Effect of recycled natural water treatment sludge and biochar on the mechanical performance and hydration kinetics of Portland cement composite

by Samuel De Carvalho Gomes

Thesis submitted in fulfilment of the requirements for
the degree of **Master of Engineering (Research)**

under the supervision of Prof. John Zhou
Co Supervisor: Doctor Wengui Li

University of Technology Sydney
Faculty of School of Civil and Environmental Engineering

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Samuel De Carvalho Gomes declare that this thesis, is submitted in fulfilment of the requirements for the award of Master of Engineering (Research), in the School of Civil and Environmental Engineering at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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LIST OF PUBLICATIONS

- **Gomes, S. D. C.,** Zhou, J. L., Li, W., & Long, G. 2019, Progress in manufacture and properties of construction materials incorporating water treatment sludge: A review. Resources, Conservation and Recycling, 145, 148-159.

- **Gomes, S. D. C.,** Zhou, J. L., Li, W., & Qu, F. (2020). Recycling of raw water treatment sludge in cementitious composites: effects on heat evolution, compressive strength and microstructure. Resources, Conservation and Recycling, 161, 104970.

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Abstract

Water treatment sludge (WTS) management is a growing global problem for water treatment plants (WTPs) and governments. This research examines the application of natural WTS and thermally modified sludge (WTS-biochar) as a construction materials ingredient by converting a waste by-product to a value-added product. Important aspects such as the physicochemical interaction of the sludge/biochar with the Portland cement, the hydration kinetics of the cement paste and the mechanical behaviour of the composite were carefully studied. The results show that for 1-2% of WTS addition, the compressive strength and heat evolution of the cement paste was well maintained being close to the reference specimen after 28 days of curing. However, for sludge addition above 5%, a delay in the hydration reaction was observed, together with about 25% reduction in compressive strength at 28 days of curing. The mineralogical and thermal analysis showed decreasing portlandite content and increasing calcite in the WTS-amended composites. Scanning electron microscope analysis demonstrated that the addition of sludge induced more porous and weak surface structures compared to the reference specimen. The thermally modified WTS (biochar) show an improvement in material kinetics and mechanical properties. The mineralogical, thermal and microscopic analysis shows several pieces of evidence of pozzolanic activity of the biochar. The samples with 2% and 5% WTS-biochar showed higher heat release than the reference material. Specimens with 1%, 2% and 5% WTS-biochar showed a slightly higher compressive strength at 28 days compared to the reference material. As a result of all these findings, this project has shown strong indications that WTS can be promoted as a sustainable and alternative resource for construction materials with less environmental impacts as well as economic savings.

Keywords: Water treatment sludge; Construction materials; Biochar; Cement mortar; Pyrolysis

Chapter 1

1. Introduction

1.1 Research background

Large quantities of water treatment sludge (WTS) are produced daily from water treatment plants (WTP), and its management is attracting attention worldwide. A major environmental challenge for water treatment is the disposal of excess sludge produced during the process. Furthermore, other problems such as the risk of water contamination with heavy metals and high costs of sludge treatment disposal are challenges faced by companies and governments around the world. In Australia, the cost associated with the disposal without transportation is between $130-200 per tonne landfill or/and sewer disposal, with an approximate cost of over $6.2 million per annum just in the state of Victoria (Maiden et al., 2015). Thus, considering the concrete industry as a potential taker of industrial and urban by-products, this can be a sustainable and alternative disposal for the WTS. Although some research has been conducted thus far on the concept of using natural WTS or calcined in cementitious composites, there are no published studies so far on the application of modified-WTS by pyrosis (biochar) as an ingredient of cement composites.

1.2 Aim and objectives

The main aim of this research is to investigate the feasibility of using WTS as a supplementary cementitious material and the mechanical performance of the product. Therefore, proving the feasibility of sludge application in cement composites can suggest a better and more sustainable destination for this by-product and also provide an additional ingredient for the concrete industry.

The specific objectives of this study are:

- To review critically the previous studies that used WTS as an ingredient of concrete and cementitious composites.
- To perform the physicochemical characterization of WTS and also the biochar made by sludge.
- To determine some mechanical properties of fresh and hardened cement paste/mortar incorporating different levels of WTS (natural and biochar).
- To analyse the impacts and interaction of natural sludge and WTS-biochar on the hydration kinetics of cement products.

1.3. Significance and innovation of the research

1.3.1 Significance

The high costs associated with the waste disposal generated in water treatment plants are concerns of both local government and water treatment companies, which is typically disposed of in landfills. By studying the feasibility of applying this sludge as cementitious material through the characterisation and mechanical performance, the application of this waste product in the concrete field can be assessed.

1.3.2 Innovation

The likely original contributions from this research are listed below:

- Extensive physicochemical characterisation of natural WTS and WTS-biochar;
- Application of WTS and WTS-biochar as a supplementary cementitious material;
- Improved mechanical and hydration kinetics of WTS-cement products.

1.4. Research methods

This research includes some research methods such as systematic review, experimental components and data analyses.

- For the literature review of this research, I used the method of literature review to provide a complete and comprehensive summary of current literature relevant to the research questions.
- The experimental part of this study consists of a laboratory investigation of the properties (fresh and hardened) of cement paste with the addition of natural WTS and WTS-biochar. A summary of the tests is shown in Figure 1.

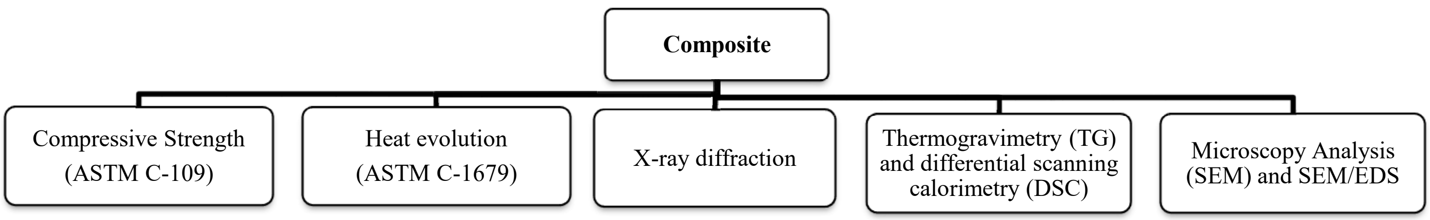


Figure 1. Summary of experimental tests conducted in this research.

Chapter 2

2. Literature Review

To protect public health, raw water is treated to a high standard at WTPs before drinking water distribution. Large quantities of WTS are produced daily by WTPs, and its management is becoming a global problem of major concern. A recent survey by Maiden et al. (2015) showed that the amount of WTS generated by Australian WTP could reach up to 43500 tonnes per year. In 2011, Japan generated more than 290000 dry tons of sludge across the country (Fujiwara, 2011), while the UK produced around 131000 tons in 2014 (Finlay, 2015). Figure 1 shows an estimated amount of sludge per capita produced in selected countries. It is estimated that an ordinary WTP generates over 10000 tons/day and 100000 tons/year of WTS (Babatunde and Zhao, 2007).

A major environmental challenge for water treatment is the disposal of excessive sludge produced in the process. The raw water quality and the treatment process are the main factors for the quantity and quality of the sludge produced. Thus, any change in the quality of natural water, seasonal change, as well as the dosage of the coagulants used in the treatment system, will alter the quantity and quality of the produced sludge (Ahmad et al., 2016).

Curiously, in the scientific literature, there is limited statistical data on the production and disposal costs associated with WTS on a global or national scale (Babatunde and Zhao, 2007; Keeley et al., 2014). Some problems such as the risk of water contamination with heavy metals, high costs of sludge treatment and disposal are challenges faced by companies and governments around the world. In Australia, the cost associated with the sludge disposal without transportation is $130-200/ton by landfill or sewer disposal, with an approximate cost of over $6.2 million per annum just in the state of Victoria (Maiden et al., 2015). The costs associated with sludge disposal in the Netherlands are on average between £30 and 40 million, as reported by Evuti and Lawal (2011), while in the UK the annual disposal costs £5.5 million (Keeley et al., 2014).

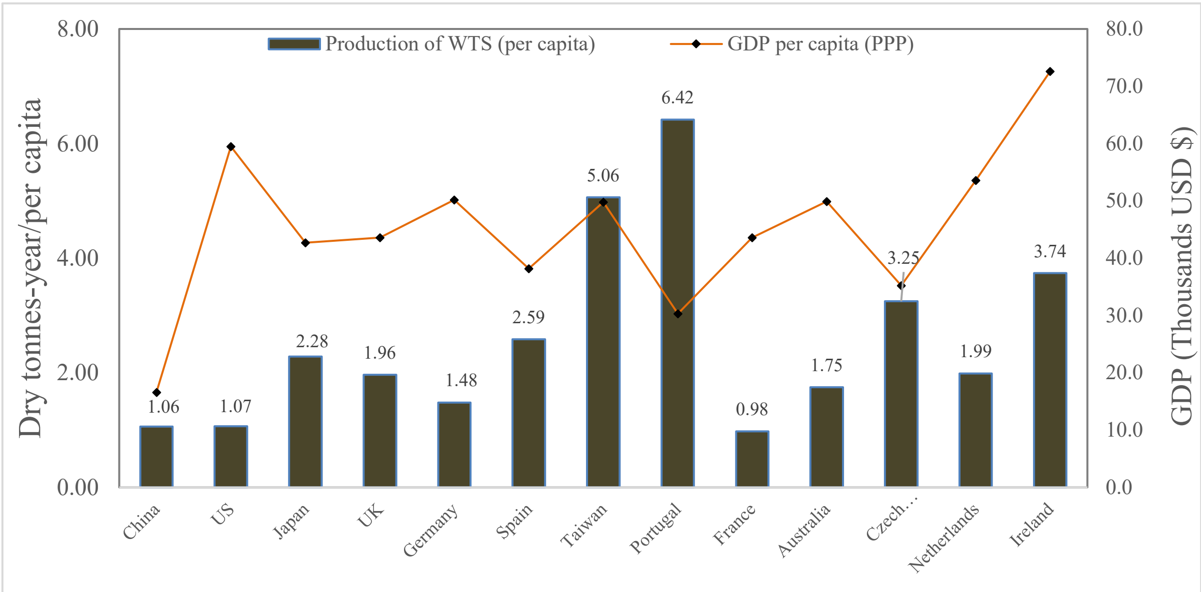


Figure 2. Estimated quantities of WTS from selected countries, compiled from Li et al. (2013), Babatunde and Zhao (2007), Finlay (2015), Dassanayake et al. (2015), Fujiwara (2011), Zamora et al. (2008), Boaventura et al. (2000), Maiden et al. (2015), Ippolito et al. (1999). GDP from Central Intelligence Agency (2017).

WTS has been used in various industrial and commercial manufacturing processes. Particularly, some studies have been conducted by using WTS for wastewater treatment as coagulant/contaminants removal, ceramic products, coagulant recovery and land application (Ahmad et al., 2016). As clay and WTS have a similar mineralogical composition (essentially hydroxides and oxides of silica, aluminium and ferric), the use of WTS has been highly encouraged to partially replace the clay used for fabrication of cement and others sintered ceramic materials (Hegazy, 2007). Furthermore, because of clay scarcity in many parts of the world and the high environmental impact generated by the clay harvesting, many studies are focused on designing and development of new sustainable materials using less conventional raw materials, with available local sources and in accordance with international standards requirements. In order to protect the environment and the limited clay resources, countries such as China have begun to limit the use of clay-bricks and publicly recommend to incorporate waste materials into the ceramic materials (Chen et al., 2011).

There are a few review articles on WTS application and reuse (Babatunde and Zhao, 2007), most of which have focused on general aspects of brick or cement production from the last decade. Furthermore, the majority of the studies do not differentiate between the different types of sludge such as iron based, aluminium-based, or lime (calcium carbonate, $CaCO_3$) which have been applied in the building materials, yet they have different properties and behaviour. This review (Gomes et al., 2019) therefore evaluated the different types of WTS and their latest applications in building materials, such as ceramic brick, paving tiles, lightweight aggregates, cement, concrete applications and composite materials. In addition, it discusses important aspects such as durability, environmental risks and cost-benefit analysis from the application of different types of WTS.

2.1 Characteristics of water treatment sludge

2.1.1 Chemical properties

In most water treatment systems around the world with elevated suspended particles, inorganic coagulants are more commonly applied. They are composed mainly of iron and aluminium salts such as aluminium sulphate ($Al_2(SO_4)_3$), ferric sulphate ($Fe_2(SO_4)_3$) and ferric chloride ($FeCl_3$). Whereas in the softening process with high levels of hardness, the main coagulant used is lime (Sales et al., 2011). These coagulants are efficient to remove a wide variety of impurities from the water, including colloidal particles and dissolved organic compounds. The final process of water filtration results in a range of by-products known as WTS, which consists of a mixture of microorganisms, organic suspended compounds, coagulant contents and chemical oxides (Babatunde and Zhao, 2007). The final composition of WTS is the result of the coagulants type and other chemical treatments used for the purification of water. The typical sludge composition can be seen in **Table 1**.

Table 1. Common composition of main types of WTS (mean values ± SD)

Parameter	Unit	Alum sludge	Ferric sludge	Lime sludge
Aluminium	% dry weight	29.7 ± 13.3	10.0 ± 4.8	0.5 ± 0.8
Iron	% dry weight	10.2 ± 12	26.0 ± 15.5	3.3 ± 5.8
Calcium	% dry weight	2.9 ± 1.7	8.32 ± 9.5	33.1 ± 21.1
Magnesium	% dry weight	0.89 ± 0.8	1.6	2.2 ± 1.04
SiO2	% dry weight	33.4 ± 26.2	nd	54.57
pH		7.0 ± 1.4	8.0 ± 1.6	8.9 ± 1.8
BOD_5	mg/L	45 (2-104)	nd	nd
P	% dry weight	0.35	0.36	0.02
Zinc	mg/kg	33.9 ± 28	18.7 ± 16.0	2.5 ± 0.7
Lead	mg/kg	44.1 ± 38.2	19.3 ± 25.3	1.87 ± 1.13
Cadmium	mg/kg	0.5	0.48 ± 0.26	0.44 ± 0.02
Nickel	mg/kg	44.3 ± 38.4	42.9 ± 39.2	0.98 ± 0.52
Copper	mg/kg	33.72 ± 32.5	18.7 ± 25.8	3.6 ± 3.1
Chromium	mg/kg	25.0 ± 20.1	25.7 ± 21.6	1.3 ± 0.2
Cobalt	mg/kg	1.06	1.61 + 1.1	0.67 + 0.05
Total solids	mg/L	(2500 - 52,345)	(2132 - 5074)	nd

Data from Babatunde and Zhao (2007). nd, no data. Data in parenthesis indicate range.

Aluminium sulphate, in particular, has been used worldwide for more than 100 years in different WTPs, due to its low cost, easy manipulation and storage (Srinivasan et al., 1999; Renault et al., 2009). Most WTPs in New Zealand and Australia use aluminium-based coagulants (Ministry of Health, 2017; Gebbie, 2006). However, the most populated NSW State in Australia uses iron-based coagulants in the majority of its WTPs due to severe manganese limits in the finished water (Gebbie, 2006). The United Kingdom uses an average of 107000 tons of aluminium-based coagulant and 165000 tons of iron per year at WTPs across the country (Henderson et al., 2009). In 1994, in the United States and Canada, 72% of all water produced came from coagulation with aluminium salts and 23% with iron salts. Several factors lead to the use of one or another coagulant in water treatment, including the search for a better quality of treated water, local availability, lower cost, a smaller volume of sludge and best dehydration conditions (Pizzi, 2010).

2.1.2 Geotechnical properties

The comprehension of WTS geotechnical properties is an essential knowledge to deal with its application (Keeley et al., 2014). Some properties such as mass loss on ignition (LOI), liquid limit (LL), plastic limit (PL), plasticity index (PI) and specific gravity are crucial not only for their identification or classification as a soil material but also to predict future behaviour of the application of this material (Basim, 1999). **Table 2** shows that the majority of geotechnical characterisation studies with WTS have demonstrated a substantial similarity with clayey soils, especially those using aluminium and iron salts. However, WTS is different from clays due to the presence of organic compounds and high concentrations of chemicals. Such organic matter in the soil usually results in high plasticity, low permeability and decreases the specific gravity (Mitchell and Soga, 2005).

O'Kelly (2008) analysed the geotechnical properties of a WTP's residuals that had aluminium as a coagulant. The study characterised the sludge as clay with high plasticity, high compressibility, and very low permeability. These characteristics were attributed to the high affinity of the coagulant metal by water and the high amount of organic particles (O'Kelly, 2008). These characteristics of natural and untreated sludge make it sometimes inappropriate for applications in building materials such as aggregates and structural elements and help to explain the difficulty of handling and transporting them. Thus, by proper treatment to the sludge and incorporating it into the most suitable material, the negative result of these characteristics can be mitigated (Keeley et al., 2014).

Table 2. Main geotechnical properties of water treatment sludge

Property	Unit	Alum sludge	Ferric sludge	Lime sludge
Liquid Limit	%	80-550	108	38-72
Plastic Limit	%	60-325	47	32-53
Plasticity Index	%	20-225	61	4-19
Specific Gravity	g/cm³	1.86–2.33	2.26-2.72	2.57–2.62
Soil Classification (USCS)	-	high-plasticity clay	high-plasticity clay	low-plasticity silt
Loss on ignition	%	15-57	24-50	35–40
Reference		Komlos et al. (2013); O'Kelly and Quille (2009); Wang et al. (1992); Watanabe et al. (2011); Richter (2001)	Wang et al. (1992); Baker et al. (2005)	Baker et al. (2005); Ramer and Wang (2000); Kashyap & Datta (2017).

2.2 Application of water treatment sludge in construction materials

2.2.1 Bricks and ceramic products

Considering the vast potential of solid waste from various industries as clay replacement for the production of ceramic artefacts (roof tiles and bricks), the latest research has focused on offering alternatives and final environmentally correct destination for these by-products. This is mainly due to the fact that materials resulting from the sintered ceramics are tolerant of additions of other raw materials even in high quantities, ensuring the solidification/immobilization of the elements with toxic potential (Dondi et al., 1997; Jonker and Potgieter, 2005). Therefore, due to the fact that clay and WTS have a similar chemical composition (essentially hydroxides and oxides of silica, aluminium and ferric), the use of WTS has been highly encouraged to partially substitute the clay used for fabrication of bricks and ceramic materials (Hegazy, 2007). This is especially the case of countries such as Brazil, where the production of sintered construction materials (bricks, tiles, blocks) is still more advantageous than cement and geopolymeric materials which will remain so for the next two decades (Monteiro and Vieira, 2014).

Figure 3. The manufacturing process for traditional fired clay bricks.

The amount of added sludge in the ceramic materials depends partly on its property (particle size, chemical and mineral composition), which will directly influence the quality of the bricks produced (Teixeira et al., 2011a). In most studies, the increase in the addition of sludge in the brick`s mix resulted in a decrease in compressive strength and higher water absorption. The high values of loss on ignition are related to the high concentration of organic matter contained in the sludge, which was burned during the sintering process, combined with the presence of inorganic components found in WTS and clay (Wolff et al., 2015).

Previous research has shown that aluminium-based sludge is more deleterious to ceramic materials than those obtained with iron-based coagulants (Teixeira et al., 2006). In general, the iron-based sludge applied in ceramic products obtained better results concerning the mechanical properties and also a reduction in the firing temperature of bricks (Anderson et al., 2003; Goldbold et al., 2003; Teixeira et al., 2006; Kizinievič et al., 2013). Furthermore, Kizinievič et al. (2013) concluded that usually, the iron-sludge conferred a more reddish colour to the bricks, acting as a natural pigment. However, the results with the addition of high proportions of aluminium-based sludge show a considerable reduction in the mechanical performance of the ceramic bodies with increasing sludge addition (Huang et al., 2001; Teixeira et al., 2006; Teixeira et al., 2011). In contrast, Benlalla et al. (2015) obtained bricks with mechanical properties higher than reference clay bricks, even with the substitution of clay by around 30% WTS at a firing temperature of 1000°C.

A significant amount of studies discussing the use of WTS in combination with other alternative materials has been reported (**Table 3**). In a study conducted in the UK, researchers investigated the incorporation of two by-products in the manufacture of bricks. This study used the sludge generated in the treatment of water and sewage, incinerated and added as partial substitutes for the traditional raw materials of the brick, in proportions of 5% (dry weight), meeting local standards and parameters for ceramic blocks (Anderson et al., 2003). On the same line of thought, a study carried out in Taiwan mixed the sludge from the water treatment with dam sediment for the production of ceramic samples. The conclusion of the study indicated that WTS rates below 20% combined with dam sediment can generate quality bricks under the Chinese National Standard (Huang et al., 2001). In a study carried out in Taiwan (Chiang et al., 2009), lightweight bricks were produced mixing the dry water treatment sludge and the calcined rice husk, obtaining improvements in mechanical properties of the ceramic bricks. Consequently, several other studies concerning the addition of materials with a high concentration of silica have been conducted (Hegazy et al., 2012; Wolff et al., 2015; Ewais et al., 2017).

In general, the addition of aluminium-based sludge decreases compressive/flexural strength and increases the water absorption of the ceramic bodies. According to the majority of the studies summarized in Table 3 (Huang et al., 2001; Teixeira et al., 2006; Teixeira et al., 2011), the replacement of the clay by the aluminium-based sludge below 10% does not significantly reduce the mechanical properties of the ceramic bodies, while above 10% significant reduction from 24.6 to 45.45% on flexural strength was observed. On the other hand, iron-based sludge increased the compressive/flexural strength of the ceramic samples compared to the reference values by 7% to 97%, for sludge additions below 10%, as shown in Table 3 (Kizinievič et al., 2013; Hassan et al., 2014). Furthermore, studies have shown that it is possible to produce ceramic bricks with mechanical properties similar to those of clay, with more considerable additions than 50% sludge, combined with a material with high silica concentration (Lin et al., 2006; Chiang et al., 2009; Hegazy et al., 2012; Wolff et al., 2015; Ewais et al., 2017).

