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Valorization of water treatment sludge waste by application as supplementary cementitious material

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HIGHLIGHTS

- WTS waste used as raw material to the production of new SCM.
- WTS waste processed by flash calcination and electrical muffle furnace.
- Different temperature and residence time investigated.
- Characterization performed to verify the potential pozzolanic activity.
- Calcined WTS shows great potential to the production of a new SCM.

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ABSTRACT

This paper investigates the potential of using calcined water treatment sludge to the development of supplementary cementitious material. Sludge samples have been collected in the drying beds of a water treatment plant located in Southern Brazil and calcined in the laboratory. Chemical and mineralogical characterization has been performed through energy dispersive X-ray spectrometry, thermogravimetric analysis, and X-ray diffraction with crystalline phases quantified by Rietveld refinement. Morphological analysis has been supported by scanning electron microscope images. Physical characterization has been carried out through specific surface area, particle size distribution, and pozzolanic activity performance with Portland cement. Results have shown that the water treatment sludge is a non-hazardous and non-inert waste without environmental restrictions for use in construction. Considering technical, environmental and economic aspects related to energy consumption, sludge samples calcined at 600 °C for 1 h present the most promising results regarding the production of supplementary cementitious material equivalent to a normal pozzolan, while highly active pozzolan requires 750 °C for 1 h. Calcined water treatment sludge showed great technical and environmental potential to be used as an alternative source of supplementary cementitious material in the near future.

1. Introduction

Aluminum salts are commonly used as a primary coagulating–flocculating agent for drinking water treatment processes due to their effectiveness and low cost. Drinking water treatment processes result in large volumes of a heterogeneous solid waste named Water Treatment Sludge (WTS) around the world [43,28]. The amount and composition of WTS depends on the volume of treated water, the treatment process and the characteristics of untreated water [32], which is influenced by the origin (surface water or groundwater through wells), type of soil and even chemical products or other materials discharged into the river [61]. Thus, it is compulsory to characterize the sludge from each water treatment plant (WTP) for recycling and reuse purposes.

The latest National Survey on Basic Sanitation [35] shows 14.4% increase in distributed volume per capita of treated water (located on premises, available when needed and free from contamination)

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in all Brazilian regions. Water treatment plants are present in 85% of the 5570 municipalities, which means approximately 7500 units distributed in 8516 million km^2. The conventional treatment process is applied in 69.2% of Brazilian water treatment plants. The Progress on Drinking Water, Sanitation and Hygiene Report [68] estimates that drinking water is supplied to 95% of Brazilian population (207.8 million people, 85% rural and 99% urban), against 96% in Latin America and the Caribbean (207.8 million people) and 71% considering the global population (5.2 billion people). Traditionally, final destinations of WTS in Brazil are the nearest water systems with no previous treatment [53], which does not comply with Federal Law 12.305 [17] that requires WTS disposal in commercial sanitary landfills.

During the last decades, the most developed countries have been converting urban sludge into fertilizer in agriculture, industrial chemicals, energy, and/or material for building [27]. Unfortunately, this is not the reality in most countries where, in general, WTS is dumped directly into rivers and streams or into drain systems, which leads to significant environmental impacts that prejudice the quality of drinking water and the health of humans and animals [11,42]. WTS can also be prepared for disposal in commercial sanitary landfills through dehydration, which involves thickening, centrifugation, and filtration operations in order to recover water and minimize volume [61]; however, this practice is expensive [14]. It is a consensus that the heavy metal contents of WTS may cause problems of human, aquatic, and terrestrial toxicity [34,32]. High concentrations of heavy metals in water has been linked to Alzheimer‘s disease [33] and children mental retardation [59]. Even when placed in landfills, problems regarding capacity limitations are very common. Incineration is an alternative solution to reduce WTS volume, immobilize heavy metals, oxidize organic matter and destroy pathogens [67], but substantial amounts of ash are produced [43].

On the other hand, various intensive practices have been employed worldwide to reuse and/or recycle WTS in an attempt to figure out how to fill the gap between successful drinking water treatment process and environmentally friendly WTS management [37,28]. The application of WTS in building material and construction is a common practice that helps to reduce the environmental degradation caused by irregular disposition. Application of WTS in the ceramic industry has been widely investigated [12,30,67,66,48,51,21,15,61,33,43,38,14,69,60]. Other applications of WTS have been reported, for instance, as mineral addition in concrete [16,32,72] or even on the production of lightweight aggregate [34]. If thermally treated, minerals present in WTS lose crystallinity and become able to release reactive silica and alumina, leading to Supplementary Cementitious Materials (SCM) by consumption of Portlandite [47]. In this sense, investigations on the possibility of using calcined WTS as SCM are scarce [55,54,32,50].

The use of SCM is one of the three pillars related to the sustainability of the cement industry [25]. This practice reduces environmental impacts and creates economic, technological, and geological benefits [71]. In Brazil, the use of SCM has become one of the main strategies to control CO_2 emissions related to the cement industry, which places the country among the ones with lower clinker to cement ratio [36]. On a global level, the clinker to cement ratio was about 75% in 2004 [26] and it is estimated that it might be 65% to 70% by 2030 and 60 to 65% by 2050 [29]. The most common SCM used in the Brazilian cement industry are fly ashes, provided by fossil fuel burning used in energy production, calcined clays, and blast furnace slags originated from steel production. However, the increasing global demand for renewable resources for energy production tends to reduce the use of fossil fuel in the near future, which may decrease the supply of fly ash [72]. Apart from that, cement production tends to step up in the next years due to the increasing global demand for housing and infrastructure in developing countries. In this perspective, searching for alternative SCM sources is one of the challenges of the Brazilian cement industry.

Up to now, the use of calcined pozzolans as SCM is common only in a few countries and in very low market shares (e.g. Brazil with 3% of the national cement market) according to the European Cement Research Academy and the Cement Sustainability Initiative [29]. The relative scarcity of the commonly used SCM or their localization, whose transport causes great economic and environmental impact, encourages the development of new materials [64]. In a long-term perspective, calcined pozzolans obtained from different sources are expected to become a relevant material group, as the global availability of the traditional pozzolans used as SCM will not be able to cover the demand for cement main constituents.

In this context, this paper investigates the potential of using of calcined Water Treatment Sludge (WTS) as Supplementary Cementitious Material (SCM) through chemical, mineralogical, morphological, and physical characterization of samples collected in the drying beds of a water treatment plant and calcined in laboratory using a pilot-scale flash calciner and an electrical muffle furnace at temperatures varying from 600 °C to 800 °C for one and two hours. The significance of this research is endorsed by the possibility of adding value to the waste while reducing the current WTS disposal into landfills, rivers, and streams. In this perspective, the increase in cement production demand for the coming decades encouraged local cement plants to invest in the development of alternative SCM source to supply the local cement market. So far, there are few reports on the use of WTS from water treatment plants in Southern Brazil as raw material to produce SCM. Apart from that, the characterization of sludges from different sources is imperative to guarantee that the properties of the calcined material will meet the requirements for recycling and reusing purposes since mineral content varies with location. Finally, the valorization of WTS by application as SCM may contribute to reduce environmental impacts related to water treatment and build a more sustainable development, which highly depends on a cleaner and sustainable production of construction materials.

2. Experimental program

2.1. WTS collection

A representative sample of WTS was collected from the drying beds of the water treatment plant named WTP II, located in a medium-sized municipality in Southern Brazil, with 518.9 km^2 and 310,000 inhabitants. WTP II supplies drinking water to 74% of the municipality residents and produces approximately 1700 m^3/day of drinking water from surface water through conventional coagulation, flocculation, and rapid sand filtration process, using poly-aluminum chloride (PAC) as the coagulant. The water treatment plant produces 85ton /month disposed of directly in the Itajaí-Açú River.

2.2. WTS classification

Based on the leaching and solubilized extracts presented in Table 1, WTS is classified as Class II-A: non-hazardous and non-inert waste, without environmental restrictions for use in construction. Solubilized extract test results show that total metal concentrations in the WTP are relatively low. However, Manganese and Surfactants exceed the limits presented in Table 1. The presence of surfactants, which are organic chemicals used in detergents, household cleaners, and personal cleansing products, is related to irregular discharges into the river. The high concentration of Manganese is related to the riverbank soil

Table 1
Results of leaching and solubilized extracts tests.

	Test Result (mg/l)	Limit* (mg/l)
Leaching Extract*		
pH	4.92	–
Arsenic	≤0.00005	1.0
Barium	2.97	70
Cadmium	0.0040	0.5
Lead	0.0040	1.0
Chromium total	0.034	5.0
Fluoride	0.06	150
Mercury	≤0.00004	0.1
Silver	0.00038	5.0
Selenium	≤0.00004	1.0
Solubilized Extract**		
pH	7.40	–
Aluminum	0.41	0.2
Arsenic	≤0.00005	0.01
Barium	0.29	0.7
Cadmium	0.00083	0.005
Lead	≤0.0001	0.01
Cyanide	≤0.01	0.07
Chloride	30.50	250.0
Copper	0.033	2.0
Chromium total	0.028	0.05
Phenol total	n.d.	0.01
Iron	0.19	0.3
Fluoride	0.22	1.5
Manganese	3.49	0.1
Mercury	≤0.00004	0.001
Nitrate (N)	0.4	10.0
Silver	0.00097	0.05
Selenium	≤0.00004	0.01
Sodium	4.12	200.0
Sulfate (SO_4)	40.0	250.0
Surfactants	1.67	0.5
Zinc	0.074	5.0

*NBR 10005 [5,3–4]; **NBR 10006 [5,3–4]; *** NBR 10.004 [5,3–4].

composition and chemical waste products from industrial processes discharged into the river. The presence of heavy metals does not prohibit its incorporation into construction materials considering that such metals can be made inert in the crystalline structure of vitreous phases formed during sintering processes [61]. WTS sludge presents a total solids content of 19.36% and 0.39% of organic matter content.

