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CALCINED SLUDGE SINTERING EVALUATION BY HEATING MICROSCOPY THERMAL ANALYSIS

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Aiming the use of the sewage sludge produced in one of the largest Brazilian wastewater treatment stations as a raw material for the ceramic industry, the sintering process of the ashes produced from its calcination was evaluated by heating microscopy thermal analysis (HMTA). From the microprocessed images, a method was developed to obtain HMTA dimensional change curves as a function of temperature, equivalent to those usually obtained from dilatometers or by thermomechanical analysis (TMA). The final product after sintering at 1050°C, characterized by X-ray fluorescence spectrometry, scanning electron microscopy and X-ray dispersive energy, indicates the presence of a vitreous phase containing phosphorus, which explains the good sintering properties of the studied calcined sludge, as shown from its HMTA dimensional change curve.

Keywords: *heating microscopy, SEM, sludge, X-ray dispersive energy*

Introduction

The processing of industry and domestic effluents in wastewater treatment plants reduces the amount of polluted material and forms reusable water and dehydrated sludge. This way landfills can be significantly reduced and the generation of hazardous municipal sludge can be decreased, as well as the impact on underground water and the risk to human health.

Untreated sewage sludge should never be permitted to enter rivers. Nowadays, treated or untreated, in some countries this is still an environmental hazard. There are resultant impacts on surface and underground water, the loss of fertile land, and offensive odour, with the risk of proliferation of disease-carrying insects, among other problems. Some wastewater treatment processes generate high levels of sludge, mainly in large metropolitan cities as São Paulo, Brazil, where 785–*t*/day production is expected by 2015 [1], which pose the question of recycling.

In Europe, a significant amount of research has investigated sewage sludge ash processing to form new materials. This residual biosolid can be used as an economic alternative in the building industry, because the disposal of sewage sludge on reclaimed land is no longer a viable solution, as occurs in Germany [2].

Dehydrated sewage sludge can be used as a component in building materials, like in the sludge–clay mixtures employed to manufacture bricks, tiles and cements [3–5]. During sludge–clay mixture firing, at usual ceramic processing temperatures, organic substances of the sludge are completely eliminated and ash is obtained [6–10]. The kinetics of the calcination process has been studied by thermogravimetry (TG) [11–13]. This ash can be used in partial replacement of clay mineral in brick manufacturing [2] in asphalted paving mixtures [14], in lightweight aggregate [15], for lightweight concrete manufacture and other applications [16, 17]. The ash can also be used as raw material in cement mortars [18, 19].

With the objective to obtain design data for further application in ceramic industry, the present paper deals with the chemical and morphological characterization of the sintered mineral components of the ash obtained from a sewage sludge, which is produced in one of the biggest Brazilian wastewater treatment plants, within São Paulo city metropolitan area. Expansion and/or shrinking curves during ceramics firing processes are usually obtained by using dilatometers [20–23] or thermomechanical analysis (TMA) [24–26]. In this work, the sintering process of the calcined sludge to obtain ceramic products was evaluated by heating microscopy thermal analysis (HMTA) and an alternative method was developed from the HMTA microprocessed data to obtain the dimensional change curve during sintering.

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Experimental

Materials and methods

Sewage sludge

The sewage sludge studied in this work, was collected in one of the biggest Brazilian wastewater treatment plants in Barueri city, which is located in São Paulo city metropolitan area, which has a population of about 16 million people. The sludge, which contains organic and inorganic materials, was sampled from the press filter residual cake of the plant. Due to the high level of humidity, it was dried at 110°C for 24 h. After drying, it was manually ground and milled to pass through sieve ASTM #100, to transform it in a homogeneous powder for the different thermal processing and characterization analysis.

Scanning electron microscopy and X-ray dispersive energy analysis

Conventional ceramic products can be obtained by sintering bodies using sewage sludge ash [3, 8]. Sintered sludge ash was obtained processing the dehydrated sludge powder at 1050°C for 3 h. The morphological aspects of the main present phases and respective surface elemental composition were analyzed by scanning electron microscopy (SEM) and by a system of X-ray dispersive energy (XDE) analysis using a Philips XL-30 model with secondary electrons detector.

