CHARACTERIZATION OF SLUDGE FROM WATER TREATMENT PLANTS (WTP) AND ITS USE IN RED CERAMIC

Silvio Rainho Teixeira
Gleyson Tadeu de Almeida Santos
rainho@fct.unesp.br
Tadeu_gtas@hotmail.com
Department of Physics Chemistry and Biology, São Paulo State University (UNESP)
Gilmar José Peixoto
gpeixoto@sabesp.com.br
SABESP

Abstract: This work presents the principal results of studies about sludge from decantation ponds of water treatment plants (WTP) in the Presidente Prudente-SP (Brazil) region. Initially the sludge was submitted to physical, chemical and mineralogical characterization. As this residue is generated by soil erosion in upstream locations, its grain-size distribution (silt, sand and clay) was studied throughout the year. Also evaluated was the influence of different chemical products used during the flocculation process. Finally, the effects of its incorporation on the properties of ceramic mass were determined. The characterization (TGA, DSC, DTA, XRD, particle size analysis and AAS) showed that this residue hás variable composition according to the WTP localization, the month of sludge production and the chemical used for flocculation. Technological tests (linear shrinkage, water absorption, flexural strength, and apparent porosity and density) of ceramic probes showed that depending on the temperature of firing and the sludge concentration, the measured values can be in accordance with the accepted limit values for the production of bricks. The sludge flocculated with aluminum chemicals was more deleterious than that obtained by using chemicals with iron. The results indicate that WTP sludge can be incorporated in raw materials used to produce red ceramics.

Keywords: WTP, Sludge, red ceramic, characterization.

1. INTRODUCTION

This work presents the results of an investigation carried out in three different periods (Teixeira et al., 2002; Teixeira et al., 2004; Teixeira et al., 2006), which evaluated sludge with regard to mineralogical composition, grain-size distribution and variation during the months of the year (seasonality). Finally, sludge from WTP obtained using different types of coagulants was incorporated into ceramic bodies with clay used to produce bricks, and the effect on technological properties was determined.

Water treatment plants (WTP) transform raw water into potable water utilizing a series of processes: coagulation, flocculation, decantation and filtration. The process of coagulation involve the use of Fe or Al salts that form floc with impurities from water, which sediment (or float) and are later filtered. This treatment produces a solid residue (sludge) with a high concentration of water whose composition depends on the origin of the raw water collected (surface water or groundwater through wells), the type of soil of the region, residues discharged in the river, chemical products, the process of treatment employed, etc. The main components of the sludge from WTP are: clay minerals, very fine-grained minerals, oxides and hydroxides of aluminum and iron, organic matter and contaminants, due to the discharge of urban and industrial effluents and other human activities. In general, this sludge is dumped directly into rivers and streams or into the drain system, causing a significant environmental impact, compromising water quality and health of the public and animal who utilize it. The growing concern of environmental organizations, due to the risks to health and to the environment, has led to the restriction or prohibition of discharging this residue into the environment (streams, landfills, soil, etc.).

Currently, there are more than 7500 complete cycle or conventional WTPs in Brazil, and the amount of sludge released into waterways is substantial. A comprehensive study was recently published (Andreoli et al., 2006) on the production, composition and constitution of sludge from WTP.

The sludge generated in WTP is a solid residue which should be properly treated and disposed without causing harm to the environment. One of the techniques applied in the preparation of sludge for disposal is dehydration, resulting in a pie with a concentration of solids of 60 to 70%. This pie can be destined for use as fertilizer, incineration, disposal in landfills for urban waste, and composting with urban waste, among other possibilities. More recently under study are alternatives, called beneficial, in which the residue is utilized or transformed into products that are useful to society. An important one among them is the utilization of residue in the fabrication of cement, ceramic masses and restoration of degraded areas. Its incorporation into ceramic masses for the production of bricks and roof tiles is a viable practice and is very interesting due to the facilities and availability of this type of industry (Portella et al.; 2003; Cosin et al.; 2002; Teixeira et al., 2002, 2004, 2006; Menezes et al., 2002; Santos et al., 2001; Ramirez et al., 2001; Oliveira et al., 2004; Ueno ET al., 2006). In a recent publication, Ingunza et al. (2006) presented a review on the use of the residues from sewage treatment in the fabrication of red ceramics. The red ceramic industry is a very important sector and is spread throughout all of Brazil.

