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QUALITY IMPROVEMENT OF CERAMIC BRICKS BY INCORPORATION OF SLUDGE FROM WATER TREATMENT UNITS

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ABSTRACT: *Sludge from water treatment units was incorporated into clay in order to produce bricks with enhanced performance on mechanical properties. The residue can be potentially reused due to mineral similarity with clay. Powder X-ray diffraction and FT-IR spectroscopy revealed that the main constituents of sludge and clay are mainly related to quartz, kaolinite, gibbsite and muscovite. Thermogravimetry assays showed good similarity on decomposition profiles, although the ash content after calcination at 1000ºC was for the sludge samples. Uppon addition of 10 to 15 % of sludge, values of compressive strength and water absorption index values reached acceptable limits, whilst the performance of pure-clay bricks performance was off-graded. These results demonstrate a potential recyclability of sludge in structural ceramic bricks, not only to comply with minimization of environmental impact but also to increase quality and market price of these products.*

KEYWORDS: Sludge from water treatment units; Ceramic; Recycling; Physical-mechanical properties.

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[1] **Abbreviations**

FT-IR – Fourier transform infrared spectroscopy
WTS – water treatment sludge
XRD – X-ray diffraction

TG/DTA – Thermogravimetric analysis coupled with differential thermogravimetric analysis
SEM – scanning electron microscopy
TEM – transmission electron microscopy
DBD – dried bulk density
WAI – water absorption index
CS – compression strength

1. INTRODUCTION

Traditional ceramic structural bricks are still on use for all types of buildings, although many alternatives are available in market. In Brazil, perforated ceramic bricks are the most common and they must have sufficient strength and must be resistant to climatic variations (Kizinievic et al., 2013). In order to achieve quality targets, the choice of good sources of raw material is critical. Traditional raw materials are clay, sand and breakstone of crushed bricks and additives may be used to improve properties of final products.

Water treatment plant sludge (WTS)[1] is a waste obtained by a series of physical-chemical processes on water treatment plants, as follows: coagulation, flocculation, sedimentation and filtration (Monteiro et al., 2008; Teixeira et al., 2006; Teixeira et al., 2011). Particularly in coagulation, colloidal particles are destabilized to form dense flocs mainly constituted of clay minerals, being attractive as an additive for ceramics production.

This sludge is usually discharged into rivers and streams or into the sewage system, causing environmental impacts as poor drinking water quality and threats to health of the public and animals that utilize it. Restrictions to WTS release made by environmental organizations and, particularly in Brazil, regulatory prohibitions do not prevent the discharge of this waste directly into water streams (Monteiro et al., 2008; Teixeira et al., 2011).

By these means, WTS presents a potential reuse as brick additive, especially to improve physical-mechanical properties. This paper reports the reuse of WTS as an additive in structural bricks in terms of physical-chemical properties, as heavy metal content, compressive strength, water absorption and density (Kizinievic et al., 2013; Monteiro et al., 2008; Oliveira et al., 2004; Teixeira et al., 2006; Teixeira et al., 2011; Vitorino et al., 2009; Weng et al., 2003).

2. MATERIALS AND METHODS

2.1. Materials

Water treatment sludge (WTS) was collected and supplied by Companhia de Saneamento de Minas Gerais (COPASA) from the water treatment plant of Patos de Minas county, Minas Gerais state, Brazil. The WTS was previously dried at room temperature prior for dryness content before milling in order to obtain a fine powder. Clay was supplied by the brick manufacturer Olaria Rio Ltda., located at Rio Paranaíba county, Minas Gerais state, Brazil and was tested as received. All reagents were used in analytical grade. The structural 8-hole bricks were produced according to Brazilian norms for all tests (ABNT, 2005a).

2.2. Characterization of clay, WTS and mixtures

X-ray diffraction (XRD) was performed in a XRD-6000, Shimadzu X-ray diffractometer (Cu-Kα1 radiation, 30 kV, 30 mA, 0.02º step). Thermogravimetric characterization (simultaneous TG/DTA) was performed in a SDT 2960, TA Instruments, at 5°C min^{-1} in dry air (100 mL min^{-1}). Fourier transform infrared spectroscopy (FT-IR) was carried out in a FT-IR 4100, JASCO spectrometer, 400 to 4000 cm^{-1} (resolution of 4 cm^{-1} and accumulation of 256 scannings). Scanning electron microscopy (SEM) was performed with a JEOL JSM-8404 scanning microscope. Elemental analysis was performed in a AA240FS, Varian spectrometer, by acid/oxidative digestion ($3HCl:1HNO_3/H_2O_2$) followed by flame atomic absorption spectroscopy. Total solids, volatile and fixed solids were determined according to American Public Health Association (APHA) standard methods (1998).