X-ray fluorescence (XRF) spectrometry

The chemical composition of the sludge ash sintered at 1050°C, was determined by X-ray fluorescence (XRF) spectrometry using a Philips-PW2510 spectrometer with type tube PW2592/15 Rh and molten pastilles with lithium metaborate and lithium tetraborate.

Heating microscopy thermal analysis (HMTA)

Heating microscopy thermal analysis (HMTA) was used to analyze dimensional changes as a function of temperature during sinterization of the calcined sludge at high temperatures. For this purpose and according to a previous work of the authors [10], dehydrated sludge powder was initially heated up to 600°C, to burnout and to eliminate all organics and to have a powder with only inorganic ceramic components for the study. The calcined powder obtained after heating the dehydrated sludge at 600°C until constant mass, was used to cast a cube of 2-mm height, in a manual press that comes with the heating microscope. Dimensional changes of the cubic pressed sample, which is heated in a temperature controlled cylindrical kiln on an alpha-alumina holder, are followed in real time by an image microprocessing system of the heating microscope, which is positioned in front of one of the sides of the kiln, allowing one to focus the internal part of the kiln where the specimen is, through a special glass window on which there is a quadriculated screen. On the other side of the kiln, a special lamp promotes the visualization of the square cross section of the cube, which appears as a shadow in the microscope image, during the heating process. The temperature of the kiln is also measured and microprocessed in real time, appearing as a legend, at the bottom of the microprocessed image. Thus, the shape and dimensional changes of the specimen cross section can be followed and registered in real time as a function of temperature.

Thermal analysis by heating microscopy was performed with a heating rate of 10°C min^{-1} from 400 to 1100°C on a static environment in a LEITZ WETZAR, (Germany) heading microscope with a VVC video-camera, to which was assembled an interface for image microprocessing and saving in real time. The temperature is measured by a THERM 2280-2 model system and temperature control is done by a THERMA TH 2131 P-201-000 model, Dimensional changes were obtained by measuring afterwards the expanded images in the monitor screen of a computer, in which they were previously recorded and saved at 1 min intervals during the thermal analysis.

Results and discussion

Chemical composition of the sintered material

Table 1 shows the oxide composition given by X-ray fluorescence (XRF) spectrometry of the sintered sewage sludge ash, which was obtained after a thermal treatment at 1050°C for 3 h. This represents the typi-

Table 1 XRF oxide composition data of the calcined sludge after sintering at 1050°C

Oxide	Mass%
SiO_2	39.68
Al_2O_3	21.89
MnO	0.10
MgO	1.86
CaO	7.23
Na_2O	0.54
K_2O	1.41
TiO_2	1.81
P_2O_5	10.35
Fe_2O_3	15.13

cal chemical composition of any ceramic body which may be manufactured from the sewage ash by conventional ceramic sintering processes. Results show that most of the oxides which compose the sintered ash, are in its identified X-ray diffraction main crystalline phases, which are quartz (SiO_2), tridimite (SiO_2), hematite (Fe_2O_3), mulite ($Al_2Si_2O_{13}$) and anortite ($CaAl_2Si_2O_8$).

Typical morphology and elemental composition

Figure 1 shows a typical SEM image of the sludge particles after being sintered at 1050°C. Figure 3 shows an XDE analysis of a typical point of the grayish phase shown in Fig. 2. The white phase presents as major components, silicium and oxygen, with a minor presence of Al, Fe and Ca, elements that are present in the crystalline phases of sintered material. Potassium (K), which was in the ilite phase ($(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$) identified in the dried sewage sludge, is also present.

Figure 2 is a micrography that details the morphology of the surface of a grayish phase particle of Fig. 1.

