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ILHA SOLTEIRA

DANILO BORDAN ISTUQUE

Study on the incorporation of sewage sludge ash in alkali-activated materials

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DANILO BORDAN ISTUQUE

Study on the incorporation of sewage sludge ash in alkali-activated materials

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Area of concentration: Science and Materials Engineering

Supervisor: Prof. Dr. Mauro Mitsuuchi Tashima

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TÍTULO DA TESE: *Study on the incorporation of sewage sludge ash in alkali-activated materials*

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“Persistence is the path to success.”

Charles Chaplin

RESUMO

O manejo sustentável e inteligente de resíduos urbanos é uma questão primordial para garantir que futuras gerações tenham as condições de viver em equilíbrio com a natureza e o meio urbano. Da mesma maneira, garantir que no futuro existam materiais alternativos e sustentáveis para a construção civil também é necessário para tal equilíbrio. Neste sentido, os materiais ativados alcalinamente são interessantes por abranger sistemas que incorporam resíduos de origem urbana, industrial e agro-industrial como matéria-prima. Por definição, os materiais ativados alcalinamente são produtos resultantes de reações químicas que se iniciam em decorrência de um ataque alcalino à precursores ricos em cálcio e/ou silica e alumina. Com base em estudos recentes que apontam estes sistemas como uma alternativa para a imobilização de cinza de lodo de esgoto (SSA), este trabalho avaliou os efeitos da incorporação de SSA como precursor em substituição ao metacaulim (MK) e à escória de alto-forno (BFS) para a produção de argamassas ativadas alcalinamente, assim como a otimização desses sistemas em termos de resistência à compressão. Inicialmente, a SSA, obtida por meio de uma auto-combustão do lodo de esgoto, foi caracterizada físico-químicamente, assim como sua reatividade química foi avaliada. O desempenho mecânico de argamassas à base de MK e SSA foi avaliado por meio de ensaios de resistência à compressão, e pastas foram quimicamente avaliadas através de análises de difração de raio-X (XRD), espectroscopia de infra-vermelho por transformada de Fourier (FTIR), termogravimetria (TG/DTG) e microscopía eletrônica de varredura (SEM). Por fim, uma otimização do ativador alcalino foi realizada por meio da pré-ativação de cinza de casca de arroz (RHA) para produção de sistemas binários de SSA e BFS, sendo estes sistemas mecanicamente avaliados por resistência à compressão. Para a caracterização destes sistemas binários (pastas), análises de XRD, TG/DTG, SEM, e porosimetria por intrusão de mercúrio foram realizadas. De acordo com os resultados, apesar de apresentar um moderado comportamento pozolânico em misturas com cimento Portland, a SSA desmonstrou um baixa reatividade em materiais ativados alcalinamente. Em geral, a substituição de MK ou BFS por SSA diminui a resistência à compressão das argamassas. Porém, em

determinadas condições, como para argamassas à base de MK e SSA em cura térmica (banho térmico, 65°C), a SSA ofereceu um retardo da perda de resistência à compressão, que ocorre devido a cristalização da matriz geopolimérica. A performance mecânica dos sistemas binários compostos por BFS e SSA foi melhorada em função da pré-ativação da RHA, empregada na forma de ativador alcalino, o que permitiu produzir argamassas com até 40% de SSA em sua constituição, alcançando uma resistência à compressão de até 30 MPa.

ABSTRACT

The sustainable and smart management of urban wastes is a key issue to ensure that future generations can live in balance with nature and the urban environment. Similarly, sustainable materials for building construction are also necessary to guarantee such a balance. Therefore, alkali-activated materials are an interesting option by incorporate by-products and urban wastes from the agro-industry as raw material. The alkali-activated materials (AAMs) result from chemical reactions that start due to an alkaline attack on precursor materials that contain calcium and/or silica and alumina in their composition. Recently, these systems have been recognized as an alternative for the immobilization of sewage sludge ash (SSA). Accordingly, in this work, the effect of SSA incorporation in AAMs by means of replacing metakaolin (MK) and blast furnace slag (BFS) was evaluated, as well as the optimization of these systems in function of the compressive strength performance. Firstly, SSA, generated by means of uncontrolled combustion of sewage sludge, was physiochemically characterised and its chemical reactivity was evaluated. The mechanical performance of mortars based on MK and SSA were evaluated by means of compressive strength tests, as well as pastes were chemically evaluated by means of X-ray diffraction (XRD), Fourier transform infra-red fluorescence (FTIR), thermogravimetry (TG/DTG), and scanning electron microscopy (SEM). The optimization of the alkaline activator, by the pre-activation of rice husk ash (RHA), to produce binary alkali-activated mortars composed of SSA and BFS as the binder, was also carried out. These binary mortars were mechanically evaluated by compressive strength tests, as well as pastes were characterised by means of XRD, TG/DTG, SEM, and mercury intrusion porosimetry (MIP) analyses. According to the results, despite the SSA presenting a moderate reactive behaviour, characterised as pozzolanic, in AAMs showed a low reactivity. Generally, as the replacement of MK or BFS with SSA increases, the compression strength of mortars decreases. However, in geopolymeric mortars based on MK and SSA thermally cured (thermal bath, 65 ° C), SSA offers a delay in the compressive strength loss, which commonly occurs due to crystallization of the geopolymeric matrix. The mechanical performance of the binary

