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Evaluation of Solid Waste From H_2S Removal Process in Natural Gas Treatment Incorporated Into Red Ceramic

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Waste incorporation into clay ceramic is a worldwide accepted recycling procedure for environmentally friendly reuse of spent industrial materials. In the present work a clay ceramic from the city of Campos dos Goytacazes, Brazil, was, for the first time, investigated with different amounts, up to 10 wt%, of a solid waste generated from the "Sulfatreat" natural gas treatment process. Both the waste and the incorporated ceramic were characterized by X-ray fluorescence and X-ray diffraction as well as vibratory sieving, gas chromatography and sedimentation method. Ceramic samples were prepared by uniaxial pressing at 18 MPa and sintered at 850°C. Physical and mechanical properties of these ceramics such as linear shrinkage, apparent density, water absorption and flexural strength were evaluated. Microstructure of the incorporated ceramics was analyzed by optical microscopy. The results showed that, within the standard deviation, the linear shrinkage and apparent density of the clay ceramic were not affected by the waste incorporation. However, the water absorption is benefitted, by decreasing, above 5 wt% incorporation, while the flexural strength is impaired for any incorporated amount. Porosity and larger waste particles observed in microstructure are proposed reasons for these advantages and shortcomings.

Keywords: *Waste incorporation, clay ceramics, Sulfatreat waste, properties.*

1. Introduction

Natural gas is a growing energy resource in Brazil associated with important applications [1-4]. Several studies have been conducted aiming at improving both quality and specification of natural gas according to the levels required by the Brazilian National Petroleum Agency, known as ANP [5,6]. The presence of contaminants existing in natural gases, such as H_2S, CO_2, N_2 and even water, imposes the need of special treatments involving separation procedures [7]. In particular hydrogen sulfide, H_2S, also called "acid gas", is an important contaminant due to its very high degree of toxicity. One of the most effective treatments to eliminate acid gas is known as the Sulfatreat™ process. This is the trade name of the iron oxide (Fe_xO_y) - based compound used in the removal of H_2S from the natural gas [8]. The treatment consists on adsorption of H_2S as the extracted natural gas flows through a vessel with a fixed bed filled with Sulfatreat™ iron oxide [8]. During this process, the adsorption occurs by chemical reaction of H_2S with Sulfatreat™ forming a by-product considered as a Sulfatretat waste (SW), classified as dangerous [9]. In fact this waste is still toxic enough to be directly disposed into the environment, which might cause ecological damage. In addition to be indefinitely kept in sealed containers, a possible destiny for the SW could be its incorporation into clay ceramics.

The incorporation of industrial wastes into clay ceramics, especially for production of civil construction materials such as red bricks, structural blocks, roofing tiles, sewage pipes and many others, has been extensively investigated [10-13]. Among the distinct types of wastes, those associated with gas and oil industries are worth mentioning [14-19]. Fernández-Pereira et al [14] investigated the application of biomass gasification fly ash and found promising results associated with its addition to bricks. Eliche-Quesada et al [15] also obtained improved technological properties in clay bricks incorporated with residues from biodiesel production. Pinheiro e Holanda [16] investigated clay ceramics incorporated with encapsulated petroleum waste. They found that, after firing at 1000°C, the linear shrinkage, water absorption and compressive strength decreased. Hajjaji and Khalfaoui [17] showed that oil shale addition into clay ceramic promoted marked changes in properties up to 12 wt%. Vieira et al [18] reported minor change in the properties of red ceramic industrial products incorporated with oily wastes.

