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# Characterization Of Sewage Sludge Ashes To Be Used As A Ceramic Raw Material

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The sewage sludge produced in one of the largest Brazilian wastewater treatment stations was characterized to evaluate it use as raw material for the ceramic industry. Sludge firing in air was evaluated by thermal analysis and by X-ray diffraction (XRD) at ceramic processing conditions. In the original dry sludge, quartz, ilite, kaolinite, dolomite, microcline and gibbsite are present. After being fired to 1050°C, Hematite, Quartz, Tridymite, Mulite and Anorthite are present in the ashes. Trace elements like Ba, Ce, Cl, Co, Cr, Cu, F, Ga, La, Nb, Nd, Ni, Pb, Rb, S, Sc, Sr, Th, U, V, Y, Zn and Zr were identified by X-ray fluorescence (XRF). Leaching test of the calcinated sludge shows very low concentration of contaminants, due to the fact that they were stabilized in the ceramic matrix and indicate that it can be used as an environmentally safe ceramic raw material.

Keywords: Sewage sludge ash, raw materials, TA, XRD and XRF.

## Introduction

Sewage sludge is being generated in an ever-increasing amount due to the urbanization (Morais et al., 2006) and higher effluent criteria implemented in recent years. Without proper treatment and disposal, it will cause a secondary pollution problem in the environment (Chen et al., 2002 and Gómez et al. 2005).

The conventional disposal options include landfill, incineration and forestry application. The heat-treated wastes had high chemical durability and would be safe for landfill or for re-use in a number of potential applications (Colombo et al., 2003 and Bingham et al., 2005).

In recent years, various uses of incinerator ash have been developed in order to ease the burden of the disposal [6]. For example, the ash has been used to replace part of the Portland cement to make construction materials, e.g. brick, paving block, tile; previous studies have show that with such treatment, heavy metal release from brick of ash considerably decreases by sintering or cement consolidation (Wiebusch et al., 1999 and Mangialardi et al., 1998).

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## Materials And Methods

### The waste and thermal analysis

Dry sludge produced in one of the largest Brazilian wastewater treatment stations in Barueri, in the metropolitan area of São Paulo, Brazil, was analyzed by simultaneous TG/DTA in a TA-Instruments model SDT2960 in platinum pan, using 100ml $min^{-1}$ of air flow, as purge gas at a heating rate of 10°C $min^{-1}$ from 25°C to 1000°C. The thermogravimetric (TG), derivative thermogravimetric (DTG) and differencial thermal analysis (DTA) curves were obtained by software.

### XRD

X-ray diffraction analysis was done in a model D5000, Siemens XRD analyzer, using copper K-$\alpha$ radiation, with $2\theta$ from 3°C to 65°, with 0.05 °C/s steps, to identify the crystalline mineral components of the sludge. X-ray patterns were interpreted by DiffracPlus software, using ICDD (JCDS) – PDF2 files, version 2001.

### XRF

The sludge sample fired at 1050C for three hours was analyzed by X-ray fluorescence spectrometry using a Philips-PW2510 spectrometer with type tube PW2592/ 15 Rh and molten pastilles with Lithium Metaborate and Lithium Tetraborate, to determine oxides and trace elements as heavy metals.

### Leaching test

A liquid-to-solid ratio of 50:1 was used to determine 0.1M $HNO_3$ extractable and distilled water extractable metals. The 0.1M $HNO_3$ sludge solution was shaken for one hour. Al, Ba, Cr, Cu, Fe, Ni and Zn leached were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, an ARL-3410, sequential spectrometer, UK).

## Results And Discussion

### Thermal analysis

Figure 1 shows the TG, DTG and DTA curves of the dry sludge in air. From TG curve it can be seen that up to 150°C, there is the residual humidity mass loss characterized by the respective DTG peak and by an endothermic DTA peak. There is a significant mass loss until 350°C in a first step, followed by a second one, which ends at 600°C, characterized by respective DTG peaks. During these steps practically occurs the total combustion of the sludge organic components, with a significant energy release as indicated by respective exothermic DTA peaks. In the second step dehydroxilation of the present clays occurs. The first exothermic DTA peak occurs after the first DTG peak, indicating that this first mass loss step begins with from volatiles release and pyrolysis of organic components, which is followed their combustion in air. Results indicate that sludge firing must be performed in air up to at least 1000°C, to assure total absence of organics in the ashes.

