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FEASIBILITY OF STEEL SLAG AS BINDER AND  
AGGREGATE IN ALKALI-ACTIVATED MATERIALS

AUTOR

VITOR ALENCAR NUNES

DIRECTORES

CARLOS THOMAS GARCÍA

PAULO HENRIQUE RIBEIRO BORGES

UNIVERSIDAD DE CANTABRIA

CENTRO FEDERAL DE EDUCAÇÃO TECNOLÓGICA DE MINAS GERAIS – CEFET-MG

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Coorientador: Carlos Thomas Garcia.

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**VITOR ALENCAR NUNES**

**FEASIBILITY OF STEEL SLAG AS BINDER AND  
AGGREGATE IN ALKALI-ACTIVATED MATERIALS**

Thesis presented in fulfilment of the requirements for the joint degree of  
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 PAULO HENRIQUE RIBEIRO BORGES  
Data: 20/11/2023 18:46:26-0300  
Verifique em <https://validar.iti.gov.br>

**Dr. Paulo Henrique Ribeiro Borges**

**Supervisor**

**Civil Engineering Department, CEFET-MG**

Firmado digitalmente por  
THOMAS GARCIA CARLOS -  
20219736E  
Fecha: 2023.11.15 08:49:16  
'+01'00

Firmado  
digitalmente  


**Dr. Carlos Thomas**

**Co-supervisor**

**Civil Engineering Department, UC**

Documento assinado digitalmente  
 PETER LUDVIG  
Data: 14/11/2023 20:24:19-0300  
Verifique em <https://validar.iti.gov.br>

**Dr. Peter Ludvig**

**Civil Engineering Department, CEFET-MG**

**Dr. João Paulo Castro Gomes**  
Assinado por: **João Paulo de Castro Gomes**  
Num. de Identificação: 07695244  
Data: 2023.11.15 08:49:16  
**Civil Engineering Department, University of Beira Interior**

**Johan Blom**  
**(Signature)**

Digitaal ondertekend  
door Johan Blom  
(Signature)  
Datum: 2023.11.15  
17:29:55 +01'00'

**Dr. Johan Blom**

**Faculty of Applied Engineering, University of Antwerp**



Digitally signed by  
AGHAJANIAN SABBAGH  
ALI - Y7480295L

**Dr. Ali Aghajanian Sabbagh**

**Civil Engineering Department, UC**

**Belo Horizonte, 30<sup>th</sup> October 2023**

## ABSTRACT

Steel slag (SS) is a solid waste generated during the steelmaking process, with annual generation of 270 million tons of SS worldwide. SS can be reused as an alternative raw material in several applications due to its chemical composition, mechanical and physical properties: in agriculture, soil stabilization, road construction and other building materials. However, the recovery rate for SS varies from 20 to 98%, depending on the country, which leads to an excessive stockpiling causing environmental harm and financial liability. So far, considerable quantities of SS are employed in road construction and internal recycling (steel making) but still with many restrictions. The construction sector appears as a potential consumer of large quantities of SS. However, the volumetric instability of SS may be an issue for application in Portland cement (PC) based products. An alternative reuse for the SS would be as raw material in the alkali-activated materials (AAM). AAM are alternative materials that could present better mechanical and durability performances; they also incorporate larger amounts of industrial wastes. This research investigated the feasibility of SS as binder and aggregate in AAM, by determining the optimum activation parameters and the pre-treatment process needed (wet-curing and carbonation). Mechanical, microstructural and durability properties were evaluated via a series of characterization methods, such as scanning electron microscopy (SEM), X-ray microtomography ( $\mu$ CT), mercury intrusion porosimetry (MIP) and autoclave expansion, among others. Results showed that SS has low reactivity but may be alkali-activated as single binder. In fact, the best mechanical results (compressive strength up to 20 MPa) were achieved by using an activator with low  $\text{Na}_2\text{O}$  concentration (4%) and intermediary silica modulus (1.50-2.22). As aggregate, the wet curing as pre-treatment of the SS is highly recommended for AAM and PC matrices to control the delayed expansion of the former, producing sound materials after accelerated testing. In addition, the ITZ showed a gel phase (most likely resulting from the reaction of the SS aggregate in the alkaline system) which promoted the bond between aggregates and paste. On the other hand, the carbonation as pre-treatment of SS strongly affected the strength development at early ages of AAM mortars due to the formation of sodium carbonate in the activator. The AAM mortar designed with neat SS as binder and aggregate presented low mechanical strength (up to 5 MPa) and high porosity. Consequently, this mortar does not have sufficient mechanical strength to be evaluated in accelerated expansion testing. The findings of this research showed that the use of SS as raw material is very promising for AAM development.

Keywords: steel slag, waste recycling, alkali-activated materials, activation parameters, pre-treatment process, volume stability.

## SPANISH ABSTRACT

La escoria de acería (EA) es un residuo sólido generado durante el proceso de fabricación del acero con generación anual de 270 millones de toneladas de EA en todo el mundo. La EA se puede reutilizar como materia prima alternativa en varias aplicaciones debido a su composición química, propiedades mecánicas y físicas: en agricultura, estabilización de suelos, construcción de carreteras y materiales de construcción en general. A pesar de este gran potencial de reutilización, la tasa de recuperación de EA varía de 20 a 98%, dependiendo del país, lo que conduce a un stock excesivo que causa daños ambientales y pasivos financieros. Hasta el momento, las principales aplicaciones que realmente consumen cantidades considerables de EA son la construcción de carreteras y el reciclaje interno (fabricación de acero), pero aún con muchas restricciones. El sector de la construcción aparece como un consumidor potencial de grandes cantidades de EA. Sin embargo, la inestabilidad volumétrica de EA puede ser un problema para la aplicación en productos a base de cemento Portland (CP). Una reutilización más ecológica para las EA sería como materia prima en los materiales álcali-activados (MAA). Los MAA son materiales alternativos que presentan mejores propiedades mecánicas y de durabilidad; también pueden incorporar mayores cantidades de residuos industriales. Esta investigación investigó la viabilidad de EA como aglutinante y árido en MAA a través de la determinación de los parámetros de activación óptimos y el proceso de pretratamiento necesario (curado en húmedo y carbonatación). Las propiedades mecánicas, microestructurales y de durabilidad se evaluaron mediante una serie de métodos de caracterización, como microscopía electrónica de barrido (MEB), microtomografía de rayos X ( $\mu$ CT), porosimetría de intrusión de mercurio (MIP) y expansión en autoclave, entre otros. Los resultados mostraron que, a pesar de la baja reactividad de la EA, se confirmaron el proceso de activación alcalina y el endurecimiento de las pastas a base de SS como aglutinante único. De hecho, los mejores resultados mecánicos (resistencia a la compresión hasta 20 MPa) se consiguieron con una combinación de baja concentración de  $\text{Na}_2\text{O}$  (4%) y módulo de silicio intermedio (1.50-2.22). En cuanto al uso como árido, el curado en húmedo como pretratamiento es muy recomendable para las matrices MAA y PC para controlar la expansión retardada de la EA, produciendo materiales endurecidos tras el ensayo acelerado. Además, la interfase presentó una fase gelatinosa (muy probablemente resultante de la reacción del árido EA en el sistema alcalino) que favorecía la interfase entre áridos y pasta. Por otro lado, la carbonatación como pretratamiento afectó fuertemente al desarrollo de la resistencia a edades tempranas de los morteros MAA debido a la formación de carbonato sódico en el activador. El mortero MAA diseñado únicamente con EA como ligante y árido presentó bajas resistencias mecánicas (hasta 5 MPa) y alta porosidad total. Como consecuencia, este mortero no tiene suficiente resistencia mecánica para ser evaluado en pruebas aceleradas. Los resultados de esta investigación demostraron que el uso de EA como materia prima es muy prometedor para el desarrollo de MAA.

Palabras clave: escoria de acero, reciclado de residuos, materiales activados alcalinamente, parámetros de activación, proceso de pretratamiento, estabilidad de volumen.

## PORTUGUESE ABSTRACT

A escória de aciaria (EA) é um resíduo sólido gerado durante o processo de fabricação do aço com uma geração anual de mais de 270 milhões de toneladas de EA em todo o mundo. Devido à sua composição química, propriedades mecânicas e físicas, a EA pode ser reaproveitada como matéria-prima alternativa em diversas aplicações como na agricultura, estabilização de solos, construção de estradas e outros materiais de construção. Apesar desse grande potencial de reaproveitamento, a taxa de recuperação de EA varia entre 20% e 98% de acordo com cada país, o que gera um estoque/empilhamento excessivo, se tornando um passivo ambiental e financeiro. Até agora, as principais aplicações que realmente consomem quantidades consideráveis de EA são a construção de estradas e a reciclagem interna na siderurgia, porém com muitas restrições. O setor da construção civil aparece como um potencial consumidor de grandes quantidades de EA. No entanto, a instabilidade volumétrica da EA pode ser um problema para aplicação em produtos à base de cimento Portland (CP). Um reaproveitamento mais sustentável da EA seria como matéria-prima nos materiais álcali-ativados (MAA). Os MAA são materiais alternativos que apresentam melhores desempenhos mecânicos e de durabilidade; também podem incorporar grandes quantidades de resíduos industriais. Esta pesquisa investigou a viabilidade da EA como ligante e agregado em MAA através da determinação dos parâmetros ótimos de ativação e do processo de pré-tratamento necessário (cura úmida e carbonatação). As propriedades mecânicas, microestruturais e de durabilidade foram avaliadas por meio de uma série de métodos de caracterização, como microscopia eletrônica de varredura (MEV), microtomografia de raios-X ( $\mu$ CT), porosimetria por intrusão de mercúrio (MIP) e expansão em autoclave, entre outros. Os resultados mostraram que, apesar da baixa reatividade do EA, o processo de ativação alcalina e o endurecimento de pastas à base de EA como um único ligante foram confirmados. De fato, os melhores resultados mecânicos (resistência à compressão de até 20 MPa) foram obtidos com uma combinação de baixa concentração de  $\text{Na}_2\text{O}$  (4%) e módulo de sílica intermediário (1.50-2.22). Com relação ao uso como agregado, a cura úmida como pré-tratamento é altamente recomendada para matrizes de MAA e PC para controlar a expansão tardia da EA, produzindo materiais endurecidos após testes acelerados. Além do mais, a interface apresentou a formação de um gel (provavelmente resultante da reação do agregado EA no sistema alcalino) que promoveu a ligação entre os agregados e a pasta. Por outro lado, a carbonatação como pré-tratamento afetou fortemente o desenvolvimento da resistência nas primeiras idades das argamassas MAA devido à formação de carbonato de sódio no ativador. A argamassa MAA produzida com apenas EA como ligante e agregado apresentou baixa resistência mecânica (até 5 MPa) e alta porosidade total. Consequentemente, essa argamassa não tem resistência mecânica suficiente para ser avaliada em testes acelerados. Os resultados desta pesquisa mostraram que o uso de EA como matéria-prima é muito promissor para o desenvolvimento de MAA.

Palavras-chave: escória de aciaria, reciclagem de resíduos, materiais álcali-ativados, parâmetros de ativação, processo de pré-tratamento, estabilidade volumétrica.

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## **1. INTRODUCTION**

### **1.1. Background and motivation**

The 2030 Agenda for Sustainable Development presents a plan of action to face the greatest global challenges toward a sustainable development. The plan is formed with 17 Sustainable Development Goals (SDGs) and 169 targets, and it seeks to balance the three dimensions of sustainable development for the future of humanity: the economic, social, and environmental [1]. The goals related to the environmental scope pursue to (i) develop a sustainable industrialization through enhancing the scientific research (Goal 9); (ii), making cities sustainable by paying special attention to waste management (Goal 11), and (iii) achieving a sustainable and efficient use of natural resources (Goal 12) [1]. In fact, according to the last annual report in 2022, only 55% of the total municipal solid wastes are managed in controlled facilities and the reliance on natural resources is increasing since 2000 (rising rate of 65%) [2].

The construction and infrastructure industries are major economic sectors that can and must contribute to achieve these environmental goals. For instance, the construction works alone consume up to 60% of all raw materials extracted worldwide [3]. Moreover, both industries contribute to the elevated demand of Portland cement (PC), which accounts for 8% of the global greenhouse gas emissions [4]. On the other side of the equation, the industrial waste management carries a significant global footprint and high maintenance costs [5,6]. The steelmaking industry generates a vast quantity of byproducts and wastes alongside the steel production. The main solid waste generated is the steel slag (SS), which is typically stockpiled in open field, causing environmental harm and financial liability [7]. The Brazilian steel industry produced approximately 35 million tons of crude steel per year, representing roughly 54% of the Latin American production and 2% of the global production. That volume of production gives a total of 4.5 million tons of SS generated every year [8].

The promotion of the reutilization of SS is the main effort to reduce the amount stockpiled. Many researchers have been investigating several types of different applications for SS, such as soil stabilizers [9,10], as wastewater treatment element [11,12], as catalyst for fuel development [13,14], as raw material to carbon capture and storage [15,16], as alternative aggregates for pavements [17–19], and as alternative raw material in PC-based products [20–22]. Despite those several possible applications, there is an enormous difference in the amounts of SS reused worldwide, e.g., Japan with 98% [23] and Brazil with only 22% [24]. In that scenario, the

investment in scientific research focused on the reutilization of an important industrial waste such as SS is vital to achieve the SDGs 9 and 11.

Most of the published studies on the development of SS as aggregate in mortars and concretes neglects the effects on the durability-related properties and the necessity of a pre-treatment on the SS, as pointed out in a recent published comprehensive review [25]. Additionally, the PC industry is accountable for a high energy consumption and a high greenhouse gas emission [4,26], which demands a more sustainable material that may replace PC for some applications. Alkali-activated materials (AAM) have been promoted as alternative greener building materials in recent decades mainly because its potential of employing industrial wastes as raw materials [27]. The global warming potential impact of AAM was estimated to be between 45% to 80% lower than PC depending on the raw materials used [28,29].

AAM typically consist of an aluminosilicate precursor mixed with an alkaline activator. The most used alkali sources are the sodium or potassium hydroxides or silicates; they are combined with an amorphous (powdered) aluminosilicate precursor to produce the AAM [30]. The precursors can be obtained from natural sources, such as metakaolin (MK) [31], or from industrial/agricultural wastes such as pulverized fly ash (PFA) [32], ground granulated blast furnace slags (GGBFS) [33], rice hush ask (RHA) [34], and waste glass [35]. It is essential to differentiate the resulting alkali-activated system: either an alkali aluminosilicate gel (N-A-S(H)) free of calcium, or a calcium aluminosilicate hydrate gel (C-A-S-H), or the coexistence of both systems [30,36]. However, the supply of those main precursors (MK, GGBFS, and PFA) is now challenging. MK is a natural resource which demands calcination, GGBFS already has a well-defined industrial route (i.e., as supplementary cementitious material in the PC production), and PFA availability was significantly reduced due to the continuous decommissioning of coal power plants worldwide [37]. Therefore, there is a need for finding alternative binders to replace these and meet the future demands of AAM.

## **1.2. Objectives and justification**

SS is placed as an important environmental liability since the world crude steel industry generated over 270 million tons of SS per year. Numerous studies have been carried out towards the development of new routes and applications for SS aiming to transform this industrial waste in a valuable raw material. The SS may act as

alternative element to natural resources, which is in line with the green supply chain and the circular economy guidelines. On this matter, the civil construction sector emerges as major consumer for this industrial waste. However, without proper treatment, the volumetric expansion of SS may cause deteriorations and negatively affect the durability of building materials. So far, the use of SS in AAM is a new topic among researchers, with still no consensus about the real influence of SS on AAM properties. Therefore, there is a demand for validation of SS as raw material (binder and aggregate) in AAM resulting in a viable construction material.

This research will develop and evaluate a AAM containing SS as both binder and aggregate; it aims to maximize the reuse and create value to this important byproduct. The main objective of this study is to determine the feasibility of SS as single raw material (precursor and aggregate) in the development of AAM (low environmental impact construction material).

The specific objectives of the study are:

- (i) Make a thorough state-of-art review mainly comprising the recent developments in the possible re-utilization of SS and highlight the potential, challenges, and research needs;
- (ii) Evaluate the feasibility of SS as binder by assessing the SS activation parameters that influence the hydration kinetics, the mechanical and microstructural properties of SS-based AAM pastes;
- (iii) Evaluate the feasibility of SS use as aggregate by assessing two SS pre-treatment methods (wet-curing and carbonation) that may affect the mechanical, microstructural properties, and volumetric stability in either AAM, GGBFS-based or PC-based mortars, comparing to natural aggregate;
- (iv) Assess the physical, mechanical, structural, microstructural properties, and volumetric stability of 100% SS-based AAM mortar containing only SS as aggregate.

### **1.3. Thesis structure**

This thesis is presented as a collection of eight chapters (Figure 1.1). Chapter 1 is a brief introduction to the subject. The literature review and state-of-art (Chapter 2) was written based in the recent advances in several applications and re-utilization of the SS. The methodology used in this research is defined in the Chapter 3. Each following

chapter (Chapters 4, 5, and 6) presents its own independent results section, which are then summarized altogether in Chapter 7. The main conclusions of the thesis and future recommendations are presented in the last chapter (Chapter 8). A more detailed description of each chapter is presented below:

- **Chapter 1** presents the background information, the motivation for this study, and a brief introduction of the topic (valorization of SS and AAM development). The chapter also includes the justification for the research, the specific objectives, and the structure of the study.
- **Chapter 2** presents the recent state-of-art studies on the advances in applications and re-utilization of the SS. It begins with a short overview about the SS production and characteristics and then presents several studies divided in sections according to type of application. Potential, challenges, and research needs are also discussed. This chapter is related to the specific objective (i). It led to the published paper: *“Recent advances in the reuse of steel slags and future perspectives as binder and aggregate for alkali-activated materials”*.
- **Chapter 3** is the methodology section of the thesis. It brings the raw materials used (binders, chemicals, and aggregates), the description of the sample’s preparation (pastes and mortars), and a detailed description of all test methods applied. The specific mix proportions (formulations) are described in their corresponding chapter.
- **Chapter 4** presents the development of SS as binder in AAM by assessing the influence of the change on the silica modulus and the sodium concentration in several properties: the early hydration process (isothermal calorimetry), the compressive strength, the apparent density, and the structure and microstructure characteristics (X-ray diffraction, thermogravimetric analysis, and scanning electron microscopy - SEM). This chapter is related to the specific objective (ii). It led to the published paper: *“Influence of activation parameters on the mechanical and microstructure properties of an alkali-activated BOF steel slag”*.

- **Chapter 5** brings the development of SS as aggregate in GGBFS-based AAM mortars by evaluating the influence of the SS aggregate pre-treatments on several properties: fresh properties (consistency test), mechanical performance (compressive and flexural strength), internal structure (X-ray microtomography -  $\mu$ CT), microstructure characteristics on the ITZ by SEM, and durability-related (volume stability by autoclave test). PC-based mortars were also evaluated as reference. This chapter is related to the specific objective (iii). It led to the submitted paper: *“Pre-treatment of BOF steel slag aggregates and effect on the mechanical and microstructure properties of alkali-activated mortars”*.
- **Chapter 6** combines the findings from Chapter 4 (the best activation parameters for SS as precursor) and from Chapter 5 (the best pre-treatment method for SS as aggregate). It presents a comparative study of a AAM mortar developed with 100% of SS as binder and as aggregate with a GGBFS AAM and a PC-based mortars. The mortars were evaluated on their fresh properties (consistency test) and early hydration process (isothermal calorimetry). Mechanical properties (compressive strength), physical properties (water absorption, apparent density, and porosity), internal structure ( $\mu$ CT), pore size distribution (mercury intrusion porosimetry), microstructure characteristics on the ITZ by SEM, and the durability-related property (volume stability by autoclave test) were also evaluated. This chapter is related to the specific objective (iv). It will lead to the following paper: *“Novel eco-friendly alkali-activated BOF steel slag-based mortar: structural and microstructural analysis”*.
- **Chapter 7** contains a summary of the main results from all the experimental work of the thesis and some complementary discussions.
- Finally, **Chapter 8** brings the overall conclusions of the thesis with some recommendations for future research in the same topic.

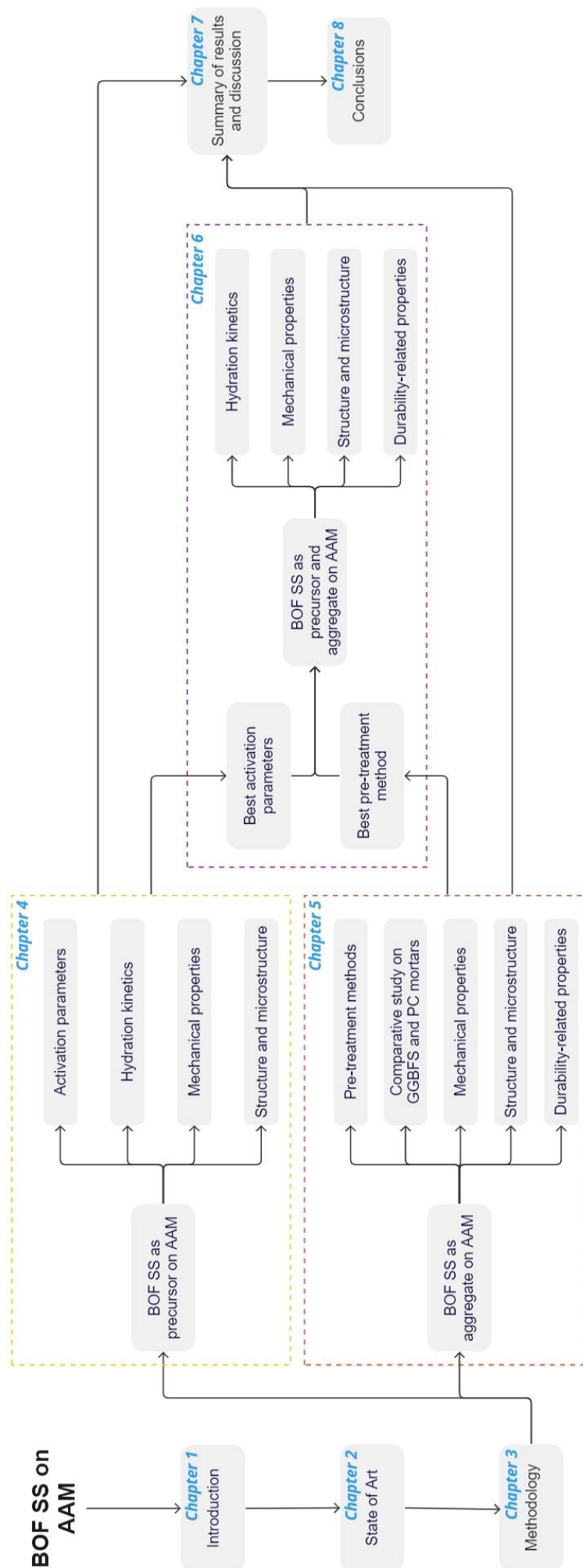


Figure 1.1 – Research structure.