2.3. Bricks manufacture and characterization

Ceramic bricks were prepared by different mixtures with amounts of 0, 10, 12.5, 15% of WTS added to the clay. Three eight-hole bricks specimens were made to be tested in the following technological properties: dried bulk density (DBD), water absorption index (WAI) and compression strength (CS). Bricks were made following standard procedures described at Associação Brasileira de Normas Técnicas (ABNT) - NBR 15270-1 (2005a). DBD was calculated by the ratio of dry mass of the specimen to its volume. WAI and CS properties were determined according to ABNT - NBR 15270-3 (2005b).

3. RESULTS AND DISCUSSION

3.1. Characterization of clay, WTS and mixtures

The WTS dry content after drying at room temperature was 96.8 %. After milling, the sludge humidity was adjusted to the same value found at clay samples (39.0 %). DBD of sludge and clay were 1.03 and 0.83 g cm^{-3}, respectively, showing that clay samples provide higher porosity than WTS.

X-ray diffraction patterns indicated the presence of mineral phases commonly associated to clay composition (Chiang et al., 2009; Kizinievic et al., 2013; Monteiro et al., 2008; Oliveira et al., 2004; Teixeira et al., 2006; Teixeira et al., 2011) in both WTS and clay samples (Figures 1 and 2, respectively). The diffractograms show that the residue composition had good similarity to clay samples, due to peaks of quartz (Q), kaolinite (K), gibbsite (G) and muscovite (M). This may be explained by the predominance of one class of soil – oxisol – at the region where WTS and clay were collected, on which the clay fraction consists of kaolinite, gibbsite and goethite (Ferreira et al., 2004). Similar chemical composition suggests that chemical bonds formed between clay and WTS may, at least, preserve the structural properties of bricks after calcination.

FT-IR spectroscopy was applied to describe the main chemical functional groups present in WTS and clay mineral phases in order to assess possible chemical analogies between the materials studied. Figure 3 shows that both WTS and clay samples are similar with respect to adsorption bands, especially for silicon groups: 3450 cm^{-1} (axial deformation of Si-OH), 990 cm^{-1} (intense absorption band of Si-O-Si), 909 cm^{-1} (angular deformation of Si-H), 513 cm^{-1} (absorption band of Si-O-Al) and around 780 cm^{-1} (symmetric stretching of O-Si-O) (Silverstein and Webster, 2000). Three out of the four main components of WTS and clay have silicon in molecular formula, explaining the main FT-IR bands attributed to siliceous groups.

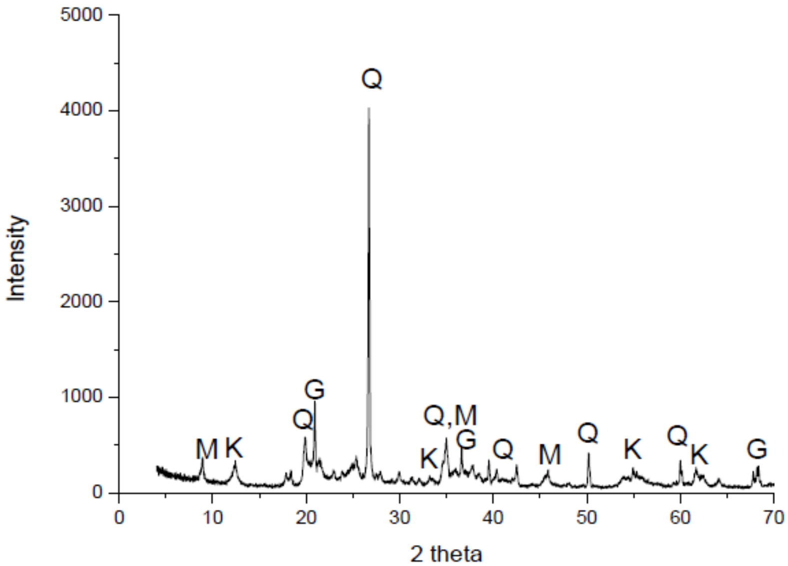

Figure 1 - X-ray diffraction patterns of WTS. Peaks are identified to following mineral phases: Q = quartz, K = kaolinite, G = gibbsite and M = muscovite.