2.2.2. Lightweight aggregates

Lightweight aggregates (LWA) are highly porous and spherical ceramic products with low density (0.8-2.0 g/cm^3) and commonly used in the manufacture of various building products (Soltan et al., 2016). The use of residual waste materials in the production of lightweight aggregates (LWA) has been largely exploited in recent years, mainly because LWA has a wide application in construction materials such as lightweight concrete/mortar (structural and non-structural), water treatment process and gardening (Dondi et al., 2016). A significant number of studies with heavy metals, sludge, and industrial waste have used the thermal stabilization process to produce composites lightweight aggregates, immobilising the contaminants through the sintering process in the matrix of the new materials, and thus reducing the migration of contaminants into the environment (Andrés et al., 1998; Huang et al., 2007; Wang et al., 2008; Corrochano et al., 2011; González-Corrochano et al., 2017).

Table 3. Summary of the main studies on the application of WTS in ceramic bricks

Ref	Type of coagulant	Clay replacement by WTS or blended with other materials (by weight)	Size of brick/Sample (mm)	Sintering temperature (°C)	Mechanical properties
1	Alum	Different contents of WTS (70–95% by weight) were mixed with bottom ash	moulded blocks	900, 1000, 1050, 1100, 1150, 1200	Compressive strength of 25Mpa and a water absorption ratio of 2.78% with 80% weight content of WTS under 1150°C,
2	Alum	The sludge concentration added to the clay ranged from 0 to 20 wt.%.	60 × 20 × 5	850, 900, 1000, 1100, 1150	Overall the WTS declined the technological parameters; however, the mix with 10% sludge allowed the manufacture of solid bricks for firing temperatures lower than 1000°C.
3	Alum and Ferric	Four mix WTS-Clay for each sludge(Alum and Iron) 0, 10, 20 e 30%	60 × 20 × 5	900, 950, 1000, 1200	For firing temperatures 950 °C, the samples with 10 % sludge-Al and 20 % sludge-Fe, are under the limits established for Brazilian standards
4	Alum	WTS mixed with rice husk ash (RHA), with ratios 25, 50, and 75% of the total weight of sludge-RHA mixture	5 0× 50 × 20	900, 1000, 1100, 1200	Bricks with 75 % of Sludge-RHA and fired at 1200 °C achieved higher compressive strength than reference brick sample, with 7,8 Mpa.
5	Alum	WTP sludge was mixed with the dam sediment. The ratio of the WTS was 0, 10 and 20%	-	950, 1000, 1050, 1100, 1150	Mixtures containing 10 and 20% WTP sludge, are still in agreement with the 1st or 2nd level criteria of Chinese Standard for the burning temperatures of 1,050°C to 1,100°C.
6	Alum	Different contents of WTS (55–85% by weight) were mixed with granite rock powder	70 × 25 × 15	850, 950, 1050	The results suggest shows that sludge can substitute the clay in the formulation of brick mixes at 850 and 950°C, for the production of interior coatings or acoustic bricks
7	Alum	Mix ranging 90 -100 % of WTS - rice husk ash (RHA), varying 0-10 %	200 × 200 × 200	800, 900, 1000, 1100, 1200	WTS can be used successfully to produce high quality insulating

					refractory bricks in accordance with Egypt standards.
8	Ferric	Addition of sludge with ratios 3%, 6%, 9% and 12% of the total weight of sludge–clay mixture	250 × 125 × 75	Burnt into a laboratory furnace at 500 °C for 12 hours and then increased for 1000°C for more 12hours	The compression strength of 3%, 6%, 9% and 12% blended brick specimens were14.1 MPa, 15.1 MPa, 9.4 MPa and 7.1 MPa, respectively.
9	Alum	Formulations of mixtures containing WTS 5% 10% 15% 20% 25% 30% of sludge–clay mixture	80 × 30 × 20	800, 900, 1000	The mechanical strength was higher than that of normal clay bricks for 30% sludge replacement at 1000°C.
10	Ferric	Mixes were prepared by incorporating from 5% to 40% of WTS additive	70 × 70 × 70	1000, 1050	The mechanical strength was higher than that of normal clay bricks for 5 and 10% sludge replacement at 1000 and 1050°C.
11	Ferric	WTS mixed with incinerated sewage sludge ash (ISSA) in various clay ratios replacement for a full-scale bricks production.	-	Maximum temperature of 1050°C	The results in accordance with the British Standard confirmed the feasibility of using the combination of these two by-products at 5% (dry) weight replacement for brick manufacture.
12	Alum	WTS mixed with rice husk ash (RHA), with ratios of 0, 5,10, 20, and 25% of the total weight of sludge-RHA mixture	20 × 20 × 55	900, 950, 1000, 1050, 1100	In the sample with 10% OF RHA, the compressive strength increased from 0,67 to 26,5 MPa when the firing temperature increase from 900 to 1100 ◦C

1- Lin et al., 2006; 2-Teixeira et al., 2011; 3-Teixeira et al., 2006; 4-Hegazy et al., 2012; 5-Huang et al., 2001; 6 - Wolff et al., 2015; 7- Ewais et al., 2017; 8- Hassan et al., 2014; 9 - Benlalla et al., 2015; 10-Kizinievič et al., 2013; 11- Anderson et al., 2003; 12- Chiang et al., 2009.

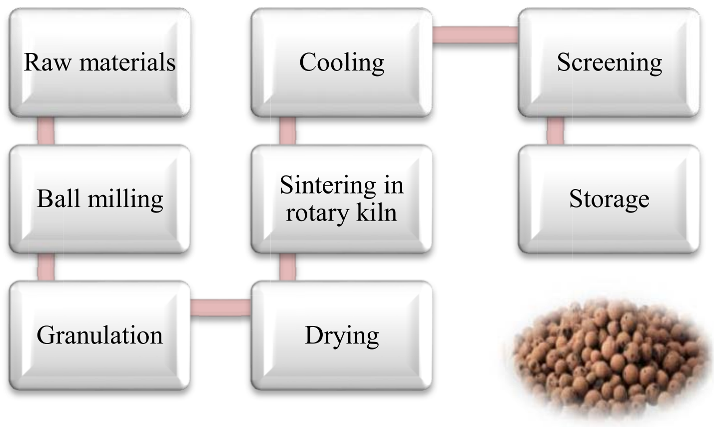


Figure 4. Manufacturing process for traditional lightweight aggregates.

2.2.2.1 Lightweight coarse aggregate

Huang et al. (2005) used the aluminum-based sludge from a Taiwanese WTP for the production of lightweight concrete coarse aggregates. Spherical samples of approximately 2 cm in diameter were produced, which were oven dried at 105°C for 24 hours and sintered at 1000, 1050 and 1100°C. The WTS-derived LWA had water absorption and specific gravity ranging from 14.47 to 37% and from 1.12 to 1.78 g/cm^3, respectively. After composite production, the LWA was applied to a concrete mix with proportions of 2:1:1 (natural sand: WTS-LWA: cement). The results, when compared to the Taiwanese construction standard, showed that only the WTS-aggregates sintered at 1100°C met the requirements of specific gravity (1.4-2.0 g/cm^3), and compressive strength (175-420 kgf/cm^2) of the concretes made with natural LWA.

Huang and Wang (2013) investigated the Alum-based sludge from 10 water treatment plants in Taiwan for the production of lightweight coarse aggregates (**Figure 5**). The researchers used the air-dry sludge mixed with an adequate amount of water and then extruded the mixture for the production of 8-12 mm diameter cylindrical pellets. The samples were sintered in two steps, the first one happened at 500°C for 5-15min and then 1150-1275°C for 7.5-15 min. The results for the LWA concrete made with WTS were satisfactory, five among ten different sludge's were classified as viable for structural and non-structural LWA production, the other five only for structural, all with similar properties of high-quality LWA, with densities ranged from (0.65-2.05 g/cm^3) and water absorption of (0.5-15%). Moreover, the researchers produced LWA in large scale using a rotary kiln with sludge from one of the water treatment plants. It was possible to produce structural and non-structural LWA with average particle densities of 1.35 g/cm^3 and apparent density of 726 kg/m^3, meeting the requirements of ASTM C330.

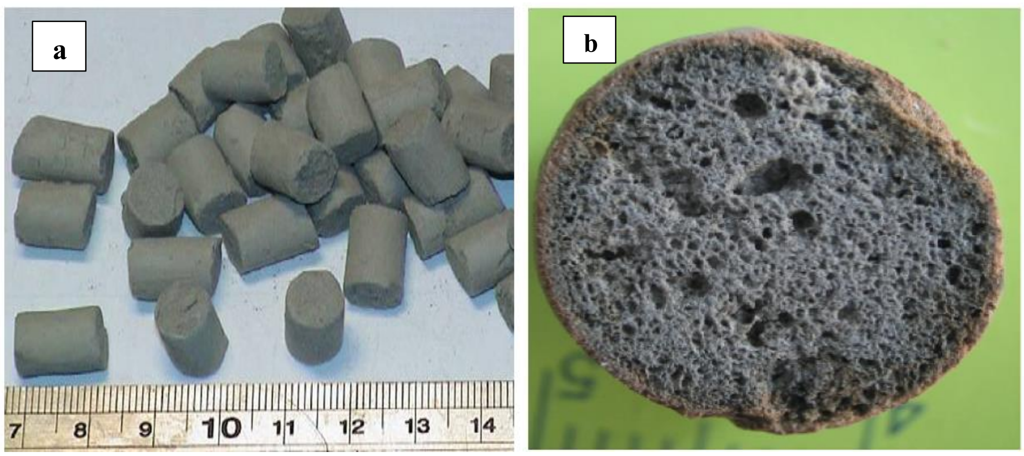


Figure 5. (a) Green pellets before firing, (b) cross-section of LWA (Huang and Wang, 2013).

In a different approach, Sales et al. (2010; 2011) produced a composite lightweight coarse aggregate for concrete with Alum-based WTS and sawdust. For the production of this lightweight composite, the dry and milled WTS was homogenized with water and sawdust in rounded samples with a diameter of 14 ± 2 mm. The proportion ratio of sawdust, WTS and water were 1: 6: 4.5. After moulding, the samples were dried at 105°C and then immersed in boiled linseed oil for 1 min. After removal, the aggregates from the oil, the samples were dried at room temperature and mixed in different concretes batches. Based on the ACI (Guide 213R-87) classification, the material produced with the lightweight coarse aggregate was in the non-structural lightweight concrete category, showing a compressive strength of 11.1 MPa and relative density of 1847 kg/m^3.

2.2.2.2 Ceramsite

Ceramsite is a type of fine lightweight aggregate that has been used as construction materials in a variety of applications, such as concrete composites, bricks, wetlands layers and filters for wastewater treatment process (Xu et al., 2008b; Jia et al., 2014). Xu et al. (2008a) tested the feasibility of ceramsite production with Alum-based WTS and Wastewater Treatment sludge (WWTS). For the production of the ceramsite, several proportions of WTS, WWTS, and water glass (sodium silicate) were used to search for the ideal ratios. The water glass's modulus was 3.2. Pelletized samples were produced with 5-8mm size and maintained at room temperature about 20°C for three days and then pre-heated to 24 hours at 110°C. The heating ramp started at 20°C and continued at a rate of 8°C/min in a muffle until reaching 1000°C for 35 min. The results showed that the optimal values for the production of ceramsite were: WTS/WWTS = 45/55, sodium silicate/ (WTS+WWTS) ratio = 20%, SiO_2 = 14-26% and Al_2O_3 = 22.5-45%, at a sintering temperature of 1000°C. For these conditions, the compressive strength of ceramsite ranged from 13.63 MPa to 16:25 MPa, above the minimum (7.50 MPa) amount required by the Chinese National Bureau of Standards (CNBS). In a similar research, Zou et al. (2009) studied the influence of different proportions of Fe_2O_3, CaO and MgO oxides on the production of ceramsite with WTS and WWTS. The methodology used was the same as used by Xu et al. (2008a), however varying and adjusting the amount of iron, calcium, and magnesium oxide. The variation of the Fe_2O_3 content directly influenced the mechanical strengths of ceramsite mixtures. The Fe content of 5-8% was considered optimal for lower water absorption and higher compressive strength, which ranged from 14.97 MPa to 15.67 MPa. The mechanical strength of the ceramsite was not influenced directly by the MgO, but an increase in the bulk density was noticed as MgO was increased, resulting in an ideal rate of 1.6-4.0%. The increase in CaO rate decreases the compressive strength of the ceramsites, so an optimal rate of 2.75% to 7% was determined.

2.2.3. Cement production

World Portland cement (PC) production is a technological activity of intense demand for natural resources. The raw materials commonly used in the manufacture of cement are limestone-calcium carbonate (75-80 wt. %) and clay (20-25 wt. %) (Bignozzi, 2011). Therefore, due to the mineral and chemical similarity of PC and WTS, some researchers have been looking for alternatives to incorporate this by-product into the cement production process or as a supplementary cementitious material.

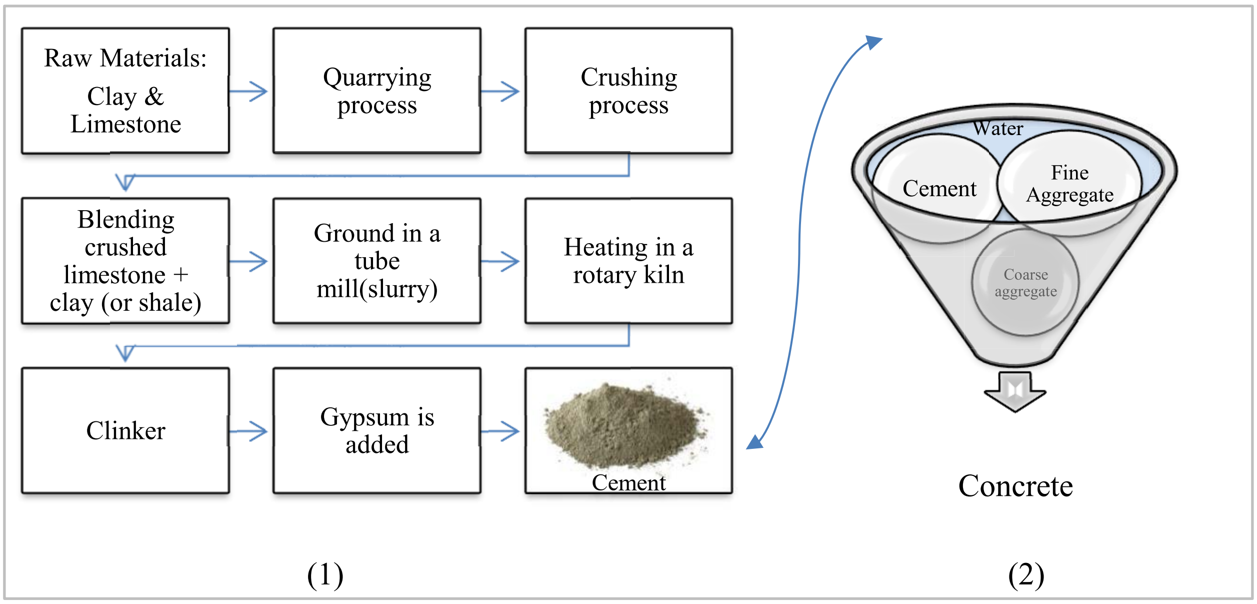


Figure 6. (1) Cement manufacturing process, (2) conventional concrete mix.

Tay and Show (1991) used an iron-based WTS mixed with different proportions of lime powder ($CaCO_3$) and sintered at a temperature of 1000 °C for 4 hours in three different blends (1:3, 1:1 and 3:1 by weight). The results indicate that cement made from Fe-sludge, with a sludge-lime mixing ratio of 1:1, sintered at 1000°C for 4 hours, can be used for general masonry work according to the American Society for Testing and Materials (ASTM). Baker et al. (2004) on an industrial scale, replaced 15% of limestone for lime sludge in a cement plant and produced around 80 tons of composite cement. The properties of the new cement were satisfactory in comparison to the

Ordinary Portland Cement. In a similar study, Pan et al. (2004) evaluated the possibility of replacing the clay used in Portland cement clinker production by using alum-sludge. The cement containing WTS as a substitute of clay showed adequate results regarding the setting time of cement paste. The compression strength of concrete increased as the sludge was incorporated, meeting the national Chinese standard requirements for first grade Portland cement.

Lin and Lin (2005) used WTS ash combined with two more industrial by-products for replacement of the Portland cement raw materials. The results regarding compressive strength and microstructure of cement paste showed that the substitution of up to 20% of these materials was feasible for the production of the clinker cement. Moreover, all hydrated compounds commonly found in an ordinary Portland cement paste ($Ca(OH)_2$ and C-S-H) were detected after the addition of these residues. Chen et al. (2010) studied the feasibility of replacing the siliceous raw material (shale) by using Alum-sludge from 4 to 10% for cement production. All specimens with WTS had higher 3-day and 7-day strength than the control specimens, and also a superior percentage of tricalcium silicate (C_3S). However, after 28-day strength, only additions below 7% had higher strengths than the control. In recent studies conducted by Dahhou et al. (2016; 2018), the researchers produced several clinker compositions with partial limestone replacements by Alum-sludge and sintering temperature ranging from 1300 to 1500°C. Regarding the flexural and compression strength of the cement pastes burned from 1450 and 1500ºC, all clinker compositions showed superior performance and also identical mineralogical values compared to ordinary Portland clicker, with a significant presence of alite (C_3S) and belite (C_2S).

The production of cement with the partial addition of sludge from a water treatment plant has been shown to be potentially applicable. Most of the studies focused on cement paste parameters such as mechanical strength, setting time, chemical and mineralogical characterization and some leaching tests. However, due to the lacking of some long-term durability testings on concrete and the presence of some substances on sludge, which are potentially deleterious to concrete such as chloride and sulphate ions, there is no guarantee that the use of this by-product will not develop expansive products (ettringite) or corrosion in the bars of reinforced concrete. More studies on this topic should be carried out to guarantee the safety and sustainable use of this residue.

2.2.4. Supplementary cementitious material and inert addition

Generally, Supplementary Cementing Materials (SCMs) are classified into two categories: Self-cementing or Pozzolanics. Self-cementing materials react similarly to hydraulic cement, they set and harden in the presence of water, forming solid cementitious products (Snellings et al., 2012), while pozzolanic materials (siliceous and aluminous composition) only hydrate and form cementitious compounds, in the presence of moisture and an activator; usually calcium hydroxide (ASTM C618, 2001).

2.2.4.1. Self-cementing

El-Didamony et al. (2014) investigated the substitution of a self-cementing material; Granulated slag (GBFS) by Alum sludge in proportions of 5%, 10% and 15% by weight for the production of composite hydraulic cement. The results showed that free portlandite increased in the first 7 days of curing and then decreased at 90 days. Furthermore, the replacement of GBFS by WTS led to increases in the chemically combined water and hydration products. Compressive strength increased by up to 5% of GBFS replacement and decreased with sludge increasing up to 15% by weight. In a similar study, Dahhou et al. (2018) investigated the partial replacement of Portland cement class CPJ55 by various amounts (5-25%) of dry Alum sludge in mortar samples with dimensions of 40 × 40 × 160 mm. It was observed that the addition of 5% of WTS in Portland cement does not affect the mineralogy of the final product. However, based on the flexural and compression tests at 28 days, mortars with 5% sludge substitution were classified as belonging to class 32.5 R according to the Moroccan standard.

2.2.4.2. Pozzolanic addition

Rodríguez et al. (2010) used the atomized-dry WTS (Aluminum-based) as a pozzolanic addition in the cement mortars. The mortars were prepared with the substitution of 10 to 30% of Portland cement by atomized sludge and tested in relation to hydration, water demand, setting time and mechanical strength. The cement replacement by the sludge considerably delayed the rates of cement paste hydration and the setting time, even in the samples with only 10% of sludge. Mortars with 10% to 30% of atomized alum-sludge showed a substantial drop in flexural strength, with a decrease of 30% and 45% respectively. Furthermore, FTIR spectra testing showed the formation of amorphous ettringite for the montars mixes with atomized sludge. Alqam et al. (2011) researched the iron-based WTS as a partial replacement of Pozzolanic Portland cement to produce paving tiles for external use. The sludge was replaced in the percentages of 10%, 20%, 30%, 40% and 50% (by cement weight), in samples of 400mm × 400mm × 35mm. The results showed that the addition of sludge did not affect the samples about the absorption of water, with an increase of only 6% for the maximum sludge replacement (50%). Except for samples with 50% sludge, all others obtained a minimum breaking strength of 2.8 MPa for external tiles according to the British Standard. Nevertheless, it was observed there was a decrease in the mechanical property as the sludge was added from 10% to 50%, ranging from 1.5% to 28% decrease in strength.

Al-Tersawy and El-Sergany (2016) compared the pozzolanic properties of calcined Ferric-Sludge and rice husk ash (RHA) in the partial substitution of cement in several concrete compositions, by ranging from 0% to 30% with two different types of aggregates (dolomite and gravel). Regarding the mechanical properties, the substitution of 10% of RHA obtained better results, with compressive and tensile strength higher than the control sample. However, the same was not observed for the replacement of calcined sludge, which obtained reductions in mechanical strength ranging from 30% to 62% after 28 days of age. The study concluded that the calcined sludge can be used in less than 10% as a filler material for concrete and still reach the minimum limits for structural concrete in Egypt. In a recent similar study, Ahmad et al. (2018) studied the feasibility of partial replacement of Portland cement by an Al-based sludge from the backwashing filtration beds, calcined at 800°C for incorporation in cement mortar and concrete. Concerning the pozzolanic activities of the sludge, the results showed that, as well as traditional pozzolanic materials, the calcined sludge reacted with Ca(OH)2 producing significant quantities of hydrated products, and it could, therefore, be classified as an artificial pozzolana. The addition of sludge had a small influence at the initial setting time; however, regarding the final setting time, an increase of 2.6% to 40% was observed. The compressive strength of the mixes decreased as the sludge was added. The results showed that even with the drop, the replacements up to 20% are meeting the India standard for the paste made by Portland pozzolana cement, IS 1489.

Table 4. Summary of the effects of WTS as a supplementary cement material

Property	Effects on concrete and mortars					
	Self-cementing		**Pozzolan**		**Sand replacement**	
	Replacement (< 5%)	Replacement (5-25%)	Replacement (<10%)	Replacement (10 - 30%)	Replacement (< 5%)	Replacement (5 - 10 %)
Compressive Strength (28 days)	▲ (10%)	▼(15 - 75%)	▼(5 - 60%)	▼(14 - 65%)	▼(11- 50%)	▼(29.3-100%)
Flexural Strength	-	▼(60%)	▼(1.5 - 30 %)	▼(28 - 45%)	▼(41 - 56%)	▼(47- 90%)
Final Setting Time	-	-	▲2.6 - 20%)	▲(40 - 200%)	-	-
Workability	-	-	▲(50 %)	▲(58 %)	▲(74 - 84.6%)	▼(100%)
Permeability	-	-	▲(5 -107%)	▲(6 - 200%)	▲(8.6 - 29%)	▲(25.21 - 45%)
Reference	El-Didamony et al. (2014); Dahhou et al. (2018)		Rodríguez et al. (2010); Alqam et al. (2011); Al-		Hoppen, et al. (2006); Lee et al. (2012); Tafarel et al.	

