1. Introduction

Ceramics are used as construction materials since the earliest days of civilization, around 5,000 B.C. Manufactured fired earth bricks had firstly been used as protection walls against invaders and fierce animals. However, during the industrial revolution on century XIX, the steam machines allowed a marked development of the ceramic industry.

The term “Ceramic” is originated from *Keramikos*, which, in Greek, means fired raw material. The most important materials used in the composition of the red ceramic bodies are clayey soils. Chemically the clay mineral is composed basically by hydrous aluminum, iron and magnesium silicates, which can be dispersed in fine particles. Presence of impurities such as ferric oxides, quartz among others plays an important role on the characteristics of the final product.

Despite its great technological advances, some industries in the developing countries have not invested in high technology in order to manufacture bricks with high durability and acceptable mechanical properties.

Therefore, for the achievement of the better quality of the ceramic bricks and in accordance with the environmental appeal, some industrial by-products have been used in the raw material in ceramic industries.

In the case presented herein, by-products from decorative stone industry have been used aiming to improve the durability of the ceramic bricks as well as their mechanical properties.

In this particular perspective, the ceramic industry emerges as a great attractive to promote the use of industrial by-products. Moreover, the use of industrial by-products, as being granulated materials, does not affect the path normally followed during ceramic processing.

As a secondary effect, but not less important, the insertion of industrial by-products can also help to save noble materials in the pit borrow, avoiding, thus, the increasing on the rate of exploration works.

2. Red ceramic materials

Red ceramic raw materials are generally taken from natural deposits of clayey soils composed by clay minerals and others organic and/or inorganic particles that are very
“reactive” in the presence of water. This property is known as plasticity, which is very dependent on chemical interaction among particles and the liquid, which percolates through the pores.

Most of ceramic materials are fragile and stiff, with very low tenacity. They have high fusion/sintering temperature and good chemical stability specially, in hostile environment, due to their strong chemical bonding between structural units.

2.1 Durability of the red ceramic materials

Despite its stable mechanical behavior, it is not rare to observe problems in ceramic bodies regarding its durability, i.e., strength against weathering.

This is commonly observed in artifacts that are fired at temperature bellow its sintering point. Cracks and weathering signs are well developed inside the ceramic body, with time, due to work done by external agents like temperature, humidity and insulation. The main problem found in construction materials regarding their durability are:

1. Deterioration in brick wall and tiles resulting in cracks and infiltration (Fig. 1);
2. Degradation of the first lines of masonry due to capillarity effect of sulphate water ($\text{Na}_2\text{SO}_4$) (Fig. 1)
3. Rapid degradation due sudden changes in temperature (Fig. 2)
4. Quickly degradation in coastal environment resulting in complete deterioration of the ceramic brick (Fig. 4)
5. Mechanical and abrasive deterioration of the floor (Fig. 4)

Fig. 1. Fast degradation of masonry and tiles

Fig. 2. Fast degradation of masonry due to sulfate water and temperature change

White stain on masonry surface (efflorescence) appears as shown in Figure 3. This is consequential from a chemical process where the cement reacts with water resulting, thus, in a soluble binder, calcium hidroxile ($\text{Ca(OH)}_2$) that adheres on the ceramic brick. As long as the mortar layer contains cement and this layer has high porosity, the free calcium
hyroxile found in its composition reacts with air (carbonic anidre). This reaction between these two components results in calcium carbonate, non-soluble white salt, which leads to the expansion of the brick (Fig. 3).

Fig. 3. Detachment of the floor brick and walls

Fig. 4. Fast degradation in masonry due to saline spray and abrasion

The process of degradation takes place when the body gets in contact with atmospheric conditions. Therefore, degradation can be understood as the effect of atmospheric agents on the ceramic bodies without crystallographic modification. Alterability is defined as the susceptibility of a ceramic body to suffer degradation. Durability, on the other hand, means the capacity in keeping its structural stability, as well as the appearance with time. Therefore, alterability and durability will be closely dependent on the material and environmental characteristics and the exposure time, as well. In tropical regions a wide range of temperature and humidity variation is commonly observed. The weathering agents that act directly on ceramic bodies are:

- Rain and air humidity
- Periodic insulation and drop of temperature in a short period of time, causing contraction and dilation, respectively.
- Air temperature favoring chemical reactions
- Wind and kinetic energy favoring abrasive deterioration.

Mechanisms that act on degradation process are the same as those that act on weathering. Dilation and contraction resulting from temperature and humidity changes can give rise to cracks that commonly leading the ceramic body to undermine. Chemical agents can flow into these cracks and pores, reducing, thus, the bond between grains, making easier the erosion process and leaching the constituent materials. These transported constituents can induce the formation of new crystals resulting from chemical reactions, mainly when soluble salts are present in the mortar. When the air humidity
penetrates into the structure, these crystals are generally dissolved and carried to the surface, provoking thus, stains on the ceramic artifact. If these salts remain inside the ceramic body, they will re-crystallize causing expansion, favoring thus, degradation of the material. These alterations can be very harmful in particular in coastal zones and industrial areas due to the saline sprays and acid rain, respectively. The intensity of the effects of these degradation processes is closely dependent on the environmental conditions and also on the level of the thermal treatment specified to the ceramic material.

3. Characterization of the materials and evaluation of the alterability and durability of ceramic mass with addition of granite waste

This chapter presents the adopted methodology in order to evaluate the durability of ceramic bricks when granite waste by-product is incorporated in the raw material. Figure 5 shows the flow chart for complete characterization of the materials used in the confection of brick ceramic.

It is presented here the test sequence for the identification of the studied raw material: the clay mass and the granite by-product.

---

Fig. 5. Flow chart for complete characterization of the raw material with different content of granite powder
Further results and information can be reached in Saboya et al (2006), Xavier (2006), Xavier (2001) and Alexandre (2000).

