROCK WASTE

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ABSTRACT

From the point of view of mechanical strength, ceramic materials exhibit dispersion results after being subjected to various levels of stress. However, there are no statistical surveys addressing the results efficiently. This study aims to assess statistically, through the use of the Minimum Lot Size, Chauvenet criterion and the Tukey range test, these results. Specifically, the mechanical strength of red ceramic incorporated with ornamental rock waste fired up to 700°C will be analyzed, before and after degradation. The pieces were subjected to degradation of up to 1,500 hours in continuous leaching and of up to 10 months in natural degradation. The results of the Tukey test, before and after the degradation showed statistical differences, ensuring that the data analysis was effective.

Key-words: red ceramic, ornamental rock waste, degradation, statistical evaluation.

INTRODUCTION

Construction and industrial processes are responsible for generating significant amounts of solid waste, despite the use of alternative technologies for optimizing the production process and better utilization of raw materials[(1)].

Today, with the focus on sustainable development, there is a worldwide trend in encouraging the recycling of household, hospital, industrial, and construction waste, among others. In the area of construction, the incorporation of solid waste into clay for the manufacturing of red ceramic pieces has been proposed by several national and international studies[(2) (3)].

The municipality of Campos dos Goytacazes, northern Rio de Janeiro state (RJ), which has a large reserve of clays and is a center of red ceramics, accounting for about 40% of the state production[(4)], emerges as object of study.

Xavier (2007)[(5)], looking for the best quality products in the mildest temperatures, indicated the use of granite waste in red ceramics for obtaining greater strength and less open porosity in firing temperatures of up to 950ºC when compared to pieces not using granite waste. However, there are no reports of the service life behavior of the ceramic materials that compare a laboratory simulation with real conditions of clay material use that incorporates granite waste.

Thus, after subjecting red ceramic samples to different degradation processes in order to analyze the variations of the mechanical characteristics, this paper presents a statistical treatment of data through the use of Chauvenet criterion, MLS (Minimum Lot Size) and Tukey tests, in order to evaluate the results and show that, even with the great dispersion of values in the individual results of each red ceramic sample, it is possible to use the average value as a reference, ensuring the reliability of the results.

MATERIALS AND METHODS

MATERIALS

For this study, we used the following materials: clay from the municipal district of Campos-RJ and ornamental rock waste from municipal district of Cachoeiro do Itapemirim, Espírito Santo state.

METHODS

Technological Tests

Sample preparation

To ensure the homogeneity of samples, the mass was reduced according to [6]. The samples were prepared with clay incorporated with three different waste contents (i.e. 0%, 5%, and 10%). Initially, the ornamental rock waste powder was sifted through #40 mesh (0.42mm) and the retained material was discarded. Next, the pass-through material was ground to pass through sieve # 20 mesh (0.25mm). The batch mixture was performed on dried material and the extrusion moisture was calculated by Equation (A) [7]:

$$Wext = \frac{LL}{2} + 2\% \qquad \text{(A)}$$

Where the **LL** is the liquid limit and $\mathbf{W_{ext}}$ is the extrusion moisture content.

After mixing the samples with 0%, 5% and 10% waste (identified as 0R, 5R and 10R, respectively) were taken to the laminator followed by the extrusion. The ceramic pieces were then molded in prismatic shapes of 11.70 cm x 2.70 cm x 1.70 cm. The number of pieces (5) and the measures was based on [8] [9] standards.

The drying and firing process involved temperatures of 110ºC, 500ºC and 700ºC in an electronic oven. After firing, the ceramic pieces were submitted to a three loading point flexural strength test according to standard procedure [8] and also to the tests according to [9]. The obtained results represent the average of 5 determinations. The three loading point flexural strength test was carried out with a loading rate of 0.5 mm/min with a distance of 9.0 cm between supports.

Degradation

The degradation was carried out at laboratory equipment degradation to be evaluated after the changes in the flexural strength (Figure 1). This equipment submit the pieces to time-controlled continuous leaching of hot distilled water (70ºC) or cold water (21ºC), with temperature control of the sample chamber, and also submits the samples to freezing up to -4ºC. Additionally, samples are subjected to vapor atmosphere every time the hot water cycle starts. The samples were submitted to degradation in equipment during up to 1.500 hours.

Fig. 1 – Laboratory equipment degradation.

Statistical Analysis

a) Minimum Lot Size (MLS): for a value obtained experimentally to be consistent, it must be representative of the sample universe. And, to know if this value is representative, it is necessary to perform the MLS test.