	Tersawy & El Sergany (2016); Ahmad et al. (2018)	(2016); Gomes et al. (2017); Fernandez et al. (2018)

▼ means a decrease in the material properties

▲means an increase in the material properties

- do not have enough information

(-) means ranging of values

2.2.4.3. Sand replacement

Hoppen et al. (2006) evaluated the partial replacement of sand by wet Al-based sludge in concrete mixtures. Four compositions of concrete-sludge were prepared with replacements of 3%, 5%, 7% and 10% based on the weight of the fine aggregate. The amount of mixing water in each mixing was adequate regarding the weight and moisture content in the sludge. The results indicated that 10% of sludge in the concrete is a limiting content for its practical application, first due to low workability, as well as low mechanical strength, being less than 15 MPa (**Figure 7**). The substitutions of 4% to 8% of sand by wet sludge in the concrete resulted in values of compressive strength higher than 27 MPa at 28 days. Thus, those researchers suggested that the possible applications for this concrete-sludges should be in non-structural concrete such as subfloor, blocks, non-load bearing walls, decorative concrete pieces, sidewalks, residential floors, among others. Using a similar methodology, Fernandez et al. (2018) obtained results similar to Hoppen et al. (2006).

Tafarel et al. (2016) also partially replaced the natural sand present in the concrete by a wet aluminium-based sludge, in proportions of up to 10% of the dry weight of the sand. Considering the results, only the samples with 5% sludge showed satisfactory compressive strength conditions when compared to the reference concrete, with 15.5 MPa at 28 days and considered a decrease in the strength close to 11%. The incorporation of sludge in the 5% and 10% contents, led to an increase in water absorption by 12% and 32%, respectively. In recent and similar research, Gomes et al. (2017) investigated the effects of aluminium-based sludge on its natural (wet) form, for sand replacement in concrete. The mixing compositions ranged from 0%, 5%, 7% and 10% of wet sludge relative to the natural sand weight. The results reveal that the addition of wet WTS reduced compression strength and increased water absorption, only 5% of sludge substitution led to a 50% drop in compressive strength and almost 45% in water absorption.

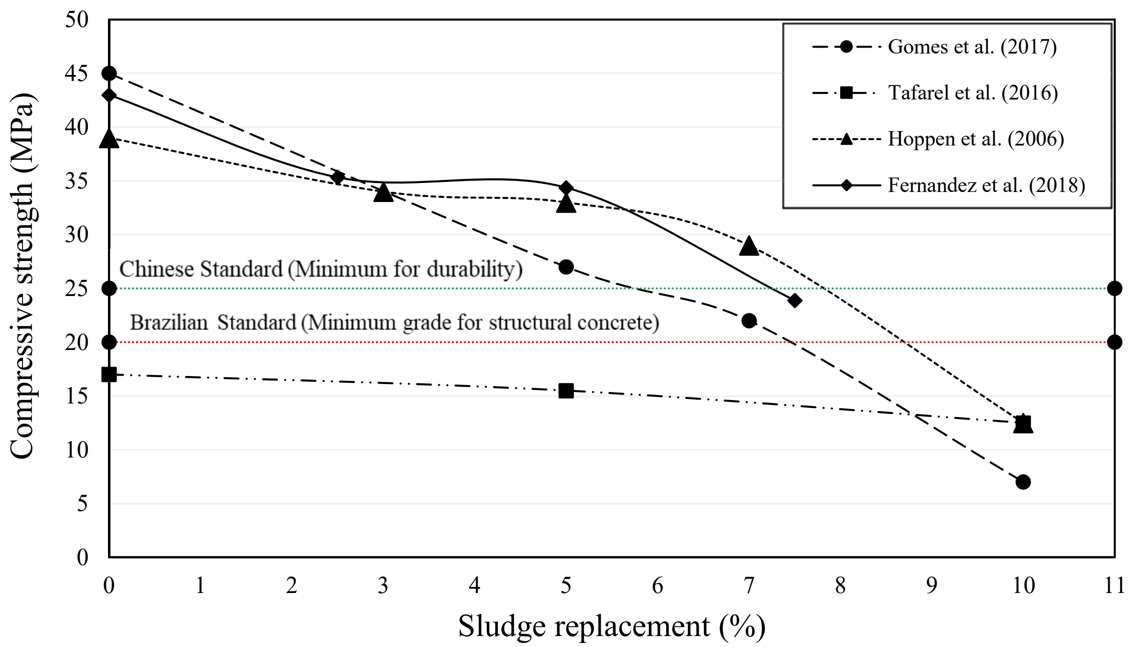


Figure 7. Effect of sand replacement by WTS on compressive strength.

Based on the studies presented, the substitution of natural sand for the production of structural and non-structural concretes was viable and satisfactory. Hoppen et al. (2006) showed that the replacement of fine aggregate by up to 5% WTS in concrete and mortar led to a slight fall in compressive strength of less than 20% compared with no sludge material (**Figure 7**). Thus, 5% substitution of fine aggregate is a critical value that could be considered safe for sludge application in structural or non-structural concretes according to the Brazilian and Chinese code (ABNT-NBR6118/2007; CCES01/2004). However, more studies have to be performed to certify the impact of sludge on water demand, hydration kinetics of Portland cement and the durability of concrete.

2.2.5. Geopolymers

Joseph Davidovits developed, in the 1970s, a cementitious material by alkaline activation that was named geopolymers (Yunsheng et al., 2010). These materials were designated in analogy to the raw materials used in their manufacture - geological elements. While carbon structures form conventional polymers, geopolymers require source materials of Si and Al (precursor), water and an alkaline reagent (activator) (**Figure 8**), which is responsible for triggering the polymerisation of the components (Davidovits, 1991). Geopolymers are considered sustainable materials, mainly because of besides geological compounds utilised for its production, others several industrial wastes and by-products can be used, such as fly ash, metallurgical slag, mining residues, activated clays, zeolites and kaolins (Phair and Van Deventer, 2002; Komljenović et al., 2010; Salwa et al. 2013; Singh et al. 2015; El-Eswed et al., 2017; Sudagar et al. 2018). Therefore, some researchers have recently conducted studies on the potential of WTS as a geopolymeric feedstock, since WTS is usually is rich in Si and Al oxides.

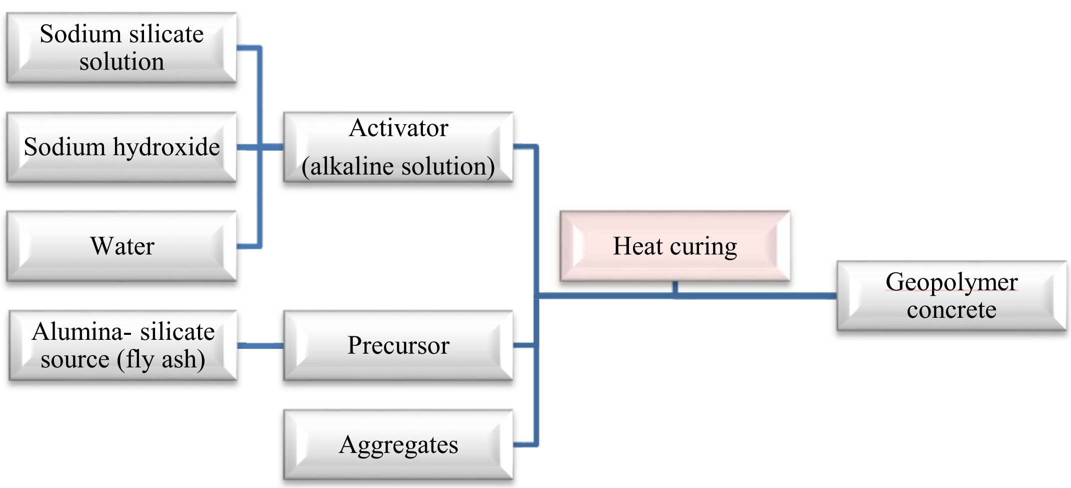


Figure 8. Geopolymer concrete manufacturing process.

Waijarean et al. (2014) studied the application of aluminium-based sludge as alumino-siliceous material to synthesise geopolymers. The primary purpose of the study was the production of a cementing material for a heavy metal waste-immobilization. The study investigated WTS compositions without thermal treatment and three calcination temperatures ranging from 600 to 900 °C, for 1 hour. The WTS obtained an initial SiO_2:Al_2O_3 ratio of 1.78. The reaction between NaOH and WTS was at a Na_2O:SiO_2 ratio of 0.25. The results showed that the non-calcined sludge did not show compressive strength in the early ages, and just after 60 days of curing, it obtained 0.76 MPa. The XRD showed that the main reason for this phenomenon was the non-occurrence of dehydroxylation of halloysite. The samples calcined at 600 and 900ºC presented lower compressive strength than sludge calcined at 800°C. The sample prepared with calcined sludge at 800°C obtained 8.8 MPa of after 60 days of curing.

Suksiripattanapong et al. (2015a) researched the mechanical performance of masonry units made with WTS-Fly ash geopolymer. The air-dried Alum sludge was used as an aggregate, Fly ash (high calcium content) was applied as a precursor combined with the alkaline activation mixture based on NaOH and Na_2SiO_3. For the production of alkaline activator liquid composition, a fixed composition by weight of 9% Na_2O, 30% of SiO_2 and NaOH with a concentration of 10 M was used. The ratio of WTS/Fly-ash was 70:30 and the Na_2SiO_3/NaOH proportions were 100:0, 90:10, 80:20, 70:30 and 50:50. Furthermore, the samples were heated at temperatures of 65, 75 and 85 °C, lasting up to 120h and then cured at room temperature (27-30°C). The best formulation results for maximum unit weight and compressive strength were at Na_2SiO_3/NaOH ratio of 80:20 and the liquid alkaline activator/fly-ash ratio of 1.3. The temperature and ideal heat period for the best results were found at the temperature of 75°C and 72 hours, generating samples with compression strength ranging to 12 - 20 MPa. Therefore, the water treatment sludge was considered feasible for the production of masonry units according to Thailand standard. In a similar study, Suksiripattanapong et al. (2015b) investigated the use of the same by-products, WTS and fly ash as an aggregate and a precursor respectively, for the production of a cellular geopolymer without using Portland cement as a cementing agent. A foaming agent based on anionic surfactants, foam stabilizers and liquid air-entraining were applied to reduce the unit-weight. The parameters used were the same as the previous study with masonry units and the influential factors studied were air content, the liquid content of alkaline activator (L) and duration of heat and cure time. The higher compressive strengths for different air contents were found at Na_2SiO_3/NaOH of 80:20 and a heat duration of 72 h at 65°C, ranging from 7.5 to 19 MPa approximately, which is related to the growth of geopolymerisation.

Nimwinya et al. (2016) studied the feasibility of a geopolymer precursor with calcined mixtures of WTS and Rice Husk Ash (RHA). Calcined aluminium sludge and RHA powder were mixed in various WTS/RHA ratios of 100: 0, 85:15, 70:30, 60:40 and 50:50. The alkaline activator solution was based on the NaOH mixture with calcium silicate (Na_2SiO_3) with fixed proportions of Na_2O equal to 8.0% and SiO_2 equal to 27.0%. A delay in the settling time was observed as the SiO_2/Al_2O_3 ratio increased, mainly because of the decrease in the WTS/RHA ratio. Thus, the initial settling time increased as RHA was increased, reaching 13.5 hours for mixture with 50% RHA. The higher 7-day compressive strength of the geopolymer paste cured at room temperature and 60°C was when the ratios of SiO_2/Al_2O_3 were 4.9 and 5.9 (30% and 40% RHA replacement, respectively), with strength ranging from 16 MPa to 24 MPa (Table 4).

Geraldo et al. (2017) investigated the partial substitution of metakaolin (MK) by WTS for the composition of geopolymeric mortar. An alternative alkaline activator solution was prepared with NaOH and RHA (replaced sodium silicate). Furthermore, due to the amount of SiO_2 was lower in the WTS compared to the MK, an extra amount of RHA was added in the mixtures to balance and increase the SiO_2/Al_2O_3 ratio. The results showed that as the proportion of WTS increased, setting time increased simultaneously. The final settling time of the samples ranged from 3.22 to 5.32 hours; these values were higher compared to fly ash geopolymers for the same temperature. The compressive strength and the workability of the samples decreased as the addition of WTS. Mechanical strengths for all specimens ages reached the minimum recommended for various types of building materials, according to the Brazilian standard.

Duxson et al. (2005) showed with aluminosilicate-base that the strength development of geopolymer matrix depended on the type of precursor and the ratio SiO_2/Al_2O_3. Thus, these few studies with WTS as a precursor had focused on improving and modifying the SiO_2/Al_2O_3 ratio when it was not satisfactory. Therefore, considering the recent research with WTS and its compatibility in the production of geopolymeric materials, the production of geopolymers with WTS would be a viable solution for the sludge application in construction materials. However, for WTS-geopolymer to be competitive and alternative for Portland cement-based materials, more studies need to be carried out to improve the mechanical strengths, setting time and workability.

2.3 Durability

Time and environment are determinate factors for the performance of engineering structures. Naturally, deterioration mechanics cause decreasing performance in materials. However, it is often considered a second or forgotten topic during the design phase (Bijen, 2003). In this topic, I will discuss the primary tests for the durability of materials incorporating WTS, based on a few studies which have been carried out on the long-term life cycle.

Table 5. Summary of main properties of geopolymers incorporating WTS

Reference	WTS usage	Activator/ Binder ratio	Molar ratio		WTS Thermal Treatment (°C)	Heat-curing Temperature (°C)	Compressive strength (MPa)	Setting Time (H)	
			SiO_2/Al_2O_3	$Na_2O:SiO_2$				Initial	Final
Waijarea et al. (2014)	Precursor	0.184	1.78	0.25	600, 800, 900	28°C for 24 hours	1.7 - 8.8	-	-
Suksiripattanapong et al. (2015a)	Aggregate	1.2 - 1.4	3.8	0.3	NA	65, 75 , 85°C for 24 - 120 hours	5.0 - 20.0	-	-
Suksiripattanapong et al. (2015b)	Aggregate	1.92 - 2.04	3.6	0.3	NA	65, 75 , 85°C for 24 - 120 hours	0 - 19.0	-	-
Nimwinya et al. (2016)	Precursor	1	3.1 - 7.3	0.296	600	28 and 60°C for 7 days	0 - 24.0	0.3 - 13.5	1.0 - 27.0
Geraldo et al. (2017)	Precursor	0.52	4.2	0.2	NA	25°C for 1 - 90 days	5.33 - 36.8	2.3 - 3.75	3.22 - 5.32

* Compressive strength: 7-60 Curing days

* NA: Not applicable

The durability of ceramic bricks depends primarily on water absorption (Huang et al., 2001; Hegazy et al., 2012; Ewais et al., 2017). According to Fernandes et al. (2010), the deterioration of the ceramic bodies is mainly due to the high capacity of the fluid to be stored in the brick, causing the reduction of the mechanical resistance and useful life. The major causes of the increase of water absorption in the bricks were the burning of the organic matter present in the WTS between 300-600°C and the decomposition of carbonates and sulphates at temperatures above 800°C, which eventually contributed to the increase of porosity (Teixeira et al., 2011; Kizinievič et al., 2013; da Silva et al., 2015). The primary test used to measure water absorption is quite similar in most of the international standards used. The majority of these standards limit the value of water absorption for load-bearing bricks for no more than 15-25% by weight (Standard IS 1077: 1992; ESS 1993; ASTM C373:2006; NBR ISO 5017:2015). The increase in water absorption was noticeable as the sludge was added to the ceramic bodies. Among the several studies evaluated in this article, the vast majority of the studies obtained values below 20% of water absorption, except in the researches where the concentration of organic material in the sludge was very high (Huang et al., 2001; Teixeira et al., 2011). However, according to Raut et al. (2011), in their review paper on ceramic bricks with the addition of residues and waste materials, accelerated weathering tests should also be done to ensure a long life-cycle for the material.

LWA and ceramsite are clay-sintered materials which exhibit similar behaviour as the ceramic bricks. The water absorption, porosity and better crystallisation are the predominant factors for the durability of the material and also for the light concrete produced with it (Huang et al., 2005; Zou et al., 2009). Huang et al. (2005) showed that among the three firing temperatures (1000, 1050 and 1100°C) used to produce LWA made from sludge, only the specimens produced at 1100°C obtained low water absorption (14.47%), similar to commercial LWA and feasible for application to concrete. Sales et al. (2010) showed that due to the high water absorption of the lightweight aggregate made with WTS, all concrete formulations had high porosity and absorption (8.8%)

compared to conventional concretes, which can affect the long-term life of the material depending on its exposure and application (**Figure 9**). Zou et al. (2009) proved that the chemical durability of ceramsite is better when their crystalline phases are more complex. Through the tests of X-ray diffraction, morphological structures analysis, water absorption and porosity, it was confirmed that the phenomenon was directly influenced by the ideal amount of iron present in the sludge that is between 6% and 8%, resulting in fewer pores and higher strength.

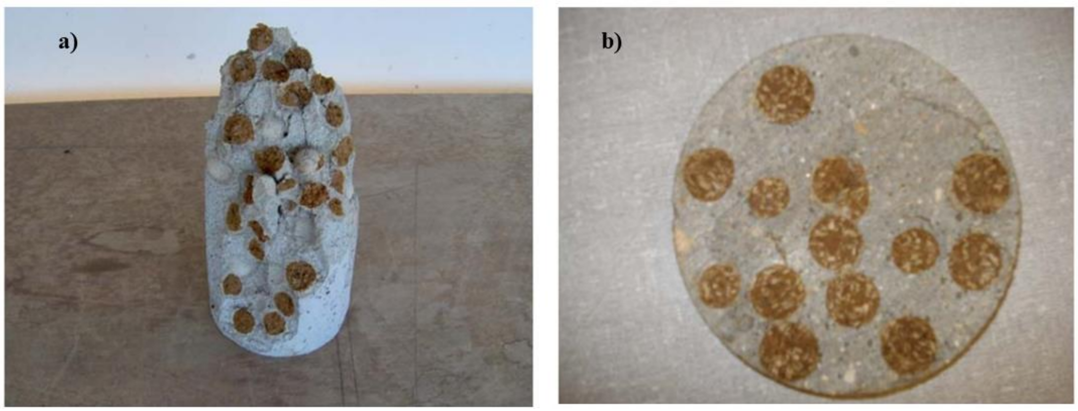


Figure 9. (a) Concrete made with WTS-composite aggregate after axial compression test, (b) Cross-section of concrete with WTS-composite (Souza, 2010; Sales et al., 2010).

Concrete is the most commonly used construction material in the world, and its combination with steel makes it a material with broad applications. However, their durability performance depends on their interaction with the environment, where the penetration of substances through the pores has a significant impact. The most common forms of deterioration of concrete are corrosion of the steel bars through the carbonation and ingress of chlorine oxides, freezing and thawing action, sulphate attack and alkali-aggregate reaction (Basheer et al., 2001). Therefore, the additions of sludge in the concrete must be evaluated for their durability, mainly because it is a by-product with the presence of organic matter, coagulants based on chlorine and sulphates and other deleterious elements. In studying the application of WTS in cement mortar, Rodríguez et al. (2010)

showed by FTIR spectroscopy test that the presence of 12–14% organic matter (mainly fatty acids) had influenced in the formation of ettringite and retardation of calcium silicate hydration process, affecting the long-term durability of concrete. Hoppen (2004) in her study on the addition of sludge to concrete found that for sludge additions above 5% showed a considerable increase in water absorption, making the material less durable and vulnerable to penetration of chloride and sulphate ions. The concrete durability tests (accelerated aging in alkaline solution and ASTM C876) with 4% of WTS obtained a result of potential corrosion similar to the reference concrete. However, the specimens with 8% of sludge showed a tendency of potential corrosion with 90% of probability occurrence, but no cracks or other defects were found in the concrete surface.

Sukmak et al. (2014) showed that concerning the sulphates attack, geopolymers based on clay-fly ash have greater durability than clay-cement materials. Using the methods for wetting and drying cycles (ASTM C599-03/ASTM 2003), Horpibulsuk et al. (2015) showed that wet-dry durability of the WTS-Fly ash geopolymer after 12 cycles was higher than that of the WTS-Cement and silty clay–cement for the same conditions. Even after 12 wet-dry cycles, WTS-FA geopolymer with better heat curing condition (85°C for 72 hours) showed a satisfactory compressive strength of 7 MPa, compatible with durable bearing masonry blocks. Geraldo et al. (2017) using the water absorption, voids and capillary absorption tests (Brazilian Standard - ABNT, 2005c), showed that the air permeability of the geopolymer with 60% substitution of metakaolin by WTS was five times higher than those specimens of 0% of sludge. The porosity of the material increased as the sludge was added, and the water absorption values were between 10.6% and 13.7%. The voids were from 9.6% to 12%, showing that the addition in massive proportions can affect the long-term behaviour of the material.

2.4. Leachability and toxicity

Considering the high possibility of applying WTS to construction materials, environmental risk assessment becomes an important issue, since the WTS may contain metals with potential consequences for the environment and human health. The most common tests for this type of evaluation are commonly called leaching tests, which evaluate the release of contaminants to the environment in the presence of water, in the different phases of the product life cycle (manufacturing, distribution, construction, use, end of life) and not only in aspects of 'passed fail tests' (Van der Sloot, 1996). When a leaching test is selected for material analysis, the shape of the building material tested should be taken into consideration, because the release mechanisms of heavy metals involved are different. For example, in monolithic elements, heavy metals will be released due to surface washing, diffusion and/or dissolution processes (NEN, 2004; Król, 2011). The most widely test applied to materials and wastes is the Toxicity Characteristics Leaching Procedure (TCLP) from the United States Environmental Protection Agency. According to Townsend et al. (2003), many chemical and physical factors control waste leaching in products. The physical factors are particle size, liquid/solid reaction, temperature, and porosity. Chemical factors include pH, the redox potential of the material, sorption processes and formation of complexes with organic or inorganic compounds.