3.1 Environmental characterization of the granite waste

The description of the results obtained from leaching test is shown in Table 1 and Table 2 where some results obtained from literature are shown in order to make the reader familiar with characteristic values and allow a direct comparison. Maximum allowed values for each chemical element are also presented aiming the classification of the material harmfulness.

| Chemical Element | Waste Granite (mg/l) | Waste Silva (1998) (mg/l) | Waste Neves (2002) (mg/l) | Maximum limits (leaching test lab) NBR-10005 (mg/l) |
|------------------|----------------------|---------------------------|--------------------------|----------------------------------|
| Ag               | <0.005               | <0.010                    | <0.010                   | 5.000                            |
| Cd               | <0.002               | <0.010                    | <0.047                   | 0.500                            |
| Cr               | 0.020                | <0.020                    | <0.010                   | 5.000                            |
| Pb               | 0.030                | <0.050                    | 2.120                    | 5.000                            |
| Ba               | 0.110                | 1.160                     | N.S.                     | 100.000                          |

Legend: N.E.: Not Specified.

Table 1. Results of the leaching test and presented in literature

| Condition test lab | Granite Waste (mg/l) | Waste Silva,1998 (mg/l) | Waste Neves,2002 (mg/l) | Maximum limits (Leaching test in laboratory) NBR-10005 (mg/l) |
|--------------------|----------------------|-------------------------|-------------------------|---------------------------------------------------------------|
| pH Begin           | 9.400                | 10.300                  | 9.400                   | N.S.                                                          |
| pH final           | 5.150                | 6.500                   | 5.500                   | N.S.                                                          |
| Vol. Acid (ml)     | 80                   | 130                     | 400                     | N.S.                                                          |
| Time (h)           | 28                   | 28                      | 28                      | N.S.                                                          |

Legend: N.S.: Not Specified.

Table 2. Conditions of the leaching test

Evaluating the results obtained in the leaching test and comparing them with the maximum limits established by the norm ABNT 10004 (1987), it is observed that none of its chemical elements of the gross mass presented superior concentrations than permitted, being the sample considered non toxic.

The pH of the leached extract from the gross mass (Table 2) falls in the interval between 5.15 and 9.4, being, thus, characterized as not corrosive (ABNT 10004, 1987).

The results of the leaching tests together with the results obtained in the literature are shown in the Table 3.

Evaluating the results obtained in Table 3 and comparing them with the maximum limits established by the norm ABNT 10004 (1987), the chemical element Pb (lead) of the mass gross has presented concentration slightly superior to the established as the maximum limit. Therefore, the residue is classified as class II, not inert.
Table 3. Results of the leaching test and some values reported in literature

The results obtained in this work are similar to those obtained by Silva (1998) and Neves (2002), which can be conclude that the granite waste is a non toxicant material, not corrosive, not inert of class II.

### 3.2 Chemical characterization

Following, the Table 4 depicts semi-quantitative chemical compositions of the standard clayey raw material granite waste.

| Raw Materials | L.O.I. (%) | SiO₂ (%) | Al₂O₃ (%) | Fe₂O₃ (%) | CaO (%) | MgO (%) | Na₂O (%) | K₂O (%) | TiO₂ (%) |
|---------------|-----------|----------|-----------|-----------|---------|---------|----------|---------|---------|
| Clay          | 15.40     | 42.30    | 32.00     | 6.87      | 0.20    | 0.70    | 0.04     | 0.94    | 1.24    |
| Granite Waste | 1.55      | 69.20    | 14.60     | 3.49      | 3.21    | 0.032   | 3.13     | 4.49    | 0.16    |

Table 4. Chemical Components of the clayey and granite waste materials

Observing the values obtained in Table 4, it is verified that for the standard clay sample, the amount of SiO₂ (42.3%) indicates the probable presence of kaolinite (Al₂O₃. 2SiO₂. 2H₂O) and illite, as well as the probable presence of free quartz in the total sample. The amount of Al₂O₃ (32.0%) almost totally is responsible for forming clay minerals, but it can also be credited to the presence of hydroxides as gibbsite (Al(OH)₃). The total value of 64.3% (SiO₂ + Al₂O₃) indicates the refractory character of the raw material.

The high amount of coloring oxide Fe₂O₃ (6.87%) characterizes it as fondant agent and also indicates the prone for the red color achieved after burning. It can also indicate the goethite presence (FeO.OH). The oxides of calcium and magnesiuim (CaO + MgO) corresponds a
Considerations about Degradation of the Red Ceramic Material Manufactured with Granite Waste

The coloring oxide Ti$_2$O in the amount of 1.24% can be credited due to the presence of rutile or anatase (Toledo, 2003) and it contributes to the yellow color of the raw material. The loss of ignition (LOI) of 15.40% indicates the loss of free, adsorbed and constitution water of the raw material and, also, the degradation of the organic content of the sample.

In the chemical analysis carried out on granite waste, it is noticed that the amount of silica is higher than 69% and the amount of Al$_2$O$_3$ can reach values higher than 14%, indicating chemical compositions of primary minerals (quartz, feldspar and minerals of the group of the mica). The traces of CaO (3.21%) and Fe$_2$O$_3$ (3.49%) come mainly from the whitewash and from the metallic particle used as lubricant and abrasive, respectively.

The oxides of sodium and of potassium (Na$_2$O + K$_2$O) in the amount of 7.62% presented by the by-product, are almost totally originated from the feldspar and mica and they are considered as fondant agents that could fill the voids. The loss of ignition (LOI) of 1.55% of the by-product is considered small indicating structural stability of the waste. However, this loss can also be credited to the degradation of the mica.

Comparison the results of the chemical analysis shown on Table 4 between the standard clay mass and that of red ceramic reported by Souza Santos (1989), Alexandre (2000) and Vieira (2001), there is a clear indication that this material is quite suitable to be used in the Brazilian industry of red ceramic.

In the same way, comparison the results of the chemical analysis shown in Table 4 for the granite waste with the chemical analyses for granite waste carried out by Neves (2002), Mothé Filho (2003) and Vieira et al. (2003), it can be shown that the incorporation of the by-product in ceramic mass can be used in the process of production of red ceramic goods without any special measure.

3.3 Thermal characterization from Differential Thermal Analysis

Observing the thermal curves of the ceramic mass and the mass with addition of waste with 5R (5%) and 10R (10%) in Figure 6, it can be detached, for each curve, two endothermic events of medium intensity very close to each other.

In this figure it is verified that the clay samples 0R, 5R and 10R present endothermic events of medium intensity between 258.50°C and 260.90°C, indicating a shift to the left of the peak values (in relation to the sample 0R) due to the presence of waste in the ceramic mass. These peaks are mainly due to the loss of OH$^-$ of the hydroxides of aluminum (Al(OH)$_3$) and iron (FeO(OH)) probably credited by the presence of gibbsite and goethite.