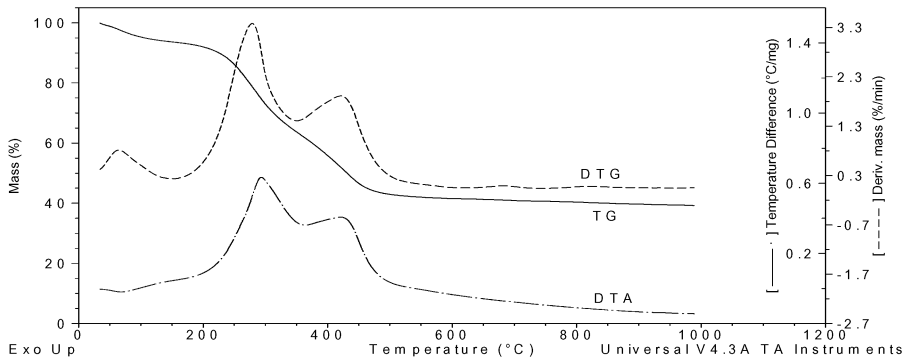


Figure 1. *TG, DTG, and DTA curves of the dried sludge at a heating rate of 10 ℃/min in air.*

**XRD**

Figure 2 presents X-Ray diffraction patterns of the sludge dried at 110°C (curve 1) and after thermal treatment in the presence of air at 350°C, 600°C, 1010°C and 1050°C (respectively curves 2 a 5). Table 1 presents the main crystalline phases identified at each firing temperature. In the product formed at 600°C, in which practically all the organics still present at 350°C were already burned out, it was verified the presence of quartz and microcline and due to dehydroxilation, ilite, caulinite and gibbsite are not present any more, as well as dolomite. The dehydroxilation reactions promote the destruction of the original crystalline structures, forming an intimate mixture of highly reactive amorphous oxides Srinivasan (1956). This explains the presence of anortite and the absence of the crystalline phase peaks identified at 350°C. At 1010°C, it is noticed the formation of tridimite, from partial quartz crystalline transformation as well as from the solid state reactions of the products formed from caulinite and ilite dehydroxilation, Norton (1973) which form the mulite at this temperature. At this temperature anortite and hematite were also identified, the latter indicating the oxidation of ferrous oxide between 600°C e 1010°C. At 1050°C, were sintering is more intense, crystalline phases are the same than those present at 1010°C.

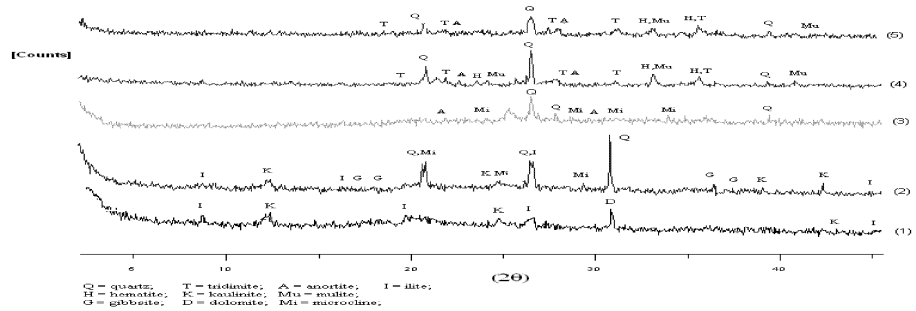


Figure 2. *X-ray diffraction patterns of the sludge dried at 110℃ (curve 1) and after thermal treatment in the presence of air at 350℃, 600℃, 1010℃ and 1050℃ (respectively curves 2 a 5).*

Table 1. Crystalline phases identified at each firing temperature.

| Minerals | Raw formula | Temperature processing | | | | |
|---|---|---|---|---|---|---|
| | | 110°C | 350°C | 600°C | 1010°C | 1050°C |
| Quartz | $SiO_2$ | | x | x | x | x |
| Ilite | $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$ | x | x | | | |
| Caulinite | $Al_2Si_2O_5(OH)_4$ | x | x | | | |
| Dolomite | $CaMg(CO_3)_2$ | x | x | | | |
| Microclíne | $KAlSi_3O_8$ | | x | x | | |
| Gibbsite | $Al(OH)_3$ | | x | | | |
| Hematite | $Fe_2O_3$ | | | | x | x |
| Tridimite | $SiO_2$ | | | | x | x |
| Mulite | $Al_6Si_2O_{13}$ | | | | x | x |
| Anortite | $CaAl_2Si_2O_8$ | | | x | x | x |

**XRF**

Tables 2 e 3 show XRF results of the sludge dried at 110°C and after sintering at 1050°C for 3 hours, expressed in oxide contents of major elements and in elemental composition of minor components. At 1050°C, the main oxides refer to those formed mainly due to the present clays dehydroxilation during simultaneous combustion of the organic components. Within the trace elements, it can be seen that after sintering, chlore presence is not significant due to the previuos volatilization in the form of chlorides. Fluor and sulphur contents also decreased significantly. When dried and sintered sludge analyses are compared, an increase of other trace elements content is noted, due to a natural concentration process in the mineral phases present in the original sludge solids.