#### 1.4. Research dissemination

This topic summarizes all the research and development disseminated during the years (2018-2023) of this doctorate:

Published papers at international journals:

- Camargos, J.S.F., Dias, E.A.P., Silva, G.M., Nunes, V.A., Borges, P.H.R. Development of sustainable foamed alkali activated materials for modular construction. J Braz. Soc. Mech. Sci. Eng. 45, 436 (2023). <https://doi.org/10.1007/s40430-023-04346-z>.
- Nunes, V.A., Suraneni, P., Bezerra, A.C.S., Thomas, C., Borges, P.H.R. Influence of Activation Parameters on the Mechanical and Microstructure Properties of an Alkali-Activated BOF Steel Slag, Applied Sciences. 12 (2022). <https://doi.org/10.3390/app122312437>.
- Nunes, V.A., Borges, P.H.R. Recent advances in the reuse of steel slags and future perspectives as binder and aggregate for alkali-activated materials, Constr Build Mater. 281 (2021) 122605. <https://doi.org/10.1016/j.conbuildmat.2021.122605>.
- Nunes, V.A., Borges, P.H.R., Zanotti, C. Mechanical compatibility and adhesion between alkali-activated repair mortars and Portland cement concrete substrate, Constr Build Mater. 215 (2019). <https://doi.org/10.1016/j.conbuildmat.2019.04.189>.

Accepted book chapter at international journals:

- Nunes, V.A., Sainz-Aja, J., Cimentada, A., Thomas, C. Microtomography of eco-efficient concrete, The Path to Green Concrete, Woodhead Publishing, Elsevier, 2023

Published work at conferences:

- Camargos, J.S.F., Dias, E.A.P., Silva, G.M., Nunes, V.A., Borges, P.H.R. On the development of sustainable foamed composites for modular construction. In: 6th Brazilian Conference on Composite Material, 2022, Tiradentes/MG.

Proceedings of the 6th Brazilian Conference on Composite Materials, 2022. p. 520-525. <https://doi.org/10.29327/566492>.

- Batista, R.P., Nunes, V.A., Trindade, A.C.C., Borges, P.H.R., Silva, F.A. On the mechanical performance of alkali-activated mortars reinforced with short PVA fibers. In: 4th Brazilian Conference on Composite Materials, 2018, Rio de Janeiro. Online Proceedings of the 4th Brazilian Conference on Composite Materials, 2018. ISBN 978-85-85083-00-7.
- Nunes, V.A., Borges, P.H.R., Zanotti, C., Batista, R.P. Compatibility and adhesion of MK/BFS alkali-activated repair mortars to Portland cement concrete substrates. In: 4th Brazilian Conference on Composite Materials, 2018, Rio de Janeiro. Online Proceedings of the 4th Brazilian Conference on Composite Materials, 2018. ISBN 978-85-85083-00-7.

#### Conference participations:

- As a plenary speaker: Nunes, V.A. Recent advances in the reuse of steel slags and the future perspectives applications in alkali-activated materials. 1st International Santander Eco-Concrete Conference, 2021. <https://www.carlosthomas.com/wp-content/uploads/2021/12/ISECC21.pdf>.
- As an attendee: International Conference on Advances in Sustainable Construction Materials and Structures, 2021. <http://rilemweek2021.uanl.mx/>.
- As a presenter: Nunes, V.A., Borges, P.H.R., Zanotti, C., Batista, R.P. Compatibility and adhesion of MK/BFS alkali-activated repair mortars to Portland cement concrete substrates. 4th Brazilian Conference on Composite Materials, 2018. <http://bccm4.com.br/2018/>.

#### Submitted documents:

- Nunes, V.A., Cimentada, A., Thomas, C., Borges, P.H.R. Pre-treatment of BOF steel slag aggregates and effect on the mechanical and microstructure properties of alkali-activated mortars. Submitted to Cement and Concrete Research, 2023.

Upcoming documents:

- Nunes, V.A., Thomas, C., Borges, P.H.R. Novel eco-friendly alkali-activated BOF steel slag-based mortar: structural and microstructural analysis.

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## **2. STATE OF ART REVIEW**

## Abstract

Steel slag (SS) is a secondary material from the production of steelmaking with little commercial value. It has several possible applications as raw material for different industrial process. However, small amounts are reused in some countries, where this material continues to be a burden to the steel industry. This chapter presents the recent advances in the utilisation of SS in activities other than steelmaking. The main focus is the potential use of SS as binder and aggregates in cement-based materials, notably in alkali-activated materials (AAM). The latter are alternative construction materials to Portland cement (PC) and sometimes with lower environmental impact. The chapter also discusses technical and commercial challenges of employing SS as raw material, e.g. legislation barriers and need for thorough treatment processing. The findings indicate that SS is a well-established material in some applications, such as agriculture and road construction. The potential use of SS as cementitious material and aggregates for concrete is highly promoted in the literature. However, the major obstacles are the variable chemical composition of SS, expansion issues, and worse fresh properties when employed as aggregates. Those issues are detrimental to mechanical strength and durability. The use of SS as binder or aggregate for AAM is still incipient albeit promising. Studies on SS-based AAM present an improved interfacial transition zone, but still, low SS reactivity as a binder. The lack of durability studies and life-cycle assessment clearly shows the demand for further investigation. Overall, a great research opportunity is the employment of SS both as binder and aggregates in AAM.

## 2.1. Introduction

The steelmaking industry produced 1.8 billion tons of crude steel worldwide in 2019. Alongside steel, byproducts and wastes such as slags, dust, sludge and gases are also generated [1]. The main solid waste (over 90% by weight) generated during crude steel production is steel slag (SS). SS is the result of impurities removal from the molten steel. It is composed mainly of silica, magnesium oxide, calcium oxide, aluminium and iron [2]. Usually, after the generation, SS is transported to a stock location, treated and magnetically separated to recover the metal iron. After that, the SS is stockpiled in an open field [3].

The excessive stockpiling of the SS causes environmental harm and financial liability. The promotion of the reutilization of SS is the main effort to reduce the amount of SS stockpiled. Because of its chemical composition, Europe began to use SS for phosphate fertilizer since 1880 [3]. The success as fertilizer led to the development of alternative soil stabilizers using SS [4,5]. Because of its porous structure and high density, SS can be applied in wastewater treatment for effluents neutralization [6,7].

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This is a slightly modified version of the author's post-print version paper "Recent advance in the reuse of steel slags and future perspective as binder and aggregate for alkali-activated materials" published at Construction and Building Materials Journal, Elsevier. Q1 (Civil and Structural Engineering) and A1 (Qualis – Engineering I). CiteScore: 12.4, Impact Factor: 7.693. DOI: <https://doi.org/10.1016/j.conbuildmat.2021.122605>.

Recent studies started to use SS as a catalyst for fuel development due to its high metal oxides [8,9]. Besides, SS may be a promising raw material to the carbon capture and storage developments because of its Ca-rich composition [10,11]. Several researchers have affirmed that SS can be used as alternative aggregates in different pavements and concretes. The former favours physical and mechanical properties, including high density, high strength and high abrasion resistance [12–18]. The presence of some mineral phases, such as dicalcium and tricalcium silicates ( $C_2S$  and  $C_3S$ ) confers SS cementitious properties and potential to be used in composite cement [19–22].

Despite several possible applications, there is a vast difference in the amounts of SS used worldwide. Industrial countries have high utilization rates, like Japan, with 98% [23], European countries with 86% [24] and the United States with 84% [3]. On the other hand, China and Brazil, two of the top nine producers of crude steel, have low rates of utilization of SS, i.e. 29.5% [3] and 22% [25], respectively. The Brazilian scenario is still far behind, characterized by a limited market for reuse of SS. The two main applications are base and subbase for payments and land levelling; yet, 30% of this amount is destined as a donation [25]. No data statistics are available for SS use as fertilizers, wastewater treatment or cementitious purposes in Brazil.

The construction sector emerges as a potential consumer of SS as supplementary cementitious material and aggregate for concretes. For example, Japan employs 30.9% of the generated SS in civil engineering works [23]. However, without proper treatment, the volumetric expansion of SS may cause deteriorations and negatively affect the durability of building materials [26]. Moreover, the Portland cement (PC) industry is responsible for 8% of the global greenhouse gas emissions [27]; a more sustainable material may replace PC and consume larger SS amounts.

Alkali-activated materials (AAM) have been promoted in recent years as alternative greener building materials. The main advantages of AAM over PC-based materials are the better mechanical and durability properties [28–30], and their potentially lower environmental impact [31–33]. SS started to be studied as potential precursor and aggregate for AAM in recent years. The results show a promising reuse route; however, the literature on this subject is still scarce and inconclusive. Therefore, further work is required to understand the role of SS in AAM development fully.

The purpose of this chapter is to present the current state-of-the-art advances in the SS reutilization. It brings an overview of the established recycling routes for SS and existing gaps and challenges for other emerging applications. We believe that this review could assist future studies and provide research opportunities in the development of construction materials. Section 2 presents the general overview of SS, briefly describing the process of generating SS and the latter's variable chemical composition. Section 3 brings the state-of-art on the applications of SS. The potential and challenges for SS recovery are discussed in Section 4, alongside proposes for future research needs emphasising AAM. Section 5 presents some conclusions.

## 2.2. Steel slag generation and composition

Steel slag (SS) is a solid waste generated during the conversion of iron into steel in a basic oxygen furnace (BOF) or during the melting of scrap to make steel in an electric arc furnace (EAF). A third type, ladle steel slag, also known as white slag or refining slag, resulting from further refining in the ladle. Its composition is quite different from that of the former [2,26,34]. The main difference between BOF, EAF and ladle process is the energy source and impurities at the end of the process (Figure 2.1) [35]. Figure 2.2 presents a flowchart combining the three types of steel slags and how they interact during the production process.

Usually, the BOF charge consists of 80–90% of molten iron and 10–20% of steel scraps, where the steel scraps play the important role of cooling down the furnace [36]. During the melting process, some fluxes (lime, dolomite) are added to the furnace to remove unwanted chemical elements, thus removing the melts impurities and generating the BOF slag [37]. On the other hand, the EAF process uses high-power electric arcs and steel scraps as a charge. CaO is also added during the melting process when the refining processes achieve the melted steel's desired chemical composition, and EAF slag is generated [26,34].

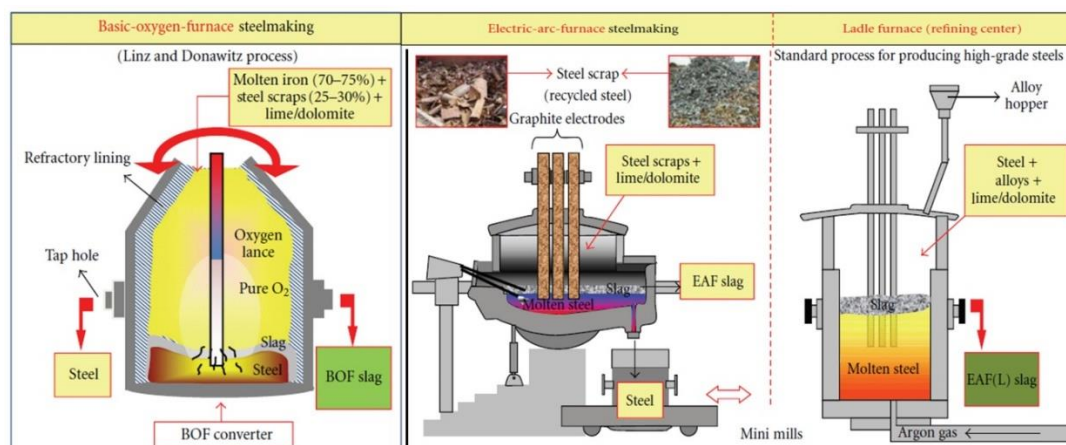


Figure 2.1 - Schematic process of steel slags generation [36].

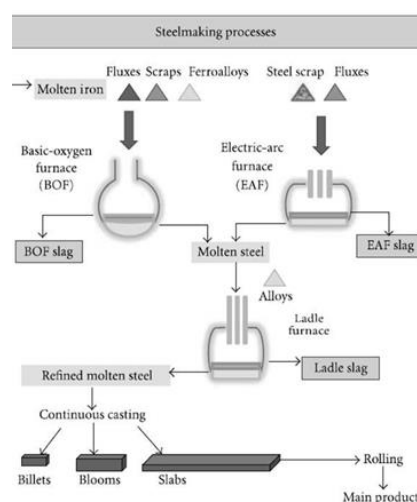


Figure 2.2 - Flowchart of steelmaking process [36].

The production amount of SS is 100–150 kg per ton of molten steel [37]. According to the World Steel Association, the world crude steel production in 2019 was approximately 1.8 billion tons, corresponding to >270 million tons of SS generated [1]. The Brazilian steel production represented roughly 54% of the Latin American production in 2019 (1st place), and 2% of the global production (9th place). Approximately 35 million tons of crude steel were produced in Brazil per year in the past five years, giving a total of 4.5 million tons of SS every year [38]. China is the world leader in crude steel production, corresponding to 51% worldwide production [38].

The SS mainly consists of CaO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, FeO, Al<sub>2</sub>O<sub>3</sub>, MgO, MnO and P<sub>2</sub>O<sub>5</sub>. Its chemical composition varies with the furnace type, steelmaking process and pretreatment method [12]. The main mineral phases are dicalcium silicate (C<sub>2</sub>S), tricalcium silicate (C<sub>3</sub>S), tetra-calcium aluminoferrite (C<sub>4</sub>AF), olivine, merwinite, CaO-FeO-MnO-MgO solid solution and free-CaO [12,37]. The ladle slag is generated during the steel refining process in which several alloys are added. Therefore, its chemical composition differs from BOF and EAF – much lower FeO content and higher Al<sub>2</sub>O<sub>3</sub> and CaO contents in the former [36]. Different BOF, EAF, and ladle chemical compositions are presented in the literature, as shown in Table 2.1.

**Table 2.1 - Chemical composition of BOF, EAF and ladle slags.**

| Reference                | Slag type | Oxide composition (%) |                                |                  |          |                                |          |           |                               | Free CaO |
|--------------------------|-----------|-----------------------|--------------------------------|------------------|----------|--------------------------------|----------|-----------|-------------------------------|----------|
|                          |           | CaO                   | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | FeO      | Al <sub>2</sub> O <sub>3</sub> | MgO      | MnO       | P <sub>2</sub> O <sub>5</sub> |          |
| Shi [34]                 | BOF       | 30 - 55               | -                              | 8 - 20           | 10 - 35  | 1 - 6                          | 5 - 15   | 2 - 8     | -                             | -        |
| Yildirim and Prezzi [36] | BOF       | 30 - 60               | 3 - 38                         | 7 - 18           | 7 - 35   | 0.5 - 4                        | 0.4 - 14 | 0.3 - 4.3 | 0.2 - 5                       | 0 - 12   |
| Yi et. al. [12]          | BOF       | 45 - 60               | 3 - 9                          | 10 - 15          | 7 - 20   | 1 - 5                          | 3 - 13   | 2 - 6     | 1 - 4                         | -        |
| Thomas et. al. [2]       | BOF       | 30 - 55               | -                              | 10 - 15          | 10 - 30  | 1 - 3                          | 5 - 15   | 1 - 5     | 1 - 3                         | 2 - 10   |
| Shi [34]                 | EAF       | 35 - 60               | -                              | 9 - 32           | 1 - 30   | 2 - 9                          | 5 - 15   | 1 - 8     | -                             | -        |
| Yildirim and Prezzi [36] | EAF       | 22 - 60               | 20 - 33                        | 6 - 34           | 10 - 40  | 3 - 14                         | 3 - 13   | 2.5 - 8   | 0 - 1.2                       | 0.5      |
| Yi et. al. [12]          | EAF       | 30 - 50               | 5 - 6                          | 11 - 20          | 8 - 22   | 10 - 18                        | 8 - 13   | 5 - 10    | 2 - 5                         | -        |
| Thomas et. al. [2]       | EAF       | 20 - 50               | -                              | 10 - 30          | 0 - 40   | 2 - 10                         | 3 - 15   | 1 - 5     | 0 - 2                         | 0.5      |
| Shi [34]                 | Ladle     | 30 - 60               | -                              | 2 - 35           | 0.1 - 15 | 5 - 35                         | 1 - 10   | 0 - 5     | -                             | -        |
| Yildirim and Prezzi [36] | Ladle     | 30 - 60               | 0.22 - 3.3                     | 2 - 35           | 0 - 15   | 4.3 - 35                       | 1 - 12.6 | 0 - 5     | 0 - 0.4                       | 0 - 19   |
| Yi et. al. [12]          | Ladle     | -                     | -                              | -                | -        | -                              | -        | -         | -                             | -        |
| Thomas et. al. [2]       | Ladle     | 35 - 60               | -                              | 5 - 50           | 0 - 5    | 1 - 30                         | 4 - 18   | 0 - 2     | 0 - 0.5                       | 2.6      |

The slag treatment processes alter the chemical and mineralogical composition, affecting the reactivity, stability and future potential use as raw materials in other applications. Usually, the steelmaking slags pass through: (i) cooling process, natural or with water spray; (ii) crushing and magnetic separation to recover metallic iron; (iii) classification to control grain-size; and (iv) ageing treatment to enhance the quality [37]. The cooling process determines the slag's morphology by regulating the

crystalline and amorphous phases, affecting its reactivity [34]. After granulation, BOF and EAF slags usually presents very complex crystalline structures resembling those of slowly cooled slags. Typically, solid solutions of wustite ( $\text{FeO}$ ) are observed as one of the main mineral phases, alongside  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$ . On the contrary, the ladle slag becomes highly amorphous after granulation, except for periclase ( $\text{MgO}$ ) [36]. Mayenite ( $\text{C}_{12}\text{A}_7$ ), tricalcium aluminate ( $\text{C}_3\text{A}$ ) and calcium-olivine are commonly observed as crystalline phases [39]. Overall the density of the SS typically is around  $3.1\text{--}3.7\text{ g/cm}^3$  [3,12]; the water absorption lower than 1% [3] and the grindability index is 0.7, in contrast of 1.0 of natural sand [12].

### 2.3. Recent advances of steel slag application

This section presents the state-of-art on the applications and reutilization of the steel slag divided in sub-section for the type of application. Emphasis is given to the development of constructions materials, mainly cement pastes and concretes. The review comprises mostly studies from 2018 to 2020. Still, previous studies are cited for providing a research background on the subject. The research bases used were Elsevier, Springer, Wiley, ASCE and MDPI.

#### 2.3.1. Agriculture

SS contains fertilizer components, such as  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{FeO}$  and  $\text{P}_2\text{O}_5$ . It has a larger specific surface area, porosity and excellent thermal stability, acting as an improving agent for acidic soil [35,40,41]. The use of steelmaking slags as raw material for fertilizer began to spread mainly in Europe in the late nineteenth century, and Japan started its studies after World War II [42]. It has recently been used in developed countries such as Germany, USA, France and Japan to produce siliceous, phosphorus and micronutrient fertilizers [12]. In China, for instance, the first SS fertilizer program with international investment started in 2011 [43]. The utilization rate of SS in agriculture is 3.0% of the generated amount in Europe and 3.9% in Japan [3].

The amount of SS used as fertilizer in agriculture is still low, which depends on market situations. Besides, natural limestone fertilizers (low market value) compete for slag use [44]. However, the employment of SS has shown comparable or even superior behaviour to natural limestone [45]. For example, it is possible to increase the soil pH and improve the soil quality and crop productivity by using a SS concentration between 1.5 and 5.0 ton/ha [46].

Several studies presented by Li and Dai [47] show that BOF and ladle slags can be used to prepare two types of fertilizers by hot slag modification method: phosphate fertilizers and phosphate silicate fertilizers. Those studies achieved the industrial trials, indicating that the modified slag is a good fertilizer with slow released properties [47]. Du et al. [48] used selective leaching–chemical precipitation process to recover phosphorus (P) from SS and successfully recover >70% of P. The authors obtained a final product with 20.2 mass % of  $\text{P}_2\text{O}_5$ , which can be applied as a good quality fertilizer [48]. According to Han and Wu [40], the application of slag fertilizer can promote the

mineralization of organic matter in soil and achieve better effects than lime when used to improve acidic soil. Three types of SS - steel, ladle and stainless steel - and three types of lime were used to assess the impact on a tropical and acidic soil chemical attributes, the generation and nutrient uptake of soybean no-tillage system [49]. These authors found that the use of SS on the soil fertility was effective compared to lime, increasing the pH, decreasing  $Al^{3+}$  concentration and providing phosphorus and silicon. Those results validate the agronomic viability of the SS for the neutralization of soil acidity.

### 2.3.2 Soil stabilization

Soil stabilization is a technique to refine and improve physical, mechanical and chemical properties of soils by adding chemical admixtures. This technique is mainly used for civil engineering applications such as sub-grade construction, road construction, backfill and foundation construction [50]. Considering the successful use of SS as a fertilizer, researchers began to look into the utilization of SS as a soil stabilization material after 2006 [51]. The first studies focused on finding alternative stabilizers to PC and controlling soil saturation with sodium [4,5,52,53].

Recently, studies have focused on the influence of SS on the strength and expansion characteristics of SS/soil mixes [50,54–58]. Cikmit et al. [55] studied several expansion tests at different rates and granulometry of SS (maximum diameter of 37.5 mm) mixed with soft clay (45%, 50%, 60%, 70% and 100%). The objective was to determine the maximum addition of SS to achieve heavy-weight geomaterial with lower volume expansion. The results of the study have shown that fine particles of SS do not affect the volume expansion. The best SS addition rate was 60%, ensuring the lower expansion ratio and a good unit weight. Furthermore, the soft clay's high void ratio was the reason for the volumetric change absorption [55].