There are also endothermic events of medium intensity between 448.50°C and 499.84°C due to the beginning of the reaction of loss of hydroxyls of the kaolinite creating, thus, an amorphous phase (metakaolinite). Endothermic bands are observed starting from 900°C. It could indicate the transformation of the metakaolinite ($\text{Al}_2\text{O}_3.2\text{SiO}_2.\text{H}_2\text{O}$) amorphous in spinally ($2\text{Al}_2\text{O}_3.3\text{SiO}_3$) forming a stable crystalline structure.

The corresponding curve of the granite waste in the Figure 6 shows an endothermic event of small intensity for 570°C, indicating the transformation of the quartz for generating expansion. At 663.18°C an endothermic peak of small intensity corresponding to the beginning of loss of OH$^-$ of the mica is verified in the sample.
4. Experimental program for natural and accelerated degradation of samples 0R, 5R and 10R

The condition of alteration of a ceramic piece depends primarily on their physical-chemical, mechanic properties and also on the characteristics that are correlated with the time of alteration. Another important features is the degradation potential caused by the aggression of the environment, affecting the durability of the material, especially, the red ceramic in tropical countries.

For the evaluation of durability of the red ceramic materials incorporated with granite waste in the proportions of 0%, 5% and 10% known herein as 0R, 5R and 10R respectively, fired at temperatures of 500ºC, 700ºC and 900ºC, it was used the methodology presented in the Figure 7, in the form of illustrative organization chart.

For the evaluation of the changes experienced by the red ceramic materials, it should be considered the following aspects (adapted from Maia, 2001):

- The characteristic of the change processes of the ceramic material used in the civil construction;
- The methodology adopted for the evaluation of the technological properties after alteration tests carried out in laboratory and in the field;
- The representatively of the considered intact and naturally altered samples,
- Correlation of the properties with the time of natural alteration, for the prediction of the potential of the damage caused by this alteration, i.e., long time prediction.

To evaluate the changes in the red ceramic materials it should identify the mechanisms that influence the natural alteration, whose processes of the evolution of the degradation are visually accompanied.
For the determination of the characteristics of the alteration of the red ceramic pieces incorporated with granite residue in the field and in the laboratory in an induced and accelerated way, it was used some procedures considered essential, as follows:

Fig. 7. Methodology for evaluation of the degradation of red ceramic samples incorporated with 0R, 5R and 10R of granite waste

4.1 Test of continuous leaching in laboratory

This particular laboratory test is considered to mimic the climatic conditions that degrade the red ceramic artifacts. When it is intended to determine the state of alteration of a rock or other natural material, the extractor Soxhlet is most suitable because the samples are submitted to leaching in distilled hot and cold water. The extractor Soxhlet allows the samples to be submitted to temperature variation in controlled periods of precipitation and water level variation.

Farjallat (1971) used the extractor Soxhlet to evaluate changes in rocks specimens using correlation with Los Angeles abrasion test.

After associating the characteristics of the rock with the quality indexes, this author compared these characteristics in different alteration stages. The quality indexes are applied in the specific quantification of measurable properties as strength, porosity, water absorption and others (Maia, 2001).

Maia (2001) has used an extractor Soxhlet of great dimensions to evaluate the alteration of rocks used in rockfill. Based on this author's work, it was manufactured in LECIV/CCT/UENF in Campos/RJ a degradation equipment (Figure 8) similar to that extractor Soxhlet.

The Equipment of Degradation developed at LECIV was designed to make possible to control periods of temperature variation and of precipitation of the solution. Distilled water is used as leaching solution. During the leaching, this solution can be monitored and, if necessary, changed.
Inside the tank, samples are subjected to environment similar to atmospheric conditions, where the material is placed on shelves of stainless-steel and submitted the temperature variations. At the same time, the samples are washed periodically with hot and cold water, simulating the natural precipitation. The wash is made by the leaching solution, coming from the pumps of hot or cold water that goes through the sprinkles placed at the top of the tank creating a saturated vapor atmosphere (this phase is only when there is the circulation of hot water).

The vapor condensation also takes place when the cycle of hot water is in operation. The equipment was programmed to work for 1 hour for each cycle of hot or cold water, meaning that when the leaching for hot water is in operation, the cold water system keeps turned off. During the cycle (hot or cold water), the water is pumped every 15 minutes.

The hot water is controlled to be kept at approximately 70°C and the cold water around 35°C. The time periods of 300 hours, 658 hours and 1500 hours were used to submit to the samples to this complete process. The equipment possesses an electronic system of operation (I-square of command) which ignores manual control of the time and water cycles.

The pump of hot water possesses a system to support high temperatures. The tanks of hot and cold water possess a capacity of approximately 200 liters (each) and the container of samples possess 500 liters of volumetric capacity. The equipment is constantly monitored by a computer and by a camera installed in the laboratory to notice possible defects during the night and weekends when the same is in operation.

Curves shown in Figure 9 depict the temperature balance inside the sample tank (500 liters) and also the temperature balance inside the hot and cold water tanks. It can be noticed that
at around 100 minutes from the beginning of the operation the balance is reached. This means that the electronic circuits work with synchrony and precision and that the samples are always under the same conditions inside the equipment.

Fig. 9. Temperature of the sample container, hot and cold water tanks with time

In the change of cycle of hot and cold water inside of the samples tank, it is noticed the continuous fall in temperature, simulating in an accelerated way the climatic conditions of temperature variation between the days and the nights, provoking dilation and retraction in the samples due to thermal gradients.

4.2 Laboratory test of wetting and drying cycles

This particular test intends to simulate, in laboratory, the aggression suffered by the ceramic when subject to environmental natural conditions. It is known that the laboratory conditions are not the same that of the field. However, the results can be somewhat representative (Maia, 2001; Cunha, 2006).

Fig. 10. Laboratory tank for wetting and drying cycling test

The washing water was monitored periodically every 15 days through pH meter aiming to assure keeping the solution as basic acidy. The environment temperature inside the room...
was controlled to keep it about 21±1°C and relative humidity of the about 64±5%. Cycling was composed of 50 and 150 cycles, representing respectively 1.200 hours and 3.600 hours of soaking and drying steps.