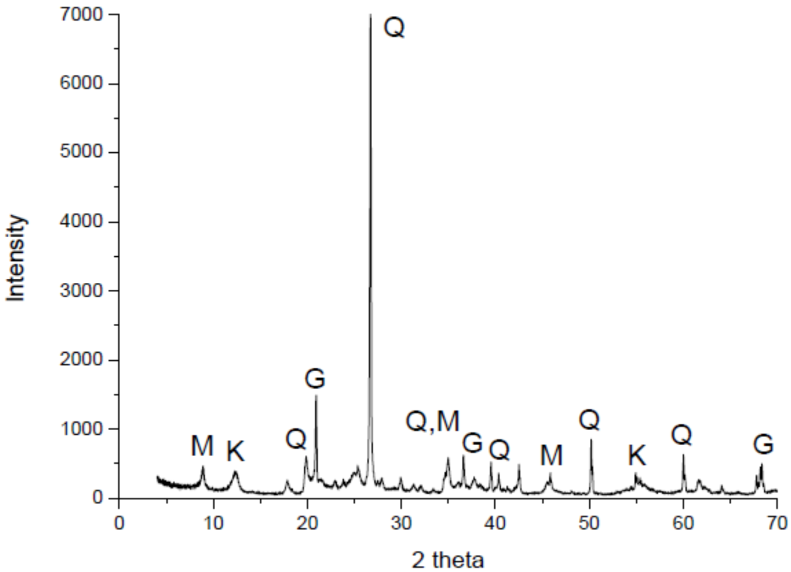

Figure 2 - X-ray diffraction patterns of clay. Peaks are identified to following mineral phases: Q = quartz, K = kaolinite, G = gibbsite and M = muscovite.

Scanning electron microscopy (SEM) of pure clay and WTS (Figures 4A and 4B, respectively) show both materials with irregular particle shapes, although grain size distribution is more homogeneous in WTS than in pure clay. Shape heterogeneity is shown in other works, varying from spherical with rounded edges to angular shaped with plain faces (Chiang et al., 2009; Kizinievic et al., 2013; Paixão et al., 2008). Aggregation of particles in denser round-edged clusters is observed in WTS (Figure 4B) suggesting that the average pore volume may be reduced in ceramic with WTS as an additive when compared with the bricks made with pure clay.

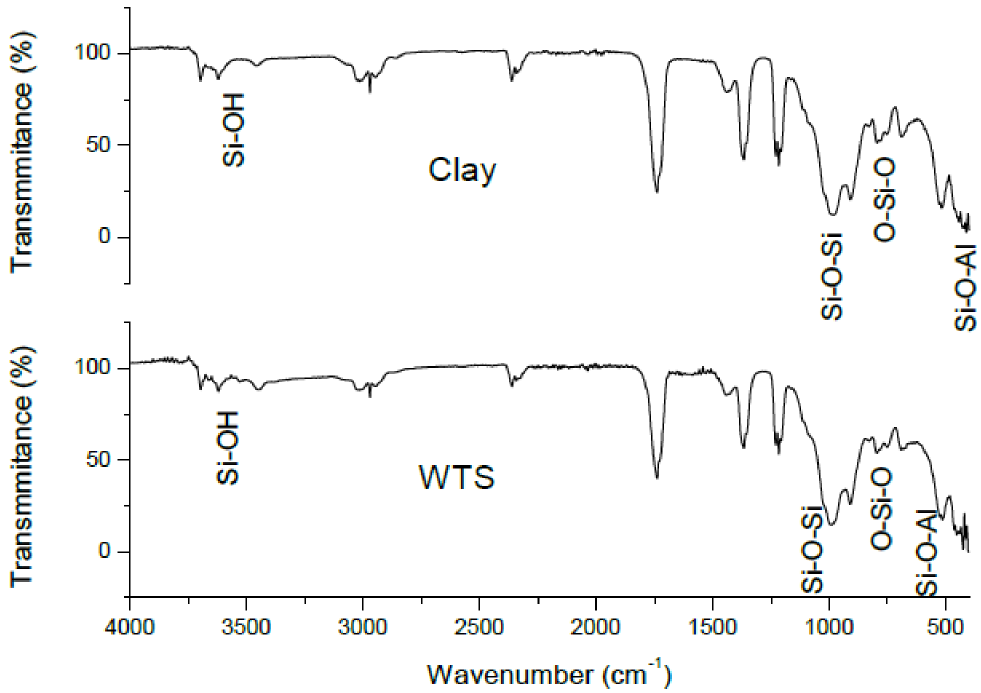

Figure 3 – FT-IR spectra of WTS and clay samples.