Gu et al. [57] evaluated the performance (compatibility, strength and expansion ratio) of different SS contents with lime soil. The authors found that the design of 50% SS, 45% soil and 5% lime has the best performance considering compatibility and expansion (SS is a great filling material for subgrade treatment). They also found that the future activation of SS with NaCl and  $Na_2SO_4$  can significantly increase the mix design's mechanical strength compared to the unreacted SS mix [57].

Behnood [50] recommended using 5% of SS fines to increase the soil's pH and the CBR index, thus improving the mechanical strength. Although the results were promising, the authors recommended combining SS with other cementitious materials (e.g. BFS, FA and rice husk ash) to produce higher strengths and control the swelling problems [50]. Kang et al. [54] studied a soft dredged clay stabilized by BOF SS as fine aggregate (<5 mm). They found that the fine particles of SS's pozzolanic reaction increased the soil's strength in the long-term [54]. Liu et al. [58] also found in their study that the introduction of SS improves the compressive strength of earthen materials. However, it decreases their thermal resistance [58].

The main advantage of using SS for soil stabilization proved to be its great filling capacity, which directly improves the soil compressive strength and stability. Moreover, the rise in pH caused by the SS presence enhances the general soil characteristics.

### *2.3.3. Wastewater treatment*

Wastewater is the general term applied to the liquid wastes collected from residential, commercial, and industrial facilities by a sewerage system to a treatment plant to remove contaminants and convert into an effluent [59]. The application of SS in wastewater treatment has received researchers' intensive attention due to the SS porous structure, large surface area, and high density [12]. The most recent studies evaluated the use of SS filters for effluents neutralization [7,60–63] and control of hazardous effluent [64,65].

The use of SS filters in small wastewater treatment plants was successfully designed by Barca et al. [60] using hydrodynamics modelling approach to upgrade phosphorus removal. These authors found that the BOF SS filter has higher hydraulic efficiency and lower dispersion than EAF SS filter. The former may be applied to treat different water plants – urban, industrial or agricultural [60]. Bove et al. [7] also develop a SS filter to effluent neutralization of other elements (not only phosphorus) but instead using CO<sub>2</sub>-enriched air. A model based on the carbonate system, CO<sub>2</sub> transfer and calcite precipitation was developed, calibrated, and validated with lab and field tests [7].

Roychand et al. [61] obtained 90% efficiency phosphate removal by granular SS into a municipal wastewater treatment plant. A significant amount of iron and manganese were filtered out by the granulated particles of SS, which was also used as aggregate in concrete applications [61]. El-Azim et al. [64] went even further. They achieved a 99% removal of cadmium and manganese from industrial wastewater treatment using a 10 µm SS particle size, showing that SS may be a promising material for heavy metals removal [64].

Promising results have been found considering the SS as a filter in wastewater treatments, with no drawbacks presented in the literature. This application may remove heavy metals such as iron, manganese and cadmium from municipal and industrial wastewater.

### *2.3.4. Fuel development*

Due to its high amount of metal oxides – Fe<sub>2</sub>O<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> and CaO – SS is an attractive material to be used as a catalyst material [66] and has gained popularity in the recent years among researchers [8]. Several recent studies focused on developing biomass, fuel gas, tar and general catalyst using SS as the primary raw material [8,9,66–71].

The synthesis of novel catalytic materials (using SS as source) upon variation of the treating agents and synthesis parameters were investigated by Kholkina et al. [8]. It was verified that low-cost catalysts made from SS could have its properties enhanced by some previous changes in the textural and structural properties of the SS. Then, the catalyst presented better characteristics during bio-oil pyrolysis [8]. Kabir et al. [9] evaluated a crushed and pulverized EAF SS (under 63  $\mu\text{m}$  particle size) as start material to obtain a zeolite catalyst for palm oil pyrolysis. The authors concluded that the catalyst derived from SS allowed molecular traffic in the bio-oils internal structure. Its activity improved the pyrolysis compared to typical zeolites [9].

Guo et al. [66,67] studied SS (particle size of 0.125–0.15 mm) as a catalyst for decomposing biomass pyrolysis tar by a calcination treatment. The results indicate that SS has potential as an efficient catalyst with excellent stability in the long-term. Song et al. [70] investigated the addition of different amounts of SS to varying temperatures into oil sludge pyrolysis in a continuous magnetic reactor to improve the quality of tar. This addition proved to be feasible for the oil pyrolysis besides bringing a high rate of recovery of SS at the magnetic reactor [70]. Jiao et al. [68] used a SS derived catalyst (powder in 120 mesh) to improve the performance of a carbon solid oxide fuel cell and, also concluded that the SS is a promising material.

SS has also been investigated as particle electrode in an electrochemical reactor [72], as an oxygen carrier for chemical combustion [73], and as desulfurization and denitration agent for flue gas [74]. All of the previous studies achieved promising results regarding this new application for SS.

### 2.3.5. *CO<sub>2</sub> capture*

Carbon capture and storage research have focused on many industrial activities, given that CO<sub>2</sub> is one of the primary greenhouse gas that contributes to climate change [12,75,76]. There are three main methods to capture CO<sub>2</sub>: solvent absorption by liquids, membrane purification, and sorption by solid adsorbents [10]. The process of mineralization of CO<sub>2</sub> using a solid Ca-rich waste material, such as SS, is known to be a promising and recent approach (most studies after 2018) to control CO<sub>2</sub> emissions [11] and also eliminate wastes and by-products simultaneously [10,77].

Sun et al. [77] investigated experiments to optimize the acidification process of SS for the preparation of a highly efficient CaO based CO<sub>2</sub> sorbents. They found that sorption performance of an optimal SS sorbent is more stable than of a natural limestone derived one, thus making this processing a promising approach. The carbonation of BOF SS in a rotary kiln reactor was evaluated by Librandi et al. [78], to demonstrate this route's efficacy in scale-up processing. The authors found that the CO<sub>2</sub> uptake values were slightly higher than those obtained in a laboratory scale, ranging between 4 and 6%. However, some future studies should focus on controlling the temperature in the reactor, the reactor's rotation speed, and the gas/solid contact to enhance CO<sub>2</sub> capture [78]. In another research, the same authors studied the reacting phases and

the CO<sub>2</sub> uptake of two different slags, i.e. BOF and EAF. Results showed that, unlike EAF, BOF SS presented a high extent of reaction with CO<sub>2</sub> in the first 15 min of the process, due to conversion of portlandite to calcite and increased CO<sub>2</sub> uptake over time [79].

Regarding SS as ultra-fine powder, the CO<sub>2</sub> sequestration and reaction rate are directly influenced by particle size, solid to liquid ratio, temperature, agitation rate and CO<sub>2</sub> flow rate during the process [80]. The high presence of non-activated Ca and Mg in SS composition increases the carbonating reaction rate, thus increasing the CO<sub>2</sub> sequestration by 20% by forming MgCO<sub>3</sub> and by 60% forming CaCO<sub>3</sub> [11,80]. Besides that the reduction of CO<sub>2</sub> content on the atmosphere has a great potential since manufacturing SS as the binder can store up to 1.76 tonnes for every 10 tonnes of binder produced [81].

Using the same concept of the CO<sub>2</sub> mineralization process, a Belgium patented technology - Carbstone Innovation – aims to convert calcium-rich slags (e.g. SS) into sustainable building materials [82,83]. The process takes place in three main steps: (i) SS is ground into an ultra-fine powder; (ii) the powder is mixed with water and natural aggregates and then pressed into a given shape, and (iii) the product is placed in an autoclave to be treated with CO<sub>2</sub> [84]. The CO<sub>2</sub> is absorbed and converted into CaCO<sub>3</sub>, providing adequate mechanical strength to the products. The technology has been tested and is currently available on an industrial scale [85].

A recent Canadian patented technology - Carbicrete – claims to enable carbon-negative concrete production using steelmaking byproducts and CO<sub>2</sub> capture. Like the Carbstone Innovation, the Carbicrete patent presents a building material by mixing SS and a silica-rich material (waste glass and/or FA) and then treating the mix by heating and CO<sub>2</sub> curing [86]. This technology is on a pilot stage of development. It is said to avoid the emission of 3 kg of CO<sub>2</sub> per standard-size concrete block, i.e. 2 kg due to the cement replacement and 1 kg due to the injection/capture during the curing process [87].

The presence of free CaO and free MgO in SS composition is the main advantage of SS for the CO<sub>2</sub> mineralization process. The extent of reaction forms calcium and magnesium carbonate, which has been observed at the laboratory and industrial scale.

#### *2.3.6. Road and pavement*

As a result of the high level of strength, high bulk density and high frictional and abrasion resistance, the SS can be used as an alternative aggregate in bases, subbases, and surface layers of different types of pavements, e.g., asphaltic and concrete [12]. As a result of those characteristics, numerous recent studies employed SS into the open-graded mix [88], rail tracks [13], subbase [89], and asphalt technologies [14,15,90–106]. A few other studies focused their development on using SS as powder or binder into the concrete pavement [107,108].

Pattanaik et al. [88] studied the influence of the natural coarse aggregate replacement by EAF SS (sizes above 2.36 mm) on the clogging phenomenon of open-graded friction course bitumen-based mixes. They concluded that up to 100% replacement with SS satisfies the performance characteristics in term of permeability for all conditions (initial, clogging and de-clogging) [88]. Delgado et al. [13] evaluated the mechanical behaviour of SS ballast for railways tracks by comparing the mechanical strength and the long-term deformability behaviour of the SS against a natural and common used aggregate - granite. They found that in both studied parameters, the SS overcame the natural aggregate and presented a lower particles breakage helping to avoid railway degradation [13].

The application of SS as mineral filler in asphalt-based materials can lead to enhancement of heat release, self-healing properties, fracture properties, rheological properties, and deformation resistance. Those behaviours were demonstrated by Li et al. [98,103] and Tao et al. [92] in their studies where limestone filler was replaced by SS filler in asphalt mastics and mortars. Results showed that SS could achieve 62.83% higher heating rate, better self-healing contribution to the asphalt mixture, and convert microwave energy into more thermal energy. Moreover, due to its higher content of  $\text{Fe}_3\text{O}_4$ , metallic iron and CaO, tougher surface texture and higher specific surface area, SS promotes the asphaltene absorption to better ductile fracture behaviour [98] and an enhanced deformation resistance [90,92,98].

Induction heating method has been given huge attention lately, thanks to its effectiveness to promote self-healing of asphalt pavement. The employment of SS as aggregate is associated with positive results as well [102,106]. According to Phan et al. [102], the substitution of 30% of conventional coarse aggregate by SS provides better healing results and higher ductile behaviour. Another recent attractive alternative in the pavement industry is the warm mix asphalt (WMA) technology which has significantly lower energy consumption and carbon footprint [14]. The mechanical performance of WMA using SS as aggregate was evaluated by Amelian et al. [14] and Martinho et al. [104]. The first compared the SS aggregate influence with three natural ones, i.e. limestone, granite and quartzite. They found out that the SS mixture (100% substitution) provided a significant resistance to moisture damage and superior mechanical behaviour (dynamic creep and resilient modulus). Martinho et al. [104], on the other hand, substituted limestone by a SS and recycled concrete aggregate (RCA). They concluded that the addition of 30% SS or 60% RCA did not implicate in any important change on the mechanical properties, fatigue resistance or water sensitivity.

Some authors evaluated the influence of fine particle size of the SS aggregate (lower than 12.5 mm) on rut resistance, tensile strength and toughness [15,95,101], moisture resistance [105], and ice and snow melting functions [94] of asphalt mixes. Kim et al. [101] found that a hot mix asphalt mixture containing SS as aggregate instead of granite (particle size distribution according to standard specification) demonstrated a significantly improved performance: (i) increased stains by 15%; (ii) dynamic modulus remained higher than the reference with granite; (iii) improvement of 121% of rut

resistance, 110% of tensile strength and 114% of toughness. A combination of gneiss (coarse aggregate) and SS (fine aggregate and filler) proved satisfactory to prepare an asphalt mixture where the SS powder improved the mix's moisture resistance. The fine aggregate surface affected the moisture stability [105].

Gupta and Sachdeva [107] investigated rigid (concrete) pavements containing SS as a PC replacement. They varied the substitution rate (10%, 15%, 20% and 25%) of cement. They evaluated the consistency, compressive strength, flexural strength, air permeability, sorptivity, abrasion resistance, acid, and sulfate attack. The authors concluded that (i) the consistency of all concretes mixes were in the range suitable for rigid pavements construction; (ii) eventual reductions of the mechanical properties (compressive and flexural strengths) were acceptable, and the employment of 25% by SS is favourable for concrete pavements which had compressive strengths higher than 40 MPa; (iii) the air permeability and the sorptivity decreased as the percentage of SS increased, which may help the development of denser and more durable concretes [107].

Overall, the replacement of either fine or coarse natural aggregates with SS particles brings positive results in flexible pavements. SS improves the mechanical behaviour (strength, dynamic modulus and toughness), long-term deformability and self-healing capacity compared to natural aggregates. Regarding rigid (concrete) pavements, finely ground SS may partially replace PC in developing durable concrete pavements, as the former tends to increase the mechanical strength and lower permeability.

#### *2.3.7. Cement and concrete*

Extensive studies have been carried out to explore the possibility of using industrial wastes to replace PC in concrete products. They were driven by the high demand for PC and concrete production worldwide and the increasing interest to reduce the depletion of natural resources [109,110]. Several studies continue to be published to evaluate SS's potential as supplementary cementitious material [111–122] and as aggregates in PC-based pastes and concretes [61,123–138].

SS must possess a sufficient volumetrically stability to be employed as a binder or aggregate. The presence of free lime (f-CaO) and periclase (free MgO) is the dominant factor contributing to its volumetric expansion [26,139]. The free unhydrated CaO and MgO react with water to form hydroxides with increased volume, depending on their content. This reaction could cause disintegration of pieces and loss of strength. Various processing and treatment methods such as rapid cooling, the addition of sand, crushing and screening, air chilling, metallic extraction, water cured, among others have been developed to ensure the proper use of SS in cement or concrete matrices [26,140].

#### 2.3.7.1. Use of SS powder as a supplementary cementitious material

SS can be incorporated in cement manufacture in two different ways. First, as a raw material for cement clinker (partial substitution of limestone) when calcined in the kiln with other natural materials [21]. Studies have shown that up to 10% BOF SS [141,142], up to 14% ladle SS [143] and up to 30% BOF SS [22] do not cause any adverse effect to the cement properties. SS is also used in a non-calcining process, by grinding SS with BFS and PC clinker to produce blended cement. Due to the potential for energy saving, the latter approach is generally preferred [21]. Additions of SS are usually in the range from 10 to 55 wt%, depending on the SS chemical and mineralogical composition [20,144–148]. Special SS cement, composed by SS, BFS and PC has been commercialized in China for >30 years now [19,34,149].

Wang and Suraneni [117] recently studied the hydraulic and pozzolanic behaviours of BOF and ladle SS, concluding that they neither consume nor produce calcium hydroxide during hydration. The ladle slag presented higher reactivity than BOF slag but strongly retarded the cement hydration due to  $C_{12}A_7$  reaction. This SS component releases a significant amount of aluminium ions, which may be adsorbed on calcium silicate surfaces, thereby retarding cement hydration. As a consequence, while BOF presented moderate compressive strength, ladle slag showed negligible strength development. The authors concluded that SS should not be used as supplementary just as it is, but rather with the addition of other beneficial materials such as gypsum [117].

Cao et al. [121] prepared a crushed SS using the high temperature treatment and rapid cooling processing to be used in the cement clinker production. The authors found out that the inert components and hard phases of SS were reduced. The soundness, grindability and reactivity were improved. They concluded that a cement clinker with 16.86% of SS in its composition had comparable characteristics to ordinary PC [121].

Humbert et al. [116] studied a clinker-free  $CO_2$  cured SS as a binder, evaluating its fineness, water to solid ratio, compacting pressure, curing temperature, partial pressure applied and carbonation duration. They concluded that the SS-based binder presented better performance than PC by achieving 76% higher compressive strength. Xu et al. [118] also studied a clinker-free prefabricated concrete using SS and BFS as binders. They evaluated the effects of the curing regime on the compressive strength. The optimum dosage of concrete was found for 3:6 SS/BFS weight ratio and 140 kg/m<sup>3</sup> water consumption, which achieved a compressive strength of 49 MPa at 28 days if cured at 45 °C at 90% relative humidity until 28 days. They also concluded that the combination of SS and BFS is viable as a substitute for PC. Their reaction generates calcium hydroxide through  $C_3S$  reaction, dissolving alumina and silica tetrahedral to form ettringite and C-S-H [118].

Jianming et al. [111] and Jiang et al. [122] evaluated the use of SS as a replacement to magnesium potassium phosphate and magnesium phosphate cement, respectively.

Those types of cement have also been widely applied in rehabilitation and rapid repair of structures and dental bone materials due to its advantages of fast hardening, high early strength, and high bonding strength [122]. Both studies found that the utilization of SS for this kind of cement promotes early hydration rate, improves early age and late strength (up to 10% of replacement), increases water resistance (up to 30% of replacement) and decreases shrinkage. New hydration products were found alongside the main ones, i.e. struvite and residual magnesia [111,122].

Mutuk et al. [120] considered the use of SS in mortar applications, by replacing PC with 2 to 10 wt% SS. The best results were achieved with 4% of replacement. The SS insertion decreased the early age strength. However, it slightly increased the long-term compressive strength with no adverse effect on the microstructure (SS particles were embedded in the cement matrix) [120]. For concrete applications, Pan et al. [119] evaluated PC replacement with 10, 20, 30, 40 and 50 wt% of SS in self-compacting concrete. The authors found that SS improved the filling and passing abilities of the self-compacting concrete, but adversely affected the segregation resistance and early age strength. They also stated that a 10% replacement ratio (higher contents showed adverse effect) showed superior mechanical properties and higher durability to chloride penetration and carbonation [119]. Zhang et al. [114] developed an ultra-high performance concrete containing 10, 20 and 30 wt% SS as a PC replacement. Results showed that the early age hydration is retarded, leading to a reduction in compressive strength development. On the other hand, the long-term compressive strength is almost unaltered. At a high content of SS they found that autogenous shrinkage is reduced, the positive filling effect is observed, the leaching toxicity is reduced and the ecological performance enhanced, the later presented by LCA [114].

Han and Zhang [115] studied the influence of SS powder in five-year-old concrete properties. They found that SS negatively affects conventional concretes with the same water to binder ratio. The concrete containing SS presented lower compressive strength, higher interconnected porosity and lower resistance to chloride ion permeability. They also observed that at later ages (five years) the microstructure still contained many unreacted particles of SS, as well as lower content of  $\text{Ca(OH)}_2$  and higher content of  $\text{CaCO}_3$  [115]. Similarly, Liu and Guo [113] studied the influence of the addition of SS and BFS as binders in the properties of a ten years old concrete. Results have shown that the hydration degree of BFS was higher than SS at all ages (up to ten years). The Ca/Si ratio of the C-S-H gel produced by BFS was lower than that one made by SS. Unlike what has been found by Han and Zhang [115], Liu and Guo [113] concluded that the  $\text{Ca(OH)}_2$  content increases over time in the hardened composite binder containing SS.

Table 2.2 summarizes the influence of SS as supplementary cementitious material in PC based materials. Most studies focus on the SS reactivity and its effect on mechanical behaviour, with some disagreements in the findings. Moreover, there is a lack of studies on the durability of the matrices.

#### *2.3.7.2. Use of SS as aggregate in PC-based pastes and concretes*

The application of SS as aggregate in PC-based concrete was not recommended since structures failure events in a Canadian building in the early 1960 s [150]. After extensive research regarding this applicability, the Japanese could patent the use of SS as replacement of natural aggregates in PC-based concrete (JAPANESE PATENT, 1982a; 1982b). Since then, several studies worldwide established the potential and benefits of SS use as aggregate on the concrete's mechanical strength and durability properties [16–18,151–158]. The primary concern on the employment of SS in PC-based pastes and concretes is associated with the volume instability caused by the free CaO and MgO. A treatment process must be placed to ensure SS stability before use [159].

Rehman et al. [123] studied the influence of a granular SS as a fine aggregate replacement (40, 60 and 80 wt%) on the fresh concrete properties (workability, density and air content) and hardened properties (compressive, flexural and split tensile strengths and modulus of elasticity). The authors found a decreasing trend in workability with the increasing of SS content, attributed to the porous and rough texture of the SS. All mechanical strengths and modulus of elasticity were improved due to the pozzolanic reaction of the SS aggregates and its higher hardness [123]. Another study focused on the influence of SS as fine aggregate in concrete under axial impact compression. The authors concluded that the addition of SS improves the static and dynamic compressive strengths, increasing the stiffness and brittleness of the concrete with an optimum replacement percentage of 20% of the natural aggregate [132].

Similarly to what was found by Guo et al. [132], Campos et al. [131] also achieved the best performance (sufficient mechanical strength and higher density) with 20% of replacement of the fine aggregate by SS. The authors also stated that higher contents of SS decrease the mechanical performance of PC-based concrete [131]. The same optimum percentage of SS (20%) was found by Chen et al. [134]. In this case, the authors evaluated four particle size ranges (<0.063 mm, 0.063–0.5 mm, 0.5–2 mm, and 2–4 mm) and their effects on the physical properties of autoclaved aerated concrete. Results have shown that particle size < 0.5 mm was successful in terms of density and compressive strength. On the contrary, SS with particle size > 0.5 mm had volume expansion after the autoclave curing, resulting in cracks. Moreover, the authors concluded that SS fines contain some iron-rich substances that should be removed by a magnetic separation process beforehand [134].