It uses common basic clays as the primary matter, totaling a consumption greater than 80 million tons/year (ABC, 2002). Sludge from WTP, mainly from the treatment of surface water, can be incorporated into ceramic masses; considering its mineralogical composition, the sludge does not significantly alter the final physical properties of the sintered pieces. The principal aspect of the incorporation of sludge in ceramic masses would be the contribution to minimizing an environmental problem, considering that at the moment clay represents na insignificant portion of the final value of the product.

This work presents the results of the characterization of sludge from WTP, obtained with different coagulants, having seasonal changes in its grain-size distribution, and the results of technological tests of ceramic probes formed with clay used to produce ceramic bricks, containing sludge from WTP. The aim of the study was to determine the possibility of incorporating sludge from WTP into ceramic masses used by the red ceramic industry for the purpose of its utilization.

2. MATERIAL AND METHODS

Samples were collected on the washing dates of decanter number one of the WTP of SABESP in Presidente Prudente, from 2001 to 2004. During this period, three different coagulants were utilized (aluminum sulfate, ferric chloride and aluminum polychloride), and samples were collected monthly in the last step for ten months. The tank was divided into six parts, and two liters of sludge were obtained from each one, totaling twelve liters per sampling. The samples were dried in an oven at 110°C, broken up and pulverized in a blade mill, and the resultant material was then passed through a # 40 sieve (0.42 mm) and mixed. Concentrations of organic matter (OM) were determined by the Walkley-Black method and the concentrations of the sand, silt and clay fractions by the pipette method, in the samples of sludge and clay, with prior oxidation of the organic matter using hydrogen peroxide (Dixon & White, 1996; Klute, 1986; EMBRAPA, 1979; IAC, 1983). The main Clay minerals present in the sludge were identified using X ray diffractometry. Chemical analysis of a sample of sludge, to test for the presence of heavy metals, was carried out using atomic absorption spectroscopy (AAS). The samples were submitted to thermal analysis (thermogravimetric,TG; calorimetric, DSC; and thermodifferential, DTA) Ceramic probes (CPs) were pressed uniaxially (19 Mpa, 60 x 20 x ~5 mm3) in triplicate, using clays from the region (Teixeira et al., 2001) with concentrations of sludge varying from 0 to 30%. After burning in a laboratory kiln at five temperatures varying from 850 to 1200 oC the CPs were submitted to technological tests for evaluation of ceramic properties: water absorption (WA), apparent specific mass (ASM), weight loss after firing (FL), apparent porosity (AP), three points flexural strength (FS) and linear shrinkage (LS) (Souza Santos, 1989).

3. RESULTS AND DISCUSSION

3.1 Grain-size distribution

Texture analysis showed that the fractions clay, silt and sand varied seasonally. The percentages of these fractions differed depending on the time of year in which the sludge was produced. Figure 1 shows the variation of the fractions and of organic matter, in the tem months of collection. Figure 2 shows the variation in the level of the river in the locality where water was drawn for WTP. The months of June to September are the ones with less incidence of rain in the region. Organic matter did not show considerable variation, while the concentration of sand and clay showed a tendency, that is, concentrations varied inversely with the level of the river. The concentration of clay in this and other steps of the work, varied 30 to 60% and was greatest in the period of greatest incidence of rain.

Based on the Winkler diagram (Pracidelli & Melchiades, 1997), summarized in Table 1, which shows the ideal grain-size distribution for each type of ceramic material, it can be seen that sludge has a concentration of clay that gives it an ideal plasticity for the fabrication of roof tiles and ridge caps. As can also be observed, concentrations of clay greater than 40% confer high plasticity to the ceramic mass, causing problems in the drying and firing process of ceramic pieces. In some cases, the concentration of sand (non-plastic material) is also very high, which worsens the properties of the ceramic material. Therefore, clay to be used to receive the sludge should show concentrations of clay and sand compatible with those in the sludge.