2.3. Calcination processes

Before calcining, WTS was kept at 110 °C for 24 h to ensure complete drying, which has been checked by successive measurements up to reach mass constancy. After the drying process, WTS was shredded and homogenized. WTS was calcined using a pilot-scale flash calciner and an electrical muffle furnace for different temperatures and exposure times. Both calcination processes have been performed in a laboratory scale. Fig. 1 shows the aspect of *in natura* and calcined WTS samples.

2.3.1. Flash calcination

Flash calcination is a process whereby a finely divided solid is heated rapidly, held at temperature for a short time, and then cooled rapidly [19], which offers a much faster and economically viable alternative to traditional calcination methods used in conventional large-scale production of SCM [52]. Flash calcination was performed in a continuous pyrolysis pilot plant adapted from Wiggers et al. [70], which is divided into air feed, pre-heating, material feed, tubular reactor, storage, and emission sections (Fig. 2). A compressor and a preheater system provide a stream of upward-flowing hot air that takes dried sludge supplied by the feed system into the tubular reactor. Thermocouples are placed along the tubular reactor as part of the control system for monitoring and temperature measuring over time. The continuous pyrolysis pilot plant allows up to 1 kg of WTS flash calcination per feeding. WTS remains about 3.4 s in the tubular reactor where average temperatures range from 732.0 °C ± 5.2 at the gas heater, 640.14 °C ± 3.37 at the first thermocouple, 580.8 °C ± 6.7 at the material inlet point, and 288.3 °C ± 4.5 at the reactor outlet. For this operating condition, the average volumetric ambient air flow rate is 3 m^3/h and the volumetric flow in the reactor is 7.30 m^3/h. The calcined sludge is then sent to air cooling cyclones where particles are cooled and retained in the first and second Hoopers. Each kg of WTS results in about 0.5 kg of flash calcined sludge. Temperature data before and after the sludge supply are recorded in a databank to estimate energy consumed during sludge calcination. This installation consumes 530 MJ/ton of WTS, much less than the energy consumed during cement production, which reaches about 3.06GJ/ton of clinker in modern plants [58,10,72].

2.3.2. Electrical muffle furnace calcination

An electrical muffle furnace (Jung LF4210, inner dimensions 300x350x400mm, rate of work 4.4 kW, maximum working temperature 1.000 °C) was used to calcine WTS samples at 600, 650, 700, 750, and 800 °C for 1 h and 2 h, with heating rate of 10 °C/min, based on previous studies reported by LaVilla et al. [39], García et al. (2008), [20], Martínez-García et al. [43], Cordeiro [24], Gastaldini et al. [32], Tantawy [59], and Tironi et al. [65]. Aiming to obtain a uniform calcining, the electrical muffle furnace

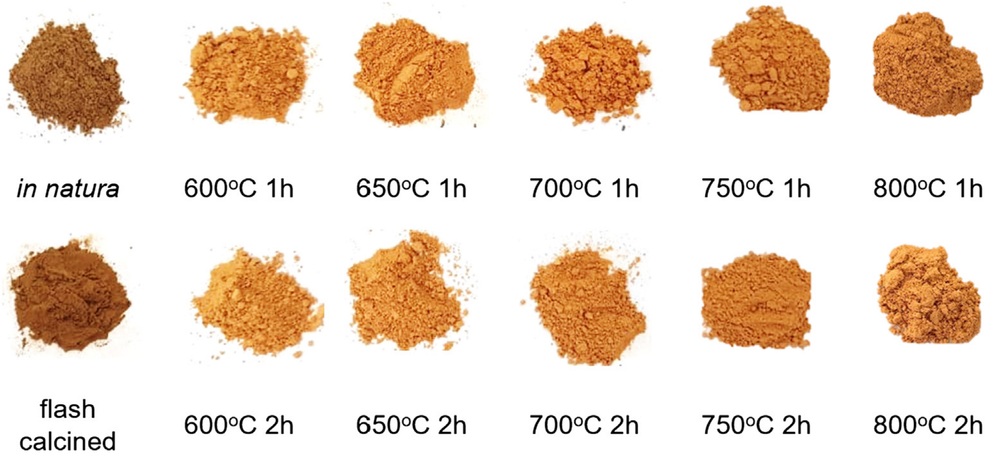

Fig. 1. The aspect of WTS samples.

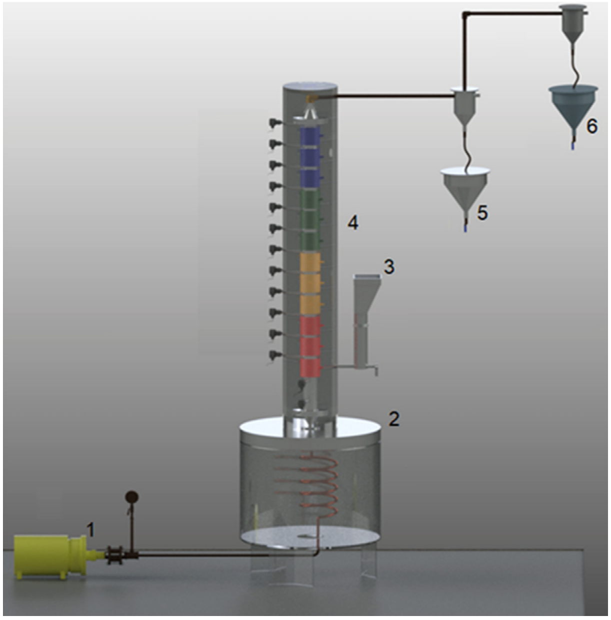

Fig. 2. Schematic diagram of the pilot plant: (1) Air feed section; (2) Pre-heating section; (3) Material feed section; (4) Tubular reactor; (5, 6) Emission and storage sections.

has been fed with 0.3 kg of WTS (6 ceramic crucibles with 0.05 kg each). Considering the operating condition of heating rate 10 °C/min, a rate of work 4,4kW, 0.3 kg per feed, calcining temperature 600 °C, and residence time 1 h, the electrical muffle furnace consumes 106GJ/ton of WTS.

2.4. WTS characterization

Quantitative chemical analysis of *in natura* and calcined WTS was obtained using the Energy Dispersive X-ray Spectrometer of the Scanning Electron Microscope (SEM) Tescan Veja 3 LHM and validated using the Energy Dispersive X-ray Fluorescence Spectrometer Shimadzu EDX 7000. X-ray diffraction patterns for mineralogical characterization were obtained using the Siemens D5000 X-ray diffractometer over a range of 10°–70° 2θ and steps of 0.02° for 3 s. Crystalline phases were quantified through Rietveld refinement. Thermogravimetric analysis and differential thermal analysis (TGA-DTG) was performed using the Shimadzu D-60 equipment under Argon. Morphological analysis was performed through images obtained by SEM.

Calcined WTS was milled in a ceramic ball mill, with a ball to sludge ratio of 5:1, for 4 h, in order to get more than 90% of particles smaller than 45 μm. The particle size distribution of the calcined WTS was determined with the Mastersizer 2000 laser granulometer. BET (Brunauer, Emmett, and Teller) specific surface area was determined by nitrogen adsorption using the Quantachrome Nova 1000e analyzer.

Chemical and physical properties have been used to evaluate the potential use of calcined WTS as SCM through the compliance with requirements of standards applicable to highly active [7] and normal pozzolans [6], selected based on the similarity of the raw material source (Table 2). Highly active and normal pozzolans follow the classification of pozzolanic materials proposed by Metha and Monteiro [45]. Both standards establish requirements for pozzolanic materials to be used with Portland cement in concrete, mortars, and paste. However, while the ABNT NBR 15894 [8,7] applies to highly-active pozzolanic materials, produced through calcination and milling of clay minerals, formed essentially by lamellar particles with predominantly non-crystalline structure, the ABNT NBR 12653 [2,6] applies to normal pozzolanic materials defined in the normative as natural pozzolans, fly ashes from thermoelectric plants, or any other pozzolanic material.

Table 2
Chemical and physical requirements.

Chemical Requirements	Highly active pozzolan*	Normal pozzolan**
CaO + MgO	≤1.5%	–
SiO_2	≥44% and ≤ 65%	–
Al_2O_3	≥32% and ≤ 46%	–
$SiO_2 + Al_2O_3 + Fe_2O_3$	–	≥70%
SO_3	≤1%	≤4%
Na_2O	≤0.5%	–
Na_2O equivalent	≤1.5%	≤1.5%
Moisture content	≤2%	≤3%
Loss on ignition	≤4%	≤10%
Physical requirements		
Percentage retained on 45 μm sieve	≤10%	≤20%
B.E.T. specific surface area	$\geq 15 m^2 g^{-1}$	–
Performance Index with cement at 7 days	≥105%	–
Performance Index with cement at 28 days	–	≥90%

*NBR 15894 [8,7]; **NBR 12653 [2,6].