Li et al. [133] evaluated the dynamic shear modulus and the damping ratio of concrete using SS as a fine aggregate. They employed particle sizes between 2 mm and 4 mm and 20, 30, 40 and 50 wt% replacement of natural aggregate to explore the effects of confining pressure, mix proportion and curing age. The authors stated that the dynamic shear modulus initially increases and decreases with SS content rise; the maximum value was achieved for 40% SS [133]. Lee et al. [136] studied the

piezoelectric sensitivity of a smart concrete containing fine SS aggregates and steel fibres under high compression. They concluded that, unlike the silica sand, the addition of SS helped enhance the piezoelectric sensitivity due to the quantum tunnelling effect [136]. Guo et al. [135] assessed the influence of unprocessed SS as fine aggregate (10, 20, 30, 40, 60, 80, 100 wt%) and the impact on normal and high strength concretes. They found a positive effect of SS in toughness and ultimate expansion ratio, thus on the energy absorption capacity. The authors also concluded that SS is more advantageous for the compressive strength of regular strength concrete (20 and 80% of replacement), but play a significant role in improving the toughness of high strength concrete (30% of replacement) [135].

The literature results show more agreement when SS is employed as a coarse aggregate [61,124,128,129,138]. Qasrawi [138] replaced the natural coarse aggregate with 50 wt% SS (optimum percentage) in a self-compacting concrete and found that (i) hot conditions harm the stability; (ii) higher amount of SS harm both the workability and stability and (iii) the use of SS increases air content and fresh density of concrete [138]. Saxena and Tembhurkar [124] also found that 50 wt% is the optimum content of SS as a replacement for coarse aggregate. At this replacement level, they observed improvements in compressive strength, flexural strength and modulus of elasticity of concrete by 33%, 9.8% and 22%, respectively. The microstructure was dense and the durability enhanced (reduced from 40 to 70% the chloride ion penetration). The authors also observed reductions in the consistency (concrete slump) and fresh density, the latter due to higher air content [124].

Sern et al. [128] conducted a more thorough study about the use of an electromagnetic separated SS (particle size 5–10 mm) as a replacement (20, 40, 60, 80 and 100 wt%) of a natural coarse aggregate of concrete. Other industrial wastes (BFS, FA) were also employed as a binder and fine aggregates. They found that 20% wt. SS is the optimum replacement level for natural coarse aggregate. The former tends to shorten both the initial and final setting times, increase the water demand for the fresh concrete, and increase the bulk density. Moreover, the addition of SS enhanced the mechanical performance (both compressive and flexural strength), the early age strength and improved the dimensional stability (lower drying shrinkage) of BFS-FA ternary blended concrete [128].

Baalamurugan et al. [129] concluded that 50 wt% SS as coarse aggregate at 10–12.5 mm is an alternative for gamma radiation shielding in the nuclear industry for fuel storage areas and hot cells. The concrete containing SS presented higher density and higher compressive strength in addition to a better shielding performance. Roychand et al. [61] employed recycled SS from water treatment (phosphorus removal) as coarse aggregate (5–10 mm) in concrete. They pointed out that the water treatment process significantly alters the chemical and mineralogical composition of the SS. These changes result in better cement paste to aggregate bond and an improvement of 17% in the compressive strength at 28 days [61].

Rooholamini et al. [126] pretreated SS by outdoor exposure for more than one year to reduce expansion. Later they assessed the effect of SS as both fine and coarse aggregate on the mechanical and fracture properties of a roller compacted concrete; the replacement levels were 25 and 50 wt% for fine natural aggregate and 50 and 100 wt% of the natural coarse aggregate. The fine aggregate replacement presented negative effect on mechanical responses and expansion behaviour probably due to (i) the high specific surface area and (ii) the presence of free CaO, respectively. On the other hand, incorporating the coarse SS increased aggregate interlock mostly due to its high angularity and roughness, promoting the mechanical and fracture properties [126]. Prasad et al. [130] also identified a better bonding between coarse aggregate and matrix, hence increased mechanical strengths. The study used SS as replacement for natural aggregates (fine SS < 4.75 mm and coarse SS < 20 mm both at 20, 40, 60, 80, 100 wt%). The best performance was at 20% fine and 80% coarse SS for compressive behaviour, 60% fine and 80% coarse SS for flexural behaviour and at 40% of both SS for split tensile behaviour. They also observed a reduction in workability due to the porous nature of SS in all cases [130].

Pervious concrete using magnesium phosphate cement and SS was investigated by Lang et al. [127]. They studied the influence of the aggregate size (2.5–5 mm, 5–10 mm and 10–15 mm) on the moulding method. They concluded that the porosity and water permeability increased for coarser aggregate sizes. The authors also pointed out that the medium particle size (5–10 mm) provided the optimum mechanical properties (compressive strength of 41 MPa and flexural strength of 8 MPa) when the vibration moulding was used [127].

Table 2.3 summarizes the primary influence found concerning SS as fine and coarse aggregates into PC-based mortars and concretes. It is possible to notice a wider variety of properties studied and more consistent results among the studies. The literature shows a better understanding of the SS role as aggregate than as binder (Table 2.2).

Table 2.2 - Summary of the influence of the use of SS as binder into PC-based materials.

| References              | Properties         |                    |           |                             |                           |               |              |                     |             |                 |                  |                   |
|-------------------------|--------------------|--------------------|-----------|-----------------------------|---------------------------|---------------|--------------|---------------------|-------------|-----------------|------------------|-------------------|
|                         | Early age strength | Long term strength | Shrinkage | Ca(OH) <sub>2</sub> content | CaCO <sub>3</sub> content | C-S-H content | Porosity     | Chloride resistance | Segregation | Filling ability | Water resistance | Toxicity leaching |
| Jianming et. al. [111]  | increase           | increase           | decrease  | -                           | -                         | -             | -            | -                   | -           | -               | -                | -                 |
| Han and Zhang [115]     | -                  | decrease           | -         | decrease                    | increase                  | -             | increase     | decrease            | -           | -               | -                | -                 |
| Humbert et. al. [116]   | -                  | increase           | -         | -                           | -                         | -             | -            | -                   | -           | -               | -                | -                 |
| Wang and Suraneni [117] | -                  | -                  | -         | decrease                    | -                         | -             | -            | -                   | -           | -               | -                | -                 |
| Xu et. al. [118]        | -                  | increase           | -         | -                           | -                         | increase      | -            | -                   | -           | -               | -                | -                 |
| Pan et. al. [119]       | decrease           | increase           | -         | -                           | -                         | -             | -            | increase            | increase    | increase        | -                | -                 |
| Cao et. al. [121]       | -                  | satisfactory       | -         | -                           | -                         | -             | -            | -                   | -           | -               | -                | -                 |
| Jiang et. al. [122]     | decrease           | increase           | -         | -                           | -                         | -             | -            | -                   | -           | -               | increase         | -                 |
| Mutuk et. al. [120]     | decrease           | increase           | -         | -                           | -                         | -             | satisfactory | -                   | -           | -               | -                | -                 |
| Liu and Guo [113]       | -                  | -                  | -         | increase                    | -                         | increase      | decrease     | -                   | -           | -               | -                | -                 |
| Zhang et. al. [114]     | decrease           | satisfactory       | decrease  | -                           | -                         | -             | -            | -                   | -           | increase        | -                | increase          |

Table 2.3 - Summary of the influence of the use of SS as aggregates into PC-based mortar and concretes.

| References                  | SS used as aggregate | Properties  |                    |                      |                   |                        |                    |                           |          |                             |                |          |             |                       |                      |           |                |
|-----------------------------|----------------------|-------------|--------------------|----------------------|-------------------|------------------------|--------------------|---------------------------|----------|-----------------------------|----------------|----------|-------------|-----------------------|----------------------|-----------|----------------|
|                             |                      | Workability | Early age strength | Compressive strength | Flexural strength | Split tensile strength | Elasticity modulus | Stiffness and Brittleness | Density  | Toughness Energy absorption | Expansion rate | Porosity | Air content | Dimensional stability | Chloride penetration | Shrinkage | Bond paste/agg |
| Rehman et. al. [123]        |                      | decrease    | -                  | increase             | increase          | -                      | increase           | -                         | -        | -                           | -              | -        | -           | -                     | -                    | -         | -              |
| Guo et. al. [132]           |                      | -           | -                  | increase             | -                 | -                      | increase           | -                         | -        | -                           | -              | -        | -           | -                     | -                    | -         | -              |
| Campos et. al. [131]        | Fine                 | -           | -                  | increase             | -                 | -                      | -                  | increase                  | -        | -                           | -              | -        | -           | -                     | -                    | -         | -              |
| Chen et. al. [134]          |                      | -           | -                  | decrease             | -                 | -                      | increase           | decrease                  | -        | -                           | -              | -        | -           | -                     | -                    | -         | -              |
| Guo et. al. [135]           |                      | -           | -                  | increase             | -                 | -                      | -                  | -                         | increase | decrease                    | -              | -        | -           | -                     | -                    | -         | -              |
| Qasrawi [138]               |                      | decrease    | -                  | -                    | -                 | -                      | -                  | increase                  | -        | -                           | -              | increase | decrease    | -                     | -                    | -         | -              |
| Saxena and Tembhurkar [124] | Coarse               | decrease    | -                  | increase             | increase          | -                      | increase           | increase                  | -        | -                           | -              | increase | -           | decrease              | -                    | -         | -              |
| Sern et. al. [128]          |                      | -           | increase           | increase             | increase          | -                      | -                  | increase                  | -        | -                           | -              | -        | increase    | -                     | decrease             | -         | -              |
| Roychand et. al. [61]       |                      | -           | -                  | increase             | -                 | -                      | -                  | -                         | -        | -                           | -              | -        | -           | -                     | -                    | -         | increase       |



### 2.3.8. Other construction materials

Other constructions materials such as blocks, ceramics and autoclaved materials have also been investigated. Some studies investigated the use of SS to develop green/eco-friendly blocks or bricks [160–164]. Abdel-Ghani et al. [160] found that it is possible to substitute 100% of the natural dolomite coarse aggregate traditionally used in fabricating interlock paving blocks. Similarly, Liu et al. [164] stated that a combination of 30% of SS and 70% of quartz sand, both as fine aggregate in the preparation of a permeable brick, showed excellent permeability and high mechanical strengths. Using SS as binder combined with gypsum in 1/16 gypsum/ SS ratio, Wang et al. [161] developed a block with compressive strength of 32 MPa and 12% of CO<sub>2</sub> uptake after 28 days of carbonation. Chang et al. [162] also used accelerated carbonation as a curing method and SS as a binder and foaming agent to develop aerated blocks successfully. Duan et al. [163] replaced 25 wt% of cement by SS powder in a ternary system (PC/FA/SS) aiming to develop an enhanced block. They found that the SS incorporation increased the compressive strength by 25.6% and reduced the water absorption by 36%, thus transforming the SS in a viable raw material for the production of construction block [163].

The application of SS into preparing ceramics was also evaluated by some researchers ([165–168]). A glass–ceramic was successfully synthesized by Zhang et al. [165] and Deng et al. [168] using SS as the primary raw material. Both studies developed a high-performance material with flexural/bending strength as 137 MPa and 176 MPa. Zong et al. [166] effectively produced a porous ceramics using high-alumina FA and SS (6:4 ratio) as raw materials by firing at 1170 °C and obtained a material with a porosity of 49.21% and flexural strength of 12.88 MPa. Teo et al. [167] evaluated the use of SS in combination with clay to produce ceramic tiles. They found that a formulation of 50% wt. SS and 50% wt. clay fired at 1180 °C yielded a ceramic tile with lower water absorption (0.16%), lower apparent density (0.48%) and higher modulus of rupture (92.4 MPa) compared with a neat clay tile.

Zhao et al. [169] studied BOF SS as binder replacement in masonry autoclaved paste. They found that the pore structure was coarsened with the SS insertion, and the thermal conductivity and thermal diffusivity decreased. The authors also observed a significantly compressive strength reduction ~ 70% at 20 wt—% of replacement of FA by SS [169].

### 2.3.9. Alkali-Activated materials

Alkali-activated materials (AAM) have been widely discussed, studied and promoted as greener binders for sustainable constructions [170]. AAM are alternative binders derived by the reaction of aluminosilicates sources with an alkaline solution [31]. Those materials are known to offer benefits such as (i) low-CO<sub>2</sub> footprint by valorizing waste materials; (ii) high mechanical performance, including rapid strength development; (iii) good performance under fire conditions; (iv) potentially low

permeability and high chemical resistance and (v) good adhesion to many substrates and the possibility to encapsulate problematic wastes [171–174]. The most commonly used alkali sources are the hydroxides or silicates of sodium or potassium (called as “alkali activator”), which are mostly provided in aqueous form and combined with a solid (powdered) aluminosilicate precursor to produce the AAM binder [171,175]. Recently, solid activator has been explored to produce “one-part” AAM [176]. This development is considered an essential step in tackling technical issues on handling large amounts of activator solutions, such as its viscosity, corrosivity, and hazardousness [177,178]. However, the first examples of “one-part” AAM have reached little commercial use [179], probably due to the often-slow strength development [170]. Commonly used aluminosilicate powders include blast furnace slag (BFS), pulverized fly ash (FA), calcined clays such as metakaolin (MK), glass waste and the combinations of two or more of these materials [171,180].

According to Provis and Van Deventer [171], the easiest way to classify alkali-activated binder structures is the binder’s calcium content, which plays an essential role in defining the type of gel that controls the structure. The reaction products (Fig. 3) are either an alkali aluminosilicate-type gel (N-A-S-H) with approximated structure of  $x\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot w\text{SiO}_2 \cdot z\text{H}_2\text{O}$  or a calcium aluminosilicate hydrate-type gel (C-A-S-H) with the approximated structure of  $x\text{Ca}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot w\text{SiO}_2 \cdot z\text{H}_2\text{O}$ ; in both cases,  $x$ ,  $y$ ,  $w$  and  $z$  vary along with the microstructure [31]. The coexistence of both gels can be identified in intermediate calcium systems where blended binders are used, represented by the middle region in Figure 2.3 [171]. Figure 2.4 presents the distinct processes of alkaline activation.

The role of SS in the development of AAM is still far from being clarified or understood by the scientific community. Some studies [181–183] began to evaluate the use of SS as a precursor for AAM and stated that SS showed a potential to act as a cementitious binder. Still, a more in-depth and thorough investigation must take place. SS has been studied as aggregate [184–187] or binder [185,188–199] in alkali-activated pastes, mortars, or concretes (see Table 2.4), as discussed in the following sections.

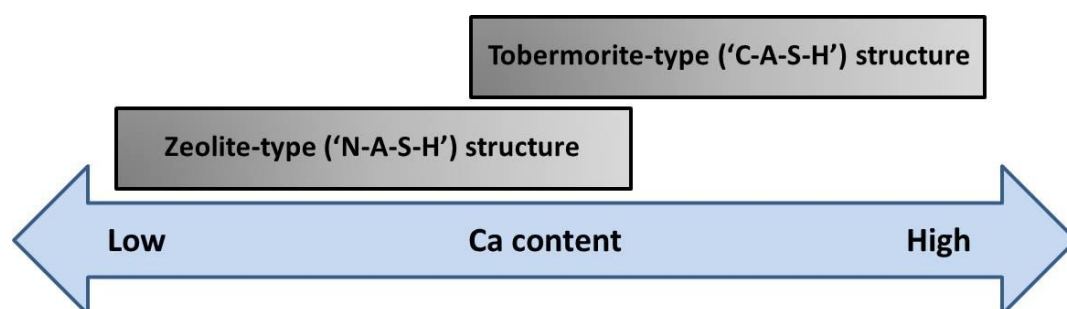
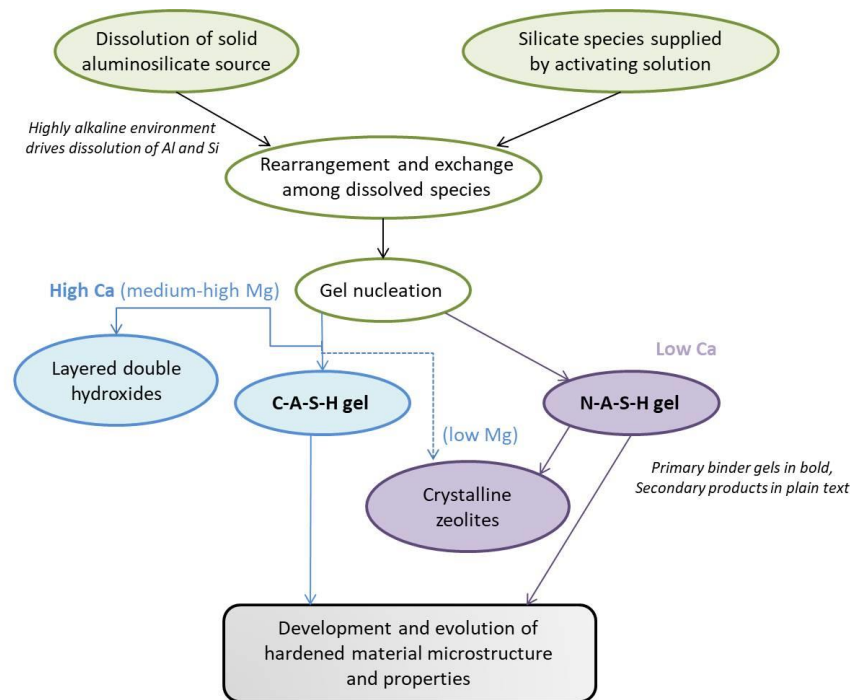


Figure 2.3 - Gel types present in alkali-activated binder systems as a function of calcium content.  
Adapted from Provis and Van Deventer [171].



**Figure 2.4 - Schematic process and reaction products of alkaline activation. Adapted from Provis and Van Deventer [171].**

#### 2.3.9.1. SS as aggregate in AAM

Manjunath et al. [187] studied SS as coarse aggregate (<12.5 mm) to develop high performance, self-compacting BFS-based alkali-activated concrete. They evaluated the rheological properties, the mechanical performance (compressive and flexural strength and modulus of elasticity) and the microstructure. The authors pre-processed the aggregate to reduce expansions due to the free lime presence. They settled the % of Na<sub>2</sub>O in the mixtures between 5 and 7% wt. to BFS, to avoid leaching of alkalis, observed in percentages higher than 8%. They used sodium phosphate as setting retarder and a water-reducing admixture to ensure the self-compacting properties [187]. According to their findings, a novel, greener, eco-friendly, and high-performance concrete (slump ~ 750 mm compressive strength ~ 80 MPa, flexural strength ~ 7 MPa, modulus of elasticity ~ 32 GPa, water absorption ~ 3%) was successfully developed with the use of 100% of SS as coarse aggregate [187].

Van Dao and Trinh [186] on the other hand, employed 100% SS as both fine (0.15 mm < x < 4.75 mm) and coarse (4.85 mm < x < 19 mm) aggregate into a FA based alkali-activated concrete. They evaluated the mechanical performance (compressive and flexural strength and modulus of elasticity) and the SS's influence in the microstructure at the interface transition zone (ITZ). Satisfactory mechanical performance was achieved, i.e. compressive strength ~ 40 MPa, flexural strength ~ 5 MPa and modulus of elasticity ~ 31 GPa. The authors also observed a chemical reaction between the SS and the alkali-activated matrix at the ITZ, which improved the bond and consequently, the mechanical properties [186].

### 2.3.9.2. SS as a binder in AAM

The potential of SS utilization as an alternative binder for AAM has been drawing more attention from researches recently than only as aggregate. Bai et al. [188] and Furlani et al. [193] assessed the role and the influence of SS on the mechanical properties and microstructure of blended pastes with alkali-activated MK. The former investigated different curing methods, compressive and flexural strengths, acid and alkali resistance and microstructure performance. They used ground SS with particle size below 75  $\mu\text{m}$ ,  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio equal to 2.80 in the activator and MK replacement levels of 10%, 20% and 30% wt. According to their findings, SS provided satisfactory performance improvement compared to neat MK-based alkali-activated paste: (i) higher early-age mechanical resistance and (ii) microstructure enhanced by the chemical interaction between SS particles and the matrix [188]. In the study of Furlani et al. [193] two particle sizes of SS (<150  $\mu\text{m}$  and < 250  $\mu\text{m}$ ) were investigated as MK replacement (20%, 40%, 60%, 80% and 100% wt.) using a  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio in the activator equal to 2.84. Results have shown that 40% wt. SS (optimum amount) increases the workability, strongly reduces the water absorption and cracks in the microstructure of the pastes. Moreover, a higher compressive strength was achieved with this percentage of replacement (40%), i.e. 67 MPa against 48 MPa of the neat MK activated paste [193].

Chen et al. [199] investigated the fresh (heat of hydration and setting time), mechanical (compressive strength) and durability properties (leachate of hazardous elements) of a ternary alkali-activated paste using MK, SS and also FA. They evaluated a wide range of combinations of the three binders (0–100 wt% of each one), different sodium solution molarities and a fixed  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio in the activator of 1.12. The best performance was achieved for a matrix with 67% FA, 30% SS and 3% MK (compressive strength ~ 65 MPa). This matrix was said to favour the early hydration process, delays the setting time and effectively immobilizes heavy metals [199].

The studies of Guo and Pan [192], Song et al. (2019b) and Guo and Yang (2020) evaluated the influence of SS in the development of alkali-activated pastes and mortars predominantly made with FA. In Guo and Pan (2018) research, the focus was to understand the influence of different fibres in the mechanical and microstructural properties using a single mortar composed by a mix of 70/30 wt% FA/SS with 10% of  $\text{Na}_2\text{O}$  to binder ratio and 2.5 aggregate to binder ratio. They developed a mortar with great mechanical characteristics (compressive strength ~ 35 MPa and flexural strength ~ 7 MPa). Still, they lacked physical and durability analysis [192]. Song et al. [196] and Guo and Yang [191] studied several rates of FA replacement by SS, i.e. 10%, 20%, 30%, 40% and 50% wt. and 7%, 14%, 21% and 28%, respectively. Both aimed to understand the role of SS in a blended alkali-activation process and its influence in various properties. The studies determined 20–21% of replacement as the SS's optimum content in the development of a blended alkali-activated paste. Besides, they found that SS increases the bulk density, the setting time and the workability while decreasing viscosity of the mixture [196]. Water absorption and apparent porosity are

also increased [191,196]. At the same time, the early age strength growth decreased [196], unlike the results in blended MK/SS pastes [193]. The good self-healing effect due to C-S-H and N-A-S-H gel [191] was also mentioned as positive effects, even though larger amounts of SS decreased the mechanical strength and increased the average pore diameter of the matrix [196].