The concentrations of the grain-size fractions obtained showed that the sludge can be considered as natural raw material for the production of ceramic materials. In general, ceramic industries mix two or more clays with different grain-size compositions to obtain the ceramic mass appropriate for each product. Thus, sludge can be one of the components of the mixture to give the desired plasticity and composition to produce a particular type of ceramic material.

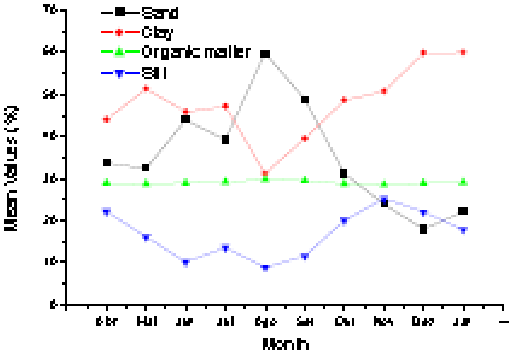


Figure 1: Monthly variation of grain-size fractions and concentration organic matter of sludge.

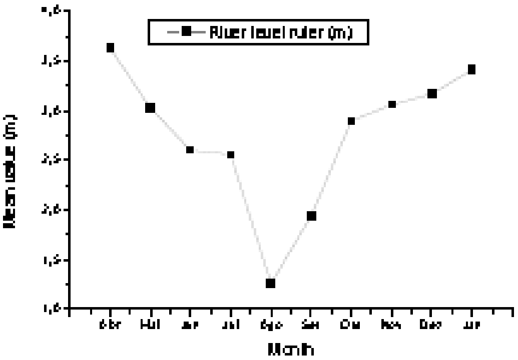
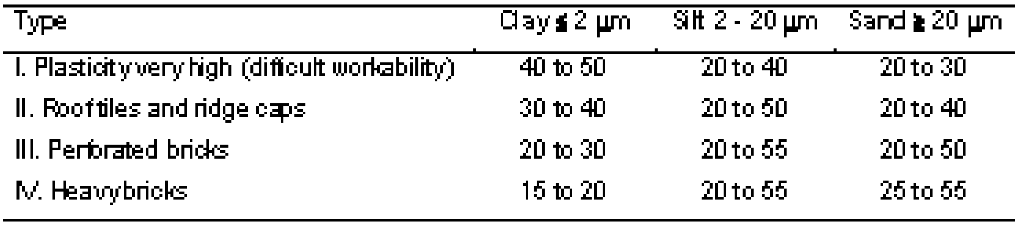


Figure 2: Measure of mean monthly water level of the river at the point of collection.

Table 1: Ideal grain-size distribution for ceramic masses according to the Winkler diagram.



Type	Clay ≤ 2 μm	Silt 2 - 20 μm	Sand ≥ 20 μm
I. Plasticity very high (difficult workability)	40 to 50	20 to 40	20 to 30
II. Roof tiles and ridge caps	30 to 40	20 to 50	20 to 40
III. Perforated bricks	20 to 30	20 to 55	20 to 50
IV. Heavy bricks	15 to 20	20 to 55	25 to 55

3.2 X-ray Diffraction and Chemical Analysis

Diffractometric analysis of the clay minerals of the region (Teixeira et al., 2001) showed that kaolinite (7.23 and 3.59 Å) is the predominant clay mineral, with the presence of mica (10.68 and 5.01 Å), goethite (4.16 Å) and quartz (3.33 Å). Some clays also have, in lower concentrations, other iron oxides, titanium oxides, gibbsite and type 2:1 clay minerals. The ceramics of the region use floodplain clays which have a similar mineralogical composition.

Therefore, from a mineral point of view, sludge also has a composition similar to that of clays used by ceramics factories. Figure 3 shows the diffractogram of the oriented clay slide of the sludge sample, collected in the month of August, obtained using aluminum polychloride as coagulant. Here, the main clay minerals noted above can be identified.