Performance Index at 7 and 28 days (Eqs. (1) and (2)) have been used to evaluate potential pozzolanic activity of the calcined WTS with Portland cement: the Performance Index at 7 days (≥105%) applies to highly active pozzolans, while the Performance Index at 28 days (≥90%) is a requirement for normal pozzolans. The potential pozzolanic performance of flash calcined WTS samples has been tested only at 7 days since it was expected to be used as a highly active pozzolan (higher added value). Indirect determination of pozzolanic activity by compressive strength meets the requirements of the mentioned standards, although more accurate methodologies are exhaustively reported in the scientific field [31,16,20,24,13,52,18].

$$PI_7 = \frac{Compressive\ Strength\ of\ Mortar\ 7B}{Compressive\ Strength\ of\ Mortar\ 7A} \tag{1}$$

$$PI_{28} = \frac{Compressive\ Strength\ of\ Mortar\ 28B}{Compressive\ Strength\ of\ Mortar\ 28A} \tag{2}$$

Mortars 7A, 7B, 28A and 28B, whose mix proportions are presented in Table 3, were produced with cement CPII-F 32, equivalent to CEM II/A-M of EN 197-1 [23], which has no SCM in its composition. Six samples of each mortar were prepared and cured into ϕ50 mm × 100 mm metallic cylindrical molds for 1 day. Then, samples were kept in saturated lime water until reaching test age. Three repetitions were considered and statistical analysis was performed using two-way ANOVA and Student *t*-test with α 0.05.

3. Results and discussion

3.1. Chemical characterization of calcined WTS

Chemical composition of the calcined WTS is shown in Table 4. Silica, alumina, and iron oxide are the major components, which is confirmed by the selected chemical mapping analysis showed in Fig. 3. The high content of Fe_2O_3 occurs mainly due to the soil characteristics in the South region of Brazil, which presents a high concentration of iron (EMBRAPA, 2004).

Fig. 4 shows TGA/DTA curves of *in natura* WTS. From room temperature up to 200 °C the release of the physically adsorbed water results in a weight loss of 4.8% and no changes in the WTS structure

Table 3
Mix proportion of mortars.

	PI_7*		PI_{28}**	
	Mortar 7A*	Mortar 7B*	Mortar 28A**	Mortar 28B**
Cement CPII-F-32	624	530	624	530
Calcinated Sludge	–	93	–	93
Sand	1872	1872	1872	1872
Water	300	300	300	300
Superplasticizer	–	adjustable	–	adjustable

* NBR 15894-2 [8,7], mortars 7A and 7B produced for compressive strength tests at 7 days. ** NBR 5752 [2,6], mortars 28A and 28B produced for compressive strength tests at 28 days. * ** amount of material in g, to produce six cylindrical ϕ50mmx100mm samples.

Table 4
Chemical composition of *in natura* and calcined WTS (%).

	in natura	flash	600 °C		650 °C		700 °C		750 °C		800 °C	
			1 h	2 h	1 h	2 h	1 h	2 h	1 h	2 h	1 h	2 h
SiO_2	52.2	53.4	54.1	55.6	57.4	58.1	54.9	57.2	57.4	57.9	58	57.5
Al_2O_3	26.7	24.9	28.2	26.7	24.9	24.1	26.1	24.2	25.2	24.5	24.5	24.3
Fe_2O_3	12.4	14.6	10.2	10.3	10.2	10.1	11.6	10.4	9.9	10	9.9	10.4
K_2O	4.2	4.0	4.2	4.3	4.3	4.4	4.0	4.5	4.0	4.2	4.3	4.3
MgO	1.5	1.2	1.4	1.3	1.4	1.4	1.3	1.4	1.4	1.3	1.4	1.3
TiO_2	2.2	1.2	1.2	1.2	1.2	1.3	1.3	1.4	1.2	1.3	1.2	1.2
CaO	0.5	0.3	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.6
MnO	0.3	0.4	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.3	0.3	0.4
Loss on ignition	–	3.55	4.50	4.20	4.70	3.80	4.60	3.50	3.60	3.00	1.90	1.70
SO_3	–	0.16	0.23	0.29	0.26	0.17	0.18	0.13	0.13	0.14	0.06	0.00

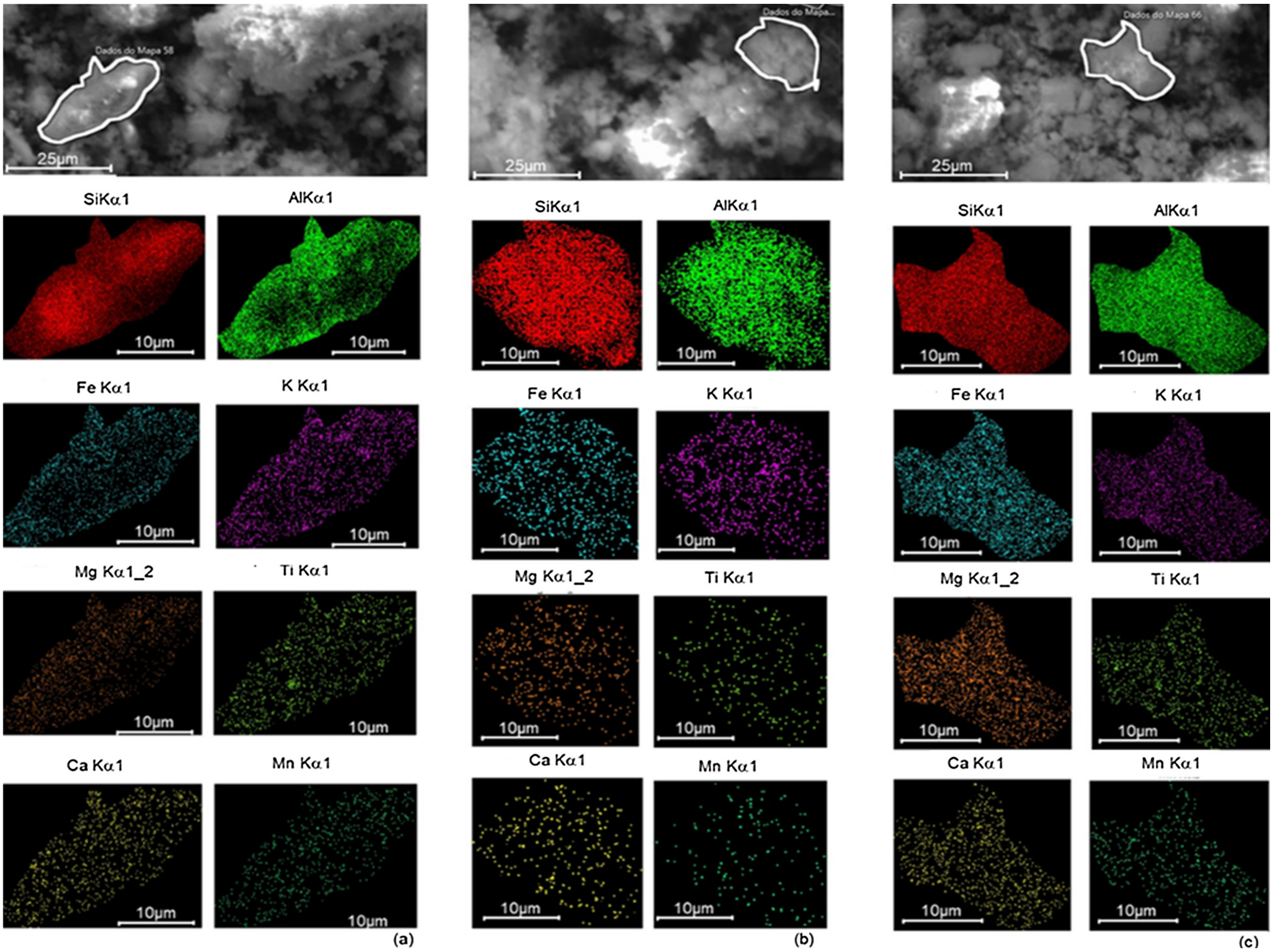

Fig. 3. Chemical mapping analysis: (a) *in natura*; (b) 600 °C 1 h; (c) 800 °C 2 h.