Elemental analysis was performed to evaluate the effects of heavy metals from WTS on bricks content. As can be seen in Table 1, the incorporation of WTS in the bricks did not affect considerably the heavy metals content, although the concentrations of some lighter metals and chemical compounds tend to double in

WTS samples. It is important to highlight that bricks made from clay/WTS mixtures may be used in all types of buildings, according to the environmental regulations for soil and water of Companhia Ambiental do Estado de São Paulo (CETESB) (2014).

The amount of organic matter should be low in ceramic bodies, because their porosity increases after calcination due to volatilization of organic compounds. In this study, organic matter was measured by volatile solids content after drying and calcination of raw material. WTS and clay volatile solids were 9.2 and 6.6% (w/w), respectively. The increase in porosity is not confirmed in our study when WTS is mixed with clay due probably to higher values of dried bulk density, as discussed above. According to literature, when calcination temperature (550 ± 50ºC) is reached, three phenomena may take place: organic matter volatilization (265-315ºC), chemically bonded water release (~510ºC) and modification of silica β-phase to α-phase (~572ºC) (Monteiro et al., 2008; Sadünas, 1999; Teixeira et al., 2006; Teixeira et al., 2008; Vitorino et al., 2009).

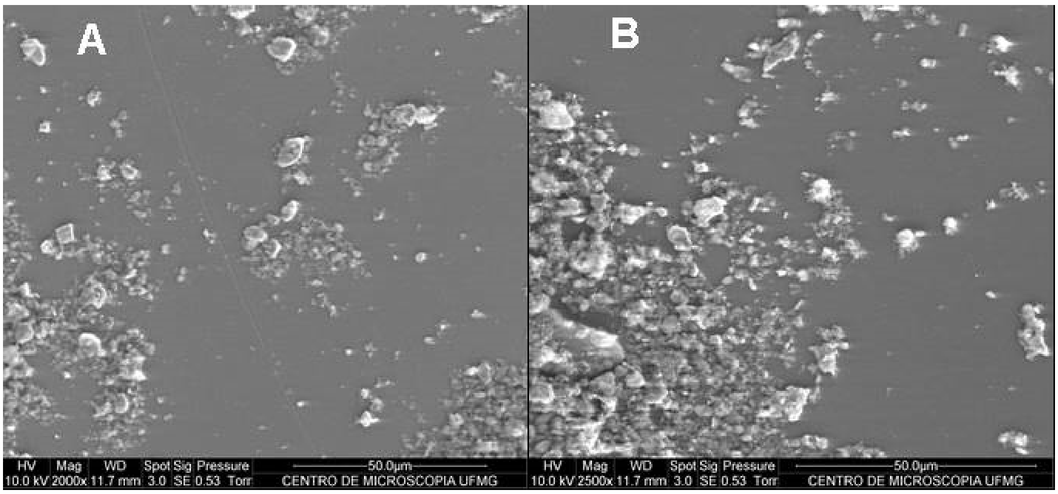

Figure 4 - Scanning electron micrographs of pure clay (A) and WTS (B).

Thermogravimetric measurements (TG/DTA) of pure clay and WTS are shown in Figure 5 and present different decomposition profiles. Pure clay and WTS present a small amount of moisture (100-200ºC), due to previous drying of clay and WTS. In the WTS thermogram, loss of water is observed at 230ºC and close to

296ºC, due to decomposition of hydroxides of aluminum and iron, calcination of organic matter and loss of interlamellar water from 2:1 clays (Monteiro et al., 2008; Teixeira et al., 2006; Teixeira et al., 2008). Clay and WTS present similar decompositions at 460-470ºC, related to kaolinite dehydroxylation (Monteiro et al., 2008; Oliveira et al., 2004; Teixeira et al., 2006; Teixeira et al., 2008; Teixeira et al., 2011).

Table 1 - Elemental analysis of clay, WTS and mixtures, in % (w/w).