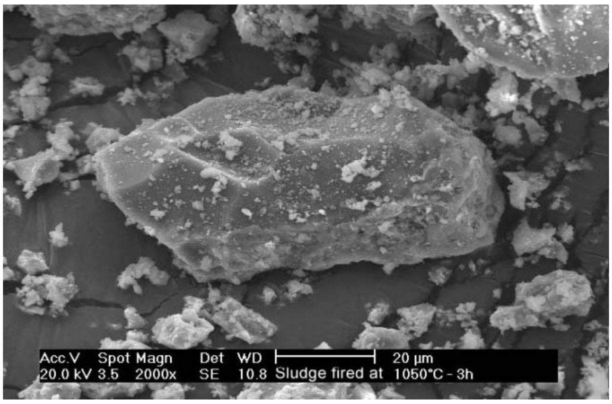

Fig. 1 Typical SEM image of sintered sludge fired at 1050°C (2000×)

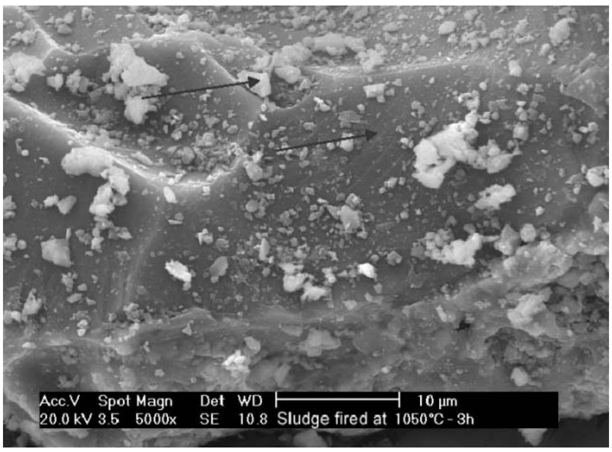

Fig. 2 Typical SEM image of sintered sludge fired at 1050°C (5000×)

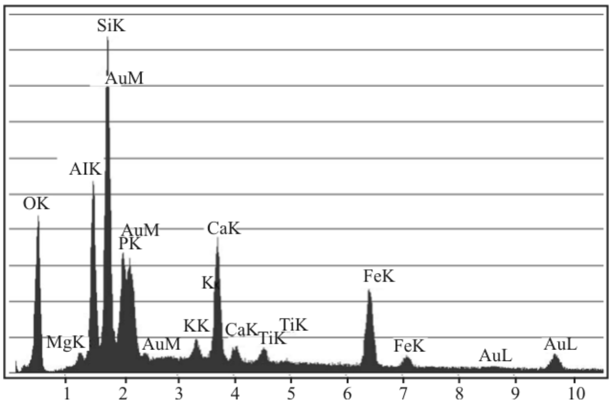

Fig. 3 XDE analysis of a typical point of the grayish phase particle of the sintered sludge at 1050°C

The XDE analysis of a typical point of this phase, is shown in Fig. 3, where phosphorus (P) is present with Si, Al, Cu and F, as major intensity peak elements and, K, Ti and Mg, as minor intensity peak ones.

As no identified crystalline phase of sintered material contains phosphorus, this fact indicates that this element is in the composition of a vitreous phase present in sintered material, which was formed during cooling of the respective liquid phase formed during sintering. The conchoidal fracture of this grayish phase particle, as shown in Fig. 2 is an additional evidence that it has vitreous characteristics.

Dimensional thermal analysis by heating microscopy

Figure 4 shows, as examples, the heating microscope images registered at 400, 750, 900, 1000, 1050 and 1100°C. In the images, the height of six squares height on the screen represents a real height of 2 mm. In the monitor screen, after zoom application, the respective expanded height of six squares was equal to 80 mm. Right and left side heights of the square image of the specimen were measured from the monitor screen to follow dimensional changes in each side, as a function of temperature.

Figure 5 shows the values of each side expanded height as a function of kiln temperature, measured from images saved every minute, during the heating microscope thermal analysis. As can be seen, right after 600°C, there is a little expansion up to 750°C, due to the effect of the gases still released from residual decomposable material of the pre-calcined sludge at 600°C in this temperature range, as evidenced by thermogravimetry in a previous work [10]. It follows an increasing shrinkage rate process, characteristic of the ashes sintering process, which is more significant from 900°C. Compared to the respective initial height of each side, there was a mean shrinkage of 18% at 1100°C, which was promoted by the presence of the liquid phase formed during the firing process.