Using exactly 5% (0.05) for the MLS test, it was considered that the cumulative frequency function was distributed in classes and the data behaved as a normal distribution.

According to [10], the Equation (B) that calculates the initial minimum number of lot is (n_0):

$$n_0 = \left[\frac{t.Sx}{r.Xm}\right]^2 \quad \textbf{(B)}$$

Where **t** is a Student tabulated value for n-1 degrees of freedom in the data set, **r** is the accuracy associated with uncertainty, $\mathbf{X_m}$ is the average of the lot and $\mathbf{S_x}$ is the standard deviation of the lot. The standard deviation and the lot average are calculated by Equations (C) and (D), respectively:

$$S_x = \sqrt{\frac{\sum(X - Xm)^2}{n-1}} \quad \textbf{(C)}$$

$$X_m = \frac{\sum_{i=1}^{n} X_i^2}{n} \quad \textbf{(D)}$$

After calculating the minimum initial lot number, the minimum lot size (MLS) is calculated using Equation (E):

$$n = \frac{n_0}{1 + \left(\frac{n_0}{N}\right)} \quad \textbf{(E)}$$

Where **N** is the number of batch data

b) Chauvenet Criterion: in this paper these are considered to be random errors associated with repetitive measurements or as representative of other phenomena.

Thus, these values that are distant from the dominant trend cannot be discarded without using consistent criterion for elimination. Therefore, this dispersion is treated with Chauvenet Criterion, in order to eliminate outlying values and to redo the calculations.

Let **n** be a large number of measurements, so that the results follow a Gaussian distribution. This distribution gives the probability that a measured value is an expected average value.

With Chauvenet Criterion, it is specified that a measurement value can be rejected if the probability **m** has a deviation related to average that is lower than **1/2n**. According to [11], there are maximum acceptable deviation values, $\mathbf{DR_0}$, relative to standard deviation for some values of **n**.

The deviation ratio is calculated by the Equation (F) [12]:

$$D_R = \frac{X - Xm}{S_x} \quad \textbf{(F)}$$

Where **DR** is the deviation ratio between maximum deviation (**X-Xm**) and the standard deviation (**Sx**), **X** is the measured value and **Xm** is the medium lot value.

If the DR calculated is greater than tabulated D_{R0} [11], the maximum or minimum value will be excluded and a new average value and a new standard deviation are calculated, without including the eliminated points.

Table 1 – Tabulated D_{R0} proposed by [11].

NUMBER OF DETERMINATIONS (n)	$\mathbf{D_{R0}}$
3	1.38
4	1.54
5	1.65
7	1.8
10	1.96
15	2.13
25	2.33
50	2.57
100	2.81
200	3.14

ROSS (2003) [13], does not recommend the repetition of this test for eliminate other points. If some points deviate of the established limit, probably the instrumentation system is inadequate or the processes are variable

After subjecting the material to the procedures for accelerated laboratory degradation (continuous leaching) and natural degradation in the field, it is necessary to verify the influence of the degradation by comparing the intact and the degraded ceramic. And to verify this contrast between the averages, the Tukey Test is used. However, the averages can be compared only after the Analysis of Variance (ANOVA).

c) Analysis of Variance (ANOVA) and F Test: the Analysis of Variance is used to simultaneously compare continuous variable samples with normal distribution, being able to compare averages of several samples or sets. The ANOVA is applied in order to reduce experimental error, where according to the several experimental designs that correspond to how the treatments are assigned to plots, the random variation is reduced as much as possible.

OTT AND LONGNECKER (2008) [14] shows that analysis of variance (ANOVA) for a completely randomized design follows the Equation (G):

$$\mathbf{Y_{ij} = m + t_i + e_{ij}} \qquad \textbf{(G)}$$

Where $\mathbf{Y_{ij}}$ is the observed value in the plot that received the treatment **i** with **j** repetitions, **m** is the overall observed average, $\mathbf{t_i}$ is the effect of treatment **i** and $\mathbf{e_{ij}}$ is the experimental error, that is, the effect of uncontrolled factors in the plot.

After calculating the ANOVA, the results are verified by the F test. If the calculated F is greater than the tabulated F, at least one average is different than expected, so, there is influence of the treatment on the samples at the level of significance required (5%). However, the ANOVA, does not identify what or which averages are different from each other. This discrimination is performed by the Tukey Test.

d) Tukey Test: This test performs the comparisons between averages to determine which sample sets are different from each other, taken 2 by 2. Thus, according to Junior (2004) [15], all contrasts ($\hat{\mathbf{C}}$) between the averages are analyzed Equation (H):

$$\hat{C} = mi - mj \quad \text{(H)}$$

Where **mi** is the parametric average of treatment **i** and **mj** is the parametric average of treatment **j**.