% (w/w)	**Clay**	**WTS**	**Clay/WTS**			**CETESB limits, % (w/w) (2014)**
			90/10	**88.5/12.5**	**85/15**	
Zn	0.5333	0.5337	0.5334	0.5387	0.5334	1.00
Cr	0.0006	0.001	0.00064	0.000656	0.00066	0.04
Ni	0.00055	0.00120	0.00062	0.00064	0.00065	0.38
Cd	ND*	ND*	ND*	ND*	ND*	0.016
Pb	ND*	ND*	ND*	ND*	ND*	0.44
MnO	0.00595	0.01662	0.00702	0.00735	0.00755	
Cu	0.00030	0.00058	0.00033	0.00034	0.00034	1.00
Fe_2O_3	1.76	3.31	1.92	1.98	2.00	
Na_2O	13.15	14.57	13.30	13.46	13.37	
K_2O	4.83	9.40	5.28	5.45	5.51	
MgO	0.03053	0.03551	0.03103	0.03146	0.03128	
CaO	0.01334	0.03766	0.01577	0.01652	0.01699	

*ND – non-detected

The mixtures of clay and WTS present very similar thermogram profiles, as observed in Figure 6, although the ash content after calcination at 1000ºC varies as shown in Table 2. According to these results, the content of organic matter is higher in clay than in WTS samples, decreasing gradually when the content of WTS in clay increases. When bricks undergo calcination, all volatile organic matter is released, thereby creating pores in the brick structure. The porosity of the material increases with increasing content of organic matter, which can be disadvantageous since high-porosity bricks may cause wearing and tearing of the overall structure, due to several factors related to structure/water interactions (Lu and Lu, 1999; Raimondo et al., 2007).

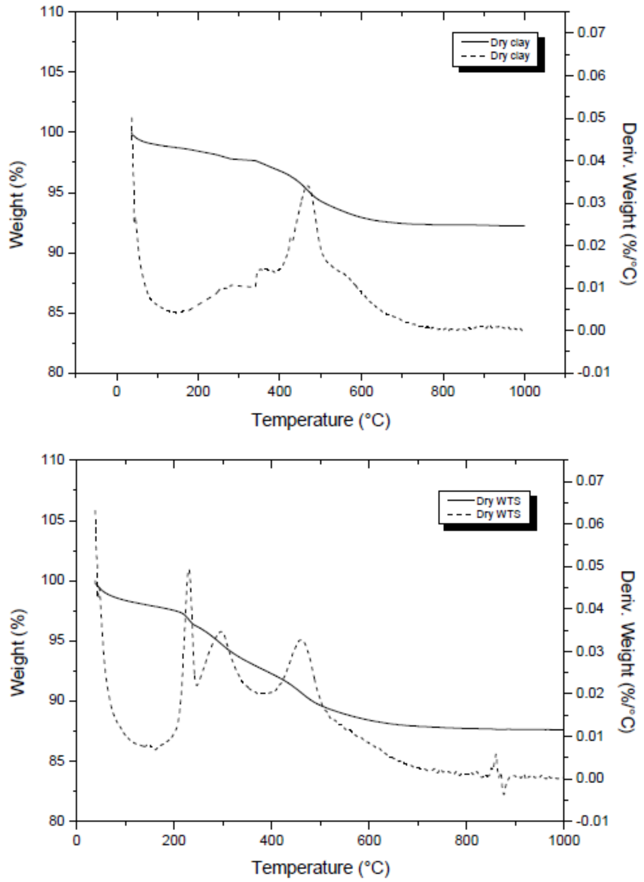

Figure 5 - TG/DTA thermograms of clay and WTS.

Table 2 - Ash content in raw materials used for bricks production.