You et al. [189] investigated the influence of 50 wt% substitution of BFS by SS and compared its performance with a neat BFS based AAM and a PC mortar. The authors used 4% Na<sub>2</sub>O to binder ratio, 1.5 SiO<sub>2</sub>/Na<sub>2</sub>O ratio in the activator, 0.5 solution to binder ratio and 2:1 aggregate to binder cured at ambient conditions; they were able to assess several properties and concluded that the incorporation of SS: (i) increases fluidity and the setting time by decreasing the hydration heat; (ii) decreases early age strength due to its low reactivity compared to BFS; (iii) slightly decreases strength but still achieved 65 MPa compressive strength and 10 MPa flexural strength; (iv) increases total porosity; and (v) significantly reduces autogenous and drying shrinkage, thus having a superior performance compared to PC mortars [189].

Neat SS based AAM was also studied to understand the activation process of this solid waste and promising results were reported for SS as binding material. Ozturk et al. [194] evaluated the influence of different silicate modulus (1.0, 1.5 and 2.0) and sodium concentrations (4%, 6% and 8%) on the compressive and flexural strengths and microstructure of several AAM mortars. According to the authors, the optimum dosage is 6% of NaOH with 2.0 of silicate modulus, achieving ~ 22 MPa compressive strength and ~ 4 MPa flexural strength. Also, a significant amount of C-SH gel and CaCO<sub>3</sub> as hydration products were identified in the matrix confirming the reactivity of SS [194]. Similar hydration products were found in the study of Sun and Chen [195] when using 2.0 silica modulus and 4% of NaOH. The authors also concluded that the hydration heat and the pore size tend to reduce when silica modulus is 2.0 [195].

Morone et al. [197] and Liu et al. [198] also employed sodium hydroxide and sodium silicate as activators, when studying the development of SS based alkali-activated paste. A low pozzolanic behaviour compared to amorphous materials such as BFS was identified by Morone et al. [197] despite the formation of C-S-H like gel and 6% CO<sub>2</sub> uptake after an accelerated CO<sub>2</sub> curing regime. Additionally, Liu et al. [198] concluded that the calcium silicates (C<sub>2</sub>S and C<sub>3</sub>S) present in the SS composition dissolved under alkaline conditions, thus emerging amorphous phases that generate NA-S-H and C-A-S-H type gels in the matrix. Differently from all previously cited studies, Cesnovar et al. [190] used a potassium silicate as activator solution and highly amorphous SS (56%) to evaluate the curing regime's influence in the mechanical performance of a SS based paste. The authors managed to develop a high-performance material with structural characteristics, i.e. compressive strength of 40 MPa and flexural strength of 15 MPa [190].

### 2.3.9.3. SS as both binder and aggregate

The studies of Lu et al. [184] and Cristelo et al. [185] went even further. They evaluated SS as fine aggregate and also as a binder in the development of an alkali-activated mortar. Lu et al. [184] replaced BFS by 20% wt. of SS, used a 4% Na<sub>2</sub>O, SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio equals to 1.0 in the activator, 0.47 solution to binder ratio and a 2.35:1 aggregate to binder ratio. The authors found that SS in AAM matrices enhances the volume stability and causes no deleterious effect, unlike in cement-based matrices. Besides, the presence of SS decreases the average pore size and maintain the mechanical strength in acceptable values (~35 MPa) [184]. On the other hand, Cristelo et al. [185] firstly evaluated the SS as a potential binder in alkali-activated pastes by replacing FA in different amounts (25%, 50%, 75% and 100%) and using only sodium hydroxide solution as an activator. In a second part of the investigation, the influence of SS as fine aggregate was evaluated in two different mortars (100% FA and 50%/50% FA/SS as binders). Pastes and mortars were assessed by compressive strength, mineralogical and microstructural analysis [185]. The experimental results showed that, as a binder, the SS reacts with the alkaline solutions to form C-A-S-H and C, N-A-S-H type gels, yielding compressive strength ~ 15–28 MPa. As aggregate, SS enhanced the mechanical performance compared to natural aggregate, (22–28 MPa mortar compressive strength for the former) by improving the bond between aggregate particles and matrix [185].

Table 2.5 summarizes the main findings in the literature cited in section 3.9, regarding the use of SS in AAM matrices combined with other binders (MK, FA and BFS) [184–189,191–193,196,199]. Additionally, other studies focused their investigation in the understanding of the role of SS as a single binder in an AAM matrix and their main findings are summarized below:

- A significant amount of C-S-H gel and CaCO<sub>3</sub> formed as hydration products, confirming the viability as binding material [194,195,197];
- Best SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio in the activator is 2.0–2.3, where hydration heat and pore size were reduced [194,195,197];
- Calcium silicates (C<sub>2</sub>S and C<sub>3</sub>S) present in the SS composition dissolve under alkaline conditions, generating N-A-S-H and CA-S-H gels [198].

**Table 2.4 - Recent studies of the use of SS into AAM.**

| Reference              | Type             | SS used as               | Particle size          | Treatment                      | Main binder | Replac./Usage wt. %    | Activators                                              | % Na <sub>2</sub> O / binder | SiO <sub>2</sub> /Na <sub>2</sub> O activator | w/b or s/b   | a/b    | Curing regime                   | Test methods                                                               |
|------------------------|------------------|--------------------------|------------------------|--------------------------------|-------------|------------------------|---------------------------------------------------------|------------------------------|-----------------------------------------------|--------------|--------|---------------------------------|----------------------------------------------------------------------------|
| Bai et. al. [188]      | Paste            | Binder                   | > 75 µm                | Grinded                        | MK          | 10, 20, 30             | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.3) + NaOH       | NS                           | 2.8                                           | 0.93         | -      | Different types                 | Compressive and flexural strength, acid and alkali erosion, FTIR, SEM, XRD |
| Guo and Pan [192]      | Mortar           | Binder                   | 400 m <sup>2</sup> /kg | NS                             | FA          | 30                     | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 1.5) + NaOH       | 10                           | NS                                            | 0.4          | 2.5:1  | Ambient conditions              | Compressive and flexural strength, fiber distribution, BET                 |
| Furlani et. al. [193]  | Paste            | Binder                   | > 150 and 250 µm       | Milled                         | MK          | 20, 40, 60, 80, 100    | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 2.94) + NaOH (8M) | NS                           | 2.84                                          | Varies       | -      | 60°C                            | Compressive strength, water absorption, BET, SEM                           |
| Lu et. al. [184]       | Mortar           | Binder<br>Fine aggregate | > 0.15 mm<br>> 4.75 mm | Crushed and magnetic separated | BFS         | 20<br>100              | Na <sub>2</sub> SiO <sub>3</sub> + NaOH                 | 4                            | 1.0                                           | 0.47         | 2.35:1 | Autoclaved                      | Compressive strength, volume stability, XRD, MIP                           |
| Cristelo et. al. [185] | Paste and mortar | Binder<br>Fine aggregate | > 80 µm<br>> 4.85 mm   | Milled                         | FA          | 25, 50, 75, 100<br>100 | NaOH (8M)                                               | NS                           | -                                             | 0.28<br>0.35 | 3:1    | 85°C<br>99% RH                  | Compressive strength, XRD, SEM/EDX                                         |
| Ozturk et. al. [194]   | Mortar           | Binder                   | > 45 µm                | Milled and magnetic separated  | SS          | 100                    | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.19) + NaOH      | 4, 6 and 8                   | 1.0, 1.5 and 2.0                              | 0.485        | 2.75:1 | 40°C and 80°C<br>45% and 98% RH | Compressive and flexural strength, XRD, SEM/EDX                            |

|                         |                  |                  |                                     |                                |                 |                    |                                                    |            |                        |             |        |                    |                                                                                                                                                   |
|-------------------------|------------------|------------------|-------------------------------------|--------------------------------|-----------------|--------------------|----------------------------------------------------|------------|------------------------|-------------|--------|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Sun and Chen [195]      | Paste            | Binder           | 624m <sup>2</sup> /kg ; d50: 6.3 µm | NS                             | SS              | 100                | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.12) + NaOH | 4.0        | 0.5, 1.0, 1.5 and 2.0  | 0.45        | -      | 25°C > 90% RH      | Compressive strength, SEM/EDX, calorimetry, TG, MIP                                                                                               |
| Song et. al. [196]      | Paste            | Binder           | d50: 22 µm                          | NS                             | High-calcium FA | 10, 20, 30, 40, 50 | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.28) + NaOH | NS         | 1.6                    | 0.65        | -      | 20±4°C 95% RH      | Fresh properties, compressive and flexural strength, elasticity modulus, sorptivity, XRD, SEM, EDS, MIP                                           |
| Morone et. al. [197]    | Paste and mortar | Binder           | > 2mm ; d50: 350 µm                 | Crushed and magnetic separated | SS              | 100                | Na <sub>2</sub> SiO <sub>3</sub> + NaOH (2M or 4M) | NS         | 0.85, 1.4, 1.7 and 2.3 | 0.2 and 0.3 | 3.33:1 | Different types    | Compressive strength, calorimetry, XRD, MIP, DTG, CO <sub>2</sub> uptake                                                                          |
| Liu et. al. [198]       | Paste            | Binder           | 440 m <sup>2</sup> /kg              | Crushed and grounded           | SS              | 100                | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 2.42) + NaOH | NS         | NS                     | 0.263       | -      | 60°C               | Calorimetry, XRD, SEM, EDS, TEM, FTIR                                                                                                             |
| Manjunath et. al. [187] | Concrete         | Coarse aggregate | < 12.5 mm                           | Pre-processed                  | BFS + QP        | 100                | Na <sub>2</sub> SiO <sub>3</sub> + NaOH            | 5, 6 and 7 | 1                      | 0.40 - 0.44 | 1.7:1  | Ambient conditions | Rheological properties, compressive and flexural strength, elasticity modulus, water absorption, XRD, SEM/EDX                                     |
| Chen et. al. [199]      | Paste            | Binder           | > 80 µm                             | Milled                         | MK + FA         | 0 - 100            | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.3) + NaOH  | NS         | 1.12                   | 0.33        | -      | Ambient conditions | Fresh properties, compressive strength, XRD, SEM, XPS, TCLP, ICP-MS                                                                               |
| You et. al. [189]       | Mortar           | Binder           | 370m <sup>2</sup> /kg ; d50: 10 µm  | NS                             | BFS             | 50                 | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 3.31) + NaOH | 4          | 1.5                    | 0.5         | 2:1    | 20±3°C 55±3% RH    | Fresh properties, calorimetry, compressive and flexural strength, autogenous and drying shrinkage, chloride diffusion, water absorption, MIP, BET |

| Cesnovar et. al. [190]  | Paste    | Binder                             | > 63 $\mu\text{m}$ ; d50:<br>6 $\mu\text{m}$ | Milled  | SS | 100           | K <sub>2</sub> SiO <sub>3</sub>                   | -  | -  | 0.5 | -     | Different types                 | Compressive and flexural strength, SEM/EDX, FTIR, MIP                           |
|-------------------------|----------|------------------------------------|----------------------------------------------|---------|----|---------------|---------------------------------------------------|----|----|-----|-------|---------------------------------|---------------------------------------------------------------------------------|
| Guo and Yang [191]      | Paste    | Binder                             | 400 m <sup>2</sup> /kg                       | NS      | FA | 7, 14, 21, 28 | Na <sub>2</sub> SiO <sub>3</sub> (Ms: 1.5) + NaOH | NS | NS | 0.5 | -     | Different types                 | Compressive strength, apparent density, tensile strength-strain, crack analysis |
| Van Dao and Trinh [186] | Concrete | Fine aggregate<br>Coarse aggregate | 0.15 mm < x < 4.75 mm<br>4.85 mm < x < 19 mm | Crushed | FA | 100           | Na <sub>2</sub> SiO <sub>3</sub> + NaOH (12M)     | NS | NS | NS  | 4.7:1 | 22 $\pm$ 4°C<br>60 $\pm$ 20% RH | Compressive and flexural strength, elasticity modulus, SEM                      |

MK: metakaolin, FA: fly ash, BFS: blast furnace slag, SS: steel slag, QP: quartz powder, Ms: modulus of silica, NS: not specified. w/b: water to binder ratio, s/b: solution to binder ratio, a/b: aggregate to binder ratio

**Table 2.5 - Summary of the influence of SS incorporation in AAM matrices.**

| Properties             | Main binder | MK           |           | FA           |           | BFS          |           |
|------------------------|-------------|--------------|-----------|--------------|-----------|--------------|-----------|
|                        | SS used as  | Binder       | Aggregate | Binder       | Aggregate | Binder       | Aggregate |
| Hydration heat         |             | -            | -         | -            | -         | decrease     | -         |
| Setting time           |             | -            | -         | increase     | -         | increase     | -         |
| Viscosity              |             | -            | -         | decrease     | -         | -            | -         |
| Workability            |             | increase     | -         | increase     | -         | increase     | -         |
| Early age strength     |             | increase     | -         | decrease     | -         | decrease     | -         |
| Bond ITZ               |             | increase     | -         | -            | increase  | -            | -         |
| Bulk density           |             | -            | -         | increase     | -         | -            | -         |
| Water absorption       |             | decrease     | -         | increase     | -         | -            | -         |
| Porosity               |             | -            | -         | increase     | -         | increase     | -         |
| Average size pore      |             | -            | -         | increase     | -         | decrease     | -         |
| Microcracks            |             | decrease     | -         | -            | -         | -            | -         |
| Shrinkage              |             | -            | -         | -            | -         | decrease     | -         |
| Volume stability       |             | -            | -         | -            | -         | increase     | -         |
| Mechanical performance |             | satisfactory | -         | satisfactory | increase  | satisfactory | increase  |

## 2.4. Potential, challenges, and future perspectives for civil engineering constructions

This section presents important topics concerning the potential and challenges found so far for the proper utilization of SS, emphasizing construction materials such as PC-based materials and AAM. The future perspectives and research needs are also discussed, focused on the development of AAM using SS as raw material.

### a. Economic and legal aspects

SS is already employed in agriculture, road construction and other civil engineering applications, but most established in countries like Japan and the USA. In contrast, the scenario is different in several countries, including the biggest producer, China. The developing countries also have a vast growth market. According to the World Resources Institute, the current world housing deficit is estimated to be equivalent to 17% of the global population [200]. According to the World Economic Forum, the infrastructure investment gap by 2040 will be around 15 trillion dollars [201].

Given the high amount of SS generated every year, enough raw material would meet the demand as an alternative material for different industrial processes. Besides, several application developments are needed, so that the consumption comes close to the generated volume. The application of SS in AAM development emerges as a sustainable solution for this environmental issue. It is not more advantageous than other applications. It is another one to help reduce the environmental burden faced by the steel industry.

Governmental legislation may be one of the significant challenges for the large scale reuse of SS in some countries, where a clear definition and differentiation should occur

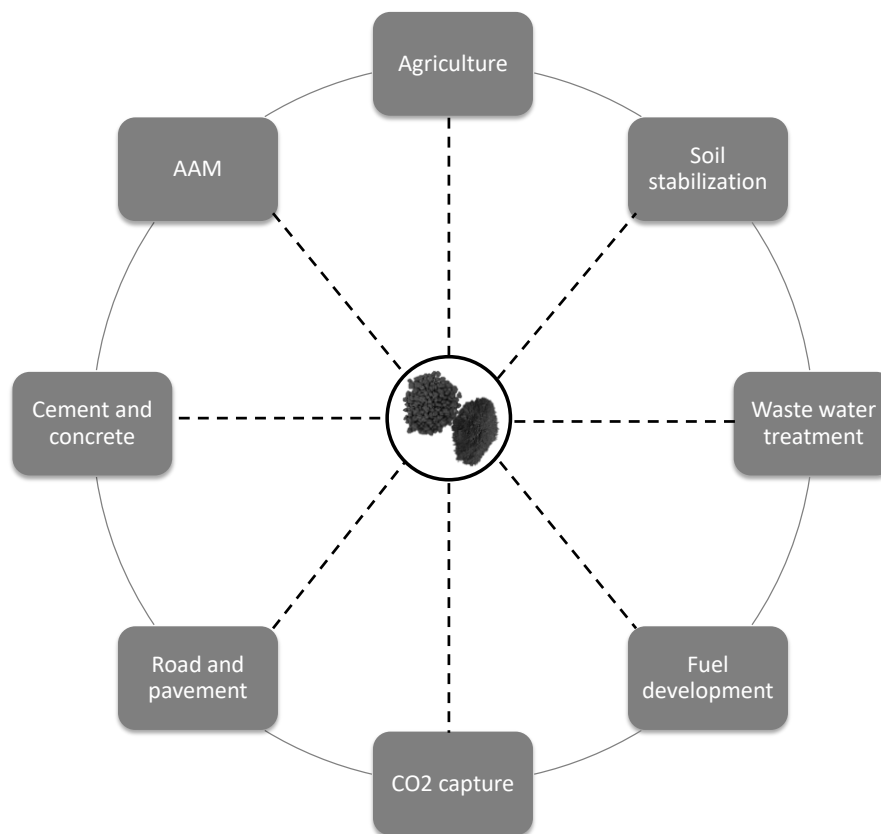
between byproducts/co-products and wastes/residues. Instead of tax incentives, stricter regulations sometimes are applied to the use of SS, as the latter is perceived as an immutably alkaline and expansive material. The steel companies must also be more proactive; they know the importance of SS treatment and processing to provide valuable raw material for other applications [26]. However, this industry is mainly focused on its core business and operations; the valorization of SS must be treated as a priority not only by plant managers but also for R&D projects [202].

#### b. Technical aspects

Nevertheless, numerous studies have been showing positive results for developing new routes and applications for this important industrial waste (SS). The previous section in this chapter highlighted the different and unrelated fields of utilization, such as agriculture, soil stabilization, wastewater treatment, fuel development, CO<sub>2</sub> capture, and civil engineering applications like road and pavement, PC and concrete productions, construction materials and AAM (Figure 2.5). Some of these areas have a more defined understanding of the fundamental characteristics and properties of the SS, probably because the studies and industrial utilization started earlier and are now well established.

The studies on the use of SS in cement and concrete (section 3.7) present some challenges and research needs. As a binder replacement, SS decreases the early age strength [114,119,120,122], which will then compromise the application for the precast industry. Besides, inconsistent results are found for the matrix porosity and permeability to chloride penetration. The literature is scarce and lacks studies on durability properties. As an aggregate replacement, SS decreases workability [123,124,130,138], thus negatively affecting pastes and concretes' fresh properties. Results on expansion rate and dimensional stability of the materials are highly inconsistent. Only a few studies discussed the effects of SS aggregate on durability properties. Single research presented that the shrinkage decreases with the employment of SS [128]. Moreover, it is a consensus in the literature that a treatment process before using SS is needed; this is also poorly addressed in recent studies.

The studies on SS for the development of AAM (section 3.9) present a clear consensus between the authors about the viability and potential use of SS as a binding material and aggregate in AAM (Figure 2.6). However, the number of publications is again scarce to establish concrete conclusions. In the limited literature available, SS may be an option to replace natural resources (sand, gneiss, clay minerals) and other industrial byproducts with already have established recycling routes (BFS, FA).



**Figure 2.5 - Potential applications for SS reuse.**

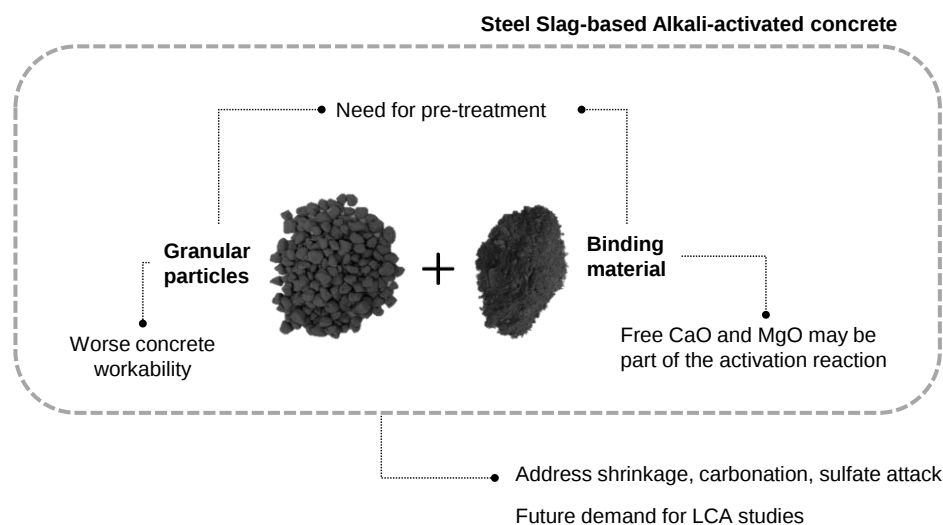
The variable chemical and morphological composition directly impact the SS reactivity; the former is likely to be the significant challenges in AAM development. The free unhydrated CaO and MgO that potentially expand in PC-based materials [21,26,139] may be part of the alkali-activated reaction, and the potential volume expansion minimized [182,184,190,194]. Some contradictory results concerning the AAM final properties confirm the need for a more in-depth and thorough investigation.

The low quantity of studies to fully understand and validate the real influence of SS on AAM properties endorses that this is still a new topic of investigation among researchers. As for PC-based materials, the SS prior treatment process and parameters are essential but poorly investigated for AAM matrices. Studies combining SS as a binder and aggregate in AAM matrices are scarce and a new promising topic [184,185]. They maximize the incorporation of SS in the final product. Future research should address this approach. Another research need is the possibility to use SS to develop one-part AAM. One-part AAM is a recent topic of investigations [176–179]. However, no publication concerning the employment of SS was found in the literature.

AAM has proven to be more durable than PC-based materials; this is valid for low-calcium based AAM, also known as geopolymers [171]. The composition of SS is somehow different, and the durability issues may be compared with alkali-activated BFS. In other words, shrinkage, carbonation, sulfate attack need to be assessed for

SS-based AAM as well. Presently, SS incorporation may reduce shrinkage [189] and increase the volume stability [184] of AAM; nothing else was investigated regarding durability.

Finally, life cycle assessment (LCA) should also be an object of future research. The environmental impact of AAM has continuously been discussed, and the ecological benefits questioned [203–208]. SS will likely have a low environmental impact for some countries and under some conditions (proximity to the SS generation). The geographic location is paramount to establish this alternative route for SS.