systems composed of BFS and SSA was improved using RHA in the activator, which guarantees to produce mortars with up to 40 wt.% SSA in their composition, reaching a compressive strength of up to 30 MPa.

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CHAPTER 1

1. INTRODUCTION

1.1. GENERAL ISSUES

New waste management policies are genuinely supported by the circular economy, which promotes a sustainable development worldwide. Related to such a subject, the current and future sewage sludge management, facing the growing sewage sludge generation, are seriously debated in the scientific journals (KACPRZAK et al., 2017). Due to the accelerated urbanization and population growth, which is expected the worldwide population exceeding nine billion people by 2050 (CORCORAN et al., 2010), a great sanitary infrastructure improvement is urgent, mainly in low and middle-income countries. Hence, jointly with the sanitary infrastructure enhancement, a growing sewage sludge generation is also expected, as it is an inevitable by-product from the conventional wastewater treatment plants (WTPs).

In countries where the processed sewage sludge is suitably managed, its three main disposal routes are landfill, agricultural use, and minimization through thermal processing (CHRISTODOULOU; STAMATELATOU, 2016; SALIHOGLU; MARDANI-AGHABAGLOU, 2020). A decade early, 53% of the sewage sludge generated by EU-15 was disposed for agricultural use and 21% was incinerated, while for EU-12 (new Member States that joined EU after 2004), the landfilling disposal was the most common sewage sludge management choice yet (KELESSIDIS; STASINAKIS, 2012). Since then, due to more restrictive laws about soil and environmental protections, sewage sludge incineration is getting more notable in some countries, like in Germany that 70% of the sewage sludge generated is incinerated (SCHNELL; HORST; QUICKER, 2020).

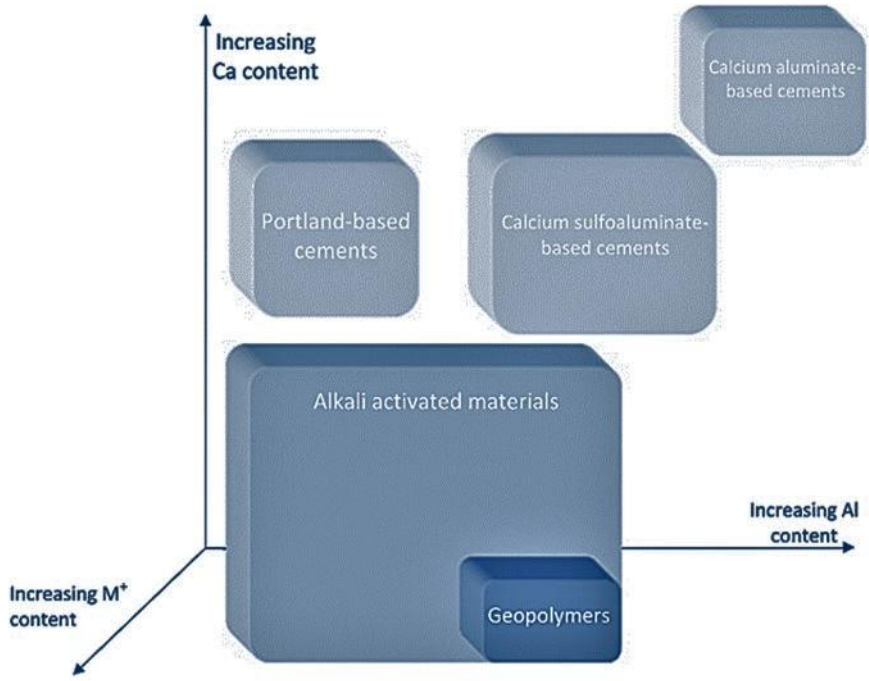
What concerning about the sewage sludge thermal treatment (incineration and pyrolysis), although offers a significant waste volume reduction, it is not the final disposal due to the sewage sludge ash (SSA). Until 2013, the global production of SSA was

estimated at 1.7 million tons yearly (DONATELLO; CHEESEMAN, 2013), and its generation is expected to increase in the future as more sewage sludge is generated as well as incinerated (KELESSIDIS; STASINAKIS, 2012).