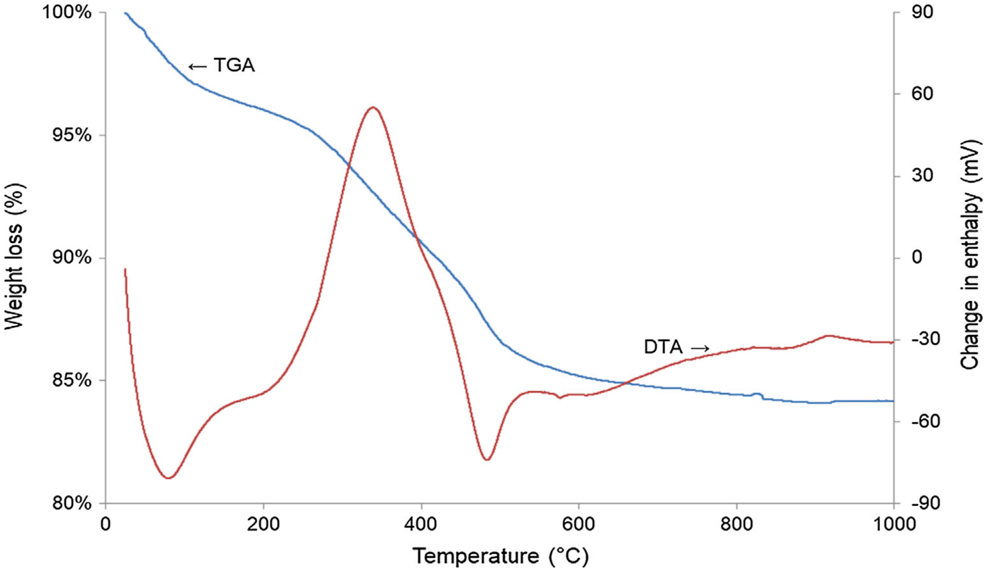

Fig. 4. TGA/DTA curves of *in natura* WTS.

[38]. Dehydration corresponds to the endothermic peak that appears at 79 °C. Decomposition of organic matter, between 200 °C and 400 °C results in a weight loss of 5.39% and the exothermic peak appears at 338 °C. The endothermic peak at 482 °C represents the phase transition or dehydroxylation of Kaolinite that occurs between 400 °C and 600 °C and the metakaolin production [43,42], accompanied by a weight loss of 5.45%. The removal of chemically bound water confers to the calcined WTS an amorphous state and a pozzolanic reactivity, which defines the efficiency of the SCM (artificial pozzolan) obtained from WTS [47]. Decarbonation occurs between 600 °C and 800 °C with CO_2 dissipation and the production of hematite, resulting in a weight loss of 1.06%. The exothermic peak at about 926 °C indicates the recrystallization of metakaolin [42], without weight loss, which is responsible for dropping the pozzolanic activity of the material [57,47].

In order to get a higher amount of amorphous phase [65] calcination temperature must be lower than the one related to recrystallization and higher than the temperature corresponding to the end of the last endothermic peak. Bratoev et al. [18] suggest temperature range of 650 °C–800 °C for calcination process because below 650 °C the intensity of the process is low and above 800 °C reactivity may start to decrease, but emphasize that optimal values should be determined experimentally in each case. In fact, the reaction time of a material depends not only on the burning temperature but also on its mineral composition. The constant and continuous weight loss that can be observed between 525 °C and 1000 °C is related to the occurrence of gradual clay minerals decomposition throughout the firing process without obvious endothermic or exothermic reaction [42]. The total weight loss of the WTS sample was 16.13%.

It is important to highlight that the most important particularities regarding pozzolanic reactivity are the quantity and type of clay minerals, calcining mode and fineness, as well as the crystallinity of kaolinite that causes different reaction rates, while structural characteristics of other generic minerals or impurities have been proved to be less important [63,18]. The most reactive state occurs when the calcining temperature leads to loss of hydroxyls and results in a collapsed and disarranged structure [56].

Fig. 5 shows XRD spectra of *in natura* and calcined WTS samples. Diffraction patterns of *in natura* WTS confirms the predominance of quartz (00-046-1045) and kaolinite (01-078-1996) and the presence of albite (00-009-0466) and leadhillite (01-080-1390). Flash calcined WTS samples present three crystalline phases: quartz, albite, and muscovite (01-072-1503). Five crystalline phases are identified in WTS calcined in the electrical muffle furnace at temperatures up to 700 °C: quartz, kaolinite, albite, muscovite, and moganite (01-079-1503). At higher temperatures (750 °C and 800 °C), kaolinite is no longer detected and hematite (01-073-0603) is identified, besides quartz, albite, muscovite, and moganite. Fig. 6 shows crystalline phases identified at main peaks for all samples.

Table 5 contains the quantitative mineralogical analysis of WTS crystalline phases, obtained by Rietveld refinement. All WTS samples present crystalline phases Quartz and Albite. *In natura* WTS presents 43.8% of Kaolinite, which is not detected after flash calcination or burning temperatures higher than 750 °C in the electrical muffle furnace. The absence of kaolinite means that the kaolin–metakaolin transformation (dehydroxylation) is complete, which is indicative of the calcination method efficiency. Presence of hematite was identified in WTS samples burned at 750 °C and 850 °C in the electrical muffle furnace. Other changes observed at calcined samples are the presence of muscovite, regardless of the burning temperature, and small amounts of moganite (1.7 to 10.6%) in samples calcined in the electrical muffle furnace.

The absence of the crystalline and not reactive phase mullite suggests no recrystallization, which is reasonable since calcination temperature did not exceed 850 °C [58,72]. One of the advantages of flash calcination is that high process temperatures enable complete calcination while the short retention time suppresses the formation if inert-temperature phases like mullite, even if the material is treated above the optimal calcination temperature [41]. Notwithstanding, only a few tenths of a second in a flash calciner at 1100 °C may lead to the formation of mullite [22]. The temperature of about 950 °C and residence time of 0.5 s are the preferred calcination conditions, which represent a good tradeoff between fast dehydroxylation and slow unwanted transformation reactions [62]. The design of the flash calcination pilot plant used in this research program still does not allow particles to reach temperatures this high.

3.2. Morphological characterization of calcined WTS

Fig. 7 shows morphological characteristics of *in natura* and calcined WTS with a residence time of 1 h, obtained by SEM. Samples

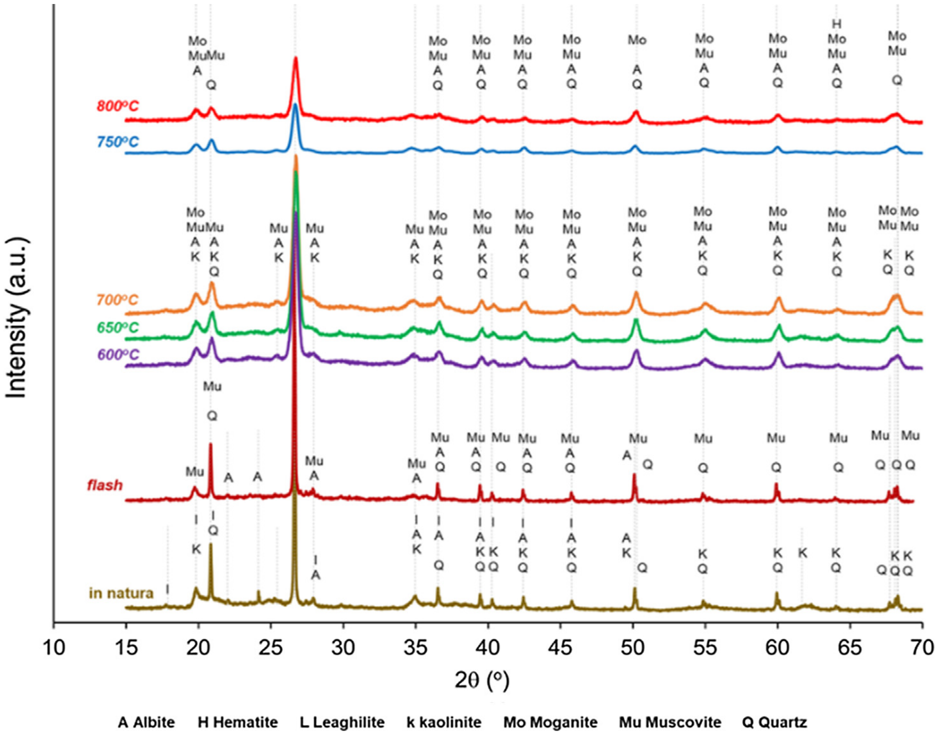

Fig. 5. Diffraction patterns of *in natura* and calcined WTS.

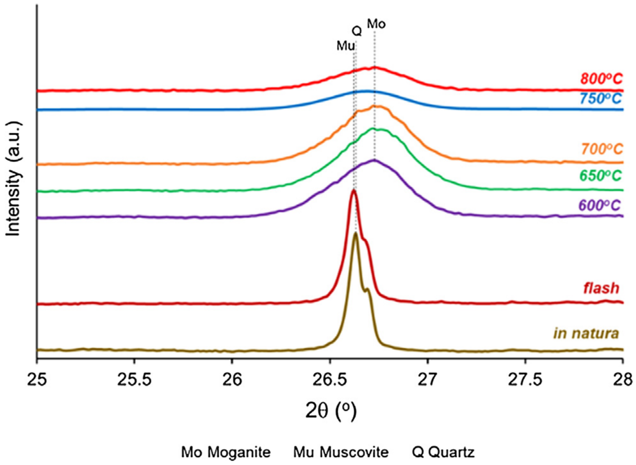

Fig. 6. Identification of crystalline phases at main peaks for all samples.

of *in natura* WTS presented in Fig. 7(a) and (b) display small clusters of agglomerates consisting mainly of mesoporous [1]. In Fig. 7(c) and (d) particles with rough texture [42] and non-homogeneous size are coupled into conglomerates. Fine particles are attached to the surface of larger particles and there are hollow areas among the coupled particles, related to the high porosity [43,11] on the sludge surface. Flash calcined particles reported by San Nicolas et al. [58] presented flat, hexagonal, and leaf-like shape originated during dihydroxylation related to the evaporation of water. Fig. 7(e) and (f) show typical characteristics of sintering processes, with slightly rounded aggregated particles. Calcination at 800 °C resulted in a decrease in the relative amount of finer particles, a decrease in BET specific surface area, and the formation of metakaolin. However, flash calcined samples of Fig. 7(c) show aggregates with lower volume, which leads to the reduction of BET specific surface area when compared to samples calcined in the electrical muffle. Fig. 7(g) to (l) show fragments of pseudo-hexagonal microstructures with flaky morphology, stacked in a less dense structure, which corroborates the results of BET specific surface area shown in Table 6.