Tukey's test is based on the least significant difference Δ, given by (15) through Equation (I):

$$\Delta = q\sqrt{\frac{QMresidue}{2}\left(\frac{1}{R_i}+\frac{1}{R_j}\right)} \quad \text{(I)}$$

Where **Δ** is the studentized range, **q** is the tabulated Tukey value, **QMresidue** is the square average of the waste, **Ri** and **Rj** are **i** and **j** repetitions, respectively.

If the contrast (**Ĉ**) is greater than the studentized range, the contrast (**Ĉ**) is significant at **r** level of probability. Otherwise, the treatments applied to the samples had no effect.

RESULTS AND DISCUSSION

Initially, the results of the flexural strength test of intact samples were evaluated by Chauvenet Criterion and Minimum Lot Size.

The Minimum Lot Size (MLS) test was used to verify that the minimum number of samples (5) established by (8) would be satisfactory due to dispersion from the central tendency. The results are shown in the following Table 2:

Table 2 – MLS of Measured Values for Flexural Strenght (MPa).

SAMPLE (nº)	MLS MEASURED VALUES FOR FS (MPa)					
	0R INTACTS		5R INTACTS		10R INTACTS	
	500ºC	700ºC	500ºC	700ºC	500ºC	700ºC
1	8.24	10.14	5.46	9.65	5.86	4.91
2	5.73	8.14	4.93	9.82	6.91	5.12
3	10.9	6.98	6.85	7.73	7.62	5.21
4	7.77	8.84	6.81	8.67	8.05	8.77
5	8.35	10.33	7.65	10.56	6.03	10.01
x_m (Average)	8.20	8.89	6.34	9.28	6.89	6.80
S_x (Standard Deviation)	1.85	1.40	1.11	1.10	0.96	2.40
v (Degrees of Freedom)	4	4	4	4	4	4
t (Table => 0,975)	2.78	2.78	2.78	2.78	2.78	2.78
r (Accuracy)	0.05	0.05	0.05	0.05	0.05	0.05
n_0	156.79	76.61	95.35	43.33	59.67	385.70
N	3.90	3.80	3.84	3.66	3.75	3.96

According to the results, it would be necessary to use at least four (4) ceramic pieces for data consistency. With this, the number of pieces utilized (5) is considered satisfactory.

Next, to analyze the data outside of the central tendency Chauvenet Criterion was used. The results are shown in the following Table 3:

Table 3 – Values of maximum and minimum deviation ratio calculated by Chauvenet Criterion for rejection or acceptation for measured values.

EXTREME VALUES	FS 0R INTACTS (MPa)		FS 5R INTACTS (MPa)		FS 10R INTACTS (MPa)	
	500ºC	700ºC	500ºC	700ºC	500ºC	700ºC
Maximum	10.90	10.33	7.65	10.56	8.05	10.01
Minimum	5.73	6.98	4.93	7.73	5.86	4.91
x_m (Average)	8.20	8.89	6.34	9.28	6.89	6.80
S_x (Standard Deviation)	1.85	1.40	1.11	1.10	0.96	2.40
Dr_{min}	1.34	1.36	1.26	1.41	1.08	0.79
Dr_{max}	1.47	1.29	1.30	1.31	1.32	1.33

Analyzing the results, it is possible to note the calculated values for minimum and maximum DR do not exceed the value of DR_0 (1.65 – Table 1) for the five determinations. So the values are assumed for the uncertainty of 5%, even with apparent dispersions.

The samples with mixtures of from 0% up to 10% of ornamental rock waste were subjected to degradations in the laboratory and in weathering. To ensure the reliability of the results, the Tukey test of flexural strength test was applied, being considered an accuracy of 5% probability of uncertainty.

At first, due to the loss of some ceramic pieces, the average values could be outside the trend. Consequently the Chauvenet and MLS tests were applied again, but, the results showed that in none of the tests were the sets rejected, indicating a minimum of 3 samples for this analysis.

Following this, the Tables 4, 5 and 6 representing the ANOVA and the Tukey test of flexural strength test is shown.

Table 4 – Analysis of Variance (500ºC).