**Figure 2.6 - Application of SS as binding material and aggregates in AAM.**

## 2.5. Concluding remarks

This chapter presented a review of the recent studies on utilizing steel slag in different applications and future perspectives for its use in alkali-activated materials. The main objective was to understand the big picture of the potential reuse of steel slag and present the state-of-art of steel slag as binding material and aggregate in alkali-activated materials matrices and some challenges and research needs. Some conclusions are:

- Some industrial application is well established for steel slag. It has a great filling capacity as fertilizer and improves the stability and characteristics of soils. The applications in agriculture and road construction have started earlier. More recently, steel slag has been considered a good filtering material for wastewater treatment, removing heavy metals such as Fe, Mn and Cd.
- For civil engineering applications, steel slag brings positive results when replacing natural aggregates in flexible pavements. The former improves the mechanical properties and self-healing capacity compared to natural aggregates. Concrete pavements may be more durable (higher mechanical strength and lower permeability) when finely ground steel slag replace Portland

cement in rigid pavements. Much of the recent literature focuses on the use of steel slag for CO<sub>2</sub> mineralization; Ca and Mg carbonates with binding properties are formed due to the reaction of free CaO and MgO with CO<sub>2</sub> and alternative building materials as masonry blocks and pavers may be developed.

- The significant challenges for steel slag application in Portland cement-based materials continue to be the potential volumetric expansion and the low reactivity, thus decreasing the mechanical strength. The steel industry must improve the steel slag process and deliver a valuable raw material for this particular application. The use of steel slag as aggregate in Portland cement-based materials negatively affects fresh properties, thus requiring a better evaluation of the particle size distribution. In general, the great uncertainty for large-scale use of steel slag in Portland cement-based materials results from the limited thorough studies on durability.
- The research on steel slag-based alkali-activated materials is incipient. It has controversial results, where steel slag mostly replaces other binders (metakaolin, fly ash, blast furnace slag). Other preliminary studies using SS as aggregate present no adverse effect on the alkali-activated materials final properties; on the contrary, steel slag seems to improve the bond at the interfacial transition zone. Similarly to Portland cement-based materials, the main challenge facing steel slag use in alkali-activated materials is the low reactivity. However, the formation of N-A-S-H and C-A-S-H gels through calcium silicates dissolution has been reported as an excellent indicative. The lack of studies combining steel slag as a binder and aggregate in alkali-activated material matrices, combined with durability studies, present a great research opportunity. These topics need to be addressed to establish concrete conclusions concerning this alternative application of steel slag.

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### **3. METHODOLOGY**

### 3.1. Introduction

The experimental program proposed in this thesis is divided into three main investigation parts, as previously presented at Figure 1.1. First, the research focused on the activation parameters and their effect on several properties of SS-based AAM pastes. The main objective was to validate the SS as precursor in AAM. Secondly, the investigation concerned the pre-treatments of the SS aggregate and their effect on various properties of the developed mortars. In a third part, a comparative study was carried out between a AAM mortar developed with 100% of SS as precursor and aggregate with other GGBFS-AAM and PC mortars.

This chapter will present a detailed overview of all raw materials used during the research, a description of the specimens' preparation, and a description of all test procedures. Figure 3.1 summarizes the materials and methods used for each part of the research.

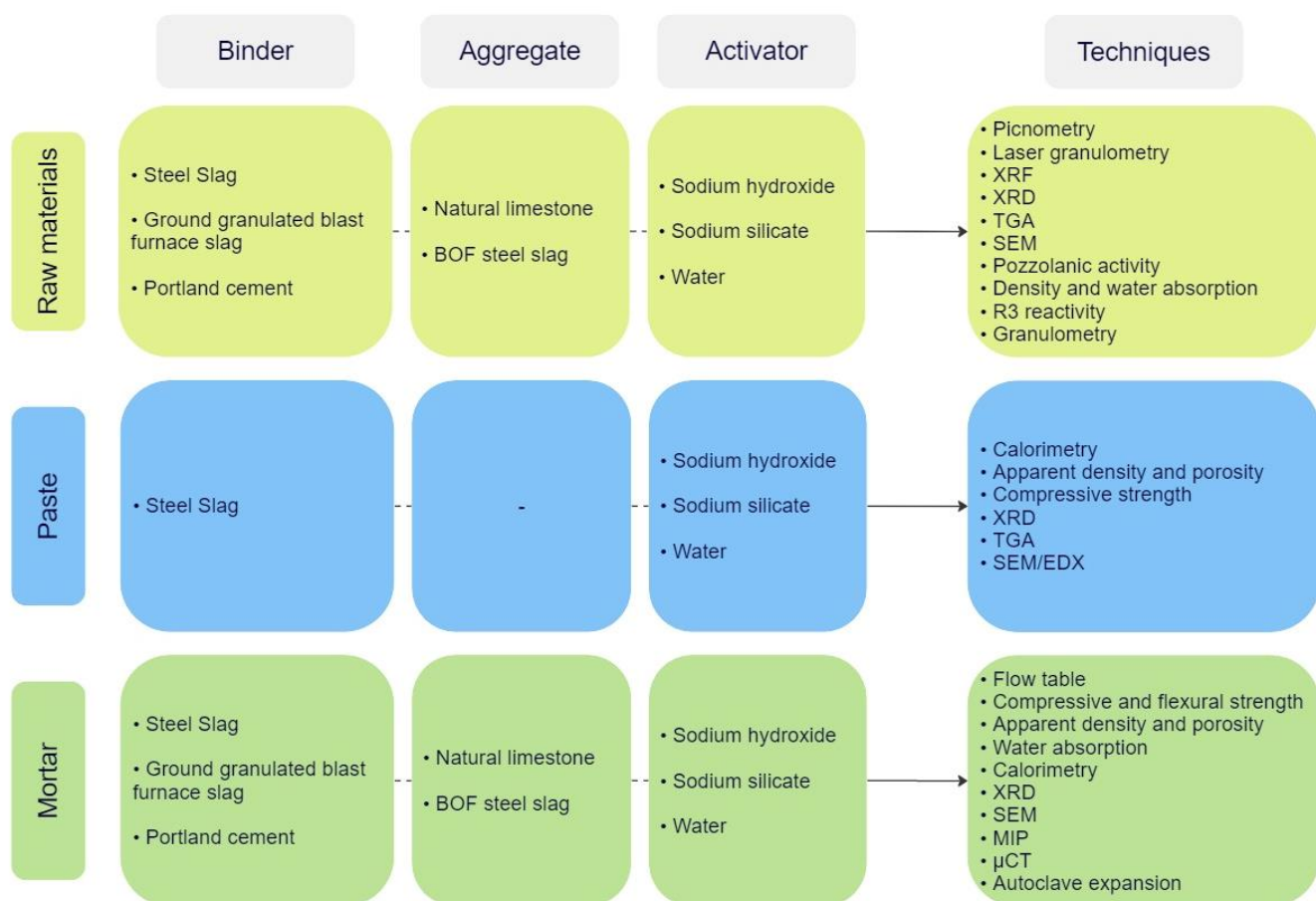


Figure 3.1 – Raw materials and experimental tests used in the research.

## 3.2. Materials

### 3.2.1. Binders

The main precursor used to produce the AAM pastes and mortars was the SS supplied by Gerdau, Brazil. The SS used in this research was a byproduct generated during the conversion of iron into steel in a basic oxygen furnace. The original SS sample had a maximum particle size of 4.8 mm, which was crushed and then ground in a ball mill for 5 hours to achieve a maximum particle size of 75  $\mu\text{m}$ . The SS sample as received and after grinding is presented in Figure 3.2.



Figure 3.2 – SS as received and after grinding.

The chemical composition (Table 3.1) was determined via X-ray fluorescence (XRF) using a Bruker S2 Ranger X-ray spectrometer. The major compounds of SS are CaO (36.66%) and FeO (24.19%), followed by SiO<sub>2</sub> (12.10%) and MgO (10.60%). The alkalinity (CaO / P<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub>) of the SS is 4.14, which favored its hydraulic activity [1], but not necessarily its cementitious behavior (the latter depends on the phases present within the chemical composition) [2]. The mineralogical phases were determined by X-ray diffraction (XRD) using a Shimadzu XRD 7000 diffractometer (scanning speed was 0.30 s/step, the length of each step was 0.02° and the scanning range was 5–80°). Rietveld refinement software (GSAS) was used for the quantitative analysis. The XRD pattern of the SS (Figure 3.3) presents several mineral phases, including larnite (C<sub>2</sub>S), srebrodolskite (C<sub>2</sub>F), brownwillerite (C<sub>4</sub>AF), portlandite (Ca(OH)<sub>2</sub>), calcite (CaCO<sub>3</sub>), quartz (SiO<sub>2</sub>), wustite (FeO) and periclase (MgO). The quantification of each phase is also presented.

Table 3.1 – Chemical composition of SS.

|    | Chemical composition by oxides (%wt.) |       |                  |       |                                |                                |      |                               |                 |
|----|---------------------------------------|-------|------------------|-------|--------------------------------|--------------------------------|------|-------------------------------|-----------------|
|    | CaO                                   | FeO   | SiO <sub>2</sub> | MgO   | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | MnO  | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> |
| SS | 36.66                                 | 24.19 | 12.10            | 10.60 | 3.84                           | 0.10                           | 4.53 | 1.11                          | 0.71            |

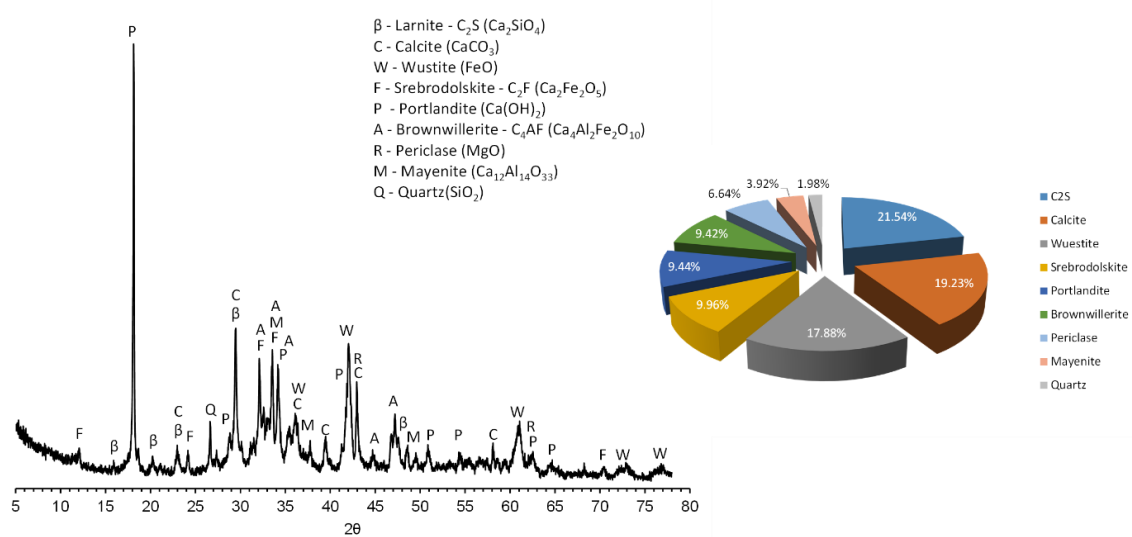


Figure 3.3 – XRD pattern and Rietveld refinement of SS.

TGA-DTA (thermogravimetric analysis coupled with differential thermal analysis) was conducted using a Hitachi STA73000 to identify and quantify the solid phases. The SS was heated from 25 °C to 1000 °C at a heating rate of 10 °C/min in a high-purity nitrogen atmosphere. Figure 3.4 shows the TG and DTG diagrams, which are divided into two main mass loss regions: (i) portlandite dehydroxylation between 350 °C and 450 °C and (ii) calcite decomposition between 600 °C and 800 °C.

The particle size distribution (PSD) of the grinded precursor was obtained via laser granulometry (Cilas 1090 Laser) using the Fraunhofer diffraction theory. The SS powder was dispersed in water (with which SS does not react) with a 60 s ultrasonic bath to increase particle dispersion. Triplicate samples were tested. The grinded precursor presented 100% of particles lower than 75 µm, with 8.11 µm as the mean diameter, as shown in Figure 3.5. The density of the SS measured using helium Pycnometry was 3.18 g/cm<sup>3</sup>.

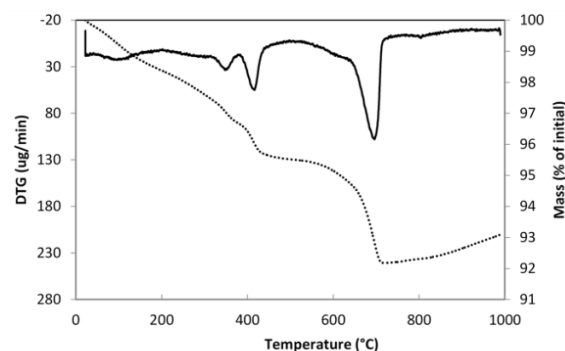
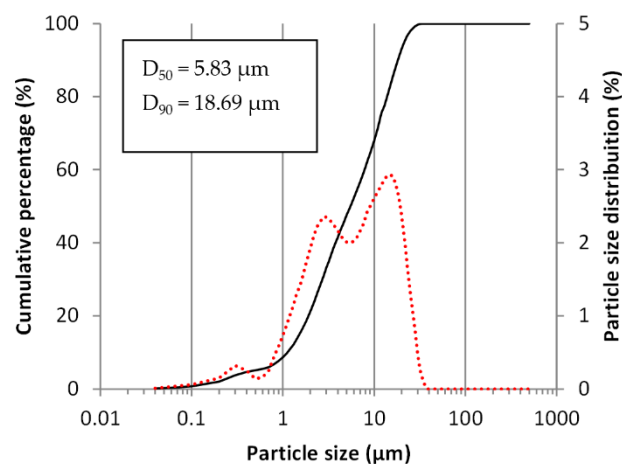


Figure 3.4 – TG (dotted line) and DTG (solid line) diagrams of SS.



**Figure 3.5 – Particle size distribution of SS.**

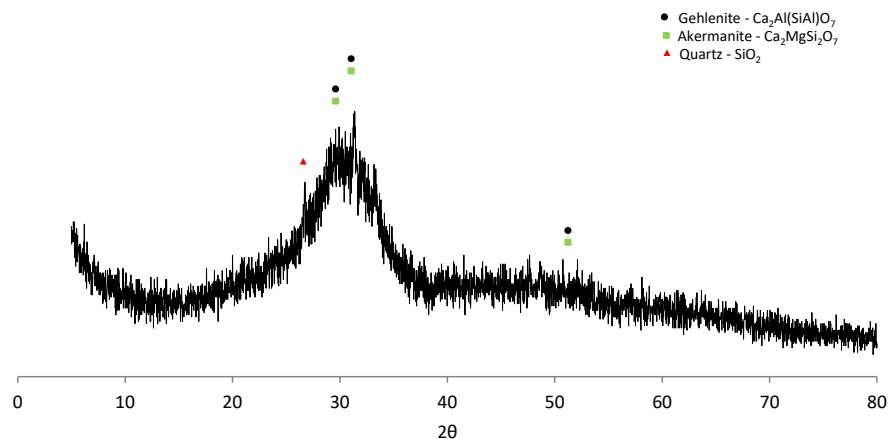
The reactivity of the SS was evaluated by two methods. (i) the standard pozzolanic activity index was determined according to the Brazilian Standard ABNT NBR 5752:2014 [3]. The pozzolanic index is the ratio between the compressive strength at 28 days of a mortar containing 25% wt. of the studied material (herein SS) replacing the Portland cement and the strength of the reference mortar containing 100% of cement. The pozzolanic index of the SS was 67.3%; therefore, it is considered a non-pozzolanic material accordingly to the Brazilian Standard ABNT NBR 12653:2014 [4]; (ii) the modified R3 reactivity test was performed to evaluate the pozzolanic activity of the supplementary cementitious material [5]. It was performed to determine the heat release and calcium hydroxide consumption in a calcium-rich simulated pore solution. The studied SS may have presented a low reactivity based on its amount of heat released and calcium hydroxide consumptions, which were 76 J/g SCM and 16 g/100 g SCM, respectively.

Another aluminosilicate used as precursor to produce AAM mortars was the ground granulated blast furnace slag (GGBFS), supplied by Mizu Cimentos Especiais, Brazil. The chemical composition of GGBFS (Table 3.2) mainly consists of CaO (41.14%) and SiO<sub>2</sub> (33.37%), followed by Al<sub>2</sub>O<sub>3</sub> (14.64%) and MgO (5.57%). Its basicity (CaO/SiO<sub>2</sub>) is 1.23, typical from a basic slag. The mineralogical pattern of the GGBFS is shown in Figure 3.6 and presents a high degree of amorphous material (98.67%) with small peaks of gehlenite, akermanite and quartz. The particle size distribution of GGBFS presented 100% of particles lower than 75 μm with a medium particle size

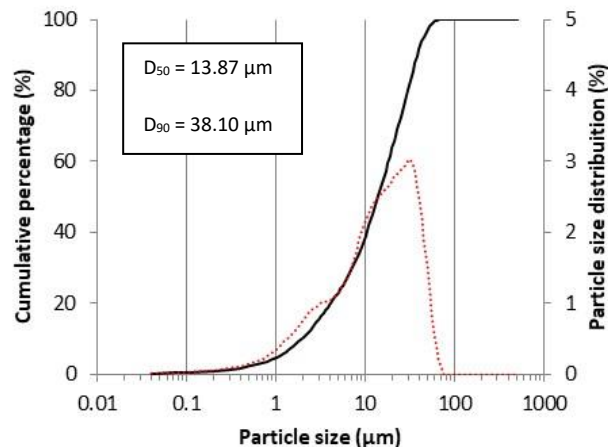
( $d_{50}$ ) of 13.87  $\mu\text{m}$ , as shown in Figure 3.7. The density of GGBFS measured by Helium Pycnometry is 2.92  $\text{g}/\text{cm}^3$ .

**Table 3.2 – Chemical composition of GGBFS.**

|       | Chemical composition by oxides (%) |                  |      |                                |                                |                   |                               |                 |                  |
|-------|------------------------------------|------------------|------|--------------------------------|--------------------------------|-------------------|-------------------------------|-----------------|------------------|
|       | CaO                                | SiO <sub>2</sub> | MgO  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | H <sub>2</sub> O |
| GGBFS | 41.14                              | 33.37            | 5.57 | 14.64                          | 1.13                           | 0.29              | 1.53                          | 1.56            | -                |
|       |                                    |                  |      |                                |                                |                   |                               |                 | LOI              |
|       |                                    |                  |      |                                |                                |                   |                               |                 | 0.50             |



**Figure 3.6 – XRD pattern of GGBFS.**

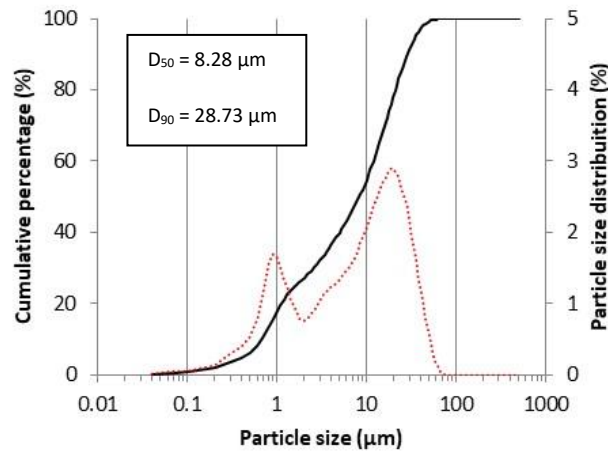


**Figure 3.7 – Particle size distribution of GGBFS.**

Reference Portland cement (PC)-based mortars were produced during the study reported in Chapter 5. A commercial rapid-hardening PC (CPV ARI type in Brazil) supplied by Lafarge-Holcim, commonly used by the prefabrication industry was used. Its chemical composition is presented in Table 3.3, as supplied by the manufacturer. The particle size distribution of the PC also presented 100% of particles lower than 75  $\mu\text{m}$  with a medium particle size ( $d_{50}$ ) of 8.28  $\mu\text{m}$ , as shown in Figure 3.8. The density of PC is 3.26  $\text{g}/\text{cm}^3$ .

**Table 3.3 – Chemical composition of PC.**

| Chemical composition by oxides (%) |       |                  |      |                                |                                |                   |                               |                 |                  |      |
|------------------------------------|-------|------------------|------|--------------------------------|--------------------------------|-------------------|-------------------------------|-----------------|------------------|------|
|                                    | CaO   | SiO <sub>2</sub> | MgO  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | H <sub>2</sub> O | LOI  |
| PC                                 | 62.53 | 18.11            | 0.60 | 4.55                           | 3.28                           | 0.14              | 0.27                          | 2.88            | -                | 5.82 |



**Figure 3.8 – Particle size distribution of PC.**

### 3.2.2. Activators

The alkaline solution used to activate the aluminosilicates (SS and GGBFS) was prepared by mixing commercially available (i) sodium silicate solution (Na<sub>2</sub>SiO<sub>3</sub>, solid content of 47.10%, SiO<sub>2</sub>/Na<sub>2</sub>O of 2.16); (ii) sodium hydroxide (NaOH, 99% purity pellets), both supplied by Getex, Brazil and (iii) water. The activator was prepared by first dissolving the NaOH pellets in water, and since this is an exothermic reaction, it was allowed to cool down prior mixing with the Na<sub>2</sub>SiO<sub>3</sub> solution.

### 3.2.3. Aggregates

Two types of aggregates were used to prepare the mortars: (i) BOF SS and (ii) natural limestone aggregate, as reference. Both are presented in Figure 3.9. The original BOF SS had a maximum particle size of 4.8 mm, and its particle size distribution is presented in Figure 3.10. The natural aggregate was sieved to the same grading of the BOF SS. The density and water absorption of the aggregates were determined according to the Brazilian Standard ABNT NBR 16916:2021 [6]. The BOF SS presented a density of 3.30 g/cm<sup>3</sup> and water absorption of 7.16%, while the natural aggregate has 2.91 g/cm<sup>3</sup> and 0.91%, respectively.