The aforementioned works have shown that hydrocarbon-based wasted might be incorporated into clay ceramics with slight reduction in strength but improvement in processing and other properties [19]. In particular, only few articles investigated the incorporation of wastes from the Brazilian petroleum industry [16,18]. To the knowledge of the authors of the present work, no investigation on the incorporation of wastes from

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the Brazilian natural gas industry has been done so far. The relevance of this specific investigation is based on the fact that the application of natural gas in Brazil is surging and the related wastes will continuously be increasing. Therefore, the objective of the present work was to incorporate SW into clay ceramics fired at a temperature of 850°C, commonly used for red bricks production. This temperature corresponds to a mean value between minimum of 600°C for ordinary red bricks and 1100°C for special ceramic tiles [10-13]. In fact, it will be shown that the SW incorporated clay ceramics fired at 850°C are associated with technical properties with values in the limits to be used for roofing tiles. This is one of the most important building construction products with a relatively higher cost per weight of clay ceramic. Clay ceramic roofing tiles are experiencing a surge in Brazil owing to current demand for popular housing.

2. Experimental Procedure

The ferrous-based solid waste resulting from Sulfatreat process, here identified as SW, was collected at a natural gas plant of Cabiúnas, Macaé, state of Rio de Janeiro, Brazil. At the Advanced Materials Laboratory of the State University of the Northern Rio de Janeiro, Campos dos Goytacazes, the SW was milled and sieved to 42 mesh. The kaolinitic clay from the same region of Campos dos Goytacazes, was collected from a local ceramic industry to be mixed with SW.

The mineral constituents of both SW and clay were obtained by X-ray diffraction (XRD) in a model URD 65 SEIFERT diffractometer operating with Cu-Kα radiation and 2θ ranging from 5 to 40º. The chemical composition analyses were performed by means of X-ray fluorescence (XRF), using a PW 2400 Phillips equipment, and the gas chromatography (GC) [5,20] in a model GC 2010-plus Shimadzu, equipped with sulfur chemiluminescence detector (SCD). The particle size distribution was determined by sieving and sedimentation methods according to the Brazilian standard [21].

Clay mixtures with 0, 2.5, 5, 7.5 and 10 wt% of SW with clay were prepared in a pan mill for 30 min. The maximum amount of 10 wt% was a limit to avoid toxic emission during the incorporated clay sintering. Specimens with dimensions of 100 x 50 x 5.5mm were produced by uniaxial pressing (18 MPa). They were dried at 110ºC for 24 hours and then sintered at 850ºC for 2h under a heating rate of 2ºC/min. A minimum of 7 specimens for each condition were tested for water absorption, apparent density, linear shrinkage and three-point bending flexural strength. The water absorption was determined according to standard procedures [22]. The linear shrinkage was obtained by measuring the sample's length, before and after the sintering stage, using a Mitutoyo caliper with an accuracy of ±0.01 mm. The three-point flexural strength was determined as per ASTM C674 standard [23] in an Instron 5582 universal testing machine, using a cross-head speed of 0.5 mm/min.

The microstructure of the sintered ceramics was evaluated by optical microscopy using a model CGA Olympus. The facture was analyzed by electron scanning microscopy (SEM) in a model SSX-550 Shimadzu microscope.

3. Results and Discussion

Figures 1 and 2 show XRD patterns of the clay ceramic and Sulfatreat Waste (SW), respectively. It is observed that the clay ceramic has predominantly peaks of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) and quartz (SiO_2), represented by K and Q letters, respectively, in Fig. 1. The presence of other minerals, such as montmorillonite ($(Al_{1,67}.Na_{0,33}.Mg_{0,33})(SiO_5)_2(OH)_2)$), gibbsite ($Al_2O_3.3H_2O$), goethite- ($FeO(OH)$), and muscovite mica ($K_2O.3Al_2O_3.6SiO_2.2H_2O$), may also be verified in Fig. 1. The very small peak attributed to gibbsite can be considered, as such, based on the typical occurrence of this mineral in the clays of Campos dos Goytacazes [24,25].