Table 5
WTS mineralogy obtained by Rietveld refinement.

	in natura	flash	600 °C	650 °C	700 °C	750°*	800 °C
Quartz, syn (SiO_2)	46.6	48.2	47.1	50.1	47.8	52.4	52.4
Kaolinite ($Al_2(Si_2O_5)(OH)_4$)	43.8	–	18.4	16.6	17.3	–	–
Muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$)	–	34.8	23.7	25.0	25.0	27.9	19.7
Albite, ordered ($NaAlSi_3O_8$)	7.0	17.0	6.8	5.5	8.1	6.1	6.7
Moganite (SiO_2)	–	–	4.0	2.8	1.7	10.6	8.7
Hematite, syn (Fe_2O_3)	–	–	–	–	–	3.1	12.5
Leadhillite ($Pb_4(SO_4)(CO_3)_2(OH)_2$)	2.6	–	–	–	–	–	–
Agreement indexes							
R expected – R_{exp} (%)	4.024	4.341	4.882	4.896	4.887	5.044	5.620
Weighted R profile – R_{wp} (%)	6.519	6.037	6.987	7.352	8.346	5.881	7.085
Goodness of fit – $X^2 = [R_{wp}/R_{exp}]^2$	2.624	1.934	2.049	2.255	2.917	1.360	1.589

Residence time 2 h; Results in % by weight; Results correspond to the crystalline phase only.

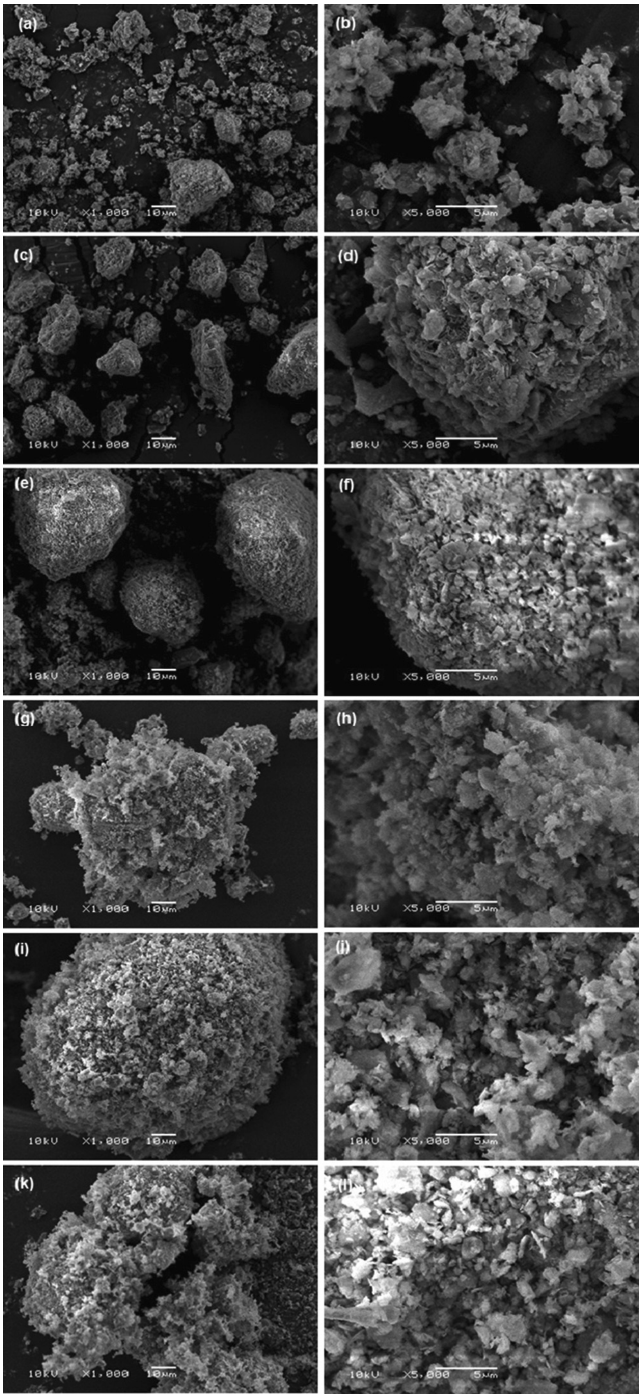

Fig. 7. SEM observation of *in natura* and calcined WTS with residence time of 1 h: (a) *In natura*, 1000X; (b) *In natura*, 5,000X; (c) Flash, 1000X; (d) Flash, 5000X; (e) 800 °C, 1000X; (f) 800 °C, 5000X; (g) 750 °C, 1000X; (h) 750 °C, 5000X; (i) 700 °C, 1000X; (j) 700 °C, 5000X; (k) 650 °C, 1000X; (l) 650 °C, 5000X.

3.3. Physical characterization of calcined WTS

Fig. 8 shows particle size distribution for all samples. BET specific surface area, average particle size (D_{50}), and percentage of WTS retained on 45 μm m sieve are shown in Table 6. Average particle size (D_{50}) of *in natura* WTS is 350 μm before grinding. All calcined WTS samples were ground for 4 h in a ceramic ball mill in order to get more than 90% of particles smaller than 45 μm.

Results show that thermal treatments at 600 °C, 650 °C, and 750 °C for 1 h resulted in WTS with higher BET specific surface area when compared to thermal treatment at the same temperatures for 2 h. The higher BET specific surface area was obtained through thermal treatment at 650 °C for 1 h. Samples burned at 700 °C and 800 °C present a lower specific surface area than samples produced with thermal treatment at 600 °C, 650 °C, and 750 °C.

Results reported by Abo-El-Enein et al. [1] show that thermal treatment at 700 °C resulted in WTS with a lower specific surface area than that of thermal treatment at 500 °C. Results of Table 7 corroborate these findings regarding the BET surface area of samples burned at 700 °C and 800 °C compared to samples burned at 600 °C and 650 °C. However, thermal treatment at 750 °C resulted in samples with BET specific surface area similar to the ones submitted to burning temperatures of 600 °C and 650 °C.

Results of Fig. 8 and Table 6 show that WTS samples do not follow the inverse relationship between average particle size and BET specific surface area after burning and grounding. BET specific surface area is highly influenced by the internal porous structure [54] and the amorphous content of the particles [9]. Flash calcined WTS sample, for instance, presents the lower average particle size (14.32 μm) and the lower BET specific surface area (21.17 m^2/g), which may indicate the formation of soft agglomerates (Fig. 7) due to short residence time of particles inside the calciner, as reported by Teklay et al. [62].

3.4. Potential pozzolanic activity with Portland cement

Results presented in Tables 4–6 show that all calcined WTS samples comply with the requirements of Table 2, related to the use of calcined WTS as SCM with properties equivalent to those of a highly active pozzolanic material, with regard to SiO_2 and SO_3 contents, percentage retained on 45 μm sieve, and B.E.T specific surface area. CaO + MgO content of samples calcined in the electrical muffle furnace is between 1.8 and 2%. The maximum CaO + MgO content of 1.5% was only obtained for flash calcination. Calcining temperatures and exposure times used to calcine WTS led to Al_2O_3 contents between 24 and 28%, lower than the required 32%. Maximum loss on ignition requirement of 4% was reached using flash calcination and electrical muffle furnace with temperatures higher than 750 °C, or 650 °C and 700 °C for 2 h. Results of Table 4 confirms the findings of Bratoev et al. [18] regarding optimum lost on ignition at 800 °C. K_2O content is related to the presence of surfactants and fertilizers irregularly discharged in the river. In fact, not complying with a certain standard requirement does not mean that the waste is unsuitable for the intended application unless unstable phases are identified through mineralogical analysis. In the case of K_2O, deleterious effects on the cementitious matrices depend on the dissolution of the crystalline phase identified in the mineralogical analysis [45]. Additionally, Leemann and Lothenbach [40] reported considerable different expansions caused by cements with same Na_2O-equivalent but different K/Na-ratio, which indicates that Na_2O-equivalent may not always accurately define the potential to cause expansion.

Fig. 9 shows the results of PI_7 calculated for all calcined WTS samples based on the results of compressive strength tests. Results show that only the mortar produced with WTS calcined at 800 °C for 1 h reached the minimum PI_7 of 105% (Table 3) desirable for the use of calcined WTS as SCM with properties equivalent to those of a highly active pozzolanic material.