4.2.1 Field natural degradation
This procedure has as the objective comparison of the degradation accelerated in laboratory to the alteration of the material under local environmental conditions. Samples were exposed to periods of 6, 8 and 10 months where variables like air temperature, relative humidity, wind speed, precipitation and the solar radiation, were recorded.
The natural degradation of the samples was carried out at the Campus of the State University of the Norte Fluminense Darcy Ribeiro - UENF, Campos of Goytacazes/RJ, with latitude of 21st 45 ' South, longitude of 41st 18 ' West and altitude of 11 m. This kind of degradation is used for the long time prediction which will serve as a base to obtain the information about the effects of the degradation of a specific material (Cunha, 2006).
The samples were fastened in a special support made of wood placed on the roof of a UENF building, according to the Illustration 11. It was placed in such way to guarantee ideal incidence and absorption of solar radiation, facilitating, thus, the effective degradation process during the research period. The supports for samples were designed to guarantee free air circulation.

Fig. 11. Samples on terrace exposed on the roof directed to the best insulation direction according to the local coordinates

The climatic conditions define the processes of degradation of ceramic materials exposed to the environment. It is naturally believed that those ceramics material that have been under more severe conditions of temperature variation and humidity are more susceptible to damage.

5. Evaluation of the alterability and durability of incorporated red ceramic pieces with granite waste

5.1 Technological properties of the intact material
The curves related to the technological properties of the standard clay for 0R, 5R and 10R after firing are presented. These curves were obtained from laboratory tests carried out on
Considerations about Degradation of the Red Ceramic Material Manufactured with Granite Waste

the so-called intact samples. These curves considered as standard are compared to the results obtained from laboratory and natural degradation process. Figure 12 presents the curves corresponding of the mean results of five determinations of the technological properties after firing. Results of the diametrical compression test are presented in Table 1.

Fig. 12. Technological Properties of the samples 0R, 5R and 10R after firing

| Values of the Diametrical compression (MPa) of the intact samples |
|---------------------------------------------------------------|
| Temp. (ºC) | 0R | σ (SD) | 5R | σ (SD) | 10R | σ (SD) |
|------------|----|--------|----|--------|-----|--------|
| 500        | 1.06 | ±0.5  | 1.99 | ±0.03  | 0.60 | ±0.09  |
| 700        | 1.69 | ±0.01  | 0.85 | ±0.10  | 1.97 | ±0.62  |
| 900        | 1.74 | ±0.16  | 1.21 | ±0.20  | 3.02 | ±0.12  |

Table 5. Values of the diametrical test on so-called intact samples
The Figure 12 also shows the tendency of the absorption of water and apparent porosities of the samples 0R, 5R and 10R after firing. It is observed that the results indicate reductions in the mean values when added 5R in the sample for all firing temperatures, however, for 700°C and 900°C this effect is accentuated indicated by smaller peak.

This behavior is closely linked to the formation of liquid phase during the thermal treatment due to presence of alkaline (Na$_2$O+K$_2$O>7%) and earthy alkaline (CaO+MgO>3%), according to the Table 4, provoking, thus, a reduction in the mean values of the absorption of water and apparent porosities, as expected.

In this case, the amount of 5% of granite waste can be used in massive bricks and ceramic blocks because of the obtained absorption lower than 25% (ABC, 2000). This represents the formation of rigid vitreous phase during cooling filling voids of the ceramic pieces.

In general, it is observed a new increase in the curves starting from the addition of 10R, revealed by the higher values of absorption of water and porosities. Extrapolating the mean values, it seems that when the amount of waste is increased, the water absorption is also increased, which means that it may not be attractive for practical use.

However, the curves of the open porosities of the green samples converge for very close values (between 33 and 35%), showing that when rising the temperature, it does not provoke significant densification of the pieces, being close to that range shown for values of open porosities.

It is observed in the Figure 12(c), that the linear retraction of the ceramic mass with 5R at 900°C, presents tendency of stabilization, being the largest values found for the samples with 0R. As expected, the higher the firing temperature, the higher the sample retraction is.

The Figure 12(d) indicates a tendency of increase of the apparent specific mass with the increase of the waste percentage, independently of the firing temperature. That increasing tendency can be justified for the granolas presence in the waste.

The convergence of the mean points for the samples is verified with 5R of addition, characterizing the densification of the ceramic pieces (Figure 12d). It is observed in the Figure 12(b) the same convergence tendency in the curves for open porosities. The tendency of these curves is to show opposite behavior, because when the open porosities are reduced the volumetric density is increased.

In Figure 12(e) and (f) it is noticed higher values for the curves of simple compression and flexural strength for sample 5R, regardless the firing temperature. The differences obtained from both tests are solely in the failure stress level. Higher mechanical strengths are achieved for sample 5R fired at 900°C.

When the thermal curves (Figure 6) are observed, it can be observed transformations in the solid state of the particles increasing, thus, stiffness and strength of ceramic bodies. Consequently, the increase of the mechanical strength with the increase of the firing temperature is independent of the addition waste amount (Figure 12e).

It is noticed that when passing from 0R to 5R of addition of granite waste for samples fired above 700°C, the strength increases considerably, which indicates that the addition of 5R for process of ceramic production can be a very acceptable value.

Observing the Table 5, it is noticed that the results of the diametrical compression strength for standard clay, show themselves varied and dispersed when compared to those obtained for incorporated samples which also depend on firing temperature, indicating that this test cannot bet conclusive, not being indicated to evaluate the material behavior. This can be explained by the presence of cracks randomly distributed in all samples provoked by air drying process.
5.2 Technological properties of the natural and accelerated altered material

5.2.1 Physical properties: Water Absorption (WA) and Apparent Porosity (AP)

Figures 13 and 14 present the variations of the absorption of water and apparent porosities with the time for both natural and laboratory degradation of the samples fired at temperatures of 500ºC, 700ºC and 900ºC and with 0, 5 and 10% of waste content in the ceramic mass. It should be stood out that the absorption of water and apparent porosities are inter-correlated properties, presenting the same pattern of variation of the degradation.

Fig. 13. Effect of the degradation type in the absorption of water for the samples with addition of granite waste for firing temperatures of 500ºC, 700ºC and 900ºC.