Among the mentioned minerals, the kaolinite and montmorillonite are responsible for a marked plasticity of the ceramic clay with added water. Quartz constitutes the major impurity present in the clay, which acts as an inert component during sintering [13]. By contrast, the gibbsite contributes to increase the clay refractory behavior and its weight loss during sintering. Regarding the muscovite mica, this is a mineral with lamellar texture that can cause defects in ceramics [26]. However, if this mineral has a reduced particle size, it may act as a fluxing

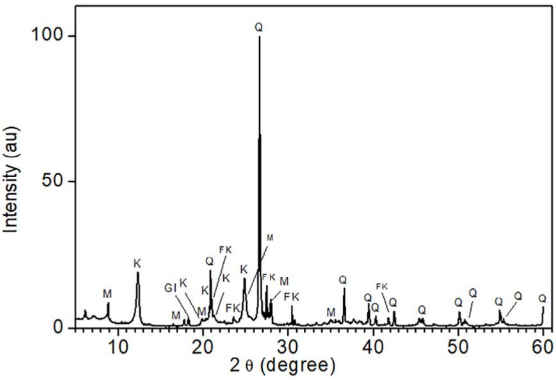


Figure 1. X-ray diffractogram of the ceramic clay. K= kaolinite; Gi = gibbsite; M = muscovite mica ; Q = quartz and FK= potassium feldspar.

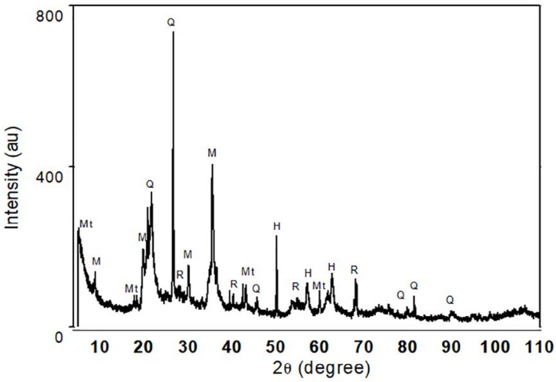


Figure 2. X-ray diffractogram of the Sulfatreat waste. M = muscovite mica ; Q = quartz, Mt = montmorillonite and H = hematite.

component due to the presence of alkaline oxides. In addition, processing problems can occur as a result of the great rehydration tendency of the montmorillonite.

The XRD diffractogram of the SW, Fig 2, shows peaks of quartz, hematite (Fe_2O_3), muscovite mica and montmorillonite. These results are in accordance with the mineralogical SW composition indicated by the supplier. It can also be noted the presence of quartz together with montmorillonite. This mineralogical combination is associated with low plasticity. The iron oxide during the sintering stage should be maintained in oxidation state as Fe^{3+}. In case the iron oxide is chemically reduced it may cause a defect known as "black heart", which occurs when vitrification takes place before complete oxidation [27]. Moreover, the iron oxide acts as a fluxing agent, reacting with silica, producing fayalite, and a glassy (amorphous phase). The glass formed produces an impermeable surface preventing gas from escaping. This might lead to bloating of the ceramic with reduction of its mechanical strength.

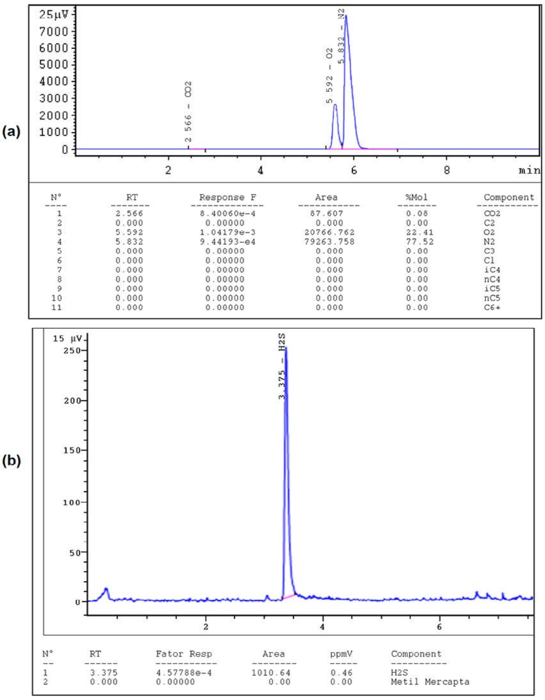
Table 1 shows the chemical compositions in terms of oxide contents, as well as the loss on ignition (LoI) for both clay ceramic and SW. It should be noted that clay ceramic exhibits a typical composition of silica (SiO_2) and alumina (Al_2O_3) [28]. Usually, these oxides are present as compounds, i.e. combination of quartz (SiO_2) and alumina (Al_2O_3), forming aluminosilicates, such as kaolinite and muscovite mica. However, according to Fig. 1, there is gibbsite, $Al(OH)_3$, in the clay ceramic. Therefore, in Table 1, not all content of alumina is associated with aluminosilicates. In addition, minor contents of Fe, Ti, Ca, Mg and K oxides are also presented in Table 1. The iron oxide is responsible for the reddish color of the ceramic. Regarding the alkaline earth oxides (CaO and MgO), they are usually associated with carbonates, such as calcite ($CaCO_3$), magnesite ($MgCO_3$) and dolomite $MgCa(CO_3)_2$. It is worth mentioning that the low amount of calcium and magnesium oxides observed in Table 1 indicates the absence of carbonates in the investigated clay. The amount of 1.24 wt% K_2O, important to reduce the porosity by viscous flux, is also present. This percentage is relatively low and typical of kaolinite clays. In clays, the Na and K oxides are commonly found as feldspar and mica.