Considering the large amount of articles evaluated in this review article. Few studies have assessed the environmental risk caused by the incorporation of various types of WTS into building materials (Table 6), possibly due to the fact that in most cases the sludge is classified as non-hazardous waste according to local standards.

Table 6. Summary of the leachability standards and key findings

Reference	Sludge Classification	Total Metal Concentrations	Sludge Use	Leaching Standard	Main Findings

Huang et al. (2001)	Non-hazardous residue	Relatively low	Ceramic brick	TCLP/USEPA (1992)	A slight increase in Cd concentration was found at increased firing temperature.
Hassan et al. (2014)	Hazardous residue	As and Fe content were very high	Ceramic brick	TCLP/USEPA (1992)	Percentages above 3% sludge-mix showed leaching
Sales et al. (2011, 2010)	Non-hazardous residue	Al content was relatively high	Lightweight composite concrete	ABNT: NBR 10004-10007	Al limit above that established by the Brazilian standard
Huang & Wang (2013)	Non-hazardous residue	Relatively low	Lightweight Aggregate	TCLP/USEPA (1992)	Concentration of heavy metals below the regulatory thresholds
Xu et al. (2010)	Non-hazardous residue	Relatively low	Ceramsite	TCLP/Chinese Standard	Concentration of heavy metals below the regulatory thresholds
Lin & Lin (2005)	Hazardous residue	Pb, Zn, Cd, Ni, Cr and Cu content were very high	Eco-cements clinkers	TCLP/SW-846-1311.	Concentration of heavy metals below the regulatory thresholds
Chen et al. (2010)	Non-hazardous residue	Cr and Zn content was relatively high	Cement clinker	TCLP/GB 5085.3-2007	Concentration of heavy metals below the regulatory thresholds
Lee et al. (2012)	Non-hazardous residue	Very low	Concrete Mix	TCLP/NIEA R201.13C (2004)	Concentration of heavy metals below the regulatory thresholds
Alqam et al. (2011)	Non-hazardous residue	Fe content was relatively high	Paving-tiles	TCLP/USEPA (1992)	Concentration of heavy metals below the regulatory thresholds

Waijarean et al. (2017)	ND	Zn, Fe and Cr content were relatively high	Geopolymers	TCLP/SW-846-1311.	Slight increase in Zn, Fe and Cr concentration when SiO_2/Al_2O_3 ratio increase

* ND : Not reported

In a study with arsenic-iron sludge for the production of bricks, Hassan et al. (2014) showed that for acidic, neutral and alkaline medium pH only sludge-mix rates of 3% shows less arsenic and iron leaching than is acceptable for Bangladesh standard and World Health Organization (WHO). The highest values for leaching of the burned brick were found at around pH 3.0, showing values above the limit values of 0.05 mg/l for arsenic. (Sales et al., 2011; 2010) studied the leaching of aluminium, iron and lead in a LWA material with Al-based WTS and sawdust. The solubilised extract of the concrete produced with the WTS-LWA showed an aluminium concentration higher than the solubilised extract concentration of the reference concrete without this composite, 19.96 mg/l and 1.12 mg/l respectively. This phenomenon was mainly due to the high concentration of aluminium (11.10 mg/l) present in the sludge. Nevertheless, the material showed the necessary limits for environmental safety according to the NBR 10004 Brazilian standard (ABNT, 2004c) and classified as non-harmful and non-inert solid wastes. Xu et al. (2008c; 2010) studied the stabilisation of heavy metals in ceramists made with Al-WTS and WWTS. Leaching tests focused on the effects of pH, oxidative condition, sintering temperature and the ratio of oxides (Fe_2O_3 + CaO + MgO)/(SiO_2 + Al_2O_3). The effect of sintering temperature and the ratio of oxides had a significant influence on the leaching and solidification, noting that above 1000°C heavy metals such as Cd, Cr, Cu, and Pb can hardly be re-released to the environment causing secondary pollution. The results also show that sample ceramsites exposed to conditions of $pH > 2$ had leaching rates below those recommended in the Chinese Standard and TCLP.

In their study on eco-cements clinkers made with two industrial wastes and Al-based WTS ash, Lin and Lin (2005) analysed the concentration and leaching of heavy metals like Pb, Zn, Cd, Ni, Cr and Cu. The results confirm a high stabilisation rate of heavy metals, and all eco-cement mixtures were below the regulatory limits established by TCLP (the characteristic leaching procedure). A similar analysis was made by Chen et al. (2010) in their study of shale replacement by WTS for clinker production. The TCLP results showed that for the hydrated samples made with the WTS-clinker, no heavy metal was detected or represented values above the normalised standard, indicating that these components were fixed and incorporated to the clinker. Lee et al. (2012) analysed the leaching effects of the substitution of natural sand by an Al-based WTS in the production of concretes. The results of TCLP and based on the NIEA R201.13C (2004), showed that no substantial quantities of heavy metals were detected in the concrete samples. Proving that, even when large quantities of sludge (30%) were added, the heavy metals were fixed and immobilised in the concrete matrix. Using TCLP, Alqam et al. (2011) evaluated the heavy metals leaching of paving tiles made from the mixture of al-sludge and cement. All results showed a very low percentage of heavy metal concentrations, even for paving tiles with 50% Al-WTS contents.
Waijarean et al. (2017) evaluated the leaching of Zn, Fe and Cr in geopolymers with compositions of Al-WTS. Only samples with SiO_2/Al_2O_3 molar ratio of 1.78 showed a safe degree of immobilisation of heavy metals in accordance with USEPA regulatory limits. It was observed that as much as the SiO_2/Al_2O_3 ratio increase, less effective is the WTS-based geopolymer as an immobilising agent. For Cr (the most toxic of the three metals), the results simulating acid rain (pH 5) showed that at SiO_2/Al_2O_3 ratio of 3 the leaching was nearly 8.9 mg/l, which is higher than the US Environmental Protection Agency recommended value of 5 mg/l.

2.5. Economic evaluation

Wolff et al. (2015) in their research on WTS application in structural ceramics showed that for every ton of clay, it would be possible to save US$318 by introducing sludge into the brick production cycle. Included in this amount is a saving of 8 US$/ton that would be transported to the landfill and others cost associated with clay extraction and energy savings. Kaosol (2010) evaluated the cost involved in the production of hollow concrete blocks with fine aggregate replacement up to 50% by using WTS in Thailand. The cost composition for the evaluation was based on the production of 1200 blocks day, 2 Laborers, machine cost, electricity and materials for normal block production (cement, sand and aggregate). In the researcher's evaluation, for the replacement of 10 and 20% of fine aggregate by WTS, the cost per unit would be reduced by Thai-Baht ฿0.64 and ฿1.05 respectively, for a hollow load-bearing concrete block. Furthermore, for the production of non-load bearing blocks with percentages of 30-50% sludge, costs would reduce from Thai baht ฿1.48-2.35 per block.

De Almeida and Zulanas (2016) performed an economic feasibility analysis for the 5% incorporation of WTS in the mix of concrete sidewalks in Cubatão city, Brazil. The analysis considered the Cubatão city daily-dry-sludge production of 1925 kilograms and a standard city block of 80 m × 274 m, (1534.4 m^3 for sidewalk 7 cm thick). According to the researchers' analysis, it would be necessary three days of sludge production to supply the required 5% addition in the 98m^3 concrete mix for 700 m of a sidewalk, and 39 days of water filtration process to achieve enough WTS to lay a city block of concrete. Thus, in 1 year with a production of 9.4 city blocks of sidewalks (365 days in a year / 39 days to produce sufficient sludge for a city block), the city could consume all its sludge production of the year. In addition, according to the researchers, the local civil construction industry could save about $543,069 per year, assuming that 1 ton of concrete gravel (washed rock) is $28.81 and 5% of WTS. Gastaldini et al. (2015) analysed the costs (US$56.04/$m^3$) of collecting/transporting the sludge from water purification plant to the landfill, and the fees applied to allocate the sludge in the Rio Grande do Sul, Brazil. According to the researchers, the price to carry a kilogram of sludge to the landfill is twice as large as the value of a

19-mm coarse aggregate (US$0.018) and 5.6 times the cost of washed and sieved sand (US$0.0083). Therefore, the 5-30% substitution of cement by WTS ash (for the same concrete strength without the addition of sludge ash) would lead to savings of 37-200 kg of cement per m^3 of concrete.

Nimwinya et al. (2016) showed that for the production of geopolymers with WTS, the cost would be twice as practised today in Thailand to send this waste to the landfill, which is US$33 /ton. This cost is mainly concentrated in the geopolymers ingredients, calcination of the sludge and the electricity used in the process, which the value is US$65-68 for geopolymers prepared at room temperature and cured at 60°C respectively.

2.6 Biochar as a cementitious material

Biochar is a carbon-rich material obtained from carbonised biomass under a low oxygen atmosphere. The thermal process commonly used for this transformation is called pyrolysis. The solid material obtained in the pyrolysis conversion is called biochar and consist of around half of the carbon from the original raw organic compounds. (Mulabagal et al. 2017). The biochar commonly presents more stabilised carbon concentration than previous raw material. Thus, the carbon contained in the biochar is less likely to be released back into the atmosphere as carbon dioxide. Furthermore, the pyrolysed biochar has shown some efficiency to reduce the emissions of greenhouse gas (GHG) in approximately 870 kg of Carbon dioxide equivalent per/tonne of dry raw material over its lifetime, and 62-66% of this reduction is due to the carbon immobilisation on biochar (Roberts et al., 2009).

The motivation for its use stems from its diversity of application in fields such as waste management, energy production, climate change mitigation and soil improvement, which individually or in combination can have positive social and financial effects(Lehmann, 2007; Steiner et al., 2008; Beesley et al., 2010). Therefore, different types of biochar have emerged, demanding different production systems such as soil amendment (Zhu et al., 2017), horticultural applications (Vaughn et al., 2017), wastewater treatment application (Gupta et al., 2016), asphalt binder (Zhao et al., 2014).

2.6.1 Biochar properties under N_2 or CO_2 Atmospheres for Pyrolysis

The studies have shown that the pyrolysis process under N_2 and CO_2 atmospheric, and temperature of 350-750°C has produced the best biochar material. The higher temperatures contribute to the increase of the porosity of the final material, as a result of the removal of volatile matter during the pyrolysis (Pereira et al., 2003; Jindarom et al., 2007). Similarly, the specific surface area increases as the temperature rises. The FTIR Spectroscopy of the pyrolysed material made with N_2 and CO_2 gas confirms a decrease in some functional groups of –OH, and – C=O at temperatures above 550 ◦C, resulting in an increase in the alkalinity of the biochar (Jindarom et al., 2007).

The main parameters of the pyrolysis process are temperature, reaction time, heating progression and raw material particle distribution. Among these parameters, the temperature has a predominant influence on the characteristic of the biochar. According to Agrafioti (2013), the ideal temperature for pyrolysis depends on the desired application of the bio-coal, in which pyrolysed biochars with low temperatures are applicable for agriculture, and high temperature will change the material porosity, increasing its mechanical capabilities.

2.6.2 Use of Biochar as an additive for concrete

Recently, there was a growing interest in the use of biochar for cementitious materials to improve its mechanical performance. Estimates show that the addition of only 1% biochar (per mass of concrete) could sequester about 0.5 Gt of CO_2 annually by the concrete industry, equivalenting of 20% of the entire annual CO_2 released by cement industry (Tommaso & Bordonzotti, 2016). Choi et al. (2012) used hardwood biochar to replace the cement partially in a mortar composite. The results show that biochar improved the mechanical performance of the mortar around 10% with only 5% cement substitution (by weight). However, the fluidity of the composite was reduced as the rate of substitution increased. The biochar contributes to an increase in the absorption and retention of the mixing water. The absorbed water in the biochar was released later at the time of mortar hardening which would stimulate the internal self-healing. In another study, the researchers investigated two types of pyrolysed byproducts, coffee powder and hazelnut shells as a nano-aggregates. The research reported that the additions of 0.80 and 1% prepared at 800◦C improved the mechanical performance of the cement paste. The study showed that the biochar acted as a microaggregate and improved the fracture energy due to the tortuosity of the cleft path. In summary, the particles of biochar changed the crack direction and created a circuitous path before fracture (Restuccia and Ferro, 2016). Similarly, Ahmad et al. (2015) reported that the addition of 0.08% of biochar made with coconut shell improved the compression and fracture strength hardness of composite in 25% and 76%, respectively. The SEM image (**Figure 10**) shows the crack tortuousness around the biochar.

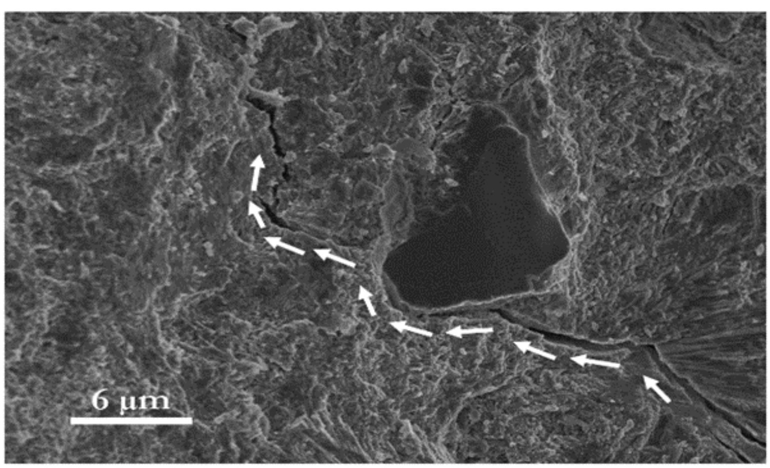


Figure 10. Crack contouring around a pyrolysed coconut shells particles addition.

Gupta et al. (2017, 2018) used biochar made from the wood and sawdust at 300°C and 500°C. The biochar was previously water-saturated before the addition of 2% in the mortar mix.

The results show that biochar application offers a significant improvement in the compressive and flexural strength of the composite. The permeability and sorptivity of the composite were significantly reduced due to the addition of bio-carbon, which indicates greater impermeability in the mortar due to the effect as a micro-filler. Akhtar and Sarmah (2018) studied the effect of biochar made from different raw materials (poultry waste, rice hulls and sludge from pulp and paper mills) in the substitution of cement up to 1% of the total volume. The results revealed that the biochar of pulp-paper sludge obtained compressive strength near the control sample. However, the substitution of only 0.1% of rice husk biochar slightly increased the tensile and flexural strength of concrete with an increase of 20% concerning the control samples.

Chapter 3

3. Experimental

3.1 Materials

3.1.1. Water Treatment Sludge

The Metropolitan of Sydney is supplied by three major water treatment plants, Prospect, Richmond and Cascade. In this study, the sludge was obtained from the Cascade Water Filtration Plant (Katoomba, NSW, Australia), as shown in **Figure 11**. The choice for the Cascade plant was due to higher sludge production (water catchment made directly from the Dam). The plant uses conventional water treatment with ferric chloride ($FeCl_3$) as the coagulant.

Figure 11. Aerial view of Cascade Water Filtration Plant (google earth, 22/05/2019)

The sludge was collected from the drying bed at four different points. The natural sludge was dried at 105 °C for 24 hours, crushed, sieved (300 μm) and stored as shown in **Figure 12**.

Figure 12. Preparation and processing of water treatment sludge.

3.1.2. Cement

The cement used in the study was a general purpose (GP) cement from Cement Australia, which fully complies with Australian Standard AS 3972-2010 (General Purpose and Blended Cements). The cement has a density of 3.0-3.2 g/cm^3, the average particle distribution 9.4 mm. Its full characterisation is shown in **Table 7**.

Table 7. Physicochemical properties of GP cement

Chemical Entity		**Proportion**
Portland clinker		< 97%
Gypsum ($CaSO_4$ $2H_2O$)		2-5%
Limestone ($CaCO_3$)		0-7.5%
Calcium oxide		0-1%
Property		Indicative GP
Setting time	Min	60-150 min
	Max	2.0-3.5 hours
Soundness	Max	< 3 mm

SO_3	Max	< 2.9%
ISO mortar	3 Day (min)	30-42 MPa
Compressive strength	7 Day (min)	43-54 MPa
	28 Day (min)	54-65 MPa

Safety datasheet, Cement Australia, 2019

3.1.3. Biochar

The natural dried and sieved sludge was used to prepare the biochar (**Figure 13**). Pyrolysis was operated in a furnace oven (Labec) at 700ºC for 2 hours. The temperature rate was 17ºC/min. To maintain a low oxygen atmosphere during the process, the gas nitrogen was injected to the reactor at a flow rate of 220 mL/min.

Figure 13. (a) Dried raw sludge powder (b) Pyrolysis reactor (c) WTS-Biochar

3.2 Cement Paste Testing

In order to ensure full hydration, cement paste was cast with water to cement ratio of 0.4, according to ASTM C305-14 (Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency). The blended pastes were prepared by mixed GP cement. Natural WTS and biochar were added at 1%, 2%, 5% and 10% based on the weight of the cement (**Table 8**).

Table 8. Cement paste experimental design mixes

Mixes	Cement (g)	WTS/Biochar (g)	Water (g)	Water/Binder
Reference	2800	0	1120	0.4
WTS -1%	2800	28	1120	0.4
WTS - 2%	2800	56	1120	0.4
WTS - 5%	2800	140	1120	0.4
WTS - 10%	2800	280	1120	0.4
WTS/Biochar-1%	2800	28	1120	0.4
WTS/Biochar- 2%	2800	56	1120	0.4
WTS/Biochar- 5%	2800	140	1120	0.4
WTS/Biochar- 10%	2800	280	1120	0.4

3.2.1 Compressive Strength

Twelve specimens of cubic moulds (50 mm × 50 mm × 50 mm) were cast for each mix. Then, the blended pastes were cured for one day at 20 °C with 95% relative humidity. After demolding, the specimens were wet-cured for 7, 14, and 28 days. The method used for the compression strength test of cube specimens was based on ASTM C109-16 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars), which provides a means of determining the compressive strength of hydraulic cement and other mortars. The compression testing was conducted on a Universal Hydraulic Test Frame (UH-500kN XR) with a REH50 load frame, Shimadzu (**Figure 14**).

Figure 14. Compressive strength test applied on cement paste.

3.2.2 Heat Evolution

The heat evolution evaluation techniques are essential for a more accurate understanding of the cement portland hydration process and the interference caused by new additions. The heating of hydration of mixing cement pastes was performed with a High Precision Calorimeter (I-Cal 4000) compliant with ASTM C1679. All the mixtures were mixed by hand for 30s, and about 25g of the paste was used for each cup mix test. The plastic cups with pastes were closed with the lids and instantly deposited into the calorimeter. The experiment was made during the first 48 hours of reaction with a controlled temperature around 20°C (**Fig. 15**).

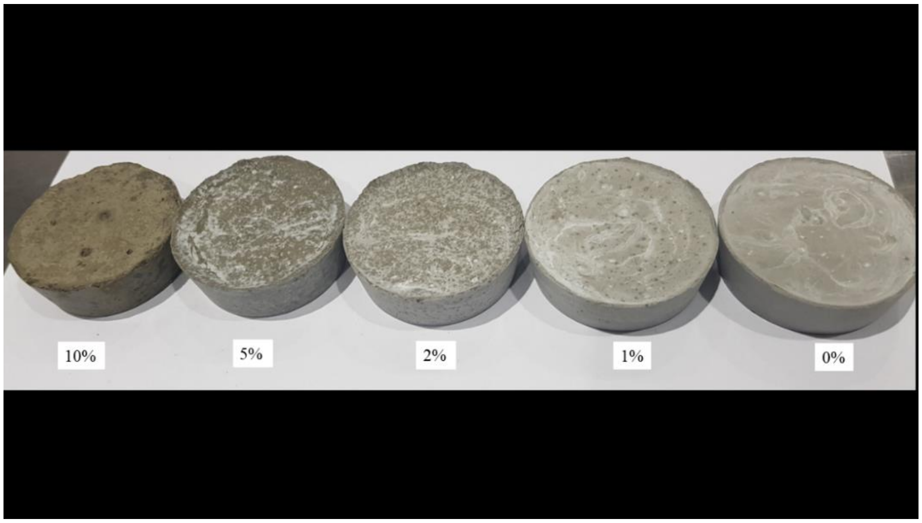


Figure 15. Heat evolution samples with raw sludge after 48 hours test.

3.2.3 Simultaneous thermal analysis

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis help the study and understanding of cementitious materials behaviour in different hydration stages and also characterise the raw materials. They have a wide variety of applications such as identification of the common cement compounds phases, studies of the hydration degree, and the analysis of pozzolanic additives (Junior et al., 2013). The simultaneous thermal analysis (TG-DSC) were performed using the *Simultaneous Thermal Analyzer – STA 449 F5 Jupiter*. For the analysis, the fragment powder of cement paste cubes 28 days were used. The simultaneous thermogravimetry used the gas nitrogen, and the gas velocity was 20 ml/min. The sample was heated from 30 to 900°C with a rate of 20°C /min.

3.2.4 X-ray diffraction

In order to identify the hydration evolution of WTS and Biochar blended cement pastes at early-age hydration, the XRD analysis was performed. The mixed cement paste from the cube specimens was grounded at the defined age of 28 days. The material was used for the crystalline characterisation of the paste by X-ray Powder Diffraction using a D8 DISCOVER X-ray diffractometer(Bruker).

3.2.5 Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM/EDS)

SEM-EDS has been one of the main research tools to analyse the complex and heterogenic structure of concrete and cement paste (Diamond, 2004). In this type of analysis, we can clearly observe the hydrated structures of the cement such as ettringite, C-S-H (Calcium silicate hydrate) among others. In addition, with this test, we can observe the behaviour of the natural WTS and biochar in the mix structure. For this experiment, the specimens at 28 days were used. The machine used in this study was a Zeiss Supra 55VP SEM.

Chapter 4

4. Results and discussion

4.1 Water treatment sludge

4.1.1 Characterization of water treatment sludge

The mineralogical composition obtained by XRD of the ferric sludge (**Fig. 16**) shows the presence of a high proportion of the amorphous phase (possibly organic). Typically, amorphous materials are challenging to be identified by XRD techniques. The main crystalline phases present in the sludge are iron hydroxides such as goethite, ferrihydrite, and hematite. These phases are present due to the use of iron-based coagulant and soil composition, which was also observed by Verrelli (2008). Manganese dioxide (MnO_2) in the form of Pyrolusite was detected. This is possibly due to the concentration of manganese in water which justifies the use of iron-based coagulant in NSW (Gebbie, 2006). Furthermore, sphalerite, a mineral with some iron phases associated with other metals, was also observed. Another dominant phase observed was the aluminium hydroxides and clay minerals such as, mullite, kaolinite, which are generally present in rivers sediments. The presence of calcite mineral is probably due to common lime incorporation practice for dewatering at the water treatment plant.