Analysis of Variance (ANOVA) - 500ºC							
Variation Source	**QS**	**Degrees of Freedom**	**QS_{total}**	**QA**	**F_{calc} test**		**$F_{tabulated}$ Test 5% probability**
Intact **Intact Waste (error)** **Total**	9.08 22.26	2 13 15	31.84	4.54 1.71	2.65	**ne**	3.81
Leaching 300 Hours **Leaching 300 Hours (error)** **Total**	38.41 3.91	2 11 13	42.32	19.21 0.36	54.00	*	3.98
Leaching 658 Hours **Leaching 658 Hours (error)** **Total**	3.71 11.95	2 13 15	15.67	1.86 0.48	3.87	*	3.81
Leaching 1500 Hours **Leaching 1500 Hours (error)** **Total**	21.38 5.84	2 12 14	27.22	10.69 0.45	23.71	*	3.89

***** calculated F is greater than tabulated F, so at least one average is different than expected.

ne: calculated F is smaller than tabulated F, so the treatment had no effect.

Table 5 – Analysis of Variance (700ºC).

Analysis of Variance (ANOVA) - 500ºC							
Variation Source	**QS**	**Degrees of Freedom**	**QS_{total}**	**QA**	**F_{calc} test**		**$F_{tabulated}$ Test 5% probability**
Intact **Intact Waste (error)** **Total**	17.74 35.76	2 13 15	53.51	8.87 2.30	3.86	*	3.81
Leaching 300 Hours **Leaching 300 Hours (error)** **Total**	60.72 0.70	2 7 9	61.63	30.46 0.10	303.25	*	4.72
Leaching 658 Hours **Leaching 658 Hours (error)** **Total**	32.93 9.04	2 12 14	41.97	16.46 0.75	21.84	*	3.89
Leaching 1,500 Hours **Leaching 1,500 Hours (error)** **Total**	83.99 1.97	2 9 11	85.96	42.00 0.15	275.87	*	4.26

***** calculated F is greater than tabulated F, so at least one average is different than expected.

Table 6 – Tukey Test of Flexural Strength.

F.S. (MPa)								
Temp. (ºC)	**TREATMENT**	**INTACT**	**CONTINUOUS LEACHING**			**TUKEY TEST INTACT X CONT. LEACHING**		
			300 h	**658 h**	**1500 h**	**300 h**	**658 h**	**1500 h**
500	Mixture (%)							
	0R	8.20	5.05	5.23	5.02	+	+	+
	5R	6.34	4.34	4.79	4.65	+	+	+
	10R	6.89	4.32	4.03	4.06	+	+	+
700	Mixture (%)							
	0R	8.89	5.82	6.28	5.51	+	+	+
	5R	9.28	5.26	5.42	5.39	+	+	+
	10R	6.80	4.32	4.74	4.69	+	+	+

+: averages followed by this signal differ one each other by the Tukey Test at the level of significance required (5%).

The Table 6 shows that the statistical significance of reductions in average values of flexural strength of the samples at 500°C and 700°C when evaluated by the Tukey test after laboratory testing, this is, the treatments applied to the samples had effect. Thus, the continuous leaching test is efficient, showing the degradation of the ceramic material and affecting their durability.

The percentage change between the values of F.S. from the intact and degraded ceramic pieces, shows that the minimum degradation value for 0R ceramic pieces appears at 700ºC and 658h of degradation. For the 5R ceramic pieces, the minimum degradation appears at 500ºC and 658h of degradation and, for the 10R ceramic pieces this behavior appears at 700ºC and 658h of degradation. This indicates that the ceramic pieces, fired up to 700ºC, undergo an ageing when subjected to 658h of degradation. The only exception is the 10R pieces, that when fired at 500ºC, shows best strength at 300h of degradation.

And, through the average of the values from the percentage changes of F.S., it can be concluded that the lowest degradation occurs in 5R ceramic pieces, fired at 500ºC, followed by 10R ceramic pieces, fired at 700ºC. So, ecologically, the use of ceramic pieces with 10% waste (10R), fired at 700°C it is more indicated.

CONCLUSION

Statistical tests are useful in the interpretation of the mechanical results in order to eliminate the doubts associated with observed values and to ensure the consistency of the minimum number of samples resulting in less dispersion of data.

This paper indicates the possibility of using ornamental rock waste incorporated in red ceramic, showing an increase of durability over the service life of the material, as well as adding value to a byproduct inappropriately discarded in the environment.

The addition of ornamental rock waste influences the degradation of red ceramic materials, providing enhanced durability to the material, especially in higher firing temperatures, keeping it more stable against weathering.

Finally, it is possible to conclude that the incorporation of 5% and 10% of ornamental rock waste in ceramic mass, when fired at 500ºC and 700ºC respectively, provides an increased the resistance of the ceramics, stabilizing the ceramic pieces to retraction by fire and expansion by moisture.

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