The SW has relatively high amounts of iron oxide and silica, as shown in Table 1. According to Fig. 2, the iron occurs in the form of hematite. The high quantity of SiO_2 (34.71 wt%) is associated, predominantly, with particles of quartz and clay minerals, such as montmorillonite and mica. Table 2 shows a qualitative analysis of the remaining composition (6.26 wt%) of SW, which may be related to several metallic elements found in natural gas and still remaining in the processed waste.

Table 2. Atomic Absorption Spectrometry (Qualitative) of Sulfatreat waste.

Majority elements	Al, Si, Fe
Small percentage elements	Mg, K, Mn
Trace elements	Na, P, S, Cl, Cs, V, Cr, Ni,Zn, Sr,Zr, Mo, Pb, Ba.

Figure 3 shows results for the SW by gas chromatography, in a Sulphur Chemiluminescence Detector (GC-SCD). These results revealed that the gas composition is similar to the atmospheric air, whose theoretical value is 78% N_2, 21% O_2, 1% CO_2. In addition, the H_2S amount obtained was 0.46 ppmv (in volume), which is below the standard value of 2 ppmv [29,30]. In other words, the existing H_2S content is acceptable.



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 N°          RT         Response F         Area          %Mol       Component
----      --------    -------------    -----------     -------     -----------
  1        2.566       8.40060e-4        87.607          0.08       CO2
  2        0.000        0.00000           0.000          0.00       C2
  3        5.592       1.04179e-3      20766.762        22.41       O2
  4        5.832       9.44193-e4      79263.758        77.52       N2
  5        0.000        0.00000           0.000          0.00       C3
  6        0.000        0.00000           0.000          0.00       C1
  7        0.000        0.00000           0.000          0.00       iC4
  8        0.000        0.00000           0.000          0.00       nC4
  9        0.000        0.00000           0.000          0.00       iC5
 10        0.000        0.00000           0.000          0.00       nC5
 11        0.000        0.00000           0.000          0.00       C6+
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N°      RT        Fator Resp      Area       ppmV     Component
--    ------     -----------   ---------    -----    ----------
1      3.375     4.57788e-4     1010.64     0.46     H2S
2      0.000     0.00000           0.00     0.00     Metil Mercapta
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Figure 3. Gas chromatography (GC-SCD) of the Sulfatreat waste.

The particle size distributions for both the clay and SW are shown in Fig 4, as per standard [31]. The particle size ranges were determined based on the following limits: particles < 2µm (clay fraction); from 2 to 20µm (silt fraction); and > 20µm (sand fraction), that correspond to 46.2 wt%, 38.4 wt% and 15.4 wt% of the clay, respectively. This result indicates that the investigated clay has a relatively high amount of clay minerals, which confers a high plasticity.