Bich et al. [16] report that a degree of dehydroxylation higher than 95% has to be achieved to yield high reactivity. Residence time and temperature show significant influence at the PI_7 at a confidence level of 95%. The residence time of 1 h showed to be 5% more effective. The residence time of 1 h presents two groups with equivalent means at a confidence level of 95% (600 °C, 650 °C, and 700 °C; 750 °C and 800 °C). The residence time of 2 h does not show any significant difference among means at a confidence

Table 6
BET specific surface area in m^2/g, average particle size (D_{50}) in μm, and percentage retained on 45 μm after grinding.

	In natura	flash	600 °C		650 °C		700 °C		750 °C		800 °C	
			1 h	2 h	1 h	2 h	1 h	2 h	1 h	2 h	1 h	2 h
D_{50}	23.35	14.32	21.59	20.54	22.06	23.23	31.26	24.31	26.48	24.18	17.69	18.90
% Retained*	–	7.48	7.77	7.32	7,05	7.70	9.66	6.30	7.20	7.00	7.38	7.42
BET	22.64	21.17	28.81	25.23	33.20	25.49	28.61	24.23	29.97	27.78	24.84	24.96

* Obtained according to the recommendations of NBR 15894-3 [8,7].

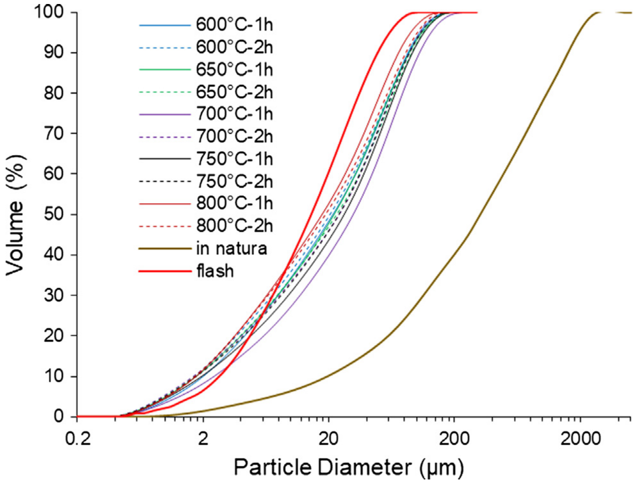

Fig. 8. Particle size distribution of *in natura* and calcined WTS.

level of 95%. PI_7 of flash calcination is statistically equivalent to that of muffle furnace for temperatures of 600 °C, 650 °C, and 700 °C with a residence time of 1 h at a confidence level of 95%. Despite the fact that the performance of flash calcination is statistically equivalent to that of muffle furnace for temperatures up to 700 °C and residence time of 1 h, energy consumption for flash calcination is much lower. Table 7 shows the ANOVA for the analyzed parameters.

It is important to highlight that, in fact, the reactivity of calcined materials obtained from waste is difficult to be controlled. Due to the mineralogical variety, it is complicated to ensure total dehydroxylation of phyllite minerals, since recrystallization and decomposition of passive phases occur at different temperatures [47]. Additionally, structural properties of a material calcined through a flash heating process or a calcination process, in which chemical and physical equilibrium are achieved, are quite different [19].

Results show that WTS sample calcined at 750 °C and 850 °C for 1 h presents the most promising performances considering environmental and economic aspects related to energy consumption and the requirements for application of calcined WTS as SCM with properties equivalent to those of a highly active pozzolanic material, even though CaO + MgO content of 1.7% does not comply with the maximum of 1.5%, nor does Al_2O_3 content of 25.2% with the minimum of 32%. These results are consistent with the mineralogical analysis presented in Table 5, which evidences the complete kaolin–metakaolin transformation (dehydroxylation) in samples calcined at 750 °C and 800 °C. The complete removal of chemically bound water results in a collapsed and disarranged structure and confers to the calcined WTS an amorphous state and, consequently, pozzolanic reactivity, which leads to a high efficient SCM [56,43,42,47].

The performance index of flash calcined WTS at 7 days (94%) is lower to the one desirable for a material to be used as highly active pozzolan (105%), although the mineralogical analysis of Table 5 has shown the complete kaolin–metakaolin transformation, identified by the absence of kaolinite. This may be related to the heterogeneous composition and porosity of the flash calcined clays, as a result of the calcining process itself due to the short residence time or the presence of a temperature gradient, for instance. In fact, dehydroxylation in flash calcined products occurs much faster than the water can diffuse, causing a build-up in steam pressure within the particle, which at the proper temperature become elastic, permitting bubble formation/internal voids [19,44]. Apart from that, the lower average particle size and BET specific surface area of flash calcined WTS samples, related to the short residence time of particles inside the calciner [62], results in high porosity, as a result of the attachment of fine particles to the surface of larger ones [43,11], shown in Fig. 7.

Regarding the use of calcined WTS as SCM with characteristics of normal pozzolan, results presented in Tables 4–6 show that all calcined WTS samples attend minimum requirements related to the content of SiO_2, Al_2O_3, and Fe_2O_3, maximum content of SO_3, maximum loss on ignition, and percentage retained in 45 μm.

Fig. 10 shows the results of PI_{28} calculated for WTS samples calcined in the electrical muffle furnace at different temperatures and residence time. Results of PI_{28} indicate that mortars produced with WTS calcined at 700 °C for 2 h and at 750 °C for 1 h do not reach the minimum of 90% required for application of calcined WTS as SCM with characteristics of normal pozzolan. It is interesting to point out that samples calcined at 700° and C750 °C present slightly higher particle size, as shown in Fig. 8 and Table 6.

As shown in Table 7, residence time does not show any significant influence at PI_{28} at a confidence level of 95%. On the other hand, the influence of temperature showed to be significant at a confidence level of 95%. Residence time of 1 h presents two groups

Table 7
ANOVA results.

		SS	DF	MS	F-test	p value
PI_7	Residence Time (A)	0.10	1	0.10	8.85	0.00335
	Temperature (B)	0.28	4	0.07	6.06	0.00014
	AB	0.13	4	0.03	2.91	0.02301
	Error	1.96	170	0.01		
PI_{28}	Residence Time (A)	0.00	1	0.00	3.90	0.89495
	Temperature (B)	0.33	4	0.08	2.42	0.00019
	AB	0.42	4	0.10	2.42	0.00002
	Error	2.41	170	0.01		

SS: Sum of Squares; DF: Degree of Freedom; MD: Mean Square.

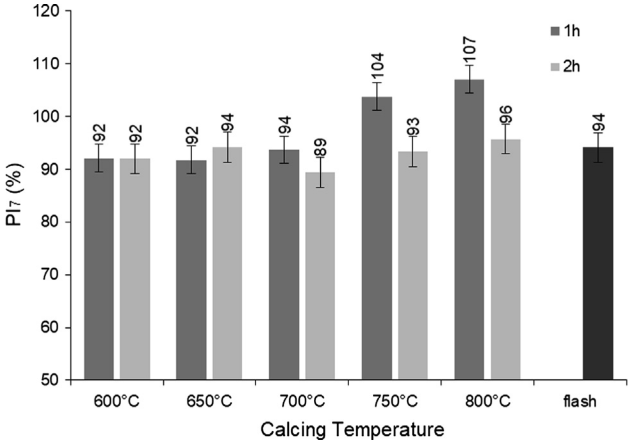

Fig. 9. Performance Index with cement at 7 days.

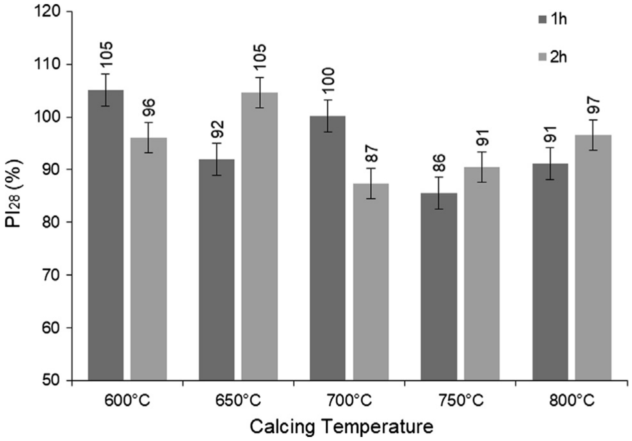

Fig. 10. Performance Index with cement at 28 days.

with equivalent means (600 °C and 700 °C; 650 °C, 750 °C, and 800 °C) and residence time of 2 h presents three groups with equivalent means (650 °C and 800 °C; 600 °C, 750 °C, and 800 °C; 700 °C and 750 °C).

WTS sample calcined at 600 °C for 1 h shows the most promising performance considering environmental and economic aspects related to energy consumption and the compliance with the requirements presented in Table 2 related to the use of calcined WTS as SCM with characteristics equivalent to those of normal pozzolans.