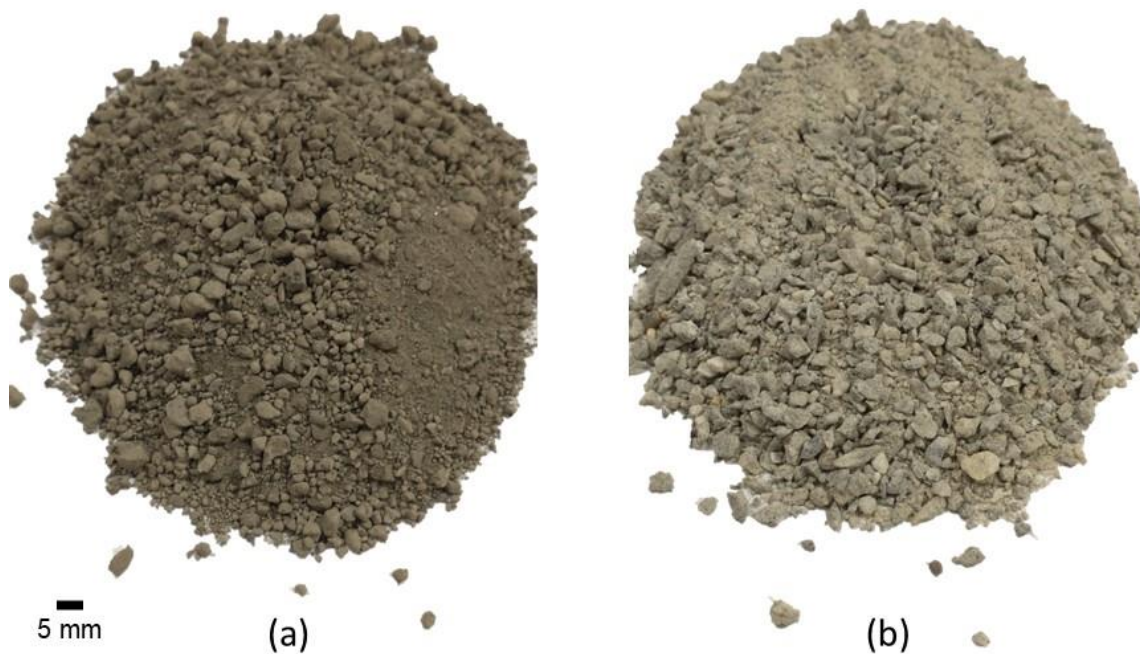


Figure 3.9 – Aggregates used: (a) BOF SS and (b) natural.

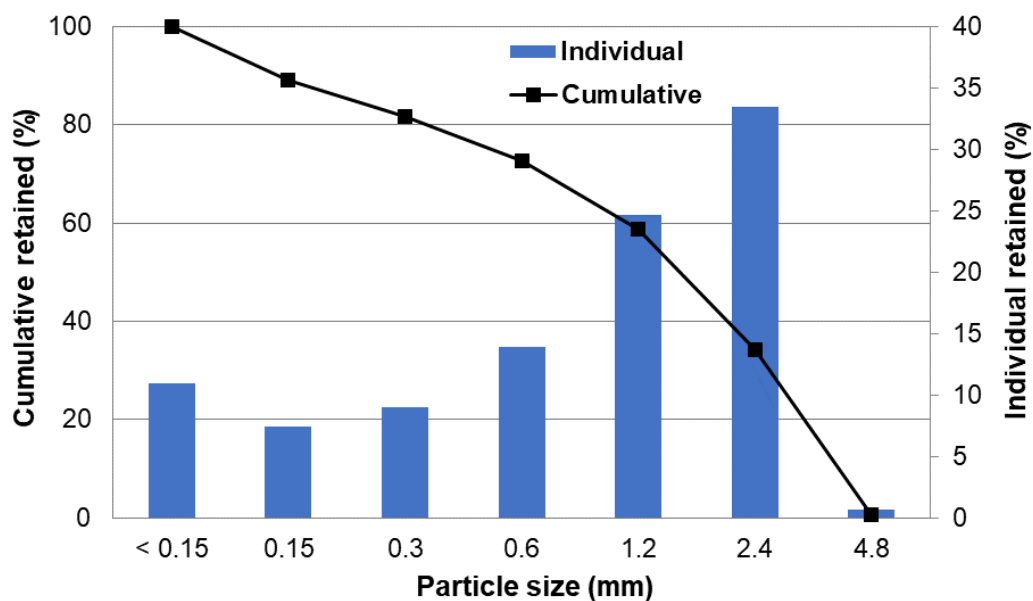


Figure 3.10 – Particle size distribution of the aggregates.

Chapter 5 reports two pre-treatment of the BOF SS aggregate concerning its volumetric instability. Firstly, the aggregate was used as received, without any pre-treatment. In that scenario, it was expected that the soluble  $\text{SiO}_2$  in the alkaline activator used to produce the AAM matrix react with f-CaO and f-MgO of the SS into stable silicates,  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$ , respectively [7]. The pre-treatment methods

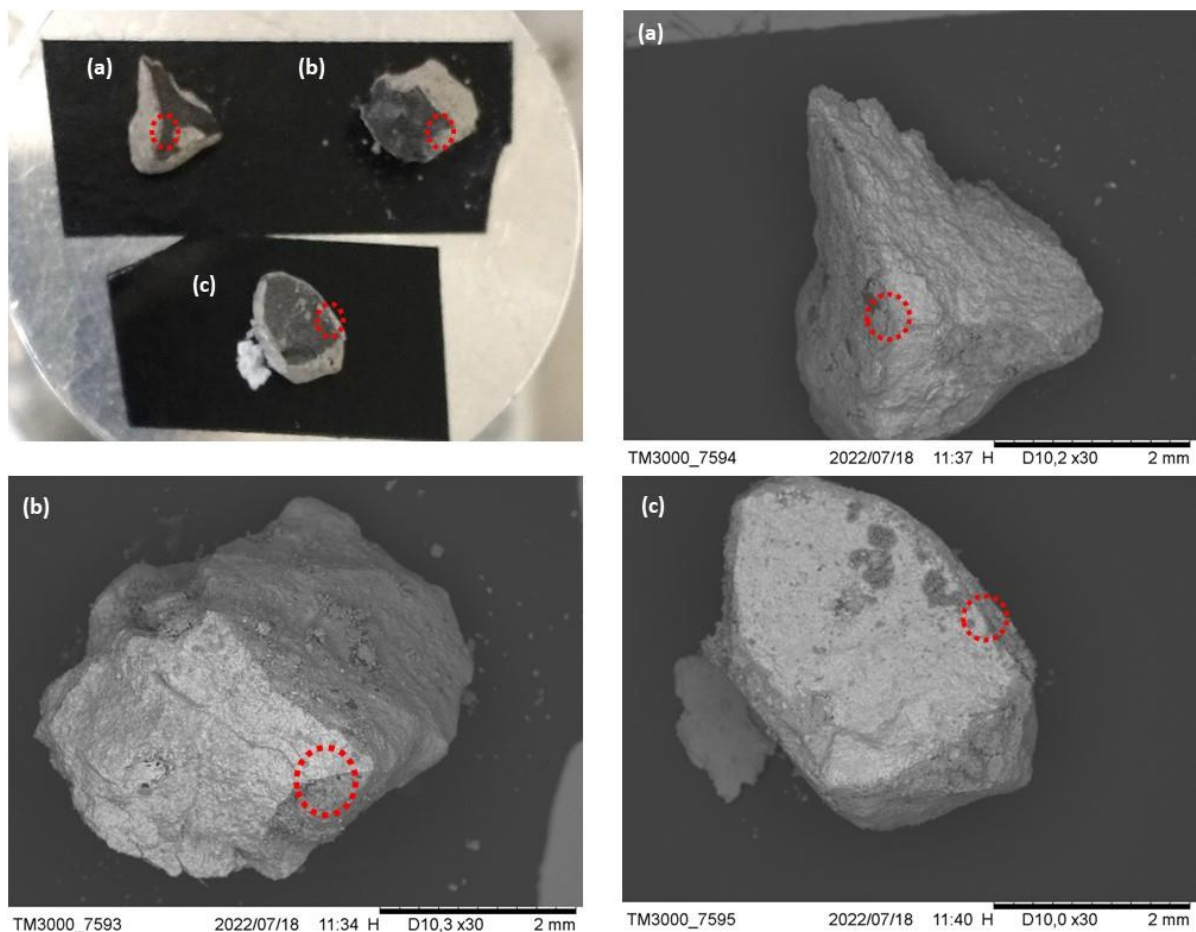
used to stabilize the BOF SS were (i) wet curing and (ii) carbonation, described as follows:

- (i) The wet curing took place for 30 days [7], where the BOF SS aggregate was completely submerged in water (Figure 3.11a). It was expected the f-CaO and f-MgO from SS to react with water (expansive hydration reaction) to form calcium hydroxide and magnesium hydroxide, respectively [8].
- (ii) The carbonation process took place inside a carbonation chamber (Climatic Chamber UUC-RH-STD-CO2-200/2018, Bass Equipment Ltd., Brazil) where the BOF SS aggregate was exposed to CO<sub>2</sub> flow gas (5% CO<sub>2</sub> concentration, 33% RH, and temperature of 35°C) for 72 h (Figure 3.11b). It was expected that the calcium oxide present in BOF SS aggregate reacted with CO<sub>2</sub> gas, leading to the formation of crystalline calcite [9], which is also an expansive reaction [8].

A microstructural analysis was carried out after the pre-treatments in order to validate the processes before using the aggregates. A Hitachi TM3000 benchtop SEM was used to assess any microstructural variation of the aggregate. An aggregate particle was broken to evaluate the difference between the interior and the surface of the particle, as shown in Figure 3.12.



Figure 3.11 – Pre-treatments: (a) wet curing and (b) carbonation chamber (CEFET-MG).



**Figure 3.12 – Microscopy set up: (a) BOF SS as received, (b) BOF SS wet cured, and (c) BOF SS carbonated.**

### 3.3. Paste and mortar preparation

The specific mix proportions (formulations) are described in their corresponding chapter. The pastes and mortars were mixed in a mortar mixer. The alkaline solution (previously mixed and cooled down) was added first, followed by the binder at a lower mix speed. After approximately 5 min, the paste was mixed for 1 min at the higher mix speed. In the case of mortars, the aggregate was added after approximately 3 min, until complete homogenization of the mix. Finally, the mortar was mixed at a higher speed for 1 min. This mixing process was carried out according to the Brazilian Standard ABNT NBR 7215:2019 [10]. The cast specimens (for hardened characterization) were cured at ambient laboratory conditions ( $\cong 24\text{ }^{\circ}\text{C}$ ,  $90 \pm 5\%$  RH); they remained in the mold for the first 24 h (placed inside sealed plastic bags) and, after demolding, were placed underwater until testing. The choice to use underwater curing was made to avoid the fast water loss that leads to potential shrinkage.

### 3.4. Characterization methods

This section describes the procedures for the characterization methods used during the research to evaluate the pastes and mortars.

#### 3.4.1. Early hydration kinetics

An isothermal calorimeter (Calmetrix I-Cal 2000 HPC, Figure 3.13) was used to assess the hydration kinetics of the fresh pastes and mortars. The pastes were made with 20 g of precursor and 8–11 g of alkaline solution. Measurements were carried out every 5 s in the first 8 h and every minute in the next 64 h. The mortars had their evaluation extended to 76 h.



Figure 3.13 – Isothermal calorimeter (CEFET-MG).

#### 3.4.2. Fresh property

The consistency of the mortars was determined with the flow table test according to the Brazilian Standard ABNT NBR 13276:2016 [11]. The results correspond to the average of the three diameter measurements, as presented in Figure 3.14.



Figure 3.14 – Flow table measurement.

### 3.4.3. Hardened properties

The hardened pastes and mortars were submitted to apparent density, water absorption and porosity tests (water saturation method) and mechanical evaluation (compressive and flexural strength). Apparent density, water absorption and porosity were determined according to the Brazilian Standard ABNT NBR 9778:2009 [12] after 28 days of curing. Cylindrical samples 25 x 50 mm (diameter x height) were used for the compressive strength tests. The compressive strength of each formulation was measured after 1, 3, 7 and 28 days of curing using a universal press Emic D30000 with a 300 kN load cell and a  $0.25 \pm 0.05$  MPa/s loading rate [10]. Prismatic samples 25 x 25 x 100 mm<sup>3</sup> (width x height x length) were used for the flexural strength tests. The flexural strength of each formulation was also measured after 3, 7 and 28 days of curing using a universal press Emic D30000 with a 300 kN load cell and a  $50 \pm 10$  N/s loading rate [13]. Five specimens were used, and the average and standard deviation were calculated and reported.

### 3.4.4. X-ray diffraction and thermogravimetry analysis

XRD and TGA were used to assess the structural analysis of the hardened pastes/mortars (Figure 3.15). The mineralogical composition (crystalline phases) was determined by XRD using a Shimadzu XRD 7000 diffractometer operating at 0.30 s/step, step size equal to 0.02° and the scanning range was 5–80°. TGA-DTG was used to quantification of the hydrates/carbonates using a Hitachi STA73000 equipment from 25 °C to 1000 °C at a heating rate of 10 °C/min in a high-purity nitrogen atmosphere. XRD and TGA/DTA were carried out at 1, 3, 7 and 28 days.



Figure 3.15 – (a) XRD and (b) TGA equipment (CEFET-MG).

### 3.4.5. Scanning electron microscopy

The microstructural analysis of the pastes was carried out using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDX) analysis operating in backscattering mode. The SEM/EDX test were carried out at 15 kV acceleration voltage with different working distances. Samples were polished for characterization. The EDX analysis were made with the support of the Centre for Innovation and Technology in Composite Materials (CITeC) at the Federal University of São João del-Rei (UFSJ), Brazil.

The mortars were also submitted to SEM to particularly observe the interface (ITZ) between aggregates and matrix. The same test conditions were used in a Hitachi TM3000 benchtop SEM. Figure 3.16 shows an example of a prepared sample and the equipment used.

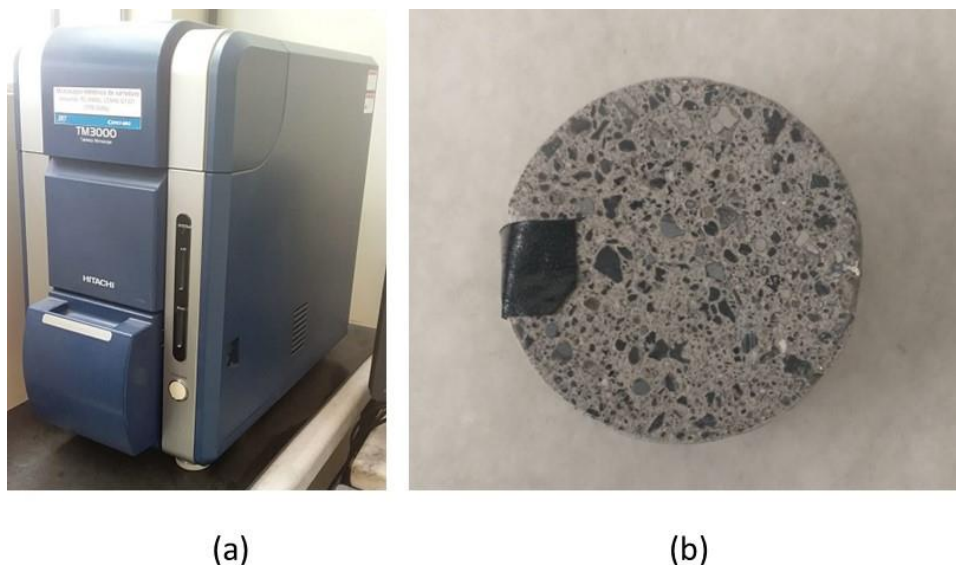


Figure 3.16 – (a) SEM equipment (CEFET-MG) and (b) sample polished for SEM.

### 3.4.6. X-ray microtomography

A computerized X-ray microtomography ( $\mu$ CT) was used to obtain both quantitative and qualitative information on mortars (chapter 5 and 6). It is possible to evaluate the volume and distribution of the different material phases of each specimen, such as volume of aggregates, volume of paste and closed porosity of the sample [14]. The  $\mu$ CT analysis consists of four steps: scanning, reconstruction, qualitative analysis, and quantitative analysis. First, during the scanning phase, a set of X-ray images are obtained while the sample rotates inside the microtomograph. A Skyscan1172  $\mu$ CT

(Bruker, Figure 3.17) with an X-ray source of 80 kV of voltage and an amperage of 100  $\mu$ A was used. The resolution (pixel size) was defined as 13.8  $\mu$ m. In the reconstruction phase, the linear absorption of each material was correlated with a shade of grey between 0 [white] and 255 [black]. The image quantitative analysis software provides the volume of the different components because the pixel intensity is proportional to the density of the material [15]. And last, the qualitative analysis, allows to evaluate how pores and aggregate are distributed all over the sample. Cylindrical samples 25 x 50 mm (diameter x height) of mortars were used.

Each phase was analyzed separately, i.e., paste, aggregate, the metallic part from the BOF SS aggregate and closed porosity. For each phase the volume represents the percent over the total volume of the sample and the closed porosity is the percent of entrapped air inside each phase. The object surface/volume ratio (OSRV) is a parameter used to describe the complexity of the structure; the higher the value, the more finely distributed is the analyzed phase within the material.



Figure 3.17 –  $\mu$ CT equipment (Universidad de Cantabria).

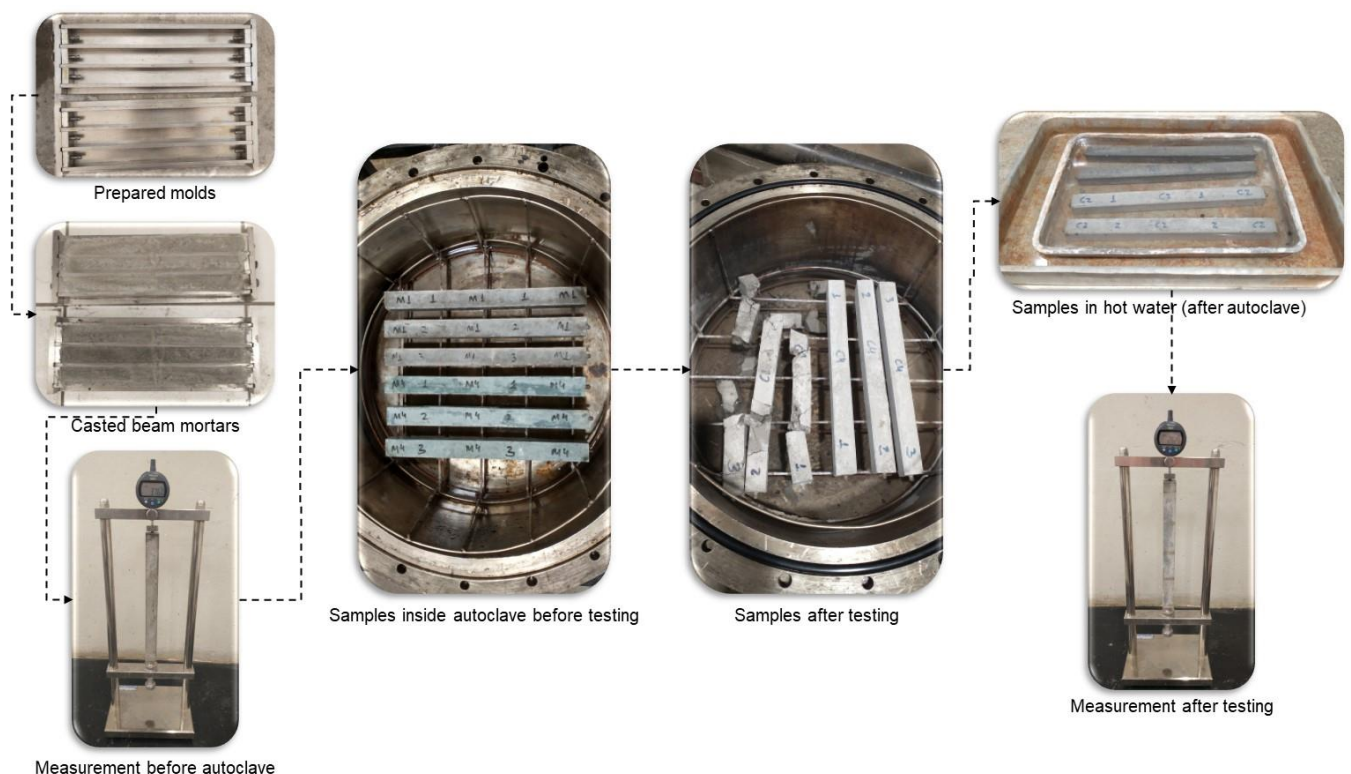
#### 3.4.7. Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) was used to determine the total porosity and pore size distribution of the mortars (chapter 6) according to the ISO 15901-1/2016 [16], using a Micromeritics AutoPore IV equipment. The parameters used were filling pressure of 0.59 Psi, maximum pressure of 59.901 Psi, a contact angle of 130°, and surface tension of mercury of 0.485 N/m. Small monoliths (about 5 mm thick) from the center of an uncrushed cylinder were used. This analysis was made with the support

of the Technological Characterization Laboratory at the University of São Paulo (USP), Brazil.

#### 3.4.8. Durability assessment: volume stability by autoclave expansion

The volume stability of the mortars (chapter 5 and 6) was evaluated using the test method similar to the autoclave expansion test of the ASTM C151 Standard [17]. Prismatic samples  $25 \times 25 \times 285 \text{ mm}^3$  (width x height x length) were used. The samples were demolded after 24 h of casting and immediately placed in the comparator reading to obtain the initial length. After that, the samples were placed inside the autoclave at room temperature so that all sides of the sample were exposed to the saturated steam. They were kept inside the autoclave for 3h at  $220^\circ\text{C}$ , maintaining the pressure of 145 psi. Afterwards, the autoclave was opened, and the samples were placed in hot water (above  $90^\circ\text{C}$ ) for 15 min. Finally, the samples were placed in the comparator reading to record final length after autoclaving. The change in length was obtained by subtracting the length before autoclaving from that after autoclaving and reported as percent of variation from the initial length. A schematic of steps from the autoclave expansion test is presented in Figure 3.18.