Regarding the SW, Fig. 4 shows the particle size after its milling and sieving (42 mesh). It should be noticed that the SW has a coarser granulometry in comparison to the clay and $d_{(50)}$ of 0.02mm, i.e., 50% of the sample mass, larger than this diameter. These results indicate that the SW is adequate

Table 1. Chemical composition (%) of the ceramic clay and Sulfatreat waste.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	MnO	CuO	ZrO_2	**LoI**
Waste	34.71	10.90	42.40	-----	0.70	1.35	1.56	0.35	0.31	1.31	0.15	-----	-----
Clay	50.20	27.88	6,00	1.06	0.24	0.74	1.24	0.01	0.18	-----	-----	0.03	12.42

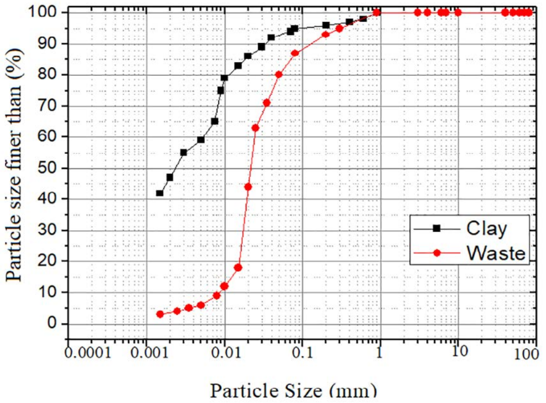

Figure 4. Particle size distribution of clay and the Sulfatreat waste.

to be mixed with clays to fabricate red ceramic products, such as bricks and roofing tiles.

Figure 5 shows the Atterberg plasticity diagram with limit and index for both the plain clay ceramic and the 10 wt% SW incorporated clay ceramic. In this diagram, one should notice that only the 10 wt% SW incorporated clay ceramic is within the accepted optimal extrusion processing for red ceramic products.

The linear shrinkage of all ceramic compositions, sintered at 850ºC, is shown in Fig. 6. In this figure a decrease in the water absorption is observed for amounts higher than 2.5 wt% of incorporated SW. Clay ceramic compositions with 7.5 and 10 wt% of waste showed a reduction of 4 and 9% water absorption, respectively. This reduction might be attributed to the high content of silt fraction in the SW, Fig. 4, which provides a convenient packing for the ceramic. In other words, these results indicate that the SW particles act as desirable filler due to their relatively coarser particle size.

Figure 7 shows the relative dry density of the clay ceramic samples as a function of the amount of SW incorporated. This relative dry density is the ratio between the apparent density by the real density evaluated by pycnometry technique. The addition of 7.5 and 10 wt% waste caused an increase of around 8% in the packing degree as a result of the high content of silt and sand in the SW. This behavior is due to the relatively higher density of the waste (2.69 g/cm^3) in comparison to the 2.65 g/cm^3 of the clay, as well as the greater packing action caused by the SW addition.

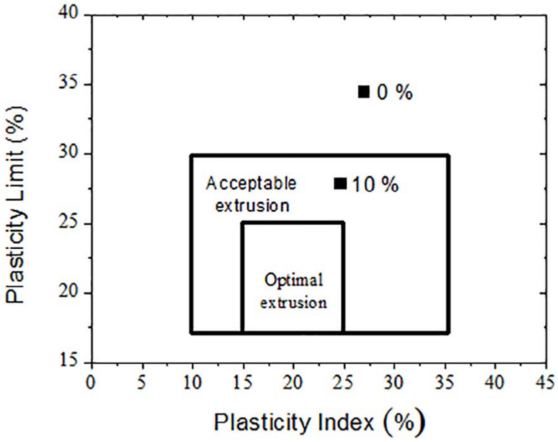

Figure 5. Plasticity index in the Atterberg diagram for plain and 10 wt% SW incorporated clay ceramic.