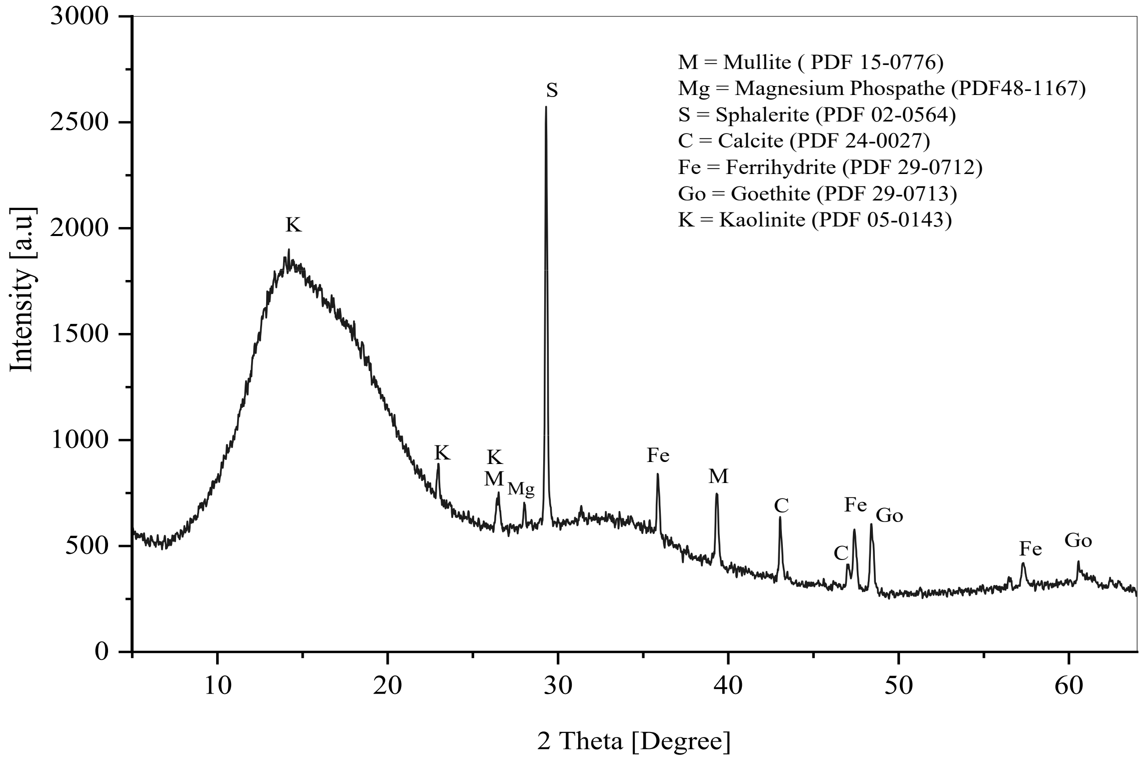


Figure 16. The mineralogical composition of ferric sludge obtained by XRD.

The TG and DSC analyses (**Fig. 17)** revealed a considerable weight loss of around 53.3% when the WTS was submitted to the thermal process until 900 °C. The first observed phenomenon is an endothermic reaction with a maximum peak at 161 °C, related to the extraction of free water from WTS. It was followed by the most significant mass loss (42.46%) with the temperature range between 250 °C and 600 °C. The first part of this considerable mass loss (between 200-400 °C) can be attributed to the burning of organic matter present in the sludge and crystallisation of amorphous phases (i.e. ferrihydrite into hematite) (Teixeira et al., 2011, Kizinievič et al., 2013). The second part of mass loss (between 450-600 °C) has a maximum exothermic peak at 562 °C, probably attributed to the loss of hydroxide (structural water) by kaolinite converted to metakaolinite (Wolff et al., 2015, De Godoy et al., 2019). In the 600–900 °C interval, the total loss observed was 19.1% of total mass, as a result of the decomposition of carbonates (calcite) with two peaks at 796 °C and 886 °C, respectively.

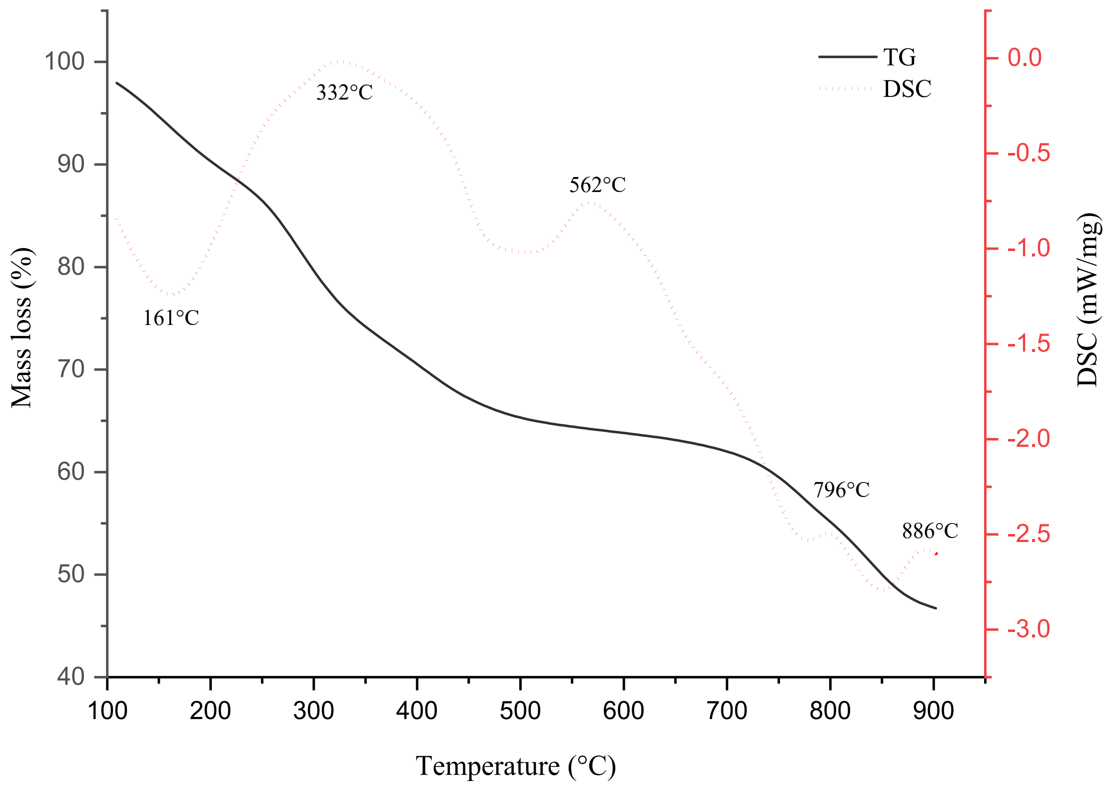


Figure 17. The Thermogravimetry (TG) and DSC analyses of Ferric sludge.

The results obtained by microscopic investigation (**Fig. 18)** of the sludge showed that the material has a heterogeneous flaky morphology, consisting of various sizes of angular and conglomerate shaped particles, and also observed by De Godoy et al. (2020). The surface of most particles is granular and semicrystalline, indicating the presence of kaolinite particles (Fungaro, 2014).

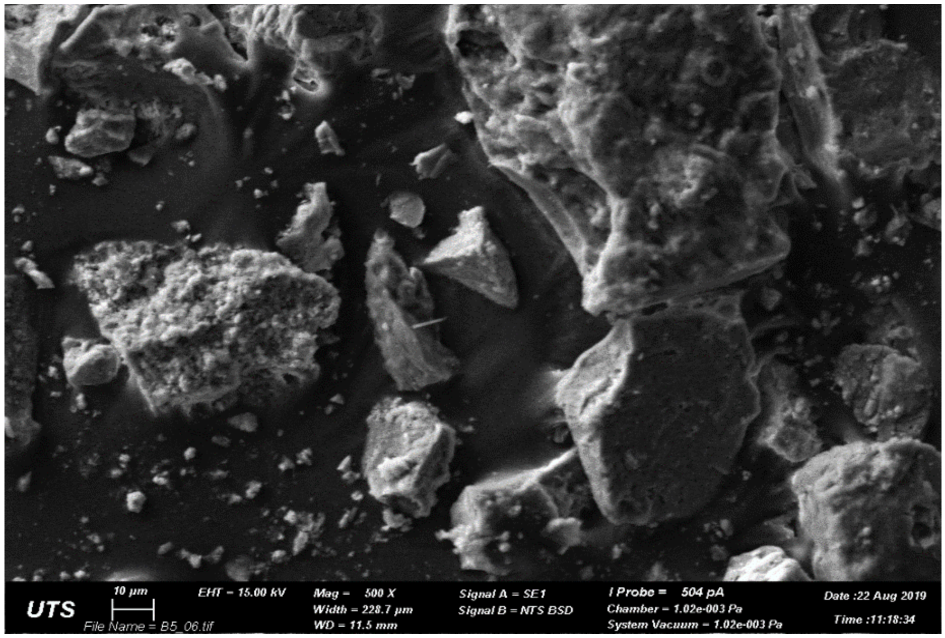


Figure 18. Scanning electron microscope (SEM) of the Ferric sludge.

4.1.2 Heat evolution of cement paste

The rate of hydration of cement and the kinetics of cement hydration were studied, and the results are discussed following the general behaviour proposed by Bullard et al. (2011). **Figure 19** shows the rate of hydration of the cement over the first few hours of reaction, with the hydration process divided into four arbitrary stages. In the first phase (1), there is a high release of heat, corresponding to the hydration of the dissolution of different types of ions and the initial hydration of tricalcium silicate (C3S) and tricalcium aluminate (C3A). In phase (2), called a dormant period, there is a reduction in chemical activity due to the lower solubility of aluminate across the presence of gypsum in the solution. This period usually occurs in the first few hours of the reaction. The reaction period corresponding to phase (3) can be divided into two parts (before and after the maximum rate) and occurs for 4-8 hours from the start of the reaction. The secondary hydration reaction of the calcium aluminates (C3A and C4AF) occurs, forming long acicular compounds of hydrated calcium detrisulfoaluminato or Ettringite (AFt). The C-S-H formed at this stage is the inner C-S-H. Soon after the maximum peak, we have the period of deceleration, with continuous slow hydration, corresponding to reactions in the solid-state. Internal C-S-H continues to form, with progressive reduction of the free space between the hydration layer and the unhydrated particle, and a new phase of aluminate, hydrated calcium monosulfoaluminate (AFm) appears on the last phase (Odler, 1998; Marchon and Flat, 2016).

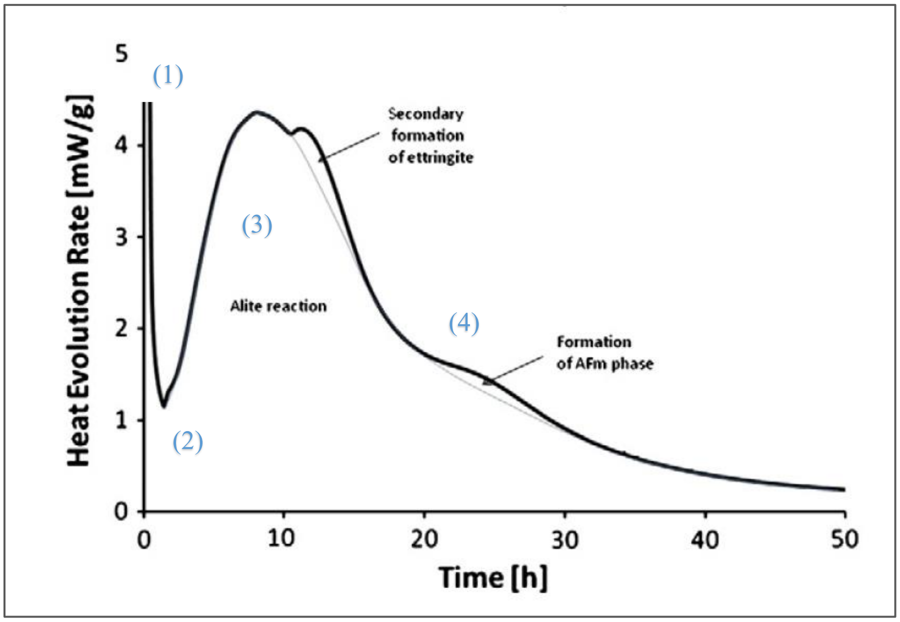


Figure 19. Calorimetry curve of modern portland cement (Bullard et al., 2011).

The interpretation of cement hydration is performed according to several steps of the heat flow analysis released by the reaction, as we mentioned in the previous topic. **Figure 20** illustrates the heat flow in cement reactions with different natural sludge ratios during the first 48 hours of hydration. For better visualisation of the heat flow graph, we do not consider the release of heat by the wetting of the particles due to inaccuracies in the first minutes of hydration and saturation of data.

Figure 20 shows clearly the curve pattern changing by the addition of sludge. Meanwhile, the samples with more natural sludge release less heat. This indicates that the hydration process of cement paste is influenced by sludge addition. The temperature also has a distinct effect on the hydration of the composite. In the curve of the rate of the heat evolution of General Portland

Cement, there are three peaks (**Figure 20**). The initial peak (first hour) is associated with the hydration of C3A, the dissolution of free lime and the wetting of Portland cement; all mixes had similar results. However, the mix with 10% of sludge showed a slightly higher level of heat than the reference. It was followed by the dormant stage (phase 2), in which it can be observed that for the reference samples (cement only) this period occurred between the first 3 hours of reaction, and as the sludge was added this dormant period increased, reaching 8 hours concerning the samples with 5% sludge and 22 hours for 10% of sludge addition.

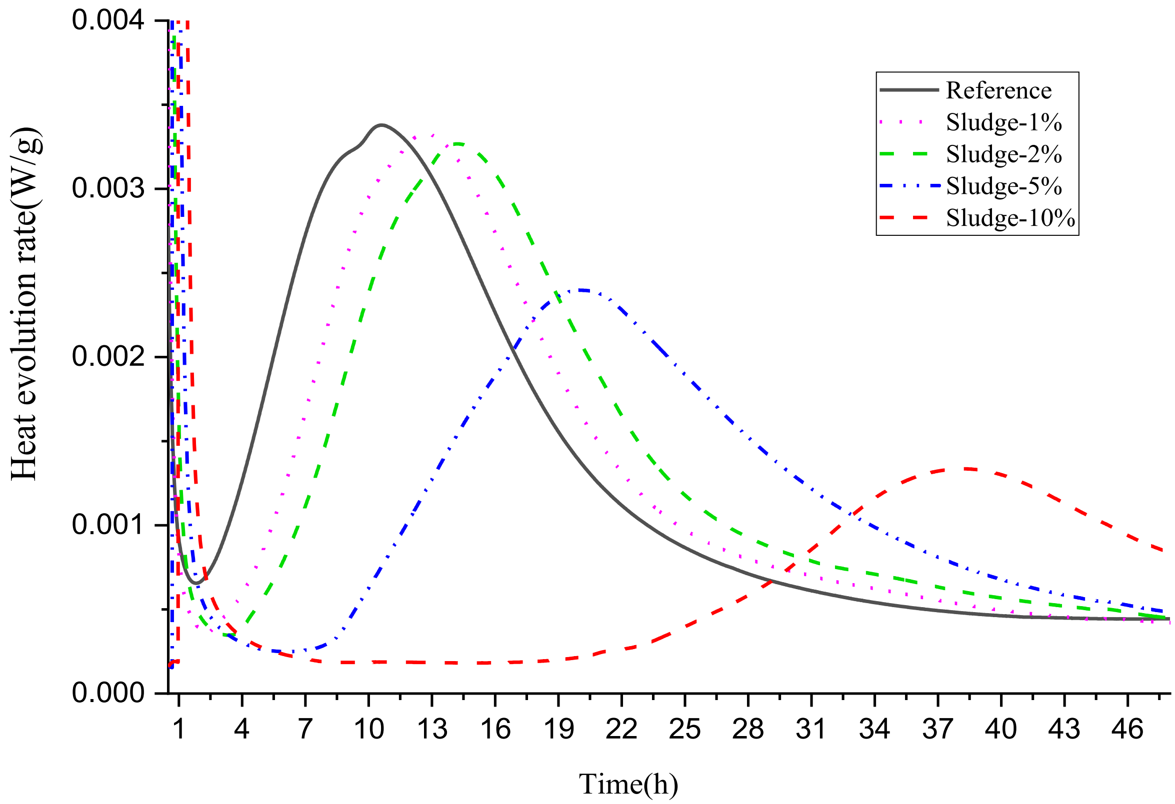


Figure 20. Hydration heat evolution flow with different additions of WTS

Similar to the reference, the curve with 1% and 2% sludge showed a maximum peak, but at a slightly lower intensity and with a delay in reaction time. These peaks correspond to rapid hydration of C_3S and C_3A respectively, followed by a deceleration period of heating. The additions of 5%

and 10% of sludge in cement pastes significantly alter the heat curve and reaction time. The specimens with 5% of sludge showed a single peak with nearly 30% less heat flow than the reference samples. Furthermore, this single peak occurred almost 20 hours after the beginning of the reaction, unlike what happened with the reference that was between 9 hours and 10 hours. Mixtures with 10% sludge showed a maximum peak after 38 hours of reaction and with 60% less heating flow. This phenomenon of delay in the reaction was also reported by Fang et al. (2019), who used the natural sludge for a low-strength composite.

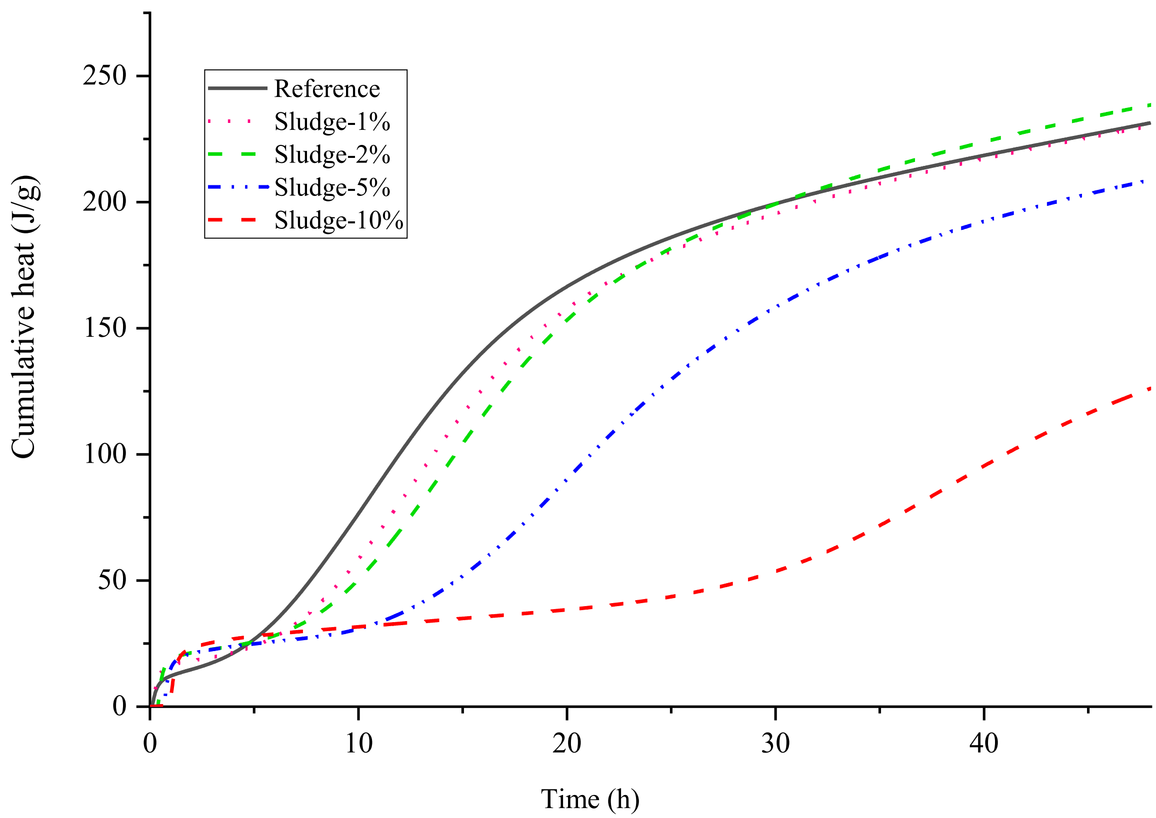


Figure 21. Cumulative heat evolution with different additions of WTS

Figure 21 shows the cumulative heat of evolution of the reference and composite pastes the first 48 hours of testing. The cumulative heat of evolution formed by the composite pastes with sludge is lower than reference cement paste, with the slight exception of the 2% blend that grew slightly after 30 hours of mixing. Increasing the WTS proportion in the mixing also led to a reduction of heating evolved for the initial hydration hours. The accumulated reaction of diluting the cement and increasing the amount of natural sludge in the composite matrix resulted in the observed data. Geraldo et al. (2017) observed a similar trend as the sludge was added on their experiments with geopolymer concrete mix. Another phenomenon associated with the increasing amount of sludge in the system is the brown/reddish colour (**Fig. 15**) related to the presence of iron oxides and detected in the mineralogical analysis (**Fig. 16)** and also observed by Lukashevich et al. (2016).

4.1.3 Compressive strength

One of the most important mechanical properties for hardened cement paste is its compressive strength. **Figure 22** presents the results of the compressive strength measurements of the cement paste with various proportions of natural oven-dried natural sludge with curing ages of 7, 14 and 28 days.