During clay-based ceramic tiles firing, liquid phase sintering occurs [27], where the densification process is due to the penetration of the liquid between other present solid grains, which are tightly hold by the solidified liquid at ambient temperatures. Considering its chemical composition and that the temperature range of wall or floor tile sintering is similar to that of the liquid phase formation during the present calcined sludge firing process [28, 29], the calcined sewage sludge is a good raw material to be used in ceramic tile compositions.

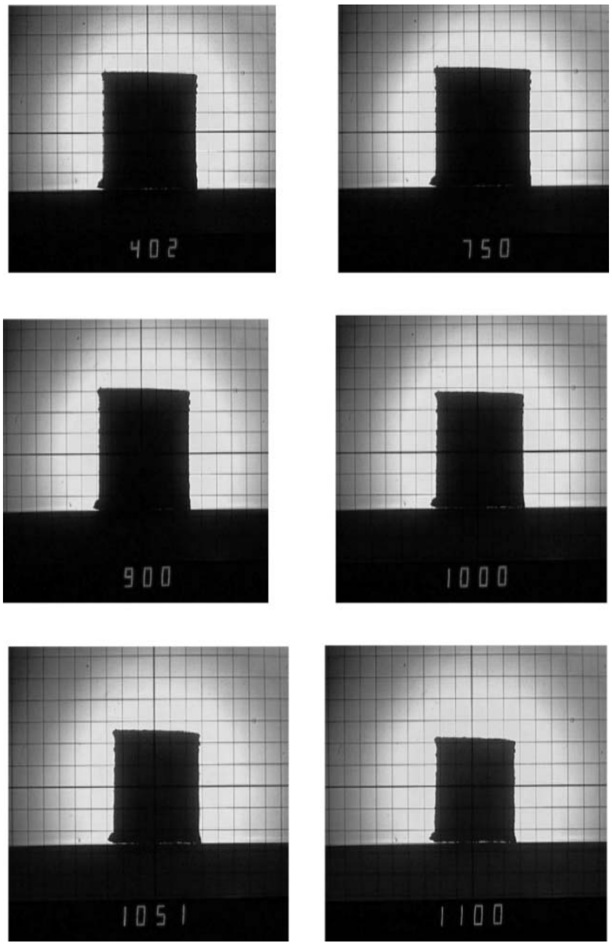

Fig. 4 Heating microscope images obtained at different temperatures

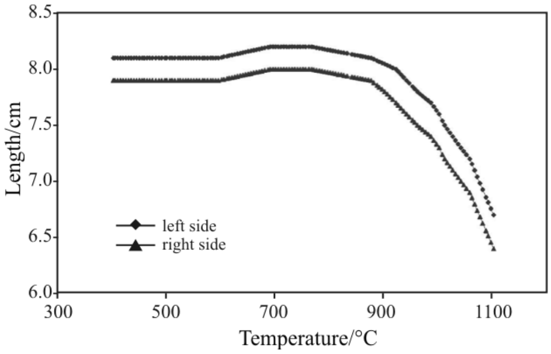

Fig. 5 HMTA curve at 10°C min^{-1} of the dry pressed cubic specimen prepared from the dehydrated sewage sludge previously calcined at 600°C

Conclusions

- HMTA is usually used to evaluate dimensional and morphological changes of ceramic bodies during their firing at particular processing temperatures. The method developed in this work enhances its use, allowing one to obtain, from microprocessed images, a HMTA dimensional change curve, equivalent to that obtained from dilatometric or thermomechanical analysis.
- Scanning electron microscopy and X-ray dispersive energy results indicate the presence of a vitreous phase containing phosphorus, non identified in the crystalline components of the sintered ash.
- The presence of this vitreous phase indicates that a liquid phase is formed during sintering, which enhances the process and causes the significant shrinkage shown by the HMTA dimensional change curve.
- The experimental sintering results and the chemical composition of the studied calcined sewage sludge indicate its use for ceramic tile raw material compositions.

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