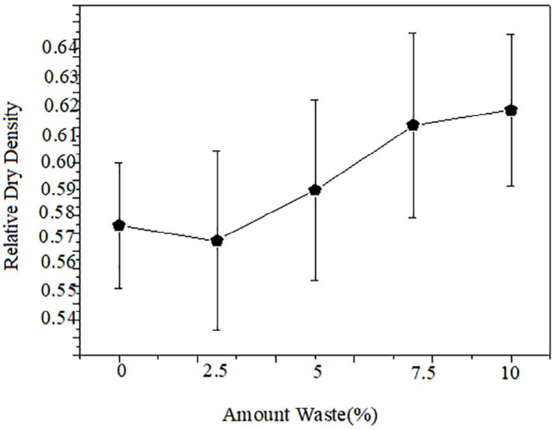

Figure 7. Apparent density of the different ceramic compositions.

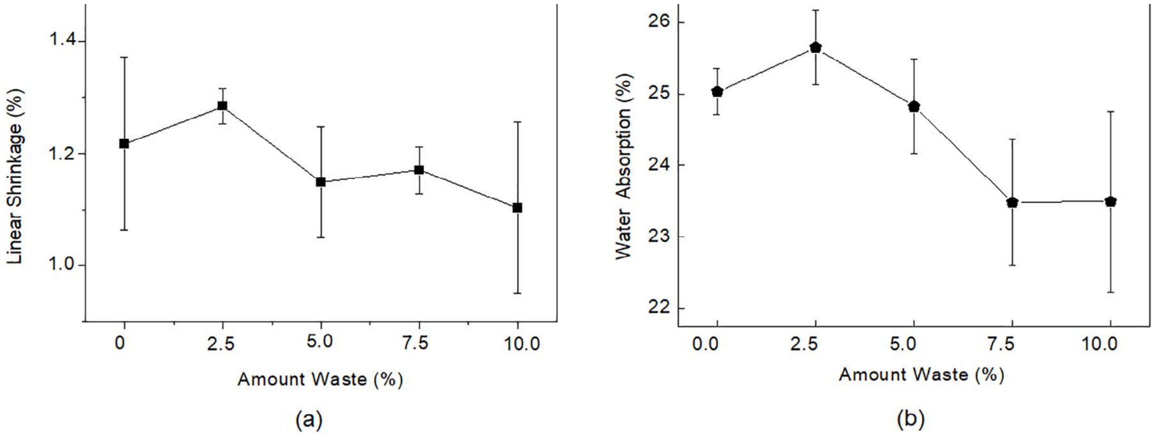

Figure 6. Linear shrinkage (a) and water absorption (b) of different ceramic compositions.

Figure 8 shows the flexural strength for different ceramic compositions sintered at 850ºC. It is important to note that all results are above the minimum value (2 MPa) recommended by the standard to produce massive bricks [32]. Although all investigated compositions attend the recommended value, it is observed a decrease in mechanical strength of the clay ceramic with incorporation of SW. This result might be assigned to the relatively coarser particle size of the SW shown in Fig. 4. Indeed, the larger quartz particles, later shown in the clay ceramic microstructure, came from SW incorporation. These polygonal-shaped particles act as stress concentration and contribute to the premature failure of the brittle ceramic at lower stress levels. Moreover, quartz would have a change in volume due to allotropic transformation at 573°C [33]. This might also contribute to cracks nucleation in the brittle ceramic, which would impair the flexural strength as shown in Fig. 8.

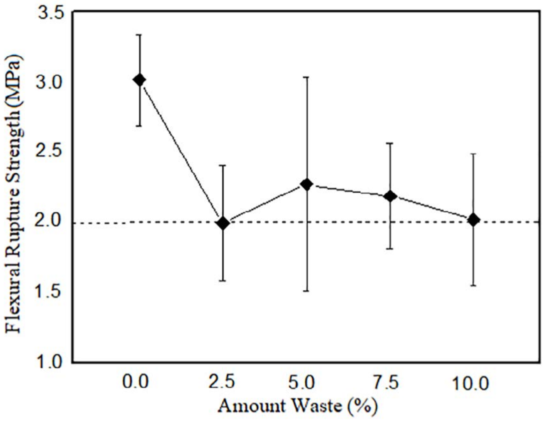

Figure 8. Flexural strength of the different ceramic compositions.