Such an issue warns of the need to increase the SSA valorisation, leading researchers to search for different alternatives for its application. One of the alternatives evaluated is the SSA application in the production of construction building materials. Such application is achievable due to its chemical composition, that depending on SiO_2, Al_2O_3 and Fe_2O_3 contents could display a moderated pozzolanic behaviour, though also can display a role as fine aggregate or filling material (DE AZEVEDO BASTO; SAVASTANO JUNIOR; DE MELO NETO, 2019; CHANG et al., 2020). A great number of studies can be found in the literature where is evaluated the SSA use to produce materials as blended Portland cement, pastes, mortars, bricks, tiles, ceramics, or glass (MONZÓ et al., 2003; LIN; LUO; ZHANG, 2007; DYER; HALLIDAY; DHIR, 2011; PEREZ CARRION et al., 2013; BAEZA-BROTONS et al., 2014; SMOL et al., 2015; CHEN; POON, 2017; TARRAGO et al., 2017; CHANG et al., 2020). In addition, in the last years, the literature has also pointed out SSA as a raw material (PAYÁ et al., 2019) to produce alkali-activated materials (AAMs), a new kind of binders (PACHECO-TORGAL, 2015), that depending on the Ca-content in their chemical composition precursors should be called “geopolymers” – a subcategory for low Ca-content AMMs as seen in Figure 1.1 (PACHECO-TORGAL; CASTRO-GOMES; JALALI, 2008; PROVIS; VAN DEVENTER, 2014).

A series of advantages are attributed to the production of AAMs: the lower carbon footprint; similar or superior mechanical properties compared to Portland Cement-based binders; and a large waste incorporation potential (PACHECO-TORGAL, 2015). In addition, depending on the type, concentration and dose of alkaline activators used to prepare the AAMs, the reduction in the carbon footprint can fall within the range of 30.0–76.0% in relation to Portland cement materials (PACHECO-TORGAL et al., 2017; YANG; SONG; SONG, 2017), or even around 90% when the whole system is entirely composed of wastes (FONT et al., 2020).

Figure 1.1 - Classification of AAMs, comparing to other cementitious binder chemistry, in terms of calcium (Ca), aluminium (Al) and alkali (M^+) content in their composition.



Source: Provis, J. L. Introduction and Scope, In. Provis, J. L.; Van Deventer, J. S. J. Alkali activated materials. Dordrecht: Springer Netherlands, 2014. v. 13.

1.2. GAP IN THE KNOWLEDGE

The design of AMMs is an interesting alternative to mitigate the increasing SSA generation and its environmental impacts. The studies on this subject are recent, being firstly reported in 2016 (ISTUQUE et al., 2016). Most of them are focused on high-calcium alkali-activated systems like BFS-based alkali-activated materials (CHAKRABORTY et al., 2017; TASHIMA et al., 2017; CHEN et al., 2018; SITARZ et al., 2020), and a few of them are related to low-calcium alkali-activated materials (geopolymers), like fly ash-based geopolymers (PAULNATH et al., 2019; SITARZ et al., 2020), rice husk ash-based geopolymers (ZAIDAHTULAKMAL; KARTINI; HAMIDAH, 2019) and metakaolin-based geopolymer (ISTUQUE et al., 2016; SUN et al., 2018).

As mentioned beforehand, there are only two studies focused on the incorporation of SSA into MK-based geopolymer. On one hand, SUN *et al* (*2*018) formulated a MK-

based geopolymer with SSA coming from controlled calcination (800°C, 1 h), which could be implied that for such findings, it is necessary a controlled SSA calcination method, demanding higher energy for its production. On the other hand, Istuque *et al.* (2016) report a short study on geopolymers with MK and SSA, in which such SSA was coming from an uncontrolled-combustion method, which is interesting due to a low energy demand during its incineration. Nevertheless, an optimisation regarding the activator parameters as NaOH concentration and SiO_2/Na_2O molar ratio in the activator of this SSA-MK geopolymer system proposed by Istuque *et al.* (2016), to better mechanical strength, is needed, as well as should be carried out mechanical evaluations for curing time superior to 7 days, which is important for understanding the long-term mechanical performance of this material.