Type of raw material	Ash content, %
Clay	87.60
WTS	92.21
Clay/WTS 85/15%	89.08
Clay/WTS 88.5/12.5%	90.28
Clay/WTS 90/10%	90.32

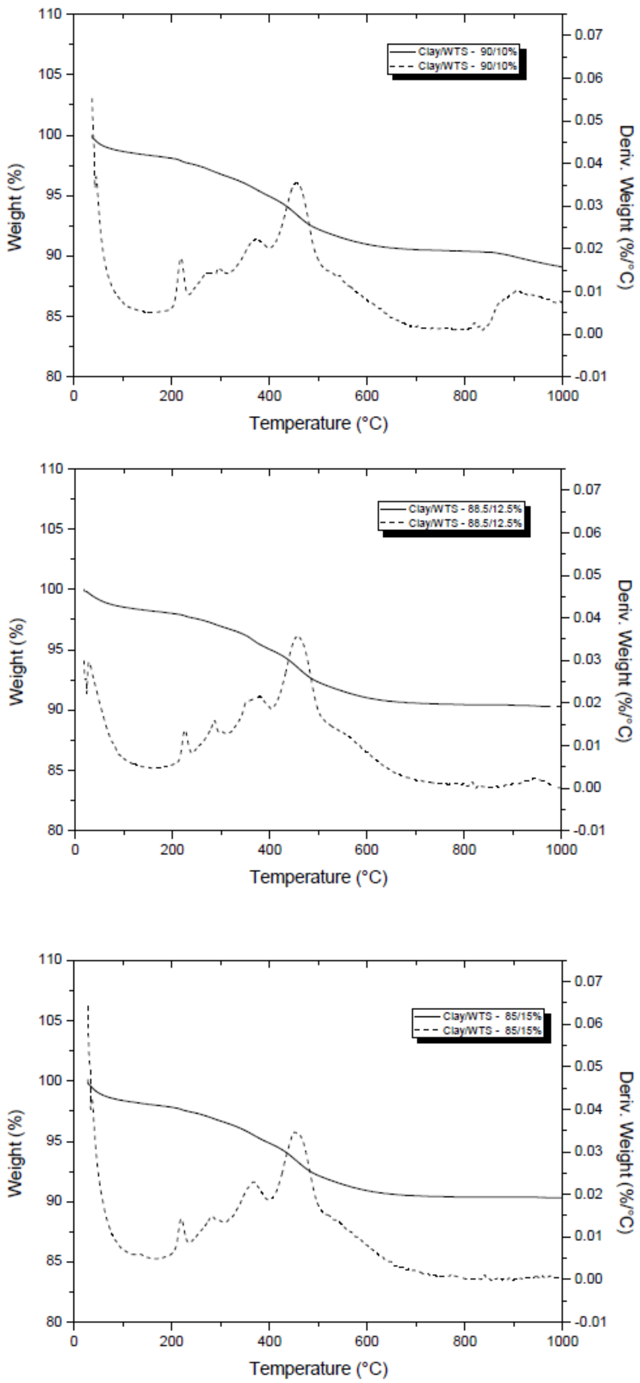

Figure 6 - TG/DTA thermograms of clay/WTS mixtures.

3.2. Bricks performance tests

Physical-mechanical properties of ceramic bodies were determined to evaluate the impact of sludge addition to their performance according to standards limits. The Brazilian norms (ABNT, 2005a; ABNT, 2005b) establish a range of 8-22% and a minimum of 1.5 MPa for WAI and CS in structural 8-hole bricks, respectively. Figure 7 shows results of CS and WAI for the bricks produced with clay and the mixtures of clay and WTS. When clay is unique as raw material, the bricks manufactured do not attend WAI and CS standard limits. On the other hand, addition of WTS to the raw material improve the performance of bricks, within the acceptable limits acceptance.

Reports in the literature indicate that CS values can decrease after 5% (w/w) of WTS added to raw material (Kizinievic et al., 2013), or can be reduced even upon addition of any amount of WTS (Vitorino et al., 2009). Other works report that water absorption increases when WTS is added to clay in brick manufacturing (Monteiro et al., 2008; Teixeira et al., 2006; Teixeira et al., 2011; Weng et al., 2003). These tendencies are attributed to the increase of pores and capillaries volumes during calcination of organic matter and water release (Kizinievic et al., 2013; Monteiro et al., 2008; Teixeira et al., 2006; Teixeira et al., 2011; Vitorino et al., 2009; Weng et al., 2003). In our study, the incorporation of WTS to the original material reduces both the amount and volume of pores and capillaries, probably due to increase in the dried bulk density (DBD) and ash content increase. These results agree with the Eshelby's equivalent inclusion method (Lu and Lu, 1999) predictions, where the inclusion (pores) and the body (material of brick) remain in a state under stress. However, the strain states in pores and brick material are heterogeneous and independent of the material composition. Since the added WTS does not affect the compressive resistance behavior, the main cause of this property improvement may be related to porosity variation due to WTS addition in bricks.