Figures 9 and 10 show optical microscopy images of the fracture surface of the ceramic with 0 and 10 wt% incorporated SW, respectively. All micrographs display a rough surface associated with some low consolidated particles. In Figure 8 it is observed small quartz particles (~50 µm) and muscovite mica elongated particles with size of 100 µm. Similar elongated muscovite mica particles are also observed in Fig 9 for the 10 wt% SW incorporated clay ceramic. In addition, some coarser quartz particles with size up to 200 µm were observed, which might significantly contribute to decrease the mechanical strength of the ceramic. It is worth mentioning that these particles in the SW act as a region of stress concentration causing small cracks around them, which is a critical factor to impair the mechanical strength of the investigated material.

In spite of the slight decrease in the mechanical strength caused by the SW incorporation, other improvements in the technical properties such as lower porosity and water absorption in association with possible reduction in cost and saving of clay extraction, strongly justify the fabrication of SW incorporated clay bricks. This first investigation on a Brazilian natural gas waste opens, for the first time, a viable solution for an increasing problem related to a relevant specific industrial waste management.

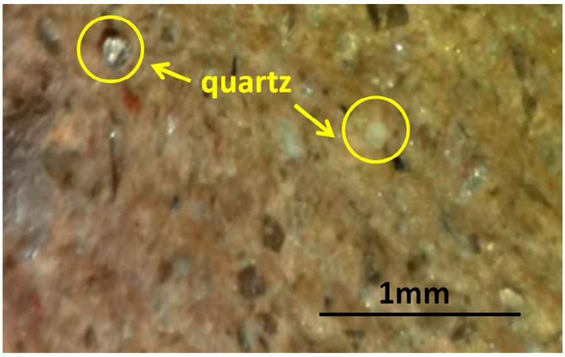

Figure 9. Fracture surface of the plain clay ceramic without incorporated waste.

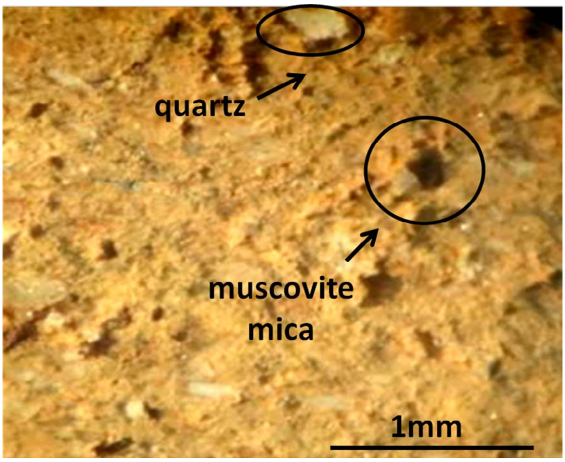

Figure 10. Fracture surface of the ceramic with 10 wt% of incorporated Sulfatreat waste.

Figures 11 and 12 show SEM images with higher magnification details of the particles associated with the fracture of the plain clay ceramic and the 10 wt% SW incorporated clay ceramic, respectively. The results in these figures corroborate those in Fig 9 and 10, particularly regarding the contribution of large elongated muscovite mica and coarser quartz particles in the 10 wt% SW incorporated clay ceramic.

Finally, Table 3 presents results of leaching and solubilization tests regarding the behavior of several metals including hazardous ones such as Mn, Cr, Zn, Pb and Ba existing in the SW, Table 2. These tests were performed at the Brazilian Institute of Technology (INT) according to the standards [34,35]. The results in Table 3 indicate that concentration of all toxic metals in the 10 wt% SW incorporated clay ceramic are below the limits imposed by the Brazilian standard [36]. Both Al and Fe are abundant in nature and not considered toxic metals.