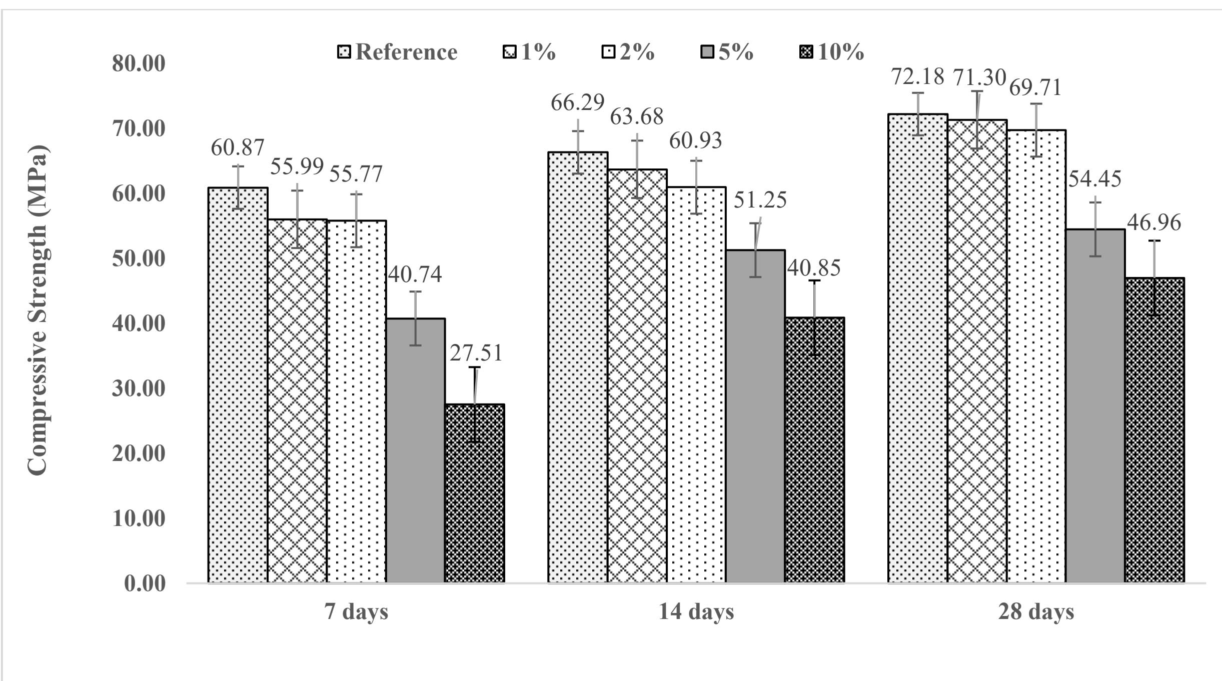


Figure 22. Compressive strength of cement paste with different addition of natural sludge.

Despite the increase in strength over time, the compressive strength of cement paste with sludge as an additive was lower than the reference cement paste. It was found that the high amount of dried natural sludge had a negative effect on the mechanical performance of the cement paste, this considering that the higher level of addition (10%) resulted in less compressive strength. (**Figure 22**). At seven days, specimens with 1% and 2% sludge showed close compressive strengths of the reference material with 100% cement. However, the additions of 5% and 10% presented a decrease close to 30% and 55%, respectively. It is important to note that the mix produced with 10% sludge demanded a demolding time longer than all blended specimens and the reference sample. The same phenomenon was observed in the literature (Hoppen et al., 2006; Gomes et al., 2017) with concrete studies. This effect was attributed to the high concentration of organic matter and iron/aluminium oxides.

Regarding the results at the age of 28 days (final parameter), a similar behaviour was observed as at 7 days, however with less intensity. **Figure 22** still shows a decreasing on compressive strength when more than 5% sludge was added. However, 5% and 10% of WTS addition presented a decrease nearly to 25% and 35%, respectively. As shown in previous studies (Gomes et al. 2017; Wang et al. 2018), significant additions of sludge with a high concentration of organic matter affect the ultimate compression strength of the material.

4.1.4 Mineralogy of hydrated products

The XRD analysis of composite cement paste mix at 28 days is shown in **Fig. 23**, presenting the main phases of hydrated products detected in 0, 1%, 2%, 5% and 10% of sludge samples. As shown in **Fig. 23**, the addition of sludge does not provide the formation of new hydrated compounds, and such as the reference graph (0% sludge) all mixtures have the main crystalline phases; calcium silicate hydrate (CSH), ettringite(Aft) and portlandite (CH). Calcite (CC) peaks are also detected, due to the presence of 7.5% limestone mineral addition on the cement (**Table 7**) and also on the sludge (**Fig. 16**).

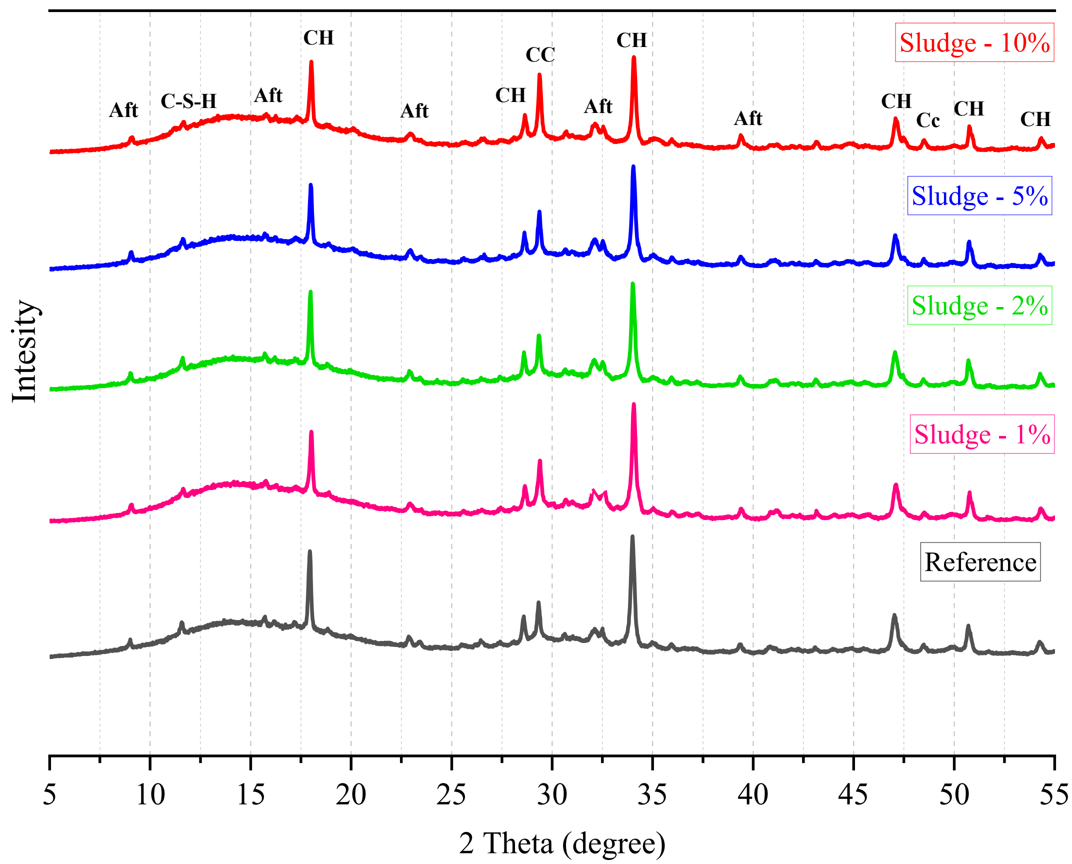


Figure 23. Ray Diffraction of hydrated mixes. Aft =Etringita, C-S-H =Calcium silicate hydrate, CH= Portlandite, CC= Calcite.

Figure 24 shows the XRD patterns comparison between the reference mix and the addition of 10% sludge. It is clear that the peaks of calcite increase with increasing in the sludge content. This is probably due to the presence of more residual calcite present in the sludge and detected in the sludge XRD (**Fig. 16**). On the other hand, the intensity of portlandite peaks decreases with increase in the ferric sludge content, indicating one of the reasons for the lower compressive strength compared to the reference mixture.

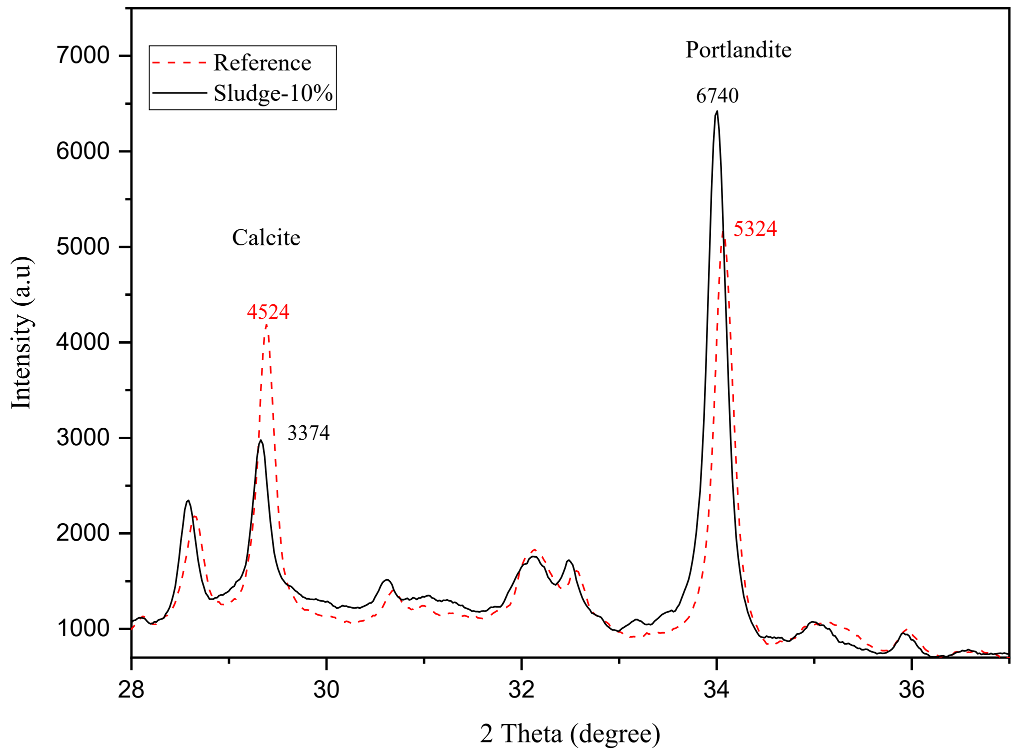


Figure 24. X-Ray Diffraction pattern of reference and 10% of sludge.

4.1.5 Simultaneous thermogravimetry and differential scanning calorimetry analyses

Figure 25 shows the TG and DSC analyses from hydrated pastes of reference, 5% and 10% of sludge addition at 28 days. The first endothermic peak is ranging between 70 °C and 250 °C, and this peak is defined in the literature as the dehydration of C-S-H (Ben Haha et al., 2011). The second endothermic peak is ranging between 420°C and 550 °C, and this peak is defined in the literature as the dehydration of portlandite (Feng et al., 2019). The third visible peak is located between temperatures of 680 °C and 790 °C and represents the decarbonation of calcite ($CaCO_3$) (Alarcon-Ruiz et al., 2005; Feng et al., 2019).

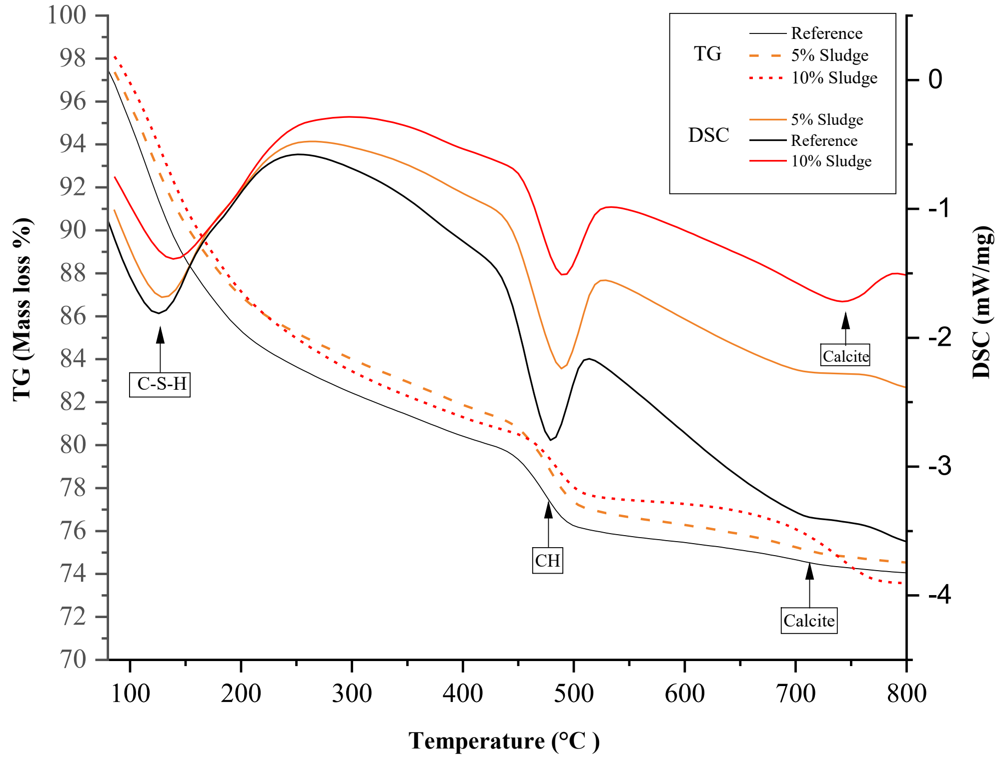


Figure 25. TG-DSC pattern of reference, 5 and 10% of sludge.

Based on the thermograms results and the evident comparison between the area and intensity of the characteristic peaks of C-S-H, Portlandite, we can note that the composite with the addition of 10% sludge had less hydrated product compared to the 5% sludge and reference material. This confirms what was observed in XRD analysis for 10% of WTS, where the peak intensity for portlandite was lower compared to the reference. Furthermore, this result underlies the mechanical strength analyses for decreasing the mechanical performance of the composite as much as sludge was added. The main reason for this low production of portlandite when increasing sludge's content is due to the high concentration of organic matter in the sludge, which prevents complete hydration of the cement compounds (Wang et al., 2018). Another observed phenomenon is the higher mass loss, and a more intense peak concerning calcite for the 10% sludge composite, a similar trend was observed in the XRD analysis.

4.1.6 Microstructure

The heterogeneity of the microstructure of cement hydration products is very complex and sometimes difficult to understand. Usually, C-S-H is the phase that gives the greatest strength to the material, which the structure often presents an amorphous morphology. Furthermore, there are other typical phases in the cement pastes such as portlandite (hexagonal prisms) and ettringite (needle-shaped crystals). Several factors can affect the morphology of these phases on SEM analyses such as curing temperature and drying sample preparation (Zhang et al., 2018). It is evident in **Figure 26(a-b)** the large formation of C-S-H and CH scattered throughout the reference cement paste structure.

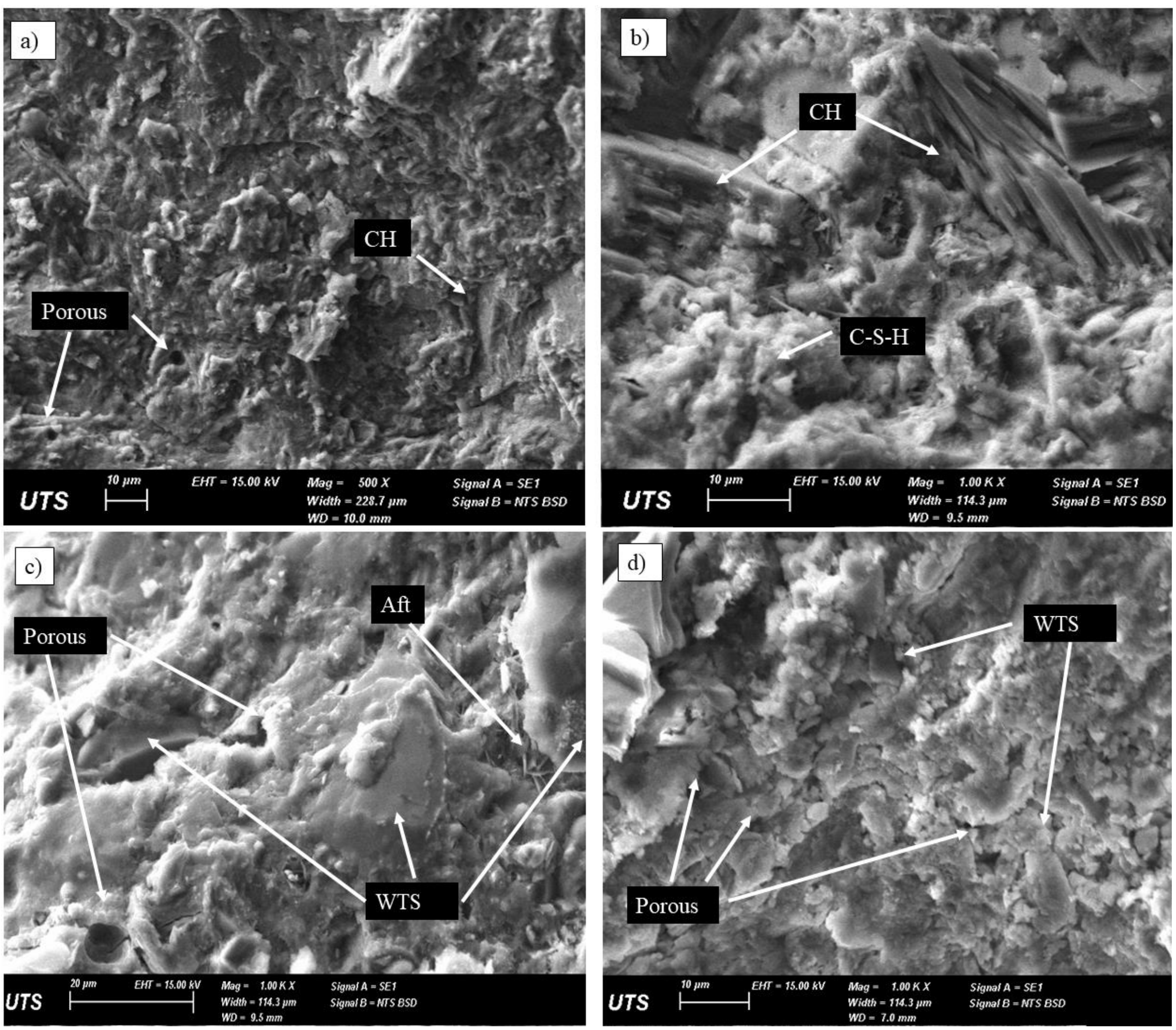
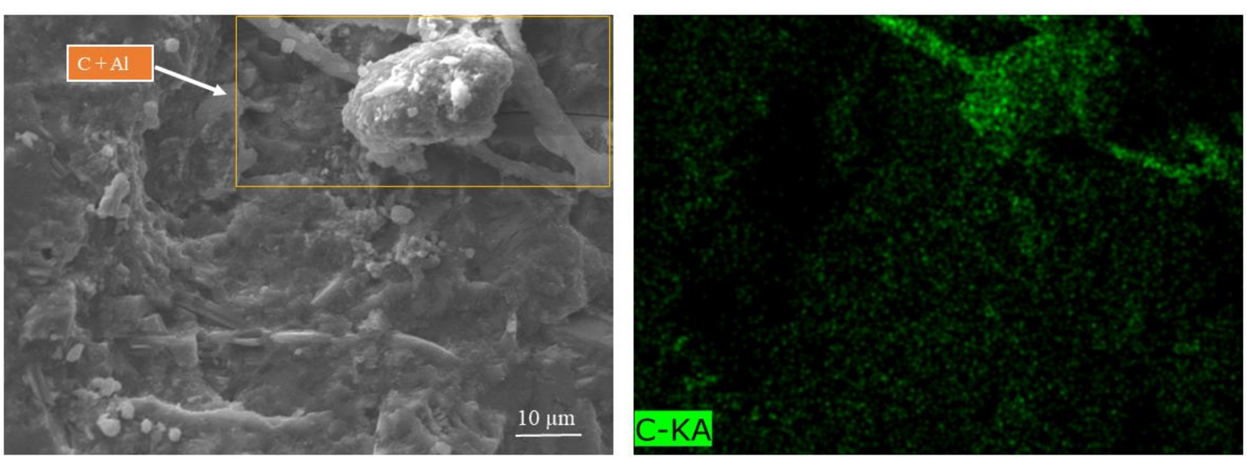


Figure 26. SEM of (a) hydrated reference cement paste (500x), (b) hydrated reference cement paste (1000

x), (c) 5% of WTS addition (1000 x), and (d) 10% of WTS addition (1000 x).

The SEM image (**Fig. 26c**) of the mix containing 5% of WTS shows a slightly less hydrated structure compared to the reference mixture (**Fig. 26a)**. It is essential to note the considerable amount of sludge particles and pores are visible in the matrix, with the formation of ettringite around some sludge particles. **Fig. 26d** shows the microstructure of cement paste with 10% of sludge. The structure has an extremely porous morphology with little or no complete bond development phase. This behaviour is in agreement with the mechanical results and also observed in other similar studies, where the absorption of cement hydration water by the sludge was appointed as the primary cause (Sales et al., 2009; Gomes et al., 2017; Tharshika et al., 2019).

The distribution of the main elements in the structure of the cement paste with the addition of sludge was examined by using the SEM-EDS elemental maps. **Figure 27** shows a high and well-distributed concentration of calcium (Ca), silicon (Si) and oxygen (O), characteristic of hydrated compounds such as calcium silicate hydrate (C-S-H) and portlandite (Ca(OH)2). A relatively high concentration of magnesium (Mg) was observed in the spectrum. Agglomerated carbon (C) particles associated with aluminium (Al) and silica (Si) were detected in cement pastes with 5% sludge, showing the presence of organic sludge in the mixture. Another visible agglomeration in the spectrum was the presence of iron (Fe), probably from the sludge waste.