Tironi et al. [63] state that, at early ages, compressive strength depends more on the specific surface, which is a physical factor, however, at later ages, the effect of structural disorder and the amorphous material derived from kaolinite content become more relevant. On the other hand, Alujas et al. [13] have proved that, for low-grade kaolinitic clays, where pozzolanic reactivity could be considered as the combined contribution of all clay minerals present in the sample, the higher the overall Al2O3 and structural OH^- content in the raw material, the higher the potential pozzolanic reactivity of calcination products.

It is important to clarify that PI_{28} is not an evolution of PI_7 in time, since mortars whose mix proportions are presented in Table 3 have been produced in two different groups: Mortar 7A as reference and mortars 7B to each calcining temperature and residence time; Mortar 28A as reference and mortars 28B to each calcining temperature and residence time.

Average carbon emission associated with clinker production in Brazil is about 855kgCO_2/t considering no allocation (waste status) for residual mineral additions. Emissions related to blended cements are about 700kgCO_2/t to 800kgCO_2/t for CPII-F and 600kgCO_2/t to 780kgCO_2/t for CPII-Z, while pozzolanic cements release about 190kgCO_2/t to 520kgCO_2/t [49]. On the other hand, the energy required to heat clay to 600 °C may vary from 800 MJ/ton to 1700 MJ/ton depending on the furnace. If calcination is achieved by the combustion of biomass rather than fossil fuels, carbon emission is about 0.091kgCO_2/MJ [46]. Considering these data, a simplified carbon saving assessment points out that emissions associated with WTS calcination are in the range of 76kgCO_2/ton to 150kgCO_2/ton. In this context, the use of calcined WTS as SCM may contribute to reducing greenhouse gases emissions and impacts related to waste discharge in watercourses.

4. Conclusions

Results presented in this paper have proved the potential for developing an SCM from the sludge waste originated in the investigated water treatment, whose waste is disposed of in the Itajaí-Açú River located in Southern Brazil. WTS is a non-hazardous and non-inert waste, mainly composed of SiO_2, Al_2O_3, Fe_2O_3 and contains essentially quartz (46.6%), moderate content of kaolinite (43.8%), albite (7.0%) and leadhillite (2.6%), without environmental restrictions for use in construction.

WTS samples calcined at 600 °C for 1 h show the most promising performance regarding the application as SCM equivalent to a normal pozzolan, considering technical, environmental and economic aspects related to energy consumption. Calcination temperatures of 750 °C and 800 °C with residence time of 1 h are the most promising processing combinations for the production of SCM from calcined WTS with properties equivalent to those of highly active pozzolanic materials, though CaO + MgO content of 1.7% does not comply with the maximum of 1.5%, nor does Al_2O_3 content of 25.2% with the minimum of 32%, which does not mean that the waste is unsuitable for the intended application.

Calcined WTS showed great technical and environmental potential to be used as an alternative source of SCM in the near future. However, the characterization of sludge from different sources is imperative to guarantee that the properties of the calcined sludge will meet the requirements for utilization as SCM. Further studies on the viability of producing calcined WTS in a commercial scale are required, with the improvement of calcination processes efficiency and an extensive microstructural investigation in order to identify hydration products and their evolution in time. Finally, it is important to address workability and durability issues related to the use of calcined WTS in cement-based materials in future studies.

Declaration of Competing Interest

None.

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References

[1] S.A. Abo-El-Enein, A. Shebl, S.A. Abo El-Dahab, Drinking water treatment sludge as an efficient adsorbent for heavy metals removal, Appl. Clay Sci. 146 (2017) 343–349.

[2] ABNT, Associação Brasileira de Normas Técnicas, 2014. Materiais pozolânicos — Determinação do índice de desempenho com cimento Portland aos 28 dias, NBR 5752, Rio de Janeiro, Brazil, 4pp.

[3] ABNT, Associação Brasileira de Normas Técnicas, 2004. Resíduos sólidos – Classificação, NBR 10004, Rio de Janeiro, Brazil, 71pp.

[4] ABNT, Associação Brasileira de Normas Técnicas, 2004. Procedimento para obtenção de extrato lixiviado de resíduos sólidos, NBR 10005, Rio de Janeiro, Brazil, 16pp.

[5] ABNT, Associação Brasileira de Normas Técnicas, 2004. Procedimento para obtenção de extrato solubilizado de resíduos sólidos, NBR 10006, Rio de Janeiro, Brazil, 3pp.

[6] ABNT, Associação Brasileira de Normas Técnicas, 2014. Materiais pozolânicos – Requisitos, NBR 12653, Rio de Janeiro, Brazil, 6pp.

[7] ABNT, Associação Brasileira de Normas Técnicas, 2010. Metacaulim para uso com cimento Portland em concreto, argamassa e pasta. Parte 1: Requisitos, NBR 15894-1, Rio de Janeiro, Brazil, 8pp.

[8] ABNT, Associação Brasileira de Normas Técnicas, 2010. Metacaulim para uso com cimento Portland em concreto, argamassa e pasta. Parte 2: Determinação do índice de desempenho com cimento aos sete dias, NBR 15894-2, Rio de Janeiro, Brazil, 3pp.

[9] Q.A. Acton, Issues on environment, health, and pollution, Scholarly Editions (2013) 1180.

[10] B. Afkhami, A. Akbarian, A.N. Beheshti, A.H. Kakaee, B. Shabani, Energy consumption assessment in a cement production plant, Sustainable Energy Technol. Assess. 10 (2015) 84–89.

[11] T. Ahmad, M. Ahmad, M. Alam, Sustainable management of water treatment sludge through 3R concept, J. Cleaner Prod. 124 (2016) 1–13.

[12] J.E. Alleman, N.A. Berman, Constructive sludge management: biobrick, J. Environ. Eng. 110 (1984) 301–311.

[13] A. Alujas, R.S. Almenares, S. Betancourt, C. Leyva, 2015. Pozzolanic Reactivity of Low Grade Kaolinitic Clays: Influence of Mineralogical Composition. In: Proceedings of the 1st International Conference on Calcined Clays for Sustainable Concrete. Lausane, Switzerland. Available at https://link.springer.com/content/pdf/10.1007%2F978-94-017-9939-3.pdf. Access on 10th February 2018.

[14] A. Benlalla, M. Elmoussaouiti, M. Dahhou, M. Assafi, Utilization of water treatment plant sludge in structural ceramics bricks, Appl. Clay Sci. 118 (2015) 171–177.

[15] E. Bernardo, R. Dal Maschio, Glass–ceramics from vitrified sewage sludge pyrolysis residues and recycled glasses, Waste Manage. 31 (2011) 2245–2252.

[16] Ch. Bich, J. Ambroise, J. Péra, Influence of degree of dehydroxylation on the pozzolanic activity of metakaolin, Appl. Clay Sci. 43 (2009) 392–400.

[17] BRASIL, 2010. Federal Law 12305: National Policy on Solid Waste. Brasília, Brazil, 20pp.

[18] Bratoev B., Doykov I., Ninov J., Lenchev A., 2017. Pozzolanic activity assessment of calcined clays with complex minerals content. Advances in Cement Research, ahead of print.

[19] D. Bridson, T.W. Davies, D.P. Harrison, Properties of flash-calcined kaolinite, Clays Clay Miner. 33 (1985) 258–260.

[20] A. Chakchouk, L. Trifi, B. Samet, S. Bouaziz, Formulation of blended cement: Effect of process variables on clay pozzolanic activity, Constr. Build. Mater. 23 (2009) 1365–1373.

[21] K.Y. Chiang, P.H. Chou, C.R. Ching-Rou Hua, K.L. Chien, C. Cheeseman, Lightweight bricks manufactured from water treatment sludge and rice husks, J. Hazard. Mater. 171 (2009) 76–82.

[22] M. Claverie, F. Martin, J.P. Tardy, M. Cyr, P. De Parseval, O. Grauby, C. Le Roux, Structural and chemical changes in kaolinite caused by flash calcination: formation of spherical particles, Appl. Clay Sci. 114 (2015) 247–255.

[23] CEN, European Committee for Standardization, 2011. Cement - Part 1: Composition, specifications, and conformity criteria for common cements, EN 197-1, Brussels, Belgium, 29pp.

[24] L.N.P. Cordeiro, A.B. Masuero, D.C.C. Dal Molin, Analysis of potential pozzolanic ash from rice husk using the technique of Rietveld refinement, Matéria 19 (2014) 150–158.

[25] CSI, 2002. Our agenda for action. Report, Genève, Switzerland, 50pp.

[26] CSI, 2016. Cement Industry Energy and CO2 Performance: Getting the Numbers Right. Database, Genève, Switzerland, 20pp.

[27] J.A. Cusidó, L.V. Cremades, Environmental effects of using clay bricks produced with sewage sludge: Leachability and toxicity studies, Waste Manage. 32 (2012) 1202–1208.

[28] K.B. Dassanayake, G.Y. Jayasinghe, A. Surapaneni, C. Hetherington, A review on alum sludge reuse with special reference to agricultural applications and future challenges, Waste Manage. 38 (2015) 321–335.

[29] ECRA & CSI, 2017. Development of state of the art techniques in cement manufacturing: trying to look ahead. CSI/ECRA Technology Papers 2017, Genève, Switzerland, 190pp.

[30] J.M.F. Ferreira, S.M. Olhero, Al-rich sludge treatments towards recycling, J. Eur. Ceram. Soc. 22 (2002) 2243–2249.