Table 2. XRF data of ash showing oxides.

| Oxides(%) | 110°C | 1050°C - 3h |
|---|---|---|
| $SiO_2$ | 15,84 | 38,33 |
| $Al_2O_3$ | 7,63 | 21,14 |
| MnO | 0,042 | 0,097 |
| MgO | 0,64 | 1,8 |
| CaO | 2,55 | 6,68 |
| $Na_2O$ | 0,02 | 0,52 |
| $K_2O$ | 0,5 | 1,36 |
| $TiO_2$ | 0,694 | 1,75 |
| $P_2O_5$ | 3,738 | 9,994 |
| $Fe_2O_3$ | 5,91 | 14,61 |

Table 3. Results of XRF data of ash for heavy metals and trace elements.

| Elements (mg.kg$^{-1}$) | 110°C | 1050°C-3h |
|---|---|---|
| Ba | 745 | 1582 |
| Ce | 115 | 214 |
| Cl | 2572 | 15 |
| Co | 14 | 25 |
| Cr | 929 | 2078 |
| Cu | 942 | 2044 |
| F | 650 | 326 |
| Ga | <9 | <9 |
| La | 46 | 103 |
| Nb | 11 | 42 |
| Nd | 27 | 47 |
| Ni | 285 | 684 |
| Pb | 109 | 176 |
| Rb | 21 | 64 |
| S | 2914 | 157 |
| Sc | 8 | 19 |
| Sr | 111 | 322 |
| Th | 25 | 43 |
| U | 3 | 3 |
| V | 60 | 122 |
| Y | 10 | 39 |
| Zn | 2846 | 6123 |
| Zr | 192 | 567 |

**Leaching tests**

Tables 4 and 5 presents the results obtained in leaching test of the sintered sludge, with respect to solubility in distilled water and to acid extraction with $HNO_3$ 0,1M in pH = 0,97. This essays show that practically there is no solubilization of the heavy metals present in the original sludge, due to their stabilization in the ceramic matrix during the sintering process (Morais et al., 2006). This result also indicates that the sludge ashes can be used as raw materials in ceramic compositions with no environmental problems.

Table 4. Water soluble elements concentrations.

| Elements | mg.kg$^{-1}$ |
|---|---|
| Al | 1.11 |
| Ba | 0.027 |
| Cr | 0.008 |
| Cu | 0.013 |
| Fe | 0.108 |
| Ni | <0.001 |
| Zn | 0.06 |

Table 5. $HNO_3$ (0.1 M) extractable concentrations.

| Elements | mg.kg$^{-1}$ |
|---|---|
| Al | 49.5 |
| Ba | 1.248 |
| Cr | 0.128 |
| Cu | 4.84 |
| Fe | 5.68 |
| Ni | 0.196 |
| Zn | 2.68 |

## Conclusions

TG and DTA analysis show that the pyrolisis and combustion in air of the organic components of the sludge occurs in two main steps, which practically end at 600ºC.
Besides the organic components, the sludge has ilite, caulinite, gibbsite and dolomite in its composition, which decompose during the combustion of the organic components.
The stabilization of the metals present in the sludge is very effective during the sintering process, which promotes their chemical insertion in the ceramic matrix formed during the thermochemical transformations of the mineral components of the sludge.
The lixiviation tests of the sludge ashes sintered at 1050ºC, indicate that the concentration of potentially toxic elements in the lixiviate is under the environmentally allowed limits for these elements, indicating their use in ceramic products composition.

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## References

Bingham P.A., Hand R.J., Forder S.D. and Lavaysierre A., 2005, Vitrified metal finishing wastes II. Thermal and structural characterization. *J. Hazar. Mat.*, 122, 129- 138.

Chen X., Jeyaseelan S. and Graham N., 2002, Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Manage.,* 22, 755-760.

Colombo P., Brusatin G., Bernardo E. and Scarinci G., 2003, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products. *Curr. Opin. Sol. State Mater. Sci.*, 7, 225-239.

Gómez-Rico M.F., Font R., Fullana A. and Martín-Gullón I., 2005, Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content. *J. Anal. Appl. Pyrolysis*, 74, 421-428.

Mangialardi T., Piga L., Schena G. and Siriri P., 1998, Characteristics of MSW incinerator ash for use in concrete. *Environ. Eng. Sci.*, 15, 291-297.

Morais L.C., Dweck J., Valenzuela Díaz F.R., Gonçalves E.M. and Büchler P.M., 2006a, Trace elements and heating value from sewage sludge, Barueri, Sao Paulo, Brazil. *Int. J. Environ. Studies*, 63, 331-336.

Morais L.C., Dweck J., Gonçalves E.M. and Büchler P.M., 2006b, An experimental study of sewage sludge incineration. *Environ. Technol.*, 26, 1047-1051.

Morais L.C., Dweck J. Gonçalves E.M. and Büchler P.M., 2006c, A case study of the ceramic matrix sintering of sewage sludge when fired at high temperatures. *Mat. Sci. Forum*, 530, 734-739.

Norton F.H., 1973, Introdução à Tecnologia Cerâmica. Edgard Blucher (ed.), Brazil, pp. 177-185.

Srinivasan N.R., 1956, Surkhi as a Puzzolana. *Road Res. Papers*, 1, 1-69.

Norton F.H., 1973, Introdução à Tecnologia Cerâmica. Edgard Blucher (ed.), Brazil, pp. 177-185.

Wiebusch B., Ozaki M., Watanabe H. and Seyfried C.F., 1998, Assessment of leaching tests on construction material made of incinerator ash (sewage sludge): Investigation in Japan and Germany. *Water Sci. Technol.*, 38, 195-205.