The variation in the magnitude of the absorption of water with the degradation time observed in the Figure 13 is, in general, not much affected by the firing temperature. It is noticed in the last alteration stages a variation of the absorption of water about 2% in relation to that of intact material. Variations of the order of 3% were noticed in the naturally degraded material with 10R.
It is observed in Figure 14 that the variation of the range of the apparent porosities with the time of degradation was not very much affected by the firing temperature. It is also observed in the last alteration stages, a variation of the open porosities about 4% in relation to that of intact material. Variations of the order of 5% were noticed in the naturally degraded material with 10R.

Fig. 14. Effect of the degradation type in the apparent porosities for samples with granite waste for firing temperatures of 500°C, 700°C and 900°C

5.2.1.1 Continuous leaching

For the leaching conditions also shown in Figures 13 and 14, the largest effect of the degradation was noticed in the samples with 0R at 700°C, which can evidence the loss of cohesion among particles due to the increase of the water absorption.

In the samples fired at 900°C under continuous leaching, the variation of the absorption of water is small due to the great influence of vitreous phase and larger changes in the present.
crystalline phases of the samples maintaining it, therefore, more resistant against leaching effects. It should be stood out that the elevation of the firing temperature is also responsible for the densification of the ceramic material due to the fondant properties of some existing oxides.

The vitreous phase is characterized by the presence of alkaline \((\text{Na}_2\text{O} + \text{K}_2\text{O})\) and earthy alkaline \((\text{Dog} + \text{MgO})\), that are fondant oxides, mainly when granite waste is added, as observed in the Table 4. When the temperature increases, a eutectic formation takes place. During cooling a plug partially or totally seals the pores, making difficult the effect of the continuous percolation of distilled water through voids of the ceramic sample.

The results of the apparent porosities are similar to the absorption of water for the intercorrelation among these properties. In general, the increments of open porosities observed in all cases provoked by the field and laboratory degradation facilitates the displacement of the particles welded by firing before submitting them to the continuous leaching. It has been observed reductions on the values obtained in the samples with 10R. Open porosity decreasing in these samples reflects on the reduction of the absorption of water of the ceramic piece, when compared to the intact samples. This is accredited to the presence of the CaO and MgO (Table 4) in the granite waste, corroborating, thus, for plugging openings.

The largest increments of the porosities opened after the continuous leaching, were observed in the samples with 0R in all range of the thermal treatment. That indicates the susceptibilities of the samples to the degradation conditions imposed by the laboratory tests and calls for the attention for the suitability of waste use, aiming to assess more durability of red ceramic goods.

### 5.2.1.2 Cycles of drying and wetting

It is verified in the Figures of 13 and 14 that the values of the water absorption are similar to those of open porosity for 0R, 5R and 10R, as expected. It can be noticed in the curves of 500°C after 50 cycles a quite similar behavior of that observed for 150 cycles with reductions of the water absorption. The samples 5R at 500°C depict significant increase in water absorption for 50 (and after) cycles.

On the other hand, the curves of the samples fired at 900°C have shown reduction in water absorption after 50 and 150 cycles when compared to those values of the intact samples. This can be credited to the severity of the tests in laboratory, mainly if the stove is used to dry samples causing increase in volumetric density, as shown later.

The largest effect of the degradation given by larger water absorption was noticed for the samples with 0R at 700°C in all conditions of wetting and drying cycles due to the loss of mass induced by these cycles which favors the cohesion reduction among particles.

The samples fired at 900°C show the reduction of the water absorption after cycling, due to the great influence of the vitreous phase and also due to the crystalline phases presented in the sample at this temperature, increasing, thus, the volumetric density as a result of pore plugging.

The tendency of increasing the open porosity is verified for 50 wetting-drying cycles for sample 5R. On the other hand, small reductions are observed for the samples 10R under same conditions. This applies for all firing temperature.

After 150 wetting-drying cycles, the sample 10R has its porosity reduced for all tested firing temperature.
The open porosity values after degradation tests for each waste addition (0R, 5R and 10R), suffered alteration in the wetting-drying cycles. The samples 0R and 10R presented higher increase in porosity, and the samples 5R did not show any change in their initial porosity.

5.2.1.3 Natural alteration (Field)

The Figures 13 and 14 show that after 8 and 10 months of field alteration the values of the absorption of water and apparent porosities are quite similar. The values for the samples molded with standard clay at 500ºC after 6 months of natural degradation, are kept unchanged. For samples 5R Increasing in water absorption can be observed. On the other hand, for samples 10R this values decreases.

The largest variation took place for samples 0R after 8 months of natural degradation. However, the samples 10R tend to converge to the same point of water absorption, slightly below 25% after 8 months. For these same samples, after 10 months of natural degradation, the mean values of water absorption rise above 25%.

The smallest values are still observed for samples 5R for all firing temperatures, revealing, thus, their stability against natural degradation. The samples 0R are more inclined to suffer natural degradation as a consequence of high values of water absorption.

It is also noticed the similarity between natural degradation and wetting-drying cycles test regarding water absorption values obtained for the two groups. These results indicate that 6 months of natural degradation can be replicated by around 50 to 150 wetting and drying cycles, revealing that such laboratory test may, somehow, represent field effects acting on degradation process.

The largest variation of open porosity is shown for samples 0R after 8 months of natural degradation. Samples 10R, after 8 months of natural degradation, tend to converge to the same values of open porosity at values slightly below 40%, staying stable after further 10 months of natural degradation.

The smallest value of apparent porosities is observed in the samples with 10R to 900ºC, revealing the stability to the natural degradation of the samples with addition of waste.

5.2.2 Mechanical properties

5.2.2.1 Index of Flexural Strength (FS)

Variation of the index of the Flexural strength (I_{FS}) with time for natural and laboratory degradation is shown in Figure 15.

This index expresses a correlation between a given material property for both intact and degraded states. The index I_{FS} which uses the flexural strength (FS) to define degradation index is defined as follows:

$$I_{FS} = \left( \frac{FS_D - ES_I}{ES_D} \right) \times 100$$

Where, subscripts “D” and “I” mean “degraded” and intact, respectively.

It can be observed that the tendency of the curve of the index Flexural strength (I_{Flexure Strength} (%) with firing temperature follows the same pattern regardless the kind of degradation. These curves present similar pattern of those obtained for water absorption and open
Considerations about Degradation of the Red Ceramic Material Manufactured with Granite Waste

porosity, as expected. This indicates that the firing temperature has little or no influence on $I_{FS}$.