What concerning the SSA-BFS alkali-activated materials, although can be found a higher number of studies in the literature, none of these works was focused on replacing the commercial sodium silicate with less carbon footprint silica source as RHA yet, which is an interesting way to increase the sustainability of such systems. Therefore, although the SSA-BFS alkali-activated materials production has been largely evaluated, more sustainability could be achieved to these systems if RHA is used in the activator to replace the commercial sodium silicate.

Therefore, in the work herein, such optimisation of the SSA-MK geopolymer system proposed by Istuque et al. (2016) and the RHA use to obtaining a non-conventional sodium silicate alkaline activator to produce more sustainable SSA-BFS alkali-activated materials are evaluated.

1.3. AIM AND OBJECTIVES

This study aimed evaluate the SSA application as a raw material in AAMs production, focusing in to achieve optimized systems in terms of compressive strength performance, SSA incorporation content and sustainability. Thus, the objectives were:

(I) To characterise SSA resulting from uncontrolled combustion by means of physicochemical analyses, as well as to evaluate its pozzolanic activity.

(II) To optimize the activator dosage in terms of SiO_2/Na_2O molar ratio and NaOH concentration to achieve higher compressive strength performance in SSA/MK – based geopolymeric mortars.

(III) To evaluate the long-term mechanical performance of SSA-MK geopolymeric mortars cured at room temperature.

(IV) To enhance the sustainability of SSA-BFS alkali-activated mortars by replacing commercial sodium silicate with non-conventional sodium silicate suspensions synthesised with RHA and NaOH.

1.4. THESIS STRUCTURE

This thesis presents 9 chapters, including the introduction, in which the motivations and goals were described (Chapter 1). Chapter 2 is a literature survey about sewage sludge and SSA generation issues, as well as the knowledge concerning AAMs. From chapter 3 to chapter 7 are presented published articles that materialise such an investigation. In chapter 3, apart from the uncontrolled-combusted SSA physicochemical characterization, the pozzolanic reactivity of this waste was evaluated. In chapter 4 is described how the compressive strength and microstructure is affected by the partial replacement of MK with SSA to prepare geopolymeric mortars cured at room temperature (25°C) and in thermal bath (65°C) for different SiO_2/Na_2O molar ratios. Chapter 5 highlights the influence of the alkaline concentration of activator on SSA-MK based geopolymeric mortars, as well as the long-term compressive strength performance of geopolymeric mortars containing MK and different contents of SSA. An evaluation of the compressive strength performance and microstructure of binary alkali-activated mortars based on BFS-SSA, in which rice husk ash (RHA) was used as a source of silica replacing commercial sodium silicate is presented in chapter 6. Finally, the general conclusion, scientific and social impact and proposal for futures studies are presented in chapter 7, chapter 8, and chapter 9, respectively.

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CHAPTER 7

7. GENERAL CONCLUSION

The aim of the work carried out herein was to evaluate the SSA application as a raw material in AAMs production, targeting the optimization of these systems in terms of compressive strength performance, SSA incorporation content and sustainability. Thus, the main findings are concluded as follows:

(I) According to the SSA physicochemical characterisation, SSA from the uncontrolled combustion of the sewage sludge generated ash with a low loss on ignition (3.72%), which highlights the efficacy of the applied incineration system in terms of organic matter removal. Such ash showed a chemical composition (main oxides: 32.72 wt.% SiO_2, 20.72 wt.% Al_2O_3, and 11.27 wt.% Fe_2O_3) similar to those reported in the literature. The reactive behaviour was mainly attributed to its Al_2O_3 content (20.72%), which guaranteed moderate pozzolanic activity based on the measure of consumption of $Ca(OH)_2$ during the hydration of Portland cement, forming hydrated compounds (C-S-H, C-A-S-H and C-A-H gel).

(II) In SSA/MK-based geopolymeric mortars, the higher compressive strength performance was reached by using NaOH-Na_2SiO_3 activator dosage with 8 $mol.kg^{-1}$ NaOH and SiO_2/Na_2O molar ratio of 1.6. Under room temperature (25°C) curing, although the incorporation of 10 wt.% SSA by MK replacement caused a delaying effect on the hardening process of geopolymeric mortars in the first curing days, after 14 curing days the mortar with 10 wt.% SSA achieved similar compressive strength (about 50 MPa) to the reference one (100 wt.% MK). Under thermal bath (65°C) curing, MK-based geopolymeric mortars lose compressive strength for a long-curing time due to the formation of Faujasite-type and Na P-type zeolites. However, the incorporation of SSA provided a retarding effect on

such zeolite formation process, indicating higher stability for geopolymeric gel.