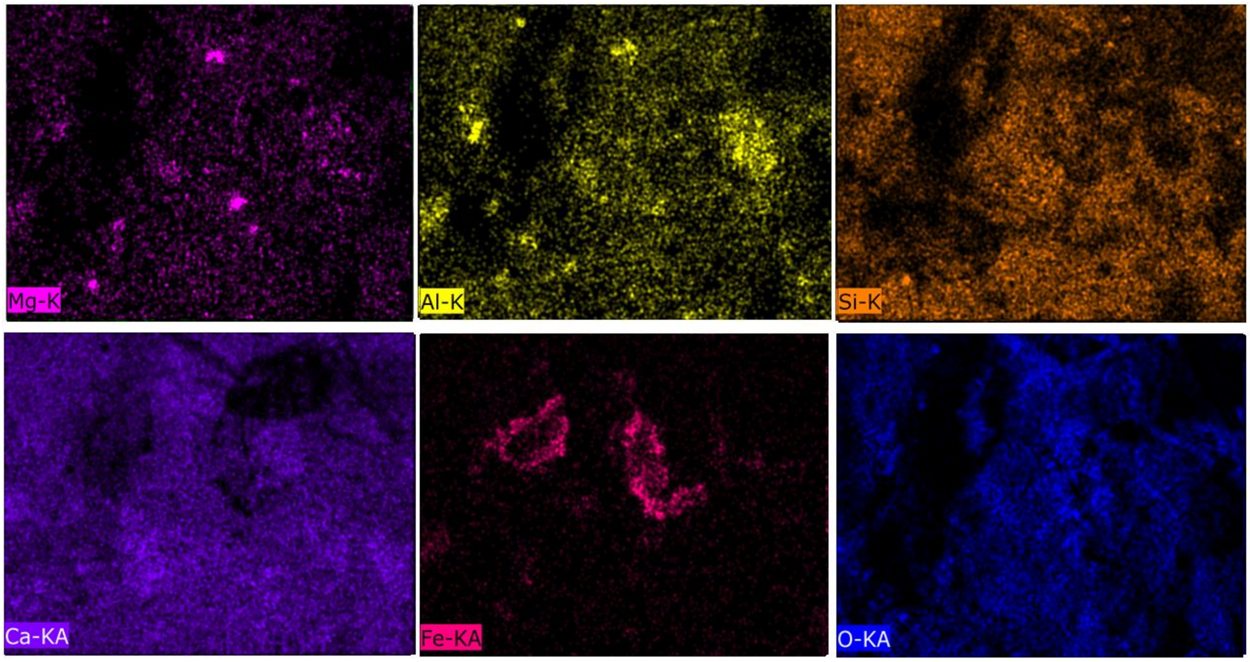


Figure 27. SEM-EDS image of the 5% of sludge and the element distribution mapping

4.2 Thermally modified sludge (WTS-Biochar)

4.2.1 Characterization of WTS-Biochar

The X-ray analysis of WTS-Biochar pyrolyzed at 700°C temperature (**Fig. 28**) shows a material with more crystalline peaks than the previous natural sludge. Most of the peaks detected were formed by the dehydroxylation and conversion of iron oxides (goethite, ferrihydrite) in hematite and magnetite (Teixeira et al., 2011; Kizinievič et al., 2013; Ozden and Dunlop, 2000). The XRD pattern shows the presence of wurtzite (ZnO), which was the convention of natural sphalerite presented on the raw WTS (Hamza et al., 2017). Furthermore, the presence of iwakiite ($MnFe_2O_4$) type is evident in the XRD pattern (**Fig. 27**), which is probably due to transformation reaction between manganese and iron oxides and described by Rzepa et al. (2016). Boehmite has been detected due to partial dehydration of amorphous aluminium oxides (Tantawy et al., 2015). The single peak of kaolinite is indicative of the transformation (dehydroxylation) of the crystalline phase into metakaolin (amorphous)(Kakali et al., 2001; De Godoy et al., 2019).

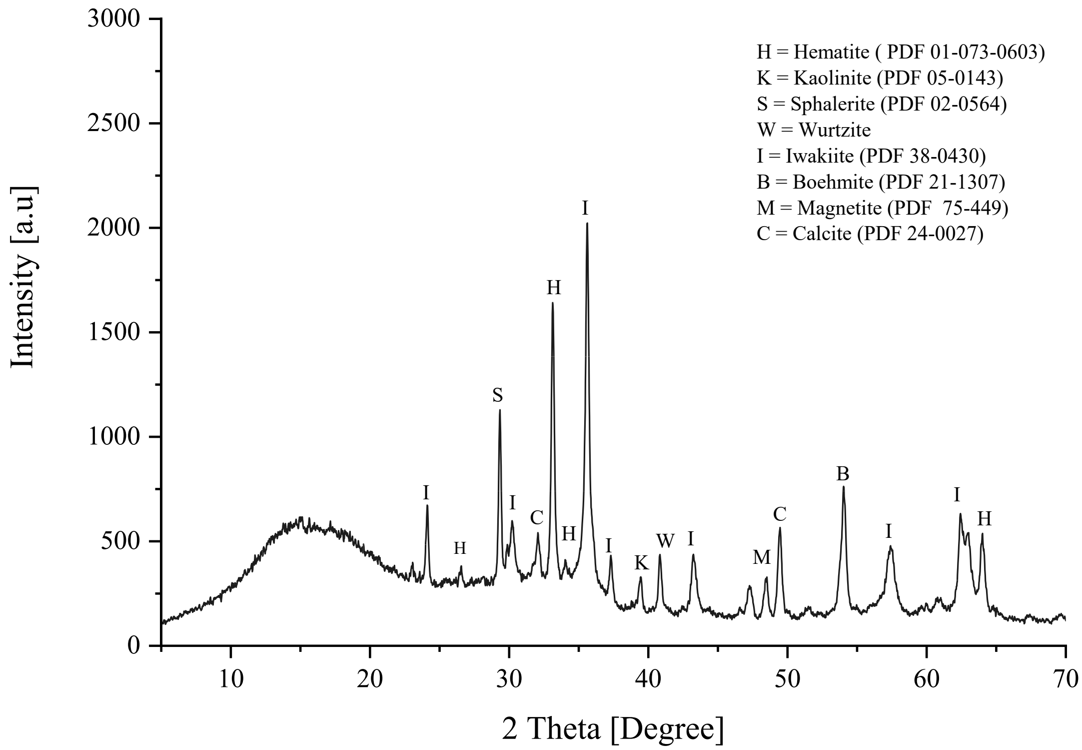
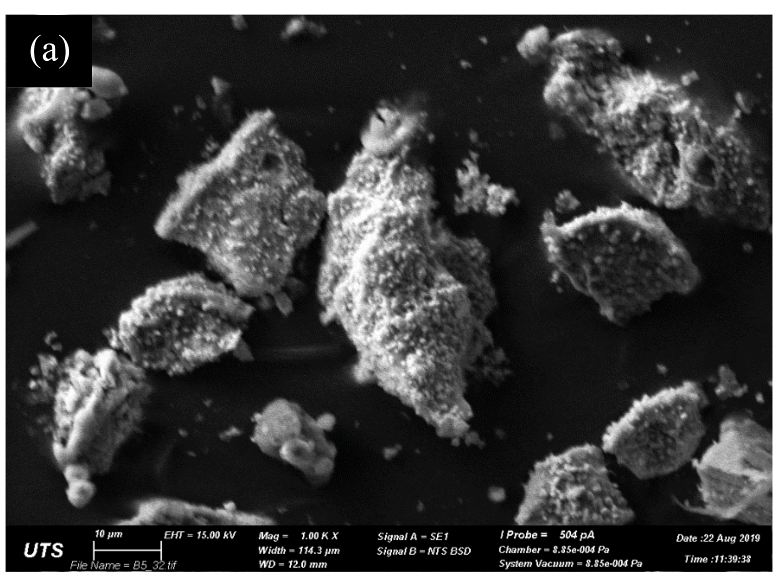


Figure 28. The mineralogical composition of WTS-biochar obtained by XRD.

Figure 29 shows the morphology of WTS-biochar. As we can see, after the thermal pyrolysis process, the sludge grains underwent a significant transformation in their structure. In general, we can observe non-homogeneous particles with development of rough texture and small clusters on the surface (San Nicolas et al., 2013; De Godoy et al., 2019).



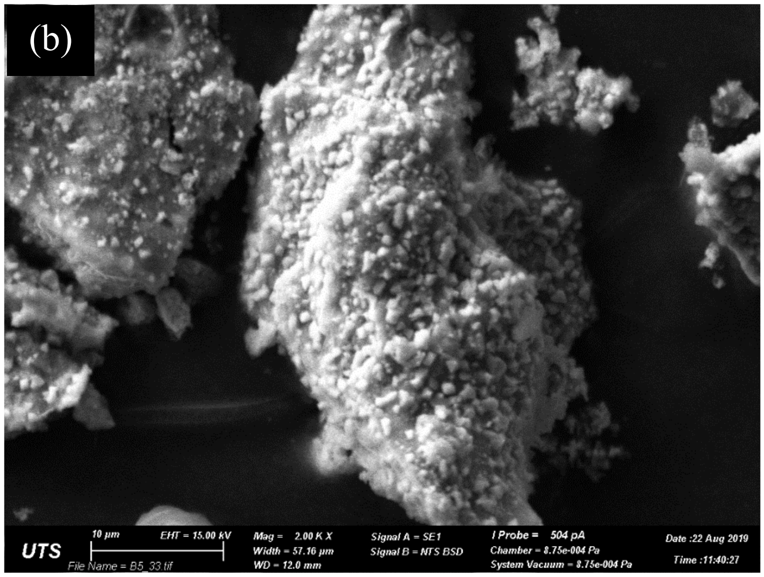


Figure 29. SEM of (a) WTS-biochar (1000 x), (b) WTS-biochar (2000 x)

4.2.2 Heat evolution of cement paste

Figure 30 shows the curve pattern changing by the addition of WTS-biochar. The samples with 2% and 5% of WTS-biochar releases more heat than the reference and also 10% of WTS-biochar. The initial peak (first hour) is associated with the hydration of C3A, the dissolution of free lime and the wetting of Portland cement, and all mixes had similar results. However, the mix with 10% WTS-Biochar showed a slight heat bigger than the reference. The dormant stage (phase 2), for the reference samples (cement only), occurred between the first 2-3 hours of reaction, and as the WTS-biochar was added this dormant period increased, reaching 5 hours concerning the samples with 10% sludge. Similar to the reference, the curve with 1% WTS-biochar showed two peaks, with the same intensity. These two peaks correspond to rapid hydration of C3S and C3A respectively, followed by a deceleration period of heating. The mixes with 2% and 5% of WTS-biochar also showed two peaks but both with higher intensity compared to the reference and 1% Biochar batches. This phenomenon is possibly associated with the filler surface effect, providing additional nucleation sites for calcium silicate hydrate (C-S-H) (Scrivener et al., 2015). The addition of 10% WTS-biochar shows almost the same hydration heat compared to the reference, but with around 2 hours of delay in the reaction. It is important to note that the thermal process applied to the original material (natural sludge) has improved hydration heat properties of the cement composites compared to the natural WTS. For example, even for the addition of 10% biochar had a similar heat peak compared to the reference, which for the same proportion of natural sludge did not happen in the first 48 hours. In addition, another vital property was the decreasing in the maximum peak delay (formation of inner C-S-H) that was previously 38 hours to 10% natural sludge addition and became 12.5 hours after the thermal treatment. In other words, the WTS-biochar had around 2 hours delay only for the maximum peak compared to the reference material.

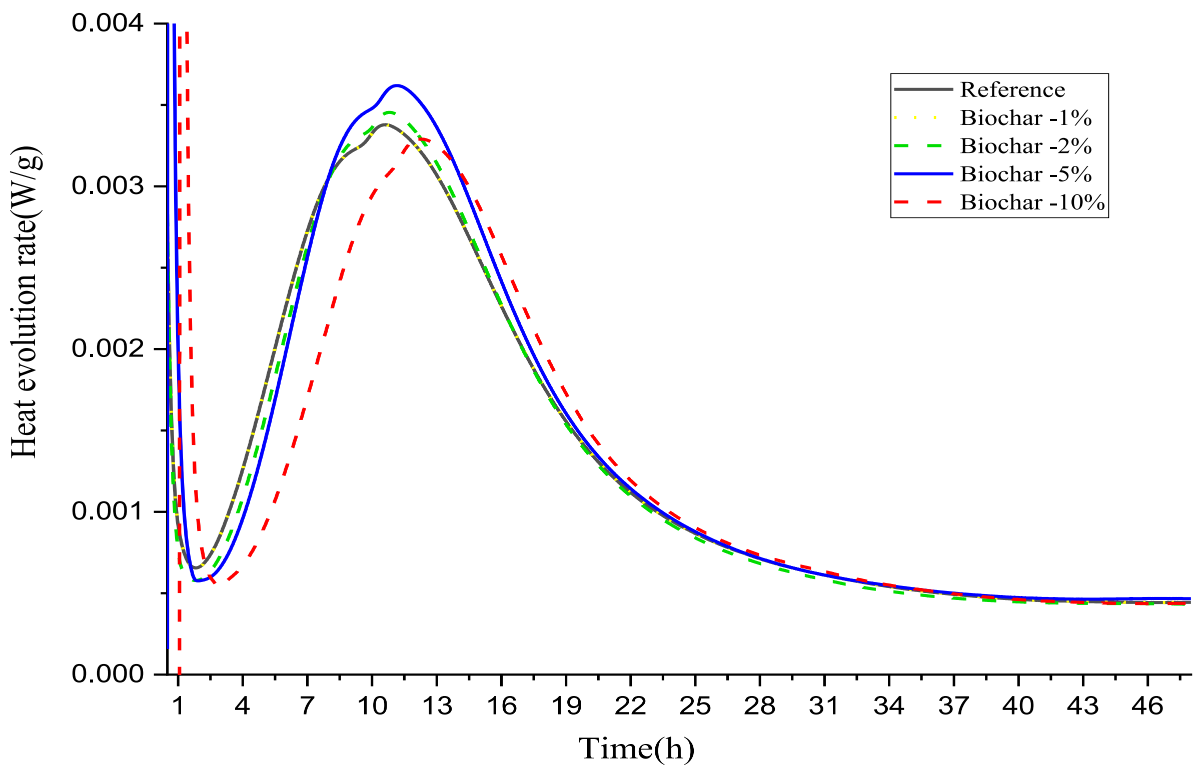


Figure 30. Hydration heat evolution flow with different additions of WTS-Biochar.

Figure 31 shows the cumulative heat of evolution of the reference and composite pastes the first 48 hours of testing. The cumulative heat of evolution formed by the blended pastes with

1%, 2% and 5% of WTS-biochar is slightly higher than the reference. Increasing the WTS-biochar content had a different behaviour compared to the natural sludge; it led to an increase in the amount of heat evolved in the system. The incorporation of 10% of WTS-biochar shows a moderate decrease in the cumulative heat of hydration compared to the reference.

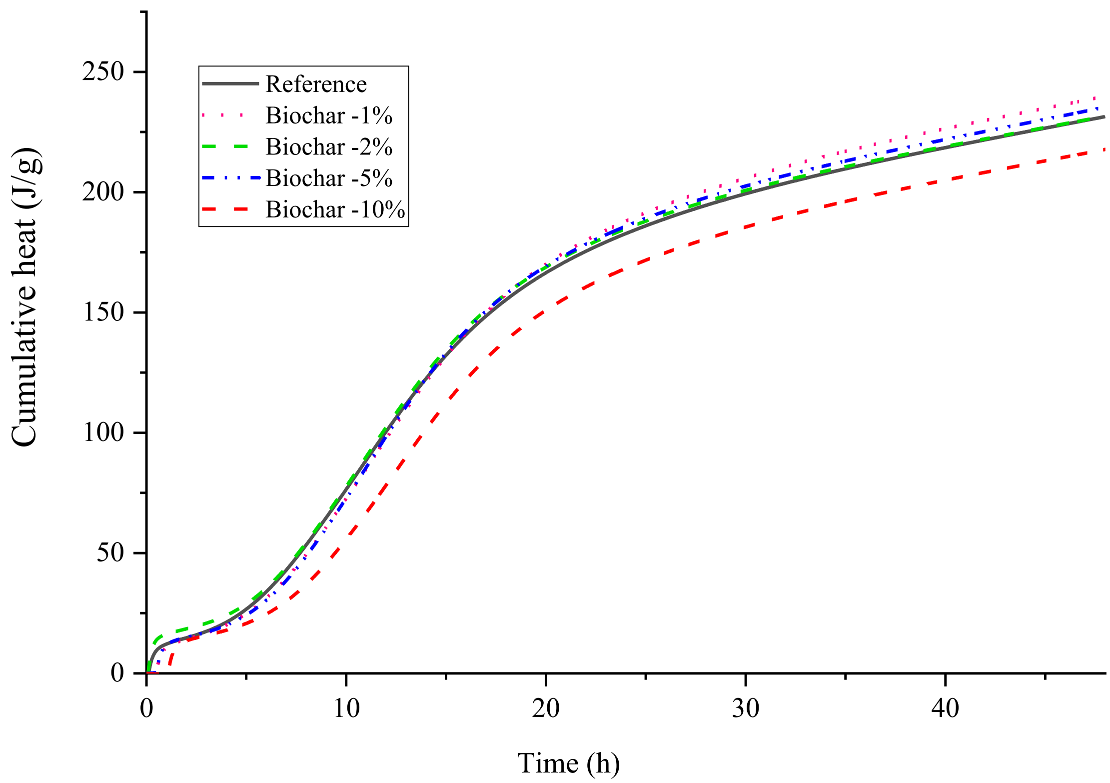


Figure 31. Cumulative heat evolution with different additions of WTS-Biochar

4.2.3 Compressive strength of WTS-Biochar composite

Figure 32 shows the increase of the compressive strength of cement pastes with biochar over time. At seven days of age, mixtures with biochar showed a little lower compressive strength than the reference material, with 18.3% less compressive strengths when 10% biochar was added. In general, there was a significant increase in the compressive strength of the composite over 28 days of age. Mixtures with 1%, 2% and 5% WTS-biochar showed a slightly higher compressive strength at 28 days compared to the reference material. Even the addition of 10% obtained a value close to that of the reference material, with only 5.5% less strength than the material with 100% cement.

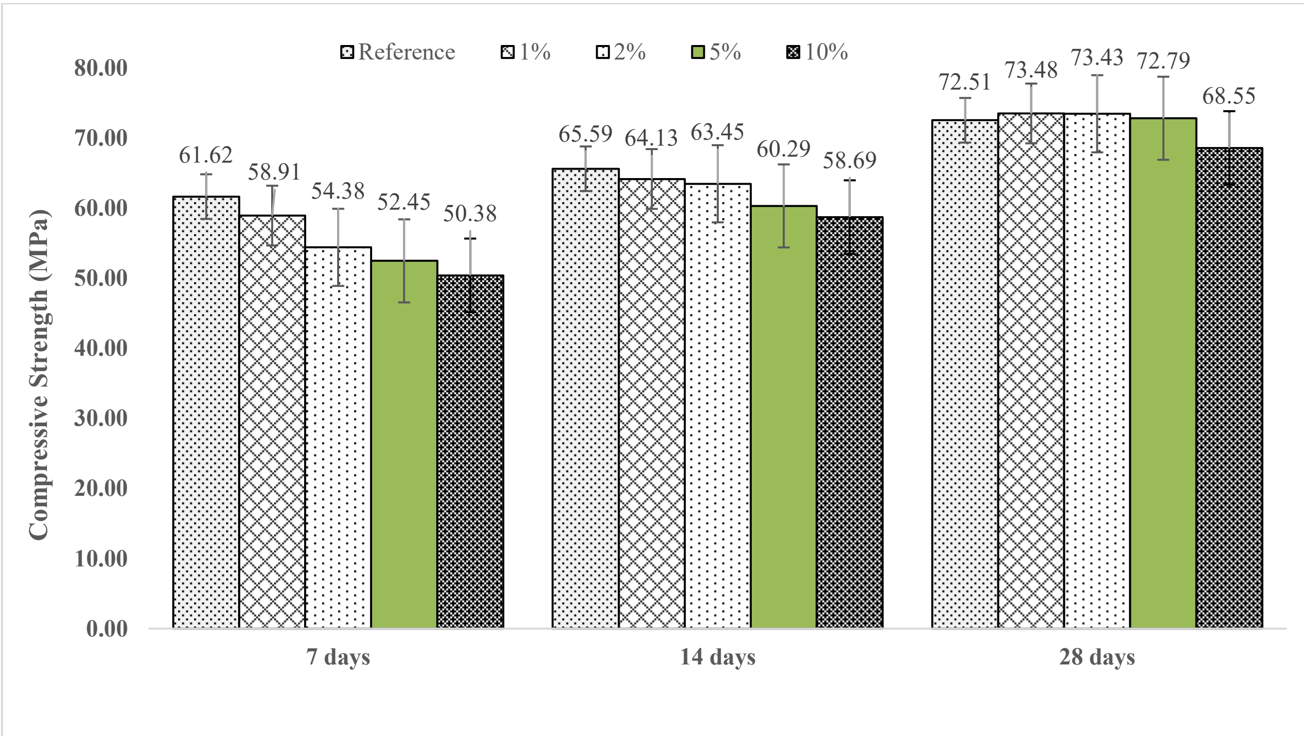


Figure 32. Compressive strength of cement paste with different addition WTS-biochar.

Regarding the results at the age of 28 days, **Figure 33** shows the comparison between the compressive strength of composites of natural sludge and WTS-biochar. For the additions of 5% and 10% WTS-biochar, there was a significant gain in the compressive strength of 37% and 46% respectively, compared to the composite with natural sludge. This improvement in the behaviour of the material was mainly due to the removal of organic matter through the thermal treatment and also possibly due to the pozzolanic activity of the biochar, even in small proportion for the age of 28 days (Kaish et al., 2018; De Godoy et al., 2019).