The variation of the $I_{FS}$ with degradation time is significantly affected by the degradation process regardless the firing temperature and waste content, as well.

![Graphs showing the effect of degradation process on the index of FS for samples with addition of granite waste fired at temperatures of 500°C, 700°C and 900°C](image)

Fig. 15. Effects of the degradation process in the index of FS for samples with addition of granite waste fired at temperatures of 500°C, 700°C and 900°C

5.2.2.2 Continuous leaching

The effect of the reduction of mechanical strength of the ceramic pieces after the continuous leaching is shown in Figure 15. It can be observed that this reduction on mechanical strength is accentuated at 500°C and 700°C, which can be explained by the low firing temperatures that are suitable for promoting coalescences among particles.

Flexural strength is reduced with leaching time for those standard clay samples (without waste content) when fired at 900°C, (300 hours). After 1500 hours of leaching, samples with
waste content (5R and 10R) did not show any loss of strength which indicates that the granite waste content is a very suitable mechanical stabilizer.

In the leaching test, the samples are submitted to the cycles of hot (≈70°C) and cold water (≈35°C). These conditions intend to simulate the temperature variations and humidity of the environment and can be efficient when it is compared to those results from natural degradation.

5.2.2.3 Wetting – drying cycles

The loss of mechanical strength is verified for the samples after 50 cycles. For 150 cycles there is a significant gain of strength of I_{FS}. The samples 5R show higher mechanical strength, once they present smaller strength indexes for all firing temperature.

Some degradation mechanisms may occur contributing for the increase of the I_{FS}: Formation of new clay minerals, restructuring, suction, arrangement of glass phase and pores clogging.

It is believed that, amongst these mechanisms involved in this process, suction and pores clogging are most presented.

5.2.2.4 Field or natural degradation

The Figure 15 depicts the values of I_{FS} for the samples 0R, 5R and 10R for firing temperatures of 500°C to 900°C. It is observed that the samples, in these conditions, show higher increase in I_{FS} after 6 months of natural degradation. After 8 months of natural degradation, the I_{FS} decreases slightly and are kept stabilized thereafter, except sample 5R which shows increase in I_{FS} after 10 months of leaching.

No significant degradation is verified for samples fired at 900°C for all waste content. This suggests high cohesion amongst the flat particles guaranteeing, thus, larger mechanical strength under the natural degradation. For samples 5R higher strength are obtained, showing, thus, that the firing temperature of 900°C or higher is suitable when waste is used.

6. Scanning electronic microscopy of the intact and degraded samples

For the evaluation of the surface morphology and texture of the intact and degraded samples, the Scanning Electronic Microscopy (SEM) was used. Images of the ceramic samples 0R, 5R and 10R, fired at 700°C in intact and degrade samples (wetting-drying cycling) were obtained and presented in Figure 16.

The Figure 16 (a, b and c) shows the evolution of the densification of the ceramic mass with and without addition of waste. It can be noticed that the absence of granite waste makes easy micro-cracks to occur and also to avoid small diameter pores clogging, characterizing the coarse texture of the sample.

The Figure 16 (b) also shows some defects associated to the pores of wide range of magnitude for samples 5R. It is observed that the texture is finer than of 0R and 10R, for the same firing temperature, indicating that 5R may be considered an optimum waste content for achieving higher densities.

The Illustration 16 (c) presents the image of the intact sample 10R, evidencing a coarse texture with pores of large diameters. It is noticed an intrusion of waste particles into the larger pores which can be attributed to waste that did not reacted to firing.

Figure 17 (a, b and c) shows SEM images from samples 0R, 5R and 10R fired at 700°C after 150 wetting – drying cycles.
Considerations about Degradation of the Red Ceramic Material Manufactured with Granite Waste

Fig. 16. SEM micrograph of the intact samples (0R, 5R, 10R) fired at 700°C

It is observed in the Illustration 17 (a) an agglomeration of free flat particles on the surface along with a micro-crack and a considerable concentration of shallow pores which are believed to be created by the wetting-drying cycles. This pore size distribution and their characteristics are strongly linked to high values of water absorption shown by these samples.

The effect of the wetting-drying cycles was more intense than that of samples 5R and 10R, causing higher strength decrease (Figure 15).

In the Figure 17 (b) sample 5R presents a smother surface texture and very few loose particles. This sample has, as expected, less porosity and less surface degradation when compared to sample 0R. This can be a clear indicative of pores clogging caused by thermal movement hysteresis and humidity variation imposed during the test.

It is also verified in the Illustration 17 (c), free particles, pores and defects on the whole surface area, aggravated by the degradation after 150 cycles.
Fig. 17. (a, b e c) SEM micrograph of the samples 0R, 5R and 10R fired at 700°C degraded after 150 wetting – drying cycles

7. Remarks

In this chapter, it was studied the behavior of the ceramic material with additions of granite waste (0R, 5R and 10R) fired at 500°C, 700°C and 900°C. The samples were submitted to artificial and natural degradation. Through these tests it was possible to obtain some response that can help the understanding the physical mechanisms associated to the mechanical behavior of the ceramic-based material used in civil construction industry. The laboratory tests, in special that of wetting and drying cycles tests showed themselves suitable for testing samples fired at 500°C and 700°C. However, for 900°C the results did not matched well with those obtained from natural degradation test, indicating that, for this temperature, the samples seemed to be somewhat stronger than those submitted to natural degradation process.
When technological properties of intact and degraded ceramic are evaluated in laboratory, it is possible to assess the mechanisms involved in this process based on changes in porosity, volumetric density, shrinkage and dilation amongst other parameters.

The images obtained in SEM allowed the analysis of the so called intact and degraded ceramic material surface, reflecting the effects suffered by the ceramic pieces, in accordance with the evolution of the degradation process imposed in laboratory and natural environment.

It was also observed that the natural and laboratory degradation causes heterogeneity on the mechanical behavior of the materials without following a pre-defined pattern.

It is verified that the granite waste addition influences in the degradation of the red ceramic materials, for propitiating them better durability characteristics, mainly for high firing temperature that, based on the results obtained herein, is the most important variable governing the ceramic materials behavior against degradation.

8. References

ABNT (Associação Brasileira de Normas Técnicas) (1987). Resíduos Sólidos – Classificação. NBR 10004.