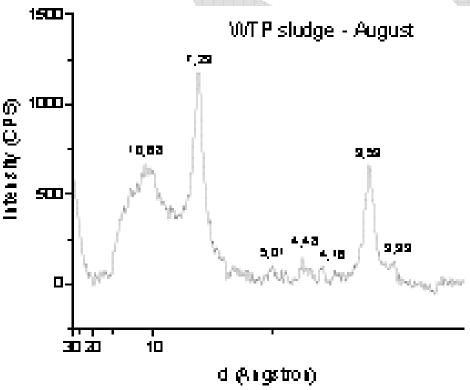


Figure 3: X-ray diffraction pattern of the clay in the WTP sludge.

Chemical analysis (X-ray fluorescence – XRF) of a sample of sludge, showed that iron, silicon, aluminum and titanium were the main components of the sample, with small concentration of calcium. Quantitative analysis by atomic absorption spectrometry (AAS) showed that the concentrations of the heavy metals Pb (0.42 ppm), Cr (4.60), Zn (31), Mn (121), Al (0.43) and Cu (15) were well below the limit values recommended by environmental oversight bodies. This result was expected since this is farming region with few industries. The concentration of Fe (130,800 ppm) is high due to the coagulant used which has an iron base. The presence of heavy metals in the sludge does not prohibit its incorporation in ceramic materials, considering that these metals can be incorporate and inertized in the crystalline structure of vitreous phases formed during the sintering process of ceramics.

3.3 Thermal Analysis

Figure 4 shows the thermograms (TG) for two samples of sludge with iron and one with aluminum, collected at different periods. The thermogravimetric analysis data showed that there was a loss of moisture of approximately 9 %, loss of water through hydroxides and burning of organic matter on the order of 7% and loss of structural water from kaolinite of 7%. Figure 5 shows the data for differential scanning calorimetry (DSC) of sludge from WTP with two different coagulants (Fe and Al), of the clay used for the production of roof tiles and of kaolin from Georgia (USA).

Comparing the diagrams, it can be seen that all three samples showed kaolinite as the main clay mineral. Besides the loss of free water (~100ºC), an exothermic band, characteristic of organic matter (200-400ºC), was also observed in all the samples. The peak of organic matter was greater in the samples of WTP sludge due to its concentration, together with the clays, in the chemical process of flocculation. The fine peak, observed at 576ºC, is characteristic of the phase transition a«b of quartz, present in the Clay sample.

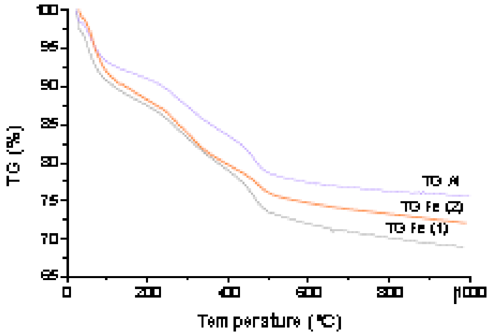


Figure 4: Thermogravimetric data of WTP sludge (using iron chloride and aluminum sulfate).

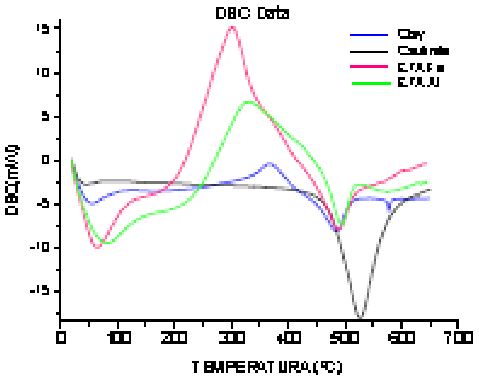


Figure 5: Differential scanning calorimetry (DSC) data of brick clay, kaolin, sludge iron and luminum.