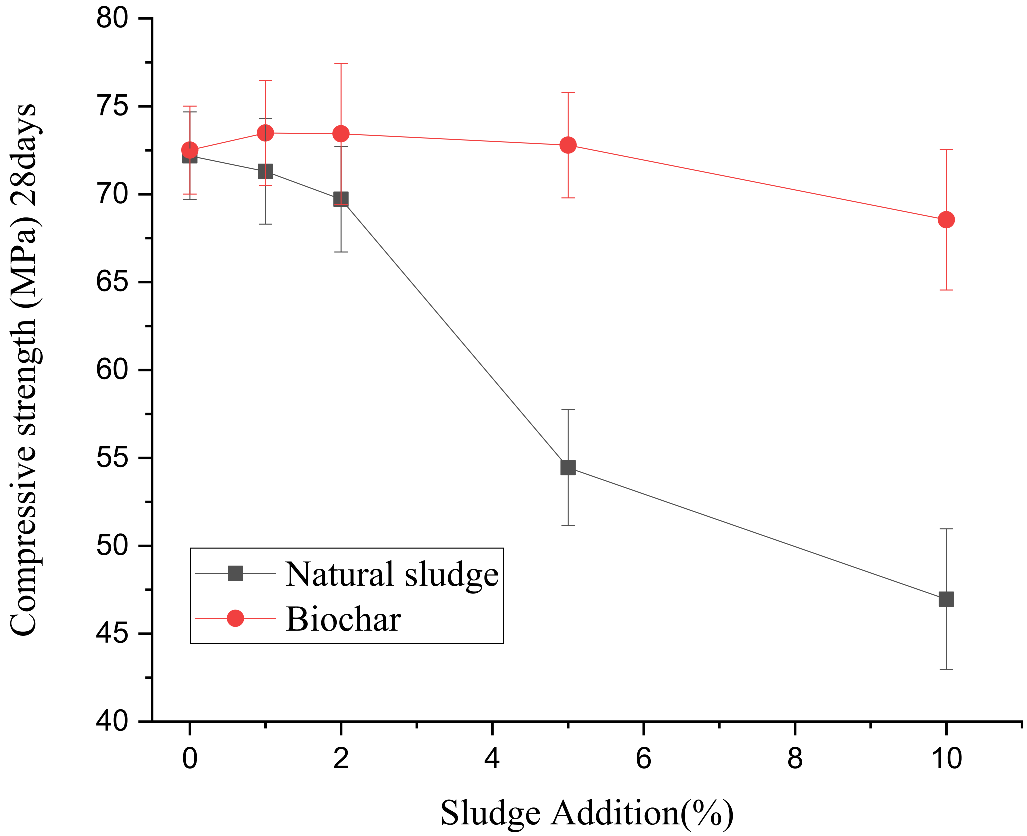


Figure 33. Comparison between the compressive strength of cement paste at 28 days of natural sludge and WTS-biochar percentages.

4.2.4 Mineralogy of hydrated products of WTS-biochar composite.

The XRD analysis of WTS-biochar composite cement paste mix at 28 days is shown in **Figure 34**. Very similar with mixes with natural sludge, the incorporation of the sludge did not create significant new crystalline phases to the composite. All mixtures have the main crystalline phases; calcium silicate hydrate (CSH), ettringite(Aft) and portlandite (CH). A single peak of calcite was detected in all mix patterns. It is important to note that there was a slight decrease in peaks and intensity of calcite on mixtures with biochar compared to blends with natural sludge (**Figure 23**).

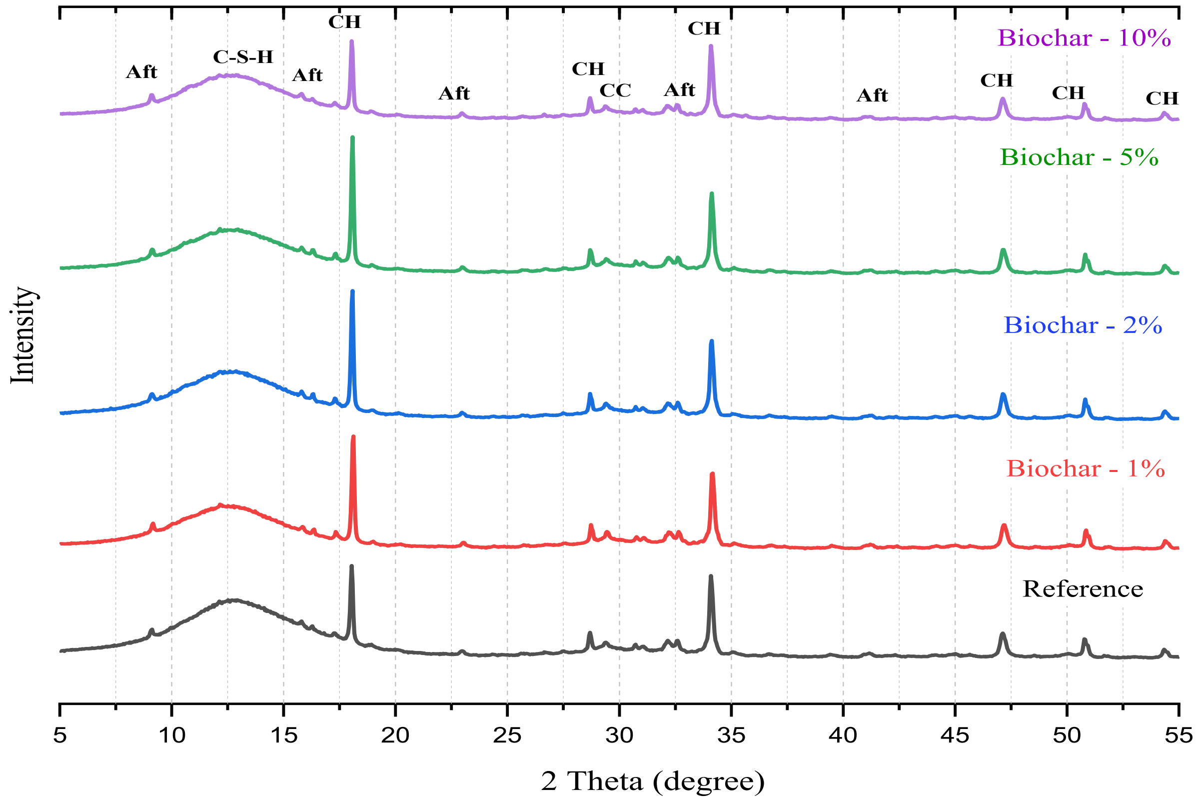


Figure 34. Ray Diffraction of WTS-Biochar hydrated mixes. Aft =Etringita, C-S-H =Calcium silicate hydrate, CH= Portlandite, CC= Calcite.

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4.2.5 Simultaneous thermogravimetry and differential scanning calorimetry analyses

Figure 35 shows a comparison of the intensities of portlandite, calcium silicate hydrate (or C-S-H) and calcite between the reference sample, 5% and 10% biochar. Analysing the first endothermic peak corresponding C-S-H, we can observe that the samples with 5% biochar remained close to the reference material and the samples with 10% biochar had a slightly lower peak compare to the reference. The second endothermic peak, related to the calcium hydroxide or portlandite (CH), we can see that reference material has a slightly higher peak than mixes with 5 and 10% biochar. However, when comparing the difference between the intensity of composites with biochar and those with natural sludge (**Figure 25**), it can be seen that the concentration of C-S-H and portlandite on the biochar composites is very close to the reference material, which does not happen with the samples with natural sludge. This is in agreement with the results of mechanical performance, wherein the mixes with biochar showed compressive strength near to the reference material at 28 days. Unlike the lower intensity of C-S-H and portlandite in the natural sludge composites (F**igure 25**) due to the organic matter concentration, the possible reason for the lower portlandite peak and compatible compressive strength with biochar is the pozzolanic reaction of the biochar. The consumption of portlandite for the production of extra calcium silicate hydrate (C-S-H) and calcium aluminium silicate hydrate (C-A-S-H) is very common in the presence of pozzolanic materials with a reasonable concentration of metakaolinite (Frias et al., 2013; Mohammed, 2017).

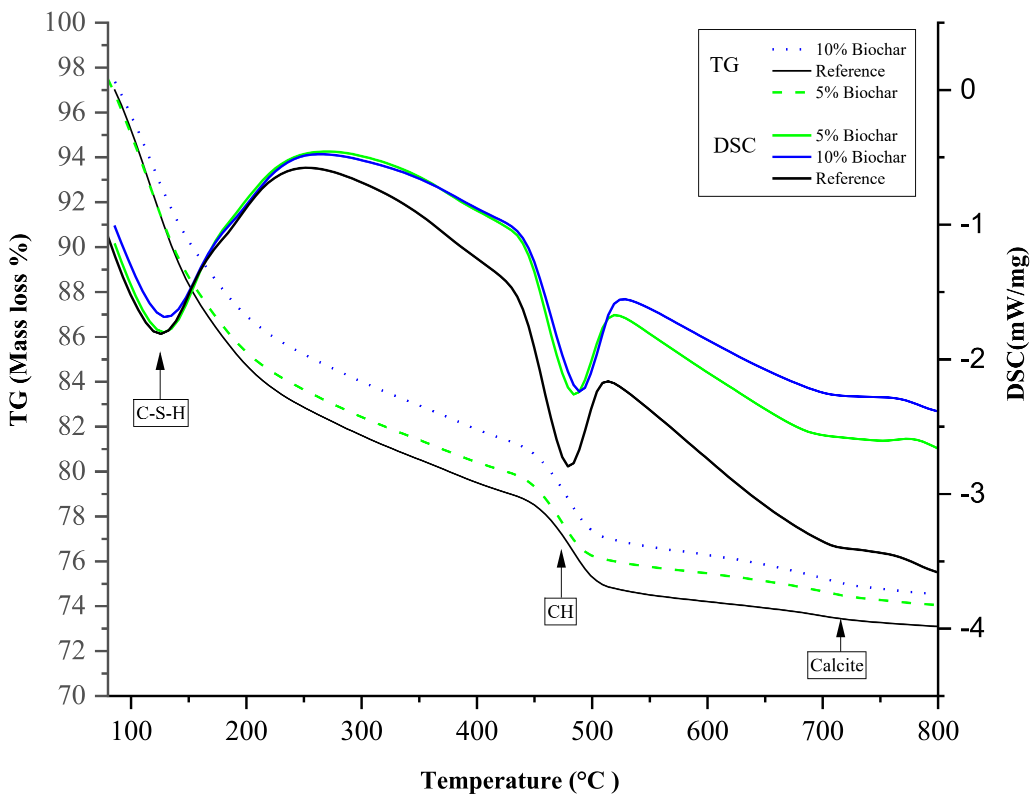
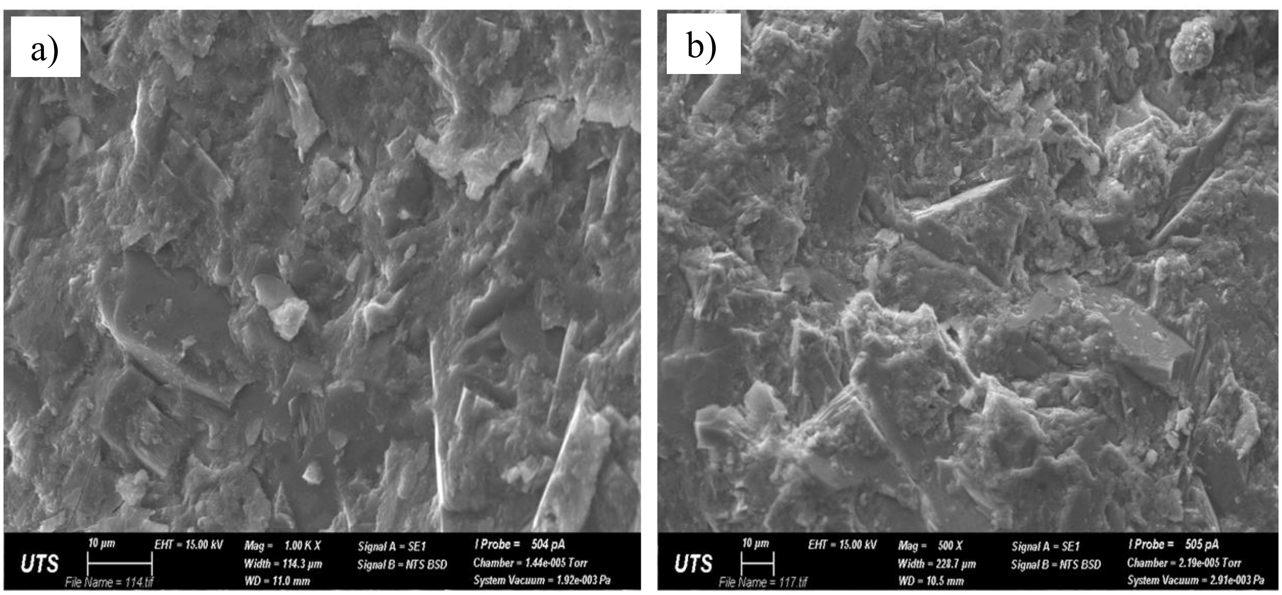


Figure 35. TG-DSC pattern of reference, 5% and 10% of biochar.

4.2.6Microstructure

The SEM image (**Fig. 36**) shows the microstructure of the hydrated composite with additions of 1%, 2%, 5% and 10% biochar. The mix containing 1% and 2% of biochar **(Fig. 36a-b)**, we can clearly see a well-developed structure with a network of defined hydrated compounds very similar to the reference material (**Fig. 26a)**. The samples with 5% biochar also showed a good and dense microstructure very similar to the reference material, with visibly hydrated compounds such as portlandite spread throughout the structure (**Fig. 36c).** For the greatest amount of biochar addition (10%), it was possible to see biochar grains added to the cement paste structure (**Fig. 36d**). It is important to note that the structure of the composite with 10% biochar proved to be well developed when compared to the low bond development structure of 10% sludge (**Fig. 26d**).



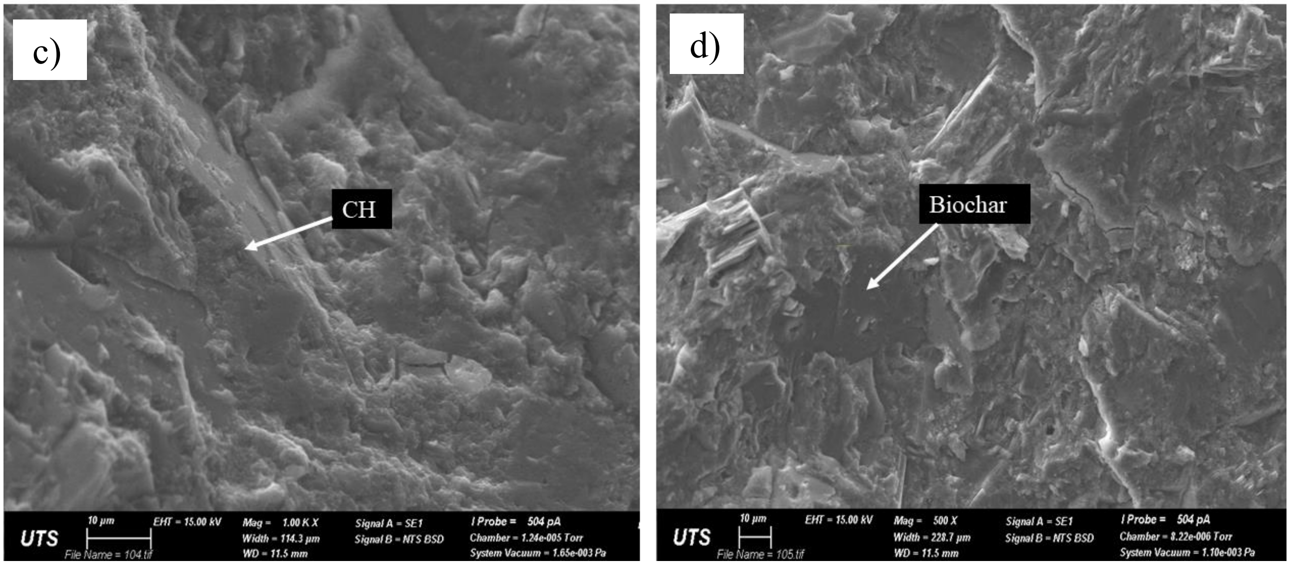


Figure 36. SEM of hydrated reference cement paste with (a) 1% biochar, (b) 2% biochar, (c) 5% biochar, and (d) 10% biochar.

In order to visualize the element distribution surface of the hardened paste with biochar, we carried out elemental mapping using SEM-EDS spectroscopy. **Figure 37** shows the map distribution of the elements for the composite with 5% biochar at 28 days. We can clearly observe the dense and predominant presence of Calcium (Ca), oxygen (O) and Silica (Si), evidencing the main cement hydrated compounds portlandite ($Ca(OH)_2$) and C-S-H. Another clear observation is the association of aluminium with other elements such as silica, indicating the presence of aluminosilicate particles such as metakaolin. The presence of this pozzolanic material in combination with Calcium possibly led to the formation of other hydrated products such as C-A-S-H (common in concretes with the addition of metakaolin) and visible in the spectrum (Avet et al., 2019)

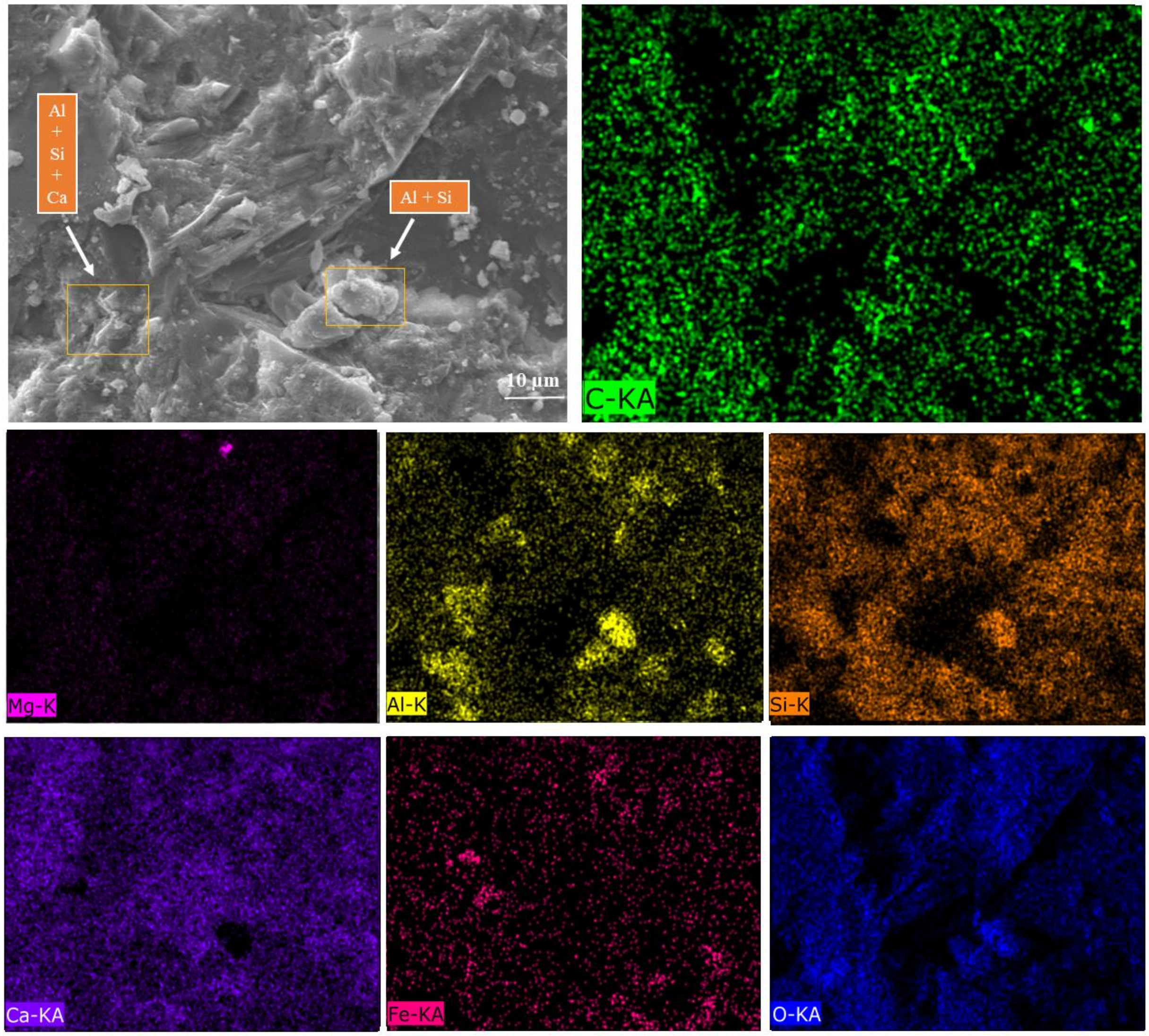


Figure 37. SEM-EDS image of the 5% of biochar and the element distribution mapping.

Chapter 5

5.1 Conclusions

Based on the research data with WTS and modified sludge (WTS-biochar), the results and effects of the application are in agreement with the literature. A summary of the key results is presented:

- WTS showed a heterogeneous morphology, with various sizes of angular particles and a semi-crystalline/amorphous structure.
- The heat evolution tests for the first 48 hours showed that the hydration process of cement paste was influenced by natural WTS addition. The dormant stage (phase 2) of hydration increased from 3 hours for the reference sample to 8 hours with 5% sludge addition, which was further increased to 22 hours for 10% sludge addition.
- Similar to the reference sample, the heat curve with 1% and 2% natural sludge addition showed one maximum peak, but at a lower intensity and with a delay in reaction time. The specimens with 5% of sludge showed a single peak with nearly 30% less heat flow than the reference sample. Moreover, this maximum peak happened almost 20 hours after the reaction, different from the reference occurring at 9-10 hours. Mixtures with 10% sludge showed a maximum peak after 38 hours of reaction and with 60% less heating flow.
- At 7 days of curing, specimens with 1% and 2% natural sludge showed comparable compressive strengths to the reference material, although samples with 5% and 10% sludge addition presented 30% and 55% decrease in the compressive strength.
- XRD and TG-DSC analyses of natural sludge identified increasing peaks of calcite with increase in WTS content, due to the presence of more residual calcite probably from the dewatering process of sludge.
- XRD and SEM-EDS analyses of biochar the analysis revealed a material with some well-

defined crystalline phases and strong indications of pozzolanic material such as methakaline.

- The thermal process applied to the original material (natural sludge) has improved hydration heat properties of the cement composites compared to the natural WTS. The samples with 2 and 5% of biochar hrelease more heat than the reference.
- The addition of 1%, 2% and 5% biochar on the composite showed a slightly higher compressive strength at 28 days compared to the reference material.
- The Compressive strength results with TG-DSC and SEM-EDS analyses indicate that the small minor presence of portlandite in the 5% and 10% biochar specimens, was probably due to the consumption of it for the reaction of C-S-H and C-A-S-H.

5.2. Recommendations

Taking into account the pioneering research and characterisation of this research project, we can affirm that the findings of this study will generate new insights into the issue and further expand our understanding of the compatibility of WTS/biochar with Portland cement. However, due to the complexity of the materials involved, further studies are required to make sure that the material can be promoted on a large scale. Below are some recommendations for future research:

- Studies with chemical or mineral additions to reduce the adverse effects of the setting time when the sludge is incorporated into the material
- Further studies are needed to explore experimental conditions on a large scale (concrete) as a combination with different types of aggregates, water/cement ratio, superplasticisers and other additions.
- Long-term and durability testings should be addressed in future studies.
- Environmental impact and life cycle assessment (LCA) studies for the incorporation of sludge and biochar in the concrete industry.

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