ABNT (Associação Brasileira de Normas Técnicas) (2004). Procedimentos para Obtenção de Extratos Solubilizados de Resíduos Sólidos. MB 2616 (1987_Lixiviação de Resíduos - Procedimento. NBR 10005).

ABNT (Associação Brasileira de Normas Técnicas) (2004). Procedimentos para Obtenção de Extratos Solubilizados de Resíduos Sólidos. NB 1067 (Solubilização de resíduos – Procedimento: antiga NBR 10006_1987).

ABNT (Associação Brasileira de Normas Técnicas) (2004). Amostragem de Resíduos Sólidos. NB 1068 (1987 NBR 10007).

ALEXANDRE, J. (1997). Caracterização das Argilas do Município de Campos dos Goytacazes para Utilização em Cerâmica Vermelha. Tese (Mestrado em Ciências de Engenharia com ênfase em Geotecnia) – Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 164p.

ALEXANDRE, J. (2000). Análise de Matéria-Prima e Composições de Massa Utilizada em Cerâmica Vermelha. Tese de Doutorado em Ciências de Engenharia – Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 174p.

ALGRANTI, E.; HANDAR, Z.; RIBEIRO, F.S.N.; BOM, A.M.T.; SANTOS, A.M. BEDRIKOW, B. (2004). Exposição a Sílice y Silicosis en Brasil (PNES). Ciência do Trabalho. Capítulo 6 (11) págs 1-13.

ASSOCIAÇÃO BRASILEIRA DE CERÂMICA (2005). Panorama Nacional da Indústria Cerâmica. Disponível: www.abceram.org.br/asp/abc_21.asp [capturado em 05 de novembro de 2005].

ASTM C 373 (American Society Tecnology Materials) (1977a). Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity and Apparent Specific Gravity of Fired Whiteware Products.

ASTM C 674 (American Society Tecnology Materials) (1977b). Standard Test Method for Flexural Properties of Ceramic Whiteware Materials.

ÁVILA JÚNIOR, M. M.; Ferreira, H. S.; Menezes, R. R.; Neves, G. A.; Lira, H. L.; Ferreira, H. C. (2002). Expansão por Umidade (EPU) de Blocos Alternativos Utilizando Rejeitos de Granito. Anais do 46º Congresso Brasileiro de Cerâmica. São Paulo – SP. 12p.
BERNETT, F.E. (1976). Effects of Moisture of Installed Quarry Tile. Ceramic Bulletin. Vol.55, n°12.

BIZERRIL, C.R.S.F.; ARAÚJO, L.M.N.; TOSIN, P.C. (1998). Contribuição ao Conhecimento do Rio Paraíba do Sul – Coletânea de Estudos. ANEEL/CPRM. Rio de Janeiro-RJ. 128p.

BUSTAMANTE, G.M.; BRESSIANI, J.C. (2000). A Indústria Cerâmica Brasileira. Revista Cerâmica Industrial. Vol. 5 (3). Maio/junho.

CABRAL, G. L.L. (2005). Metodologia de Produção e Emprego de Agregados de Argila Calcinada para Pavimentação. Dissertação de Mestrado. Rio de Janeiro-RJ. IME – Instituto Militar de Engenharia. 358p.

CASTRO, E.M. (2005a). O que esperar para o setor em 2006? Editorial. Revista Rochas de Qualidade. Edição 185: pág. 06.

CASTRO, E.M. (2005b). Um ano bom que poderia ser melhor. Editorial. Revista Rochas de Qualidade. Edição 180: pág. 07.

CALLISTER, W. D. J. (2000). Materials Science and Engineering, 5ª Edição, New York-USA, Editora John Wiley & Sons, Inc. 852p.

CEN (Comité Européen de Normalisation). (1995) – Methods of Testing Cement – Part X: Determination of the Resistance of Cements to Attack by Sulphate Solution and by Seawater, PR ENV 196-X.

CHIODI FILHO, C. (2001). Situação brasileira do setor de rochas ornamentais. Revista Rochas de Qualidade, Edição 158: págs. 87-106.

CUNHA, V. P. (2006). Estudo da Degradação de Geotêxteis Tecidos. Dissertação de Mestrado em Engenharia Civil - Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 151p.

FALCÃO BAUER, R.; RAGO, F. (2000). Expansão por Umidade em Placas Cerâmicas para Revestimento. Revista Cerâmica Industrial. São Paulo-SP. 5(3), maio/junho. 5p.

FARJALLAT, J. E. S.; DE BARROS, F.P. YOSHIDA, R.; DE OLIVEIRA, J. A. N. 1972. Alguns Problemas de Desagregação dos Basaltos da Barragem de Capivara, Rio Paranapanema. 4ª Semana Paulista de Geologia Aplicada, São Paulo, vol. II A, pp. 73-102.

FRASCA, M.H.B.O. (2005). Durabilidade e Alterabilidade em Rochas Ornamentais e para Revestimento. Revista Rochas de Qualidade. Edição 180: pág. 178-188.

GUIMARÃES, J. E. P. (1998). A Cal. São Paulo. Editora PINI. 285p.

ISRM – International Society for Rock Mechanics. (1981). Rock Characterization Testing and Monitoring. – ISRM Suggested Methods, Ed. E. T. Brow, Pergamon Press, Oxford, pp. 51-60.

JOHN, V.M. (2000). Reciclagem de Resíduos na Construção Civil: Contribuição à metodologia de Pesquisa e Desenvolvimento. Tese (Livro Docente) de Doutorado – São Paulo – SP. Universidade de São Paulo. 102p.

JOHN, V.M.; Zordan, S.E. (2001). Waste Management 21. 213-219.

LUZ, A. B. (2005). O setor de rochas ornamentais. Revista Rochas de Qualidade, Edição 180: pág. 129.

MACHADO, M. A. (2002). “O Setor de Rochas Ornamentais”. “Rejeitos”. Palestra apresentada no CREA/ES sobre rejeitos da Indústria de Rochas Ornamentais. Cachoeiro de Itapemirim-ES.
MAIA, P. C. A. (2001). Avaliação do Comportamento Geomecânico e de Alterabilidade de Enrocamentos. Tese de Doutorado – Rio de Janeiro-RJ. Pontifícia Universidade Católica do Rio de Janeiro. 351p.