3.4 Technological Tests

In general, the results of the technological tests showed that the incorporation of sludge from WTP consistently worsened the technological properties of the ceramic materials. The results with sludge obtained using the coagulant aluminum sulfate (sludge-Al) were always poorer than those with ferric chloride (sludge-Fe). In general, aluminum increased the refractivity and friability of samples, while iron reduced them in addition to being able to react with mica and to form glass. However, since sludge was collected at different periods, other factors such as mineralogical composition and texture could have influenced these results.

Considering flexural strength and water absorption, it was observed that for firing temperatures ³ 950 oC, the addition of 10 % sludge-Al and 20 % sludge-Fe, still yielded values within the limits established for technical standards (Teixeira et al, 2006). In the work carried out with samples collected monthly, sludge obtained using the coagulant aluminum polychloride, the clay used for the incorporation of sludge was different than before. Figures 6 to 9 show the results of technological tests for clay with sludge (10, 15 and 20%) collected in the month of August, which had a greater concentration of sand (Fig.1). The variation in the properties of the samples was approximately equal for the additions of 15 and 20% sludge, which was greater than that for 10%. The graphs show that the incorporation of sludge increased water absorption, decreased flexural strength and the apparent specific mass. This effect is due mainly to the high concentration (29 %)

of organic matter in sludge, which increases the porosity of the sample during firing (Teixeira et al, 2006).

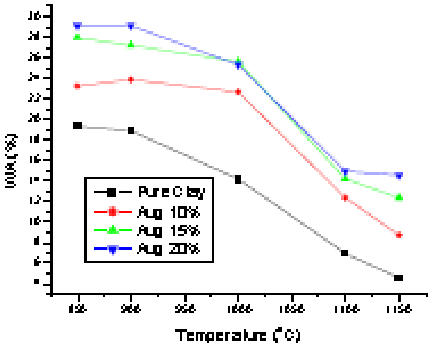


Figure 6: Water absorption (WA) by ceramic probes with incorporated sludge (August).

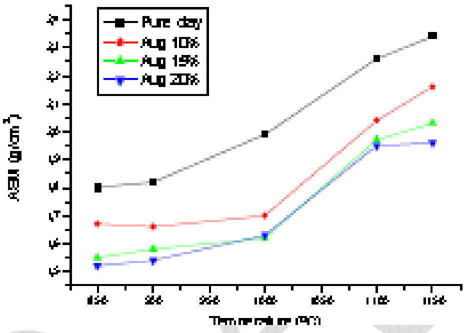


Figure 7: Apparent specific mass (ASM) ceramic probes with incorporated sludge.

The high concentration of sand in this sludge decreased linear shrinkage and also contributed to the worsening of other technological properties of the ceramic probes: increase in water absorption, decrease in apparent specific mass and flexural strength. In the clay with 10 % sludge, the variation of these properties with temperature was similar to the behavior of the property curves for pure clay. All the properties of clay with sludge have little variation below 1000 oC. At this temperature up to 1100 oC, the variation was abrupt, and then for the greater concentrations of sludge, the properties tended to stabilize. This effect, better ceramic properties with increase in temperature, was already expected since a liquid phase occurs above 1000 oC, with greater densification of the ceramic probe. However, the slowdown reaction between 1100 and 1150 oC was not expected, indicating that with sludge the densification reactions occurred at temperatures lower than those for pure clay and crystallization of new phases could have occurred with the production of microfissures. These microfissures tend to increase water absorption and decrease apparent specific mass, mechanical resistance and linear shrinkage.

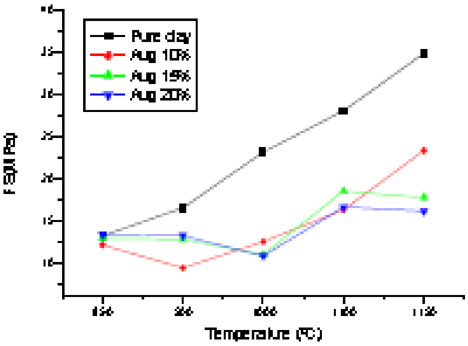


Figure 8: Three-point flexural strength (FS) for ceramic probes with incorporated sludge.