(III) For long-term compressive strength evaluation, the SSA/MK-based geopolymeric mortar containing 10 wt.% SSA (activator dosage: 8 mol.kg^{-1} NaOH and SiO_2/Na_2O molar ratio of 1.6), when it is maintained in room temperature (25°C) and controlled moisture (95%), achieved a compressive strength of 60.7±4.3 MPa for 720 curing days at 25°C, which was close to the reference geopolymeric mortar (100 wt.% MK), whose compressive strength was 66.9±2.9 MPa for the same curing conditions. The delaying effect caused by SSA on the mechanical development of MK-based geopolymeric mortars was most apparent to those ones with high SSA content. For the mortar with the highest SSA content (30%), the strength gain over time (from 3 to 720 days) was about 143.6%, achieving 40 MPa, while for the reference one, which achieved the higher compressive strength (67 MPa), was 43.9%. In addition, the incorporation of SSA into the geopolymer matrix morphologically changed the microstructure of the gels. Those geopolymers with SSA presented fewer N-A-S-H type gel with the same morphology as that one observed for the reference sample with MK only. Such behaviour was considered key to explain the differences in compressive strength development.

(IV) Regarding the use of RHA as a silicate source to prepare AMMs based on BFS, the RHA pre-activation in NaOH solutions improved the compressive strength of the BFS–based alkali-activated mortars by 4.5-fold, that achieved 46.9 MPa, being 36.5 MPa higher than the value reached by the mortars with 100 w.t% BFS with no RHA pre-activation (10.4 MPa). Using sodium silicate suspensions, made by means of RHA pre-activation, to prepare the binary SSA-BFS alkali-activated mortars conferred at least a compressive strength of 30 MPa after 28 curing days at 20°C, even replacing a large quantity of BFS by SSA (40 wt.%). Such good mechanical performance and high SSA incorporation content were only granted

because of the strength boost provided by RHA pre-activation, as the increasing SSA content leads to compressive strength decreasing.

CHAPTER 8

8. SCIENTIFIC AND SOCIAL IMPACTS

This study expands the scientific knowledge on SSA incorporation into AAMs based on MK (geopolymer) and BFS, providing an understanding of how SSA affect the mechanical performance of these materials when cured at room temperature or thermal bath environment. The uncontrolled combustion process applied to generate SSA for this work showed a reasonable efficacy in terms of generating ash with low organic matter and chemical composition similar to those SSA from incineration plants or controlled combustion in an oven. Such fact, establish a base for new hypotheses as to how to plan the incineration of sewage sludge in the future and applying the resulting ash in AAMs production. In addition, the RHA pre-activation associated with SSA incorporation into AMMs based on BFS showed to be a good alternative to give more sustainability in these systems, apart from contributes to developing a mortar with high SSA content maintaining compressive strength superior to 30 MPa, which could be suitable for many applications in building construction.

The social impact of this work is related to the promotion of alternative disposal of sewage sludge by means of its incineration and production of AMMs with the resulting ash, avoiding its critical disposal in the environment that could affect the health of the human being. Moreover, the valorisation of SSA towards the production of new materials to building construction could directly dilute the environmental impacts due to the high demand for Portland cement, apart from agreeing with the principles of the circular economy that aims to avoid waste disposal, driving more sustainable practices for the future generations.

CHAPTER 9

9. PROPOSALS FOR FUTURE STUDIES

Based on the findings herein, to broaden the knowledge on the subject, the proposals for future studies on SSA application for geopolymer and AMMs production are:

(I) As SSA commonly presents a poor content of amorphous silica, it seems interesting complement such a component by means co-incineration with silica-rich biomasses as rice husk and sugar cane bagasse and straw, for examples. Such co-incineration could supply more reactive behaviour for the outcoming ashes, then leading to lower compressive strength decrease when replacing MK or BFS.

(II) Evaluate AAMs with SSA into their composition, being the activator 100% composed of wastes to confer even more sustainability to these systems. Some studies have been pointed at the production of sodium or potassium silicates based on a pre-activation of wastes blends that contain silica, potassium, or sodium alkaline salts. Such a kind of activators could offer the possibility of formulating a one-part alkali-activated system containing SSA.

(III) Regarding a possible one-part alkali-activated systems containing SSA, evaluate their durability and toxic elements leachability, and their real application in different ways as for structural repair, masonry, pre-moulded structure elements, etc.

(V) Finally, evaluate the economic viability and Life Cycle Analysis of these alkali-activated systems containing SSA to validate their sustainability.