[31] R. Garcia, R.V. La Villa, I. Vegas, M. Frias, M.I.S. Rojas, The pozzolanic properties of paper sludge waste, Constr. Build. Mater. 22 (2008) 1484–1490.

[32] A.L.G. Gastaldini, M.F. Hengen, M.C.C. Gastaldini, F.D. Amaral, M.B. Antolini, T. Coletto, The use of water treatment plant sludge ash as a mineral addition, Constr. Build. Mater. 94 (2015) 513–520.

[33] B.E.D.B. Hegazy, A. Fouad, A.M. Hassanain, Brick manufacturing from water treatment sludge and rice husk ash, Aust. J. Basic Appl. Sci. 6 (2012) 453–461.

[34] C.H. Huang, S.Y. Wang, Application of water treatment sludge in the manufacturing of lightweight aggregate, Constr. Build. Mater. 43 (2013) 174–183.

[35] IBGE, 2010. National Survey on Basic Sanitation. Report, Brasilia, Brazil, available at <http://www.sidra.ibge.gov.br/bda/pesquisas/pnsb/default.asp?o=23&i=P>.

[36] Y. Kihara, G. Visedo, Economia de baixo carbono: uma visão para o futuro da indústria brasileira de cimento, Concreto Construções 77 (2015) 86–91.

[37] M. Kyncl, Opportunities for Water Treatment Sludge Reuse, GeoScience Engineering, LIV, 2008, pp. 11–22.

[38] O. Kizinievic, R. Zurauskiene, V. Kizinievic, R. Zurauskas, Utilization of sludge waste from water treatment for ceramic products, Constr. Build. Mater. 41 (2013) 464–473.

[39] R.V. LaVilla, M. Frías, M.I.S. Rojas, I. Vegas, R. García, Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace, Appl. Clay Sci. 36 (2007) 279–286.

[40] A. Leemann, B. Lothenbach, The influence of potassium-sodium ratio in cement on concrete expansion due to alkali-aggregate reaction, Cem. Concr. Res. 38 (10) (2008) 1162–1168.

[41] J. Lemke, C. Berger, Thermal processing of calcined clay, Proceedings of the 2nd International Conference on Calcined Clays for Sustainable Concrete, 2018.

[42] Y.P. Ling, R.H. Tham, S.M. Lim, M. Fahim, C.H. Ooi, P. Krishnan, A. Matsumotoc, F.Y. Yeoh, Evaluation and reutilization of water sludge from fresh water processing plant as a green clay substituent, Appl. Clay Sci. 143 (2017) 300–306.

[43] C. Martínez-García, D. Eliche-Quesada, L. Pérez-Villarejo, F.J. Iglesias-Godino, F. A. Corpas-Iglesias, Sludge valorization from wastewater treatment plant to its application on the ceramic industry, J. Environ. Manage. 95 (2012) S343–S348.

[44] R.H. Meinhold, H. Atakul, T.W. Davies, R.C.T. Slade, Flash calcination of kaolinite studied by DSC, TG and MAS NMR, J. Therm. Anal. 38 (1992) 2053–2065.

[45] P.K. Metha, P.J.M. Monteiro, Concrete – Microstructure, Properties, and Materials, Third Edition, Mc Graw Hill, 2006.

[46] MME, 2009. Studies for elaboration of the geology, mining and mineral transformation duodecenal plan (2010 - 2030). Report, Brasilia, Brazil, available at http://www.mme.gov.br/documents/1138775/1256650/P23_RT32_Perfil_da_Argila.pdf/b6fc71dc-3c0a-4eb1-b2a5-df62b2c3bec0.

[47] S. Mohammed, Processing, effect and reactivity assessment of artificial pozzolans obtained from clays and clay wastes: a review, Constr. Build. Mater. 140 (2017) 10–19.

[48] S.N. Monteiro, J. Alexandre, J.I. Margem, R. Sánchez, C.M.F. Vieira, Incorporation of sludge waste from water treatment plant into red ceramic, Constr. Build. Mater. 22 (2008) 1281–1287.

[49] V.C.H.C. Oliveira, B.L. Damineli, V. Agopyan, V.M. John, Estratégias para a minimização da emissão de CO_2 de concretos, Ambiente Construído 14 (2014) 167–181.

[50] J.M. Paris, J.G. Roessler, C.C. Ferraro, H.D. DeFord, T.G. Townsend, A review of waste products utilized as supplements to Portland cement in concrete, J. Cleaner Prod. 121 (2016) 1–18.

[51] M.O. Ramadan, H.A. Fouad, A.M. Hassanain, Reuse of water treatment plant sludge in brick manufacturing, J. Appl. Sci. Res. 4 (2008) 1223–1229.

[52] Rasmussen K. E., Moesgaard M., Køhler L. L., Tran T. T., Skibsted J., 2015. Comparison of the Pozzolanic Reactivity for Flash and Soak Calcined Clays in Portland Cement Blends. In: Proceedings of the 1st International Conference on Calcined Clays for Sustainable Concrete. Lausane, Switzerland. Available at https://link.springer.com/content/pdf/10.1007%2F978-94-017-9939-3.pdf. Access on 10th February 2018.

[53] L.P. Rodrigues, J.N.F. Holanda, Recycling of water treatment plant waste for production of soil cement bricks, Procedia Mater. Sci. 8 (2015) 197–202.

[54] O. Rodríguez, L. Kacimi, A. López-Delgado, M. Frías, A. Guerreiro, Characterization of Algerian reservoir sludges for use as active additions in cement: New pozzolans for eco-cement manufacture, Constr. Build. Mater. 40 (2013) 275–279.

[55] N.H. Rodríguez, S. Martínez-Ramírez, M.T. Blanco-Varela, M. Guillem, J. Puig, E. Larrotcha, J. Flores, Evaluation of spray-dried sludge from drinking water treatment plants as a prime material for clinker manufacture, Cem. Concr. Compos. 33 (2011) 267–275.

[56] B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined clays a pozzolans for concrete: a review, Cem. Concr. Compos. 23 (2001) 441–454.

[57] S. Salvador, Pozzolanic properties of flash-calcined kaolinite: a comparative study with soak-calcined products, Cem. Concr. Res. 25 (1) (1995) 102–112.

[58] Nicolas R. San, M. Cyr, G. Escadeillas, Characteristics and applications of flash metakaolins, Appl. Clay Sci. 83 (84) (2013) 253–262.

[59] M.A. Tantawy, Characterization and pozzolanic properties of calcined alum sludge, Mater. Res. Bull. 61 (2015) 415–421.

[60] M. Tarrago, M. Garcia-Valles, M.H. Aly, S. Martínez, Valorization of sludge from a wastewater treatment plant by glass-ceramic production, Ceram. Int. 43 (2017) 930–937.

[61] S.R. Teixeira, G.T.A. Santos, A.E. Souza, P. Alessio, S.A. Souza, N.R. Souza, The effect of incorporation of a Brazilian water treatment plant sludge on the properties of ceramic materials, Appl. Clay Sci. 53 (2011) 561–565.

[62] A. Teklay, C. Yina, L. Rosendahla, L.L. Køhler, Experimental and modeling study of flash calcination of kaolinite rich clay particles in a gas suspension calciner, Appl. Clay Sci. 103 (2015) 10–19.

[63] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Kaolinitic calcined clays: factors affecting its performance as pozzolans, Constructing Build. Mater. 28 (2012) 276–281.

[64] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, Cem. Concr. Compos. 37 (2013) 319–327.

[65] A. Tironi, F. Cravero, A.N. Scian, E.F. Irassar, Pozzolanic activity of calcined halloysite-rich kaolinitic clays, Appl. Clay Sci. 147 (2017) 11–18.

[66] T. Toya, A. Nakamura, Y. Kameshima, A. Nakajima, K. Okada, Glass-ceramics prepared from sludge generated by a water purification plant, Ceram. Int. 33 (2007) 573–577.

[67] C.H. Weng, D.F. Lin, P.C. Chiang, Utilization of sludge as brick materials, Adv. Environ. Res. 7 (2003) 679–685.

[68] WHO & UNICEF, 2017. Progress on Drinking Water. Sanitation and Hygiene: 2017 update and SDG baselines. Report, Genève, Switzerland, 116pp.

[69] E. Wolf, W.K. Schwabe, S.V. Conceição, Utilization of water treatment plant sludge in structural ceramics, J. Cleaner Prod. 96 (2015) 282–289.

[70] V.R. Wiggers, A.J.R. Wisniewski, L.A.S. Madureira, A.A.C. Barros, H.F. Meier, Biofuels from waste fish oil pyrolysis: continuous production in a pilot plant, Fuel 88 (2009) 2135–2141.

[71] J.K. Yamamoto, Y. Kihara, A.M. Coimbra, T.J. Montanheiro, Environmental impact reduction on the production of blended Portland cement in Brazil, Environ. Geosci. 4 (1997) 192–206.

[72] D. Zhou, R. Wang, M. Tyrer, H. Wong, C. Cheeseman, Sustainable infrastructure development through use of calcined excavated waste clay as a supplementary cementitious material, J. Cleaner Prod. 168 (2017) 1180–1192.