Linear firing shrinkage (Fig. 9) changed little at low temperatures due to the high concentration of sand (non plastic material) in sludge. Above 1000 oC, there was a substantial increase in linear shrinkage due the formation of a liquid phase, up to 1100 oC. At these temperatures, it is more evident for CPs with sludge due the presence of fluxing material (mica and goethite) in sludge (Fig. 3). Again, there was a change in behavior at 1150 oC for samples with a greater (15 and 20 %) concentration of sludge.

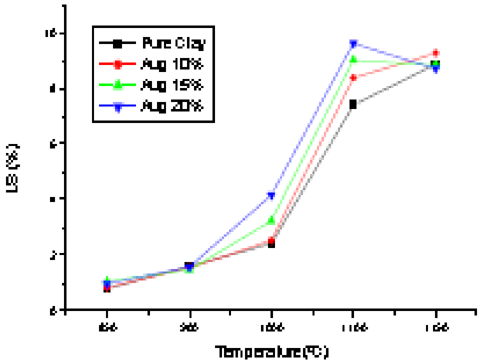


Figure 9: Linear firing shrinkage of ceramic probes with incorporated sludge.

Despite that sludge worsens the technological parameters, some of these are still within the limit values (minimal or maximal) established for the production of bricks and roof tiles. The quantity of sludge that can be incorporated is determined by the properties of the sludge and mainly of the ceramic mass used as the matrix.

4. CONCLUSIONS

The chemical and mineralogical composition of WTP sludge is similar to the natural primary matter used by the regional red ceramic industry. It is a plastic material due to the high concentration (> 30 %) of clay minerals and organic matter. Therefore, it can be incorporated into ceramic masses.

The concentration of sludge to be incorporated will depend on its properties (grain-size distribution, chemical and mineral composition), and mainly on the properties of the bonding clay (matrix) of the sludge. The type of coagulant used can also influence the properties of the sintered ceramic material.

Acknowledgements

The authors thank SABESP of Presidente Prudente for the collaboration, FAPESP for fellowships and grant support and CNPq/PIBIC program for the students' scientific initiation grants. To under graduation students (S. A. Souza, N. R. Souza and P. Alessio) for the collaboration and to Dr. A. Leyva for help with the translation and editing of the manuscript

REFERENCES

Andreoli, C. V. (Coord.), 2006. Alternativas de uso de resíduos do saneamento, Projeto PROSAB, vol. 4 Biossólidos, ABES, Rio de Janeiro, 398 p.

ABC, Associação Brasileira de Cerâmica, Anuário Brasileiro de Cerâmica, 2002. Cerâmica Vermelha, São Paulo, pp. 74-78.

Cosin, S., Kozievitch, V. F. J., Tavares, D. T., Vianna, M. M. G. R., Toffoli, S. M., Santos, P. S. & Diaz, F. R. V., 2002. Incorporação de lodo de estação de tratamento de água em massa cerâmica. In ABC 46º Congresso Brasileiro de Cerâmica (46° CBC) , São Paulo – SP (CD-ROM).

Dixon, J. B. & white, G. N., 1996. Soil Mineralogy Laboratory Manual, Soil & Crop Sciences Department, Texas A & M University, College Station – Texas, 139 p.

EMBRAPA, 1979. Serviço Nacional de Levantamento e Conservação de Solo, Manual de Métodos de Análise de Solo, Rio de Janeiro.

IAC, Instituto Agronômico de Campinas, Boletim no 81,1983. Método de Analise de Solos para Fins de Fertilidade, B. Van Ray & A. J. B. Quaggio, São Paulo.

Ingunza, M. P. D., Andreoli, C. V., Nascimento, R. M., Tinoco, J. D., Hoppen, C. & Pegorini, E. S., 2006. Uso de resíduos do saneamento na fabricação da cerâmica vermelha. In Andreoli, C. V. (Coord.), Alternativas de uso de resíduos do saneamento, pp 283-359.
ABES/PROSABE.

Klute, A. (Ed.), 1986. Methods of Soil Analysis: Physical and Mineralogical Methods Part 1, Second Edition, Soil Science Society of America Book Series, n. 9 (Part 1) Agronomy Series, Madison, Wisconsin, USA.