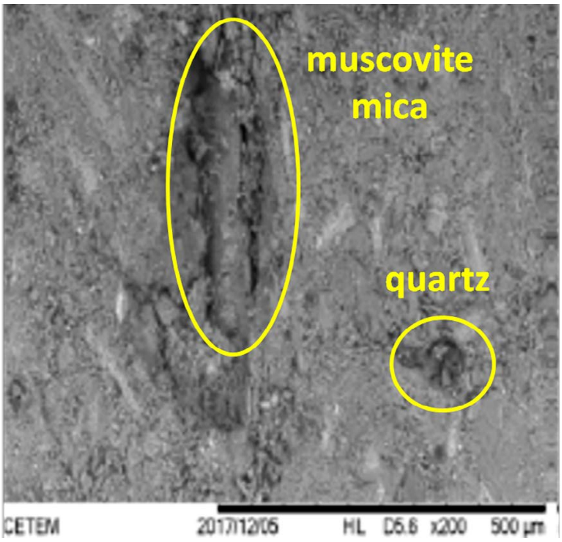

Figure 11. SEM fractography of the plain clay ceramic.

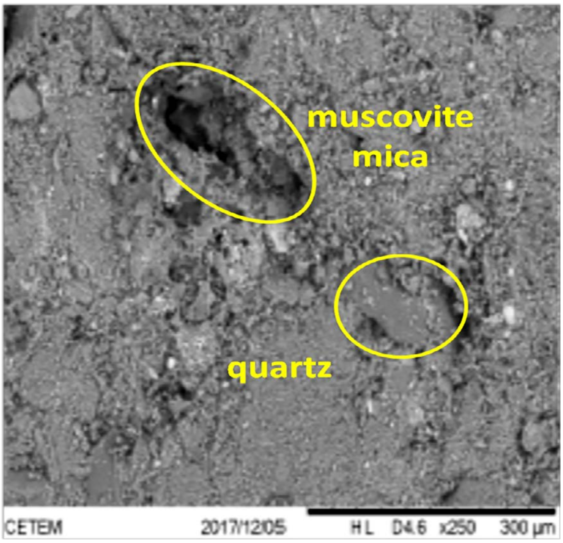

Figure 12. SEM fractography of the 10 wt% Sulfatreat waste incorporated clay ceramic.

Table 3. Results of leaching and solubilization tests.

	Concentration Leaching (mg/L)		Lim. Max. (mg/L) NBR 10004 [36]	Concentration Solubilization (mg/L)		Lim. Max. (mg/L) NBR 10004 [36]
	0%	10%		0%	10%	
Al	-	-	-	-	-	0.2
As	<0.008	<0.008	1.0	<0.008	0.025	0.01
Ag	<0.005	<0.005	5.0	<0.005	<0.005	0.05
Ba	0.19	0.04	70.0	0.11	0.19	0.7
Cd	<0.0004	<0.0004	0.5	<0.0004	<0.0004	0.005
Cr	0.011	0.010	5.0	<0.001	0.008	0.05
Cu	-	-	-	<0.004	0.168	2.0
Fe	-	-	-	0.11	-	0.3
Hg	<0.009	<0.009	0.1	<0.009	<0.009	0.001
Mn	-	-	-	0.006	0.035	0.1
Na	-	-	-	4.645	6.045	200.0
Pb	<0.008	<0.008	1.0	<0.008	<0.008	0.01
Se	<0.008	<0.008	1.0	<0.008	<0.008	0.01
Zn	-	-	-	0.054	0.107	5.0

4. Conclusions

- The Sulfatreat waste (SW) displays a particle size suitable for incorporation into red clay ceramics. The high amount of silt fraction in the SW promotes an increase of the green clay body packing, which contributed to decrease both the porosity before and after sintering. Consequently, the SW incorporation reduces the water absorption.
- The mineralogical composition of the SW also contributes to decrease the clay plasticity to an appropriate condition for the manufacture of special red ceramics such as roofing tiles.
- Clay specimens were successfully incorporated with up to 10 wt% of SW and sintered at 850ºC attending the recommended value for massive bricks, in spite of a decreased in the mechanical strength of the ceramic.
- The large production of SW in gas treatment units makes it a useful waste material to be incorporated into red clay ceramics and so becomes a viable and environmental friendly byproduct.

5. Acknowledgments

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