MOTHÉ FILHO, H.F.; POLIVANOV, H.; MOTHÉ, C.G. (2002). O Uso do Resíduo do Mármore e Granito para Indústria da Cerâmica Vermelha. Anais do 46º Congresso Brasileiro de Cerâmica. São Paulo – SP. 8p.

MOTHÉ FILHO, H.F. (2003). Caracterização e Aplicação Tecnológica do Rejeito da Indústria do Mármore e Granito. Tese de Doutorado em Geologia – Rio de Janeiro – RJ. Universidade Federal do Rio de Janeiro – UFRJ. 137p.

MOTTA, J.F.M.; ZANARDO, A.; CABRAL, M.J. (2001). As Matérias-primas Cerâmicas. Parte I: O Perfil das principais Indústrias Cerâmicas e seus Produtos. Revista Cerâmica Industrial. Vol. 6 (2). Março/Abril.

NEVES, G.A. (2002). Reciclagem de Resíduos da Serragem de Granitos para Uso como Matéria-Prima Cerâmica. Tese de Doutorado em Engenharia de Processos – Campina Grande – PB. Universidade Federal de Campina Grande – UFCG. 242p.

NITES – Núcleo Regional de Informação Tecnológica do Espírito Santo. (1994). Desperdício na Indústria de Mármore e Granito. Rochas de Qualidade. São Paulo. Ed. 118, p. 27-32.

PEITER, C.C.; CARANASOS, A.; VIDAL, F.W.H.; ALBUQUERQUE, G.S.C.; FERREIRA, G.E.; FILHO, C.C.; CALAES, G.; VALE, E. (2001). Rochas ornamentais no século XXI. CETEM, ABIROCHAS. (Relatório Técnico sobre o Setor de Rochas Ornamentais do Brasil, TR – 30/07). 113p.

PESAGRO/RIO (2005). Boletim de Dados Climatológicos da Região de Campos dos Goytacazes-RJ. Estação Automática Thies-Clima.

ROC MAQUINA. (1989). Referências arqueológicas sobre a explotación de piedras naturales em época romana de España. Cuarto trimestre.

SABOYA, F.A.J., XAVIER, G. C., ALEXANDRE, J. (2006). The Use of the Powder Marble By-Product to Enhance the Properties of Brick Ceramic. In: Construction and Building Materials, Vol. 20, pág. 1-8.

SILVA, S.A.C. (1998). Caracterização de Resíduo da Serragem de Blocos de Granito. Estudo Potencial de Aplicação na fabricação de Argamassas de Assentamento e de Tijolos de Solo-Cimento. Tese (Mestrado em Engenharia Ambiental) – Vitória – ES. Universidade Federal do Espírito Santo – UFES. 159p.

SMITH, W.F. (1998). Princípios de Ciência e Engenharia dos Materiais. 3ª Edição, Lisboa-Pt, Ed. Mc GRAW-HILL, 892p.

SOUZA SANTOS, P. (1989). Ciência e Tecnologia das Argilas. 2ª Ed. São Paulo: Editora Edgard Blucher Ltda. Vol. 1, 499p.

TOLEDO, R. (2003). Técnicas Fototérmicas e de Raios-X para o Monitoramento de Sólidos e Gases em Materiais Cerâmicos. Tese (Doutorado em Engenharia e Ciência dos Materiais) – Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 315p.

VIEIRA, C.M.F. (2001). Caracterização de Argilas de Campos dos Goytacazes Visando à Fabricação de Revestimento Cerâmico Semiporoso. Tese de Doutorado em Engenharia de Materiais – Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 118p.
VIEIRA, C.M.F.; SOARES, T.M.; SÁMCHEZ, R.; MONTEIRO, S.N. (2003). Incorporation of Granite Waste in Red Ceramics. Materials Science & Engineering. Campos dos Goytacazes - Brazil. 7p.

WARREN, J. (1999). Conservation of Brick. New York, Oxford University.

WIKPEDIA, (2005). História da Cerâmica. Disponível: http://www.en.wikipedia.org/wiki/brick. [capturado em 20 de março de 2005].

WINGER, R.J.J. (1965). In place permeability tests use for subsurface Drainage investigation. Division of Drainage and Groundwater Engineering, Denver, Colorado-USA. 9p.

XAVIER, G.C. (2001). Utilização de Resíduos de Mármore e Granito na Massa de Conformação de Cerâmica Vermelha. Dissertação de Mestrado em Ciências de Engenharia - Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 285 p.

XAVIER, G.C. (2006). Resistência, Alterabilidade e Durabilidade de Peças Cerâmicas Vermelhas Incorporadas com Resíduo de Granito. Tese de Doutorado em Engenharia Civil – Campos dos Goytacazes – RJ. Universidade Estadual do Norte Fluminense – UENF. 201 p.
The current book consists of eighteen chapters divided into three sections. Section I includes nine topics in characterization techniques and evaluation of advanced ceramics dealing with newly developed photothermal, ultrasonic and ion spattering techniques, the neutron irradiation and the properties of ceramics, the existence of a polytypic multi-structured boron carbide, the oxygen isotope exchange between gases and nanoscale oxides and the evaluation of perovskite structures ceramics for sensors and ultrasonic applications. Section II includes six topics in raw materials, processes and mechanical and other properties of conventional and advanced ceramic materials, dealing with the evaluation of local raw materials and various types and forms of wastes for ceramics production, the effect of production parameters on ceramic properties, the evaluation of dental ceramics through application parameters and the reinforcement of ceramics by fibers. Section III, includes three topics in degradation, aging and healing of ceramic materials, dealing with the effect of granite waste addition on artificial and natural degradation bricks, the effect of aging, micro-voids, and self-healing on mechanical properties of glass ceramics and the crack-healing ability of structural ceramics.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Xavier Gustavo de Castro, Saboya Fernando, Maia Paulo Cesar de Almeida and Alexandre Jonas (2011). Considerations about Degradation of the Red Ceramic Material Manufactured with Granite Waste, Advances in Ceramics - Characterization, Raw Materials, Processing, Properties, Degradation and Healing, Prof. Costas Sikalidis (Ed.), ISBN: 978-953-307-504-4, InTech, Available from: http://www.intechopen.com/books/advances-in-ceramics-characterization-raw-materials-processing-properties-degradation-and-healing/considerations-about-degradation-of-the-red-ceramic-material-manufactured-with-granite-waste