Menezes, R. R., Neves, G. A. & Ferreira, H. C., 2002. O estado da arte sobre o uso de resíduos como matérias-primas cerâmicas alternativas, *Revista Brasileira de Engenharia Agrícola e Ambiental*, vol. 6, pp. 303-313.

Oliveira, E. M. S., Machado, S. Q. & Holanda, J. N. F., 2004. Caracterização de resíduo (lodo) proveniente de estação de tratamento de água visando sua utilização em cerâmica vermelha, *Cerâmica*, vol. 50, pp. 324-330.

Portella, K.F., Andreoli, C.V., Hoppen, C., Sales, A. & Baron, O., 2003. Caraterização físicoquímica do lodo centrifugado da estação de tratamento de água Passaúna, Curitiba – Pr. In ABESA *22º Congresso Brasileiro de Engenharia Sanitária Ambiental (22° CBESA)*, Joinvile – SC (CD-ROM).

Pracidelli, S. & Melchiades, F. G., 1997. Importância da Composição Granulométrica de Massas para Cerâmica Vermelha, *Cerâmica Industrial* , vol. 2, pp. 31-35. Ramires, M. V. V., Santos, I. S. S., Kazmierczak, C. S., Silva, H. C., Kern, A. P., Camargo, S. A., 2001. Incorporação do resíduo (lodo) da ETA de São Leopoldo-RS nas misturas de argilas para a fabricação de componentes cerâmicos conformados por prensagem.
In ABC *45º Congresso Brasileiro de Cerâmica (45° CBC)* Florianópolis – SC (CD-ROM).

Santos, I. S. S., Ramirez, M. V. V., Kazmierczak, C. S., Silva, H. C., Kern, A. P., Camargo, S. A., 2001. Reciclagem do resíduo (lodo) da estação de tratamento de água de São Leopoldo-RS, visando a produção de componentes cerâmicos. In ABC *45º Congresso Brasileiro de Cerâmica (45° CBC)* Florianópolis – SC (CD-ROM).

Souza Santos, P., 1989. *Ciência e Tecnologia de Argilas*, vol 1 e 2, 2a Edição, Ed. Edgard Blücher Ltda.

Teixeira, S. R., Souza, S. A. & Moura, C. A. I., 2001. Mineralogical Characterization of Clays Used in the Structural Ceramic Industry in West of S. Paulo State, Brazil, *Cerâmica*, vol. 47, pp 204-207.

Teixeira, S. R., Souza, S. A., Souza, N. R., Job, A. E., Gomes, H. M., Heitzmann Neto, J. F.,2002. Caracterização de resíduos de estação de tratamento de água (ETA) e de esgoto (ETE) e o estudo da viabilidade de seu uso pela indústria cerâmica. In *XXVII Congresso Interamericano de Engenharia Sanitaria y Ambiental*, Cancun-México (CD-ROM).

Teixeira, S. R., Souza, S. A. & Nobre, M. A. L., 2004. Physical and mechanical properties of ceramics from clays of the west of S. Paulo State, Brazil, *Cerâmica*, vol. 50, pp. 268-273.

Teixeira, S. R., Aléssio, P., Santos, G. T. A., 2006. Efeito da adição de lodo de estação de tratamento de água (ETA) nas propriedades de material cerâmico estrutural, *Cerâmica*, vol. 52, pp. 215-220.

Teixeira, S. R., 2006. *Caracterização de argilas usadas para produção de cerâmica vermelha e estudo das alterações nas suas propriedades pela adição de resíduos sólidos*. Tese de Livre Docência, Universidade Estadual Paulista – UNESP, Presidente Prudente – SP.

Ueno, O. K. & Leite, V. M. B., 2006. Estudo da viabilidade técnica de incorporação do lodo proveniente do processo de tratamento de água para abastecimento na confecção de produtos de cerâmica vermelha. In *50° Congresso Brasileiro de Cerâmica (50° CBC)* , Blumenau – SC (CD-ROM)