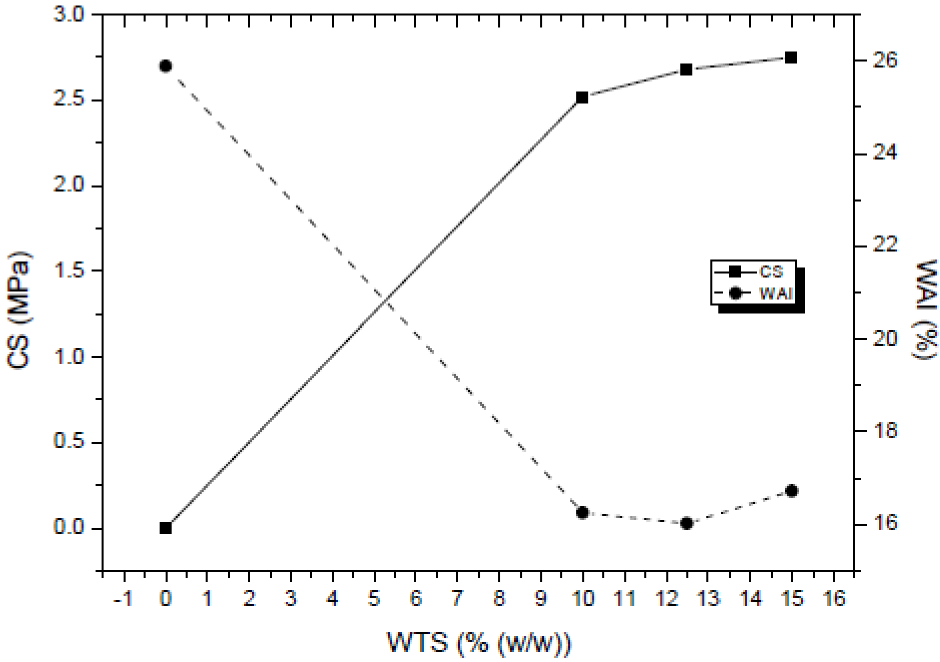

Figure 7 - WAI and CS of structural bricks.

4. CONCLUSIONS

In this work, the effect of the incorporation of sludge from water treatment units on the mechanical properties of clay bricks was examined. The sludge presented a mineral composition which is very similar to the clay used as raw material, although the content of heavy metal is higher in the waste. When the sludge is added in proportions up to 15 % (w/w), no significant environmental impact is observed in terms of heavy metals exposure. Compressive resistance increased and water absorption decreased continuously upon addition of sludge between 10 and 15 % (w/w), when compared with pure clay, at the same calcination temperature. The results confirmed that the quality of modified bricks was enhanced by complying with the minimum limits required by current legislation, showing that sludge from water treatment units is a valuable material for the production of structural ceramics.

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MELHORIA DA QUALIDADE DE TIJOLOS CERÂMICOS ATRAVÉS DA INCORPORAÇÃO DE LODO DE ESTAÇÕES DE TRATAMENTO DE ÁGUA

RESUMO: *Neste trabalho, lodo de estações de tratamento de água foi incorporado a argila para a produção de tijolos cerâmicos com elevado desempenho quanto a propriedades mecânicas. O resíduo possui potencial reúso devido à semelhança mineralógica com a argila. As técnicas de difração de raios-X no pó e espectroscopia vibracional na região do infravermelho com transformada de Fourier revelaram que os principais constituintes do lodo e da argila são principalmente relacionados aos minerais quartzo, caulinita, gibsita e muscovita. A análise termogravimétrica mostrou diferenças consideráveis nos perfis de decomposição, embora o teor de cinzas após calcinação a 1000ºC apresentou valores mais elevados na amostra de lodo. Após a adição de 10 a 15% de lodo, os valores de resistência à compressão e do índice de absorção de água alcançaram valores aceitáveis, enquanto os tijolos a partir de argila pura foram desclassificados pelo desempenho nestas propriedades. Estes resultados mostraram um potencial reúso de lodo como matéria-prima para tijolos cerâmicos, não somente para minimizar o impacto ambiental do resíduo, mas também para melhorar a qualidade e o valor agregado daqueles produtos.*

PALAVRAS-CHAVE: Lodo de estação de tratamento de água; Cerâmica; Reciclagem; Propriedades físico-mecânicas.