**Figure 3.18 – Autoclave expansion procedure (CEFET-MG).**

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#### **4. BASIC OXYGEN FURNACE STEEL SLAG AS PRECURSOR ON ALKALI-ACTIVATED MATERIALS**

## Abstract

Steel slag (SS) is a secondary material from steelmaking production with little commercial value. Its volumetric expansion and low reactivity limit the use of SS in Portland cement (PC)- based materials. This study investigated the potential use of basic oxygen furnace (BOF) slag as a single precursor in alkali-activated matrices (AAMs). Six AAM pastes were assessed by changing the silica modulus (0.75, 1.50 and 2.22) and the sodium concentration (4% or 6% Na<sub>2</sub>O—wt. SS). The early hydration was assessed using isothermal calorimetry (IC), followed by the assessment of the mechanical performance (compressive strength), apparent porosity, and structure and microstructure characterization (X-ray diffraction, thermogravimetric analysis and scanning electron microscopy). The results indicated that although the BOF slag may be considered a low-reactivity material, the alkaline environment effectively dissolved important crystalline phases to produce hydrates (reaction products). An optimized combination of activator sources was achieved with 4% Na<sub>2</sub>O and a silica modulus of 1.50–2.22, with a compressive strength up to 20 MPa, a significant amount of reaction products (C-S-H/C-A-S-H gels), and low initial and cumulative heat release. Those properties will help to promote SS recycling use in future engineering projects that do not require high-strength materials.

## 4.1. Introduction

Regarding the development of AAMs, most recent studies were carried out using SS as a partial replacement in blends with other precursors [1–10] or using SS as the sole precursor in the matrix [11–18]. The latter is gaining researchers' attention due to the possibility of increasing the reuse of SS as an alternative, environmentally friendly application [19]. The number of publications is still scarce, and thus, it is difficult to establish concrete conclusions about the real influence of SS and activation parameters on the final properties of AAMs. However, some significant findings were reported, as follows. Liu et al. [15] found that the calcium silicates (C<sub>2</sub>S and C<sub>3</sub>S) present in the SS composition dissolve under alkaline conditions to form reaction products. Ozturk et al. [12], Sun et al. [13] and Morone et al. [14] concluded in their studies that significant amounts of C-S-H-type gel and CaCO<sub>3</sub> are formed as hydration products, and the best SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio in the activator was between 2.0–2.3. Sun et al. [13] only evaluated the effect of the silica modulus variation using the same Na<sub>2</sub>O concentration (only 4%) and Morone et al. [14] evaluated the carbon storage capacity of BOF slag using CO<sub>2</sub> curing by assessing mortars and not pastes. They also used different activation parameters (molar ratio, activator type) and a different curing regime, and the focus was not on the influence of the activation parameters.

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This is a slightly modified version of the author's post-print version paper "Influence of activation parameters on the mechanical and microstructure properties of an alkali-activated BOF steel slag", published at Applied Sciences Journal, MDPI. Q2 (Engineering) and A1 (Qualis – Engineering I). CiteScore: 4.5, Impact Factor: 2.838. DOI: <https://doi.org/10.3390/app122312437>.

Additionally, contradictory results were published, confirming the need for a more thorough investigation of the alkaline activation of SS [19].

This study aimed to tackle some of the issues stated in the last paragraphs, i.e., the need for alternative binders, the necessity for further reuse of steel slag and the scarce number of investigations on steel slag activation. It investigated the influence of activation parameters on the mechanical and microstructural properties to validate the use of BOF slag as a single precursor in AAM. Six different AAM pastes were produced by changing the silica modulus and the sodium concentration. The fresh properties were evaluated using the heat of hydration and the mechanical properties were evaluated using compressive strength. The pastes were also submitted to XRD, TGA and SEM to assess the microstructure changes, i.e., the mineral composition, crystalline and solid phase variation, pore structure and variation in the reaction products.

## 4.2. Experimental program summary

The complete description of the materials and methods used in this chapter is presented in chapter 3. The alkaline solutions were prepared using NaOH pellets (99% purity),  $\text{Na}_2\text{SiO}_3$  (solid content of 47.10%,  $\text{SiO}_2/\text{Na}_2\text{O}$  of 2.16) and water. Six different pastes were studied by combining different silica modulus in the activator (0.75, 1.50 and 2.22) and the percentages of  $\text{Na}_2\text{O}$  (4% and 6%), as presented in Table 4.1. The water-to-binder ratio (w/b) was varied to ensure the same workability between all the pastes.

**Table 4.1 - Mix proportions.**

| Formulation | Modulus | $\text{Na}_2\text{O}/\text{binder}$ (%) | Water/binder | Steel Slag (g) | Water (g) | $\text{Na}_2\text{SiO}_3$ (g) | NaOH (g) |
|-------------|---------|-----------------------------------------|--------------|----------------|-----------|-------------------------------|----------|
| 0.75M-4%    | 0.75    | 4                                       | 0.35         | 540            | 159.03    | 48.78                         | 18.68    |
| 1.50M-4%    | 1.50    |                                         | 0.35         | 540            | 135.34    | 97.57                         | 9.19     |
| 2.22M-4%    | 2.22    |                                         | 0.38         | 540            | 128.59    | 144.40                        | -        |
| 0.75M-6%    | 0.75    | 6                                       | 0.35         | 540            | 144.04    | 73.18                         | 28.02    |
| 1.50M-6%    | 1.50    |                                         | 0.40         | 540            | 135.50    | 146.35                        | 13.79    |
|             | 2.22    |                                         | 0.40         | 540            | 101.39    | 216.60                        | -        |

## 4.3. Results and Discussions

### 4.3.1. BOF Slag Pozzolan/Reactivity Behavior

The pozzolanic index (PI) of the BOF slag was 67.29%; therefore, this SS was considered a non-pozzolan material accordingly to the Brazilian Standard ABNT NBR 12653:2014 [20]. Basic GGBFS, typically a pozzolan material, has a much higher PI of approximately 95%. In contrast, acidic GGBFS has a lower PI, comparable to the BOF slag, between 65 and 85%. A low pozzolan behavior of the BOF slag was expected based on the high content of crystalline phases, as highlighted by the XRD (Figure 3.3).

The modified R<sup>3</sup> reactivity test results of the BOF slag are summarized in Table 4.2, where a comparison is made with typical results from other raw materials, i.e., another BOF slag, a ladle furnace steel slag (LFS), GGBFS and limestone [21,22]. It is possible to see a significant difference in the reactivity of SCMs and even between different samples of BOF slags. The studied BOF slag may be considered to have a low reactivity based on its amount of heat released and calcium hydroxide consumptions, which were 76 J/g SCM and 16 g/100 g SCM, respectively.

**Table 4.2 - Results of modified R3 reactivity test.**

|                       | Heat release (J/g SCM) | Calcium hydroxide consumption (J/g SCM) |
|-----------------------|------------------------|-----------------------------------------|
| BOF slag              | 76                     | 16                                      |
| Another BOF slag [21] | 210                    | 9                                       |
| LFS [21]              | 490                    | -11.5                                   |
| GGBFS [21,22]         | 500                    | 32                                      |
| Limestone [22]        | 20                     | -5                                      |

The difference in terms of heat release and calcium consumption of both BOF slags was related to the inherent variability of steel slags. Due to the processing and cooling effects on the chemical and mineralogical compositions, such as the amorphous phases, there was considerable variability in their behavior. The heat released from the LFS and GGBFS were similar and significantly greater than both BOF slags. This may have been due to the more significant amounts of amorphous phases in the formers compared with the present BOF slag [21], which was demonstrated by its crystalline nature (Figure 3.3). The calcium hydroxide consumption of the LFS and the limestone were negative, which meant that they generated calcium hydroxide possibly because of the reaction of the existing free lime in their composition. GGBFS had the highest calcium hydroxide consumption due to its higher amorphous content compared with the others.

#### *4.3.2. Early Hydration Results via Calorimetry*

Figure 4.1a,b show, respectively, the heat flow rate and the cumulative heat release during the activation of the BOF slag. The alkali-activated BOF slag pastes present different behavior depending on the activation parameters. In general, the hydration process of alkali-activated SS may be divided into five stages similar to cement-based materials and GGBFS-based AAM: the rapid initial dissolution, induction/reorganization, acceleration, deceleration and stabilization periods [3,13,17]. However, the changes in both the silica modulus and Na<sub>2</sub>O concentration in the activator clearly modified the BOF slag activation kinetics.

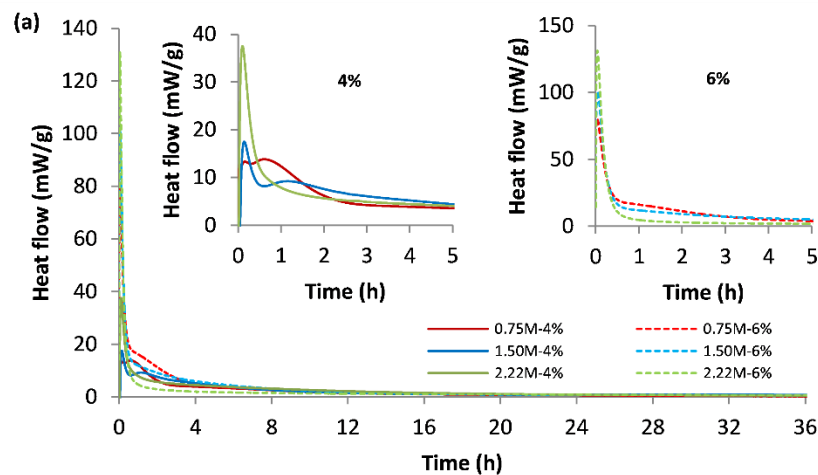


Figure 4.1 - Hydration kinetics of the pastes: (a) heat flow and (b) cumulative hydration heat.

The rapid dissolution of the slag particles (calcium silicate and calcium aluminate) led to the first exothermic peak observed in all mixtures despite differences in intensity, as shown in Figure 4.1a. This stage is characterized by the formation of the initial dissolved silicate and aluminate units [13]. The type and concentration of the alkali activator are known to influence the duration and intensity of each stage during the reaction [23]. Figure 4.1 shows that the intensity of the first peak varied between 13 and 38 mW/g when the  $\text{Na}_2\text{O}$  concentration was 4%. Conversely, the values were much higher for the 6% concentration, varying between 80 and 130 mW/g. Those results indicated that the higher the alkalinity in the solution, the faster the initial dissolution and the higher the initial heat release rate [13]. The effect of the silica modulus on the first stage was also evident for a fixed  $\text{Na}_2\text{O}$  percentage. The rise in the silica modulus from 0.75 to 2.22 also increased the intensity and speed of the heat release [14].

The induction period was characterized by low reactivity and shortened when  $\text{NaOH}$  +  $\text{Na}_2\text{SiO}_3$  were used as activators. Moreover, these activators are thought to make a small contribution to the total heat [23]. Since the aluminum phase in the BOF slag does not form crystalline products, such as ettringite, no delayed reaction occurs and the induction period is short [17]. The induction period was only identified for the 0.75M-4% and 1.50M-4% curves. The acceleration and deceleration periods (second peak) are related to the formation of hydration products, including reaction gels and  $\text{Ca}(\text{OH})_2$ , that result from the hydration of the calcium silicate present in the slag [3]. Similarly, regarding the induction period, the second peak was only identified for 0.75M-4% and 1.50M-4%. These results do not necessarily indicate the absence of  $\text{Ca}(\text{OH})_2$  or reaction gels in the other formulations. Actually, the acceleration start point was significantly delayed and the reaction rate was reduced as the silica modulus increased, which indicated that  $\text{Na}_2\text{SiO}_3$  had a retarding effect on the early reaction of the BOF slag [24].

As shown in Figure 4.1b, the cumulative heat output of the formulations varied between 13.19 and 21.51 J/g, which was a slight difference between matrices. Those values are considered very small compared with other cementitious materials, such as GGBFS-based AAM (80–150 J/g) [25] and cement-based materials (250–350 J/g) [26]. These results from our study are in line with the findings of the  $R^3$  reactivity test; the lower heat generation of the studied SS was probably associated with the slight presence of active components on the BOF slag mineralogical composition (Figure 3.3).

#### 4.3.3. Hardened Properties

Figure 4.2 presents the average results for the compressive strength of the studied pastes at 1, 3, 7 and 28 days. The error bars represent the standard deviation. Considerable development in strength from 1 to 28 days was observed for all formulations. The increases in strength from 1 to 28 days for 0.75M-4%, 1.50M-4%, 2.22M-4%, 0.75M-6%, 1.50M-6% and 2.22M-6% were 336.49%, 209.74%, 233.67%, 386.52%, 297.50% and 759.78%, respectively. These results confirmed the alkali activation process of the BOF slag and the hardening of all pastes, such as those presented by Morone et al. and Sun et al. [13,14].

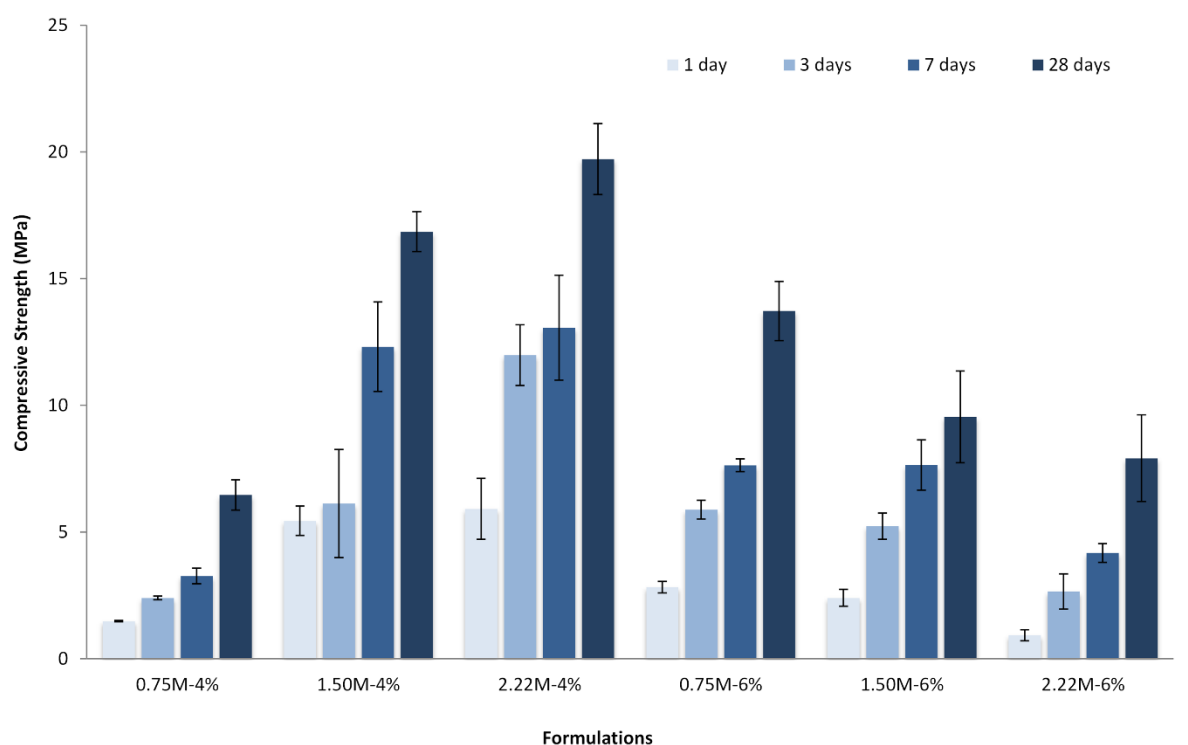


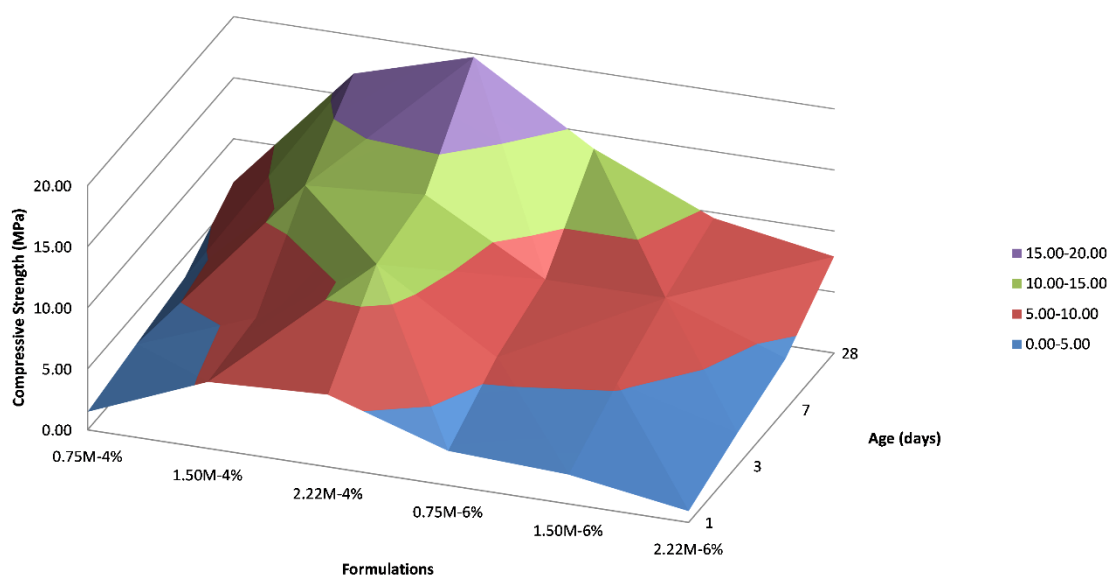
Figure 4.2 - Compressive strengths of the pastes.

It is possible to notice that the increase in silica modulus within the same  $\text{Na}_2\text{O}$  concentration had different impacts on the compressive strength for each case (4% or 6%). For 4%  $\text{Na}_2\text{O}$ , the higher the silica modulus, the higher the strength of the pastes. A rise in the modulus provided more silicate (higher Si/Al molar ratio in the matrix),

which promoted strength development [27]. However, the opposite behavior occurred when 6%  $\text{Na}_2\text{O}$  was employed. In the latter situation, the strength of pastes decreased for a higher silica modulus. This will be further discussed in the following section (Section 3.4).

Similarly, the increase in  $\text{Na}_2\text{O}$  concentration within the same modulus only enhanced the strength in the case of a low modulus (0.75M). In the other cases (1.50M and 2.22M), the increase in  $\text{Na}_2\text{O}$  negatively affected the mechanical behavior. Wang et al. [28] observed a threshold above which the alkali concentration compromises the strength development. Shi et al. [29] also pointed out that a high silica modulus may decrease the liquid alkalinity provided by the high alkali concentration and consequently reduce the extent of activation and compressive strength.

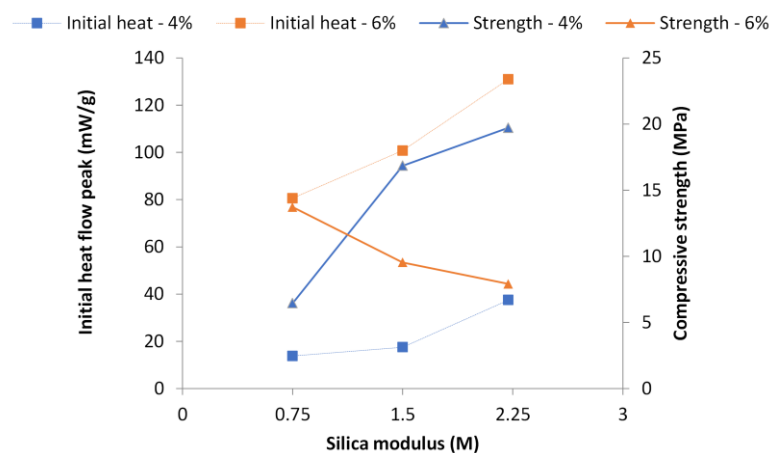
The trend of the compressive strength results is presented in Figure 4.3, where all variables are gathered. The figure graphically shows that the lowest strength values were found for extremes in the activator's content: a low alkali concentration combined with a low silica modulus or a high alkali concentration combined with a high silica modulus. Better strength performance could be achieved when an optimized combination of activator sources was considered. In this study, a low  $\text{Na}_2\text{O}$  concentration (4%) with an intermediary silica modulus (1.50–2.22) presented the best mechanical results, increasing the compressive strength up to 20 MPa. The compressive strength of the pastes was lower than the conventional ones (based on the activation of GGBFS); however, it is essential to emphasize that BOF slag is an industrial waste that presents economic and environmental benefits. The compressive strength results are helpful for material design in future engineering projects that do not require high-strength materials.



**Figure 4.3 - Compressive strength distribution with respect to the formulation and curing age.**

Similar results were presented by Sun and Chen [13] in their study, where 4% Na<sub>2</sub>O was combined with an optimal silica modulus of 2.0 to develop an alkali-activated SS paste with compressive strengths of 15 MPa and 25 MPa at 28 and 180 days, respectively. On the other hand, Ozturk et al. [12] successfully developed an alkali-activated SS mortar with considerably high strength (22 MPa) by employing a higher Na<sub>2</sub>O concentration and an intermediate silica modulus of 6% and 2.0, respectively.

Figure 4.4 presents the mean compressive strength at 28 days and the initial heat release found using calorimetry (Section 3.2) plotted against the silica modulus and Na<sub>2</sub>O concentration (4% and 6%). The graphs do not have the same trend. A rise in the silica modulus increased the initial heat release irrespective of the Na<sub>2</sub>O concentration. However, a high silica modulus combined with a high concentration of Na<sub>2</sub>O (6%) was detrimental to the strength development. The first reason for this was the relatively fast loss of consistency observed for those pastes during the molding process (i.e., 1.50M-6% and 2.22M-6%), which was in line with the high initial heat release (orange curves in Figure 4.4). This may have compromised the casting and directly affected the strength. The second reason was an excess amount of silicate and OH<sup>-</sup> in the mixture, which inhibited the activation reaction by limiting the diffusion of ions [30]. Thus, the reaction of Ca<sup>2+</sup> with Si<sup>4+</sup> was negatively affected, along with the strength development.



**Figure 4.4 - Influence of the activator parameters on the relation between the initial heat release and compressive strength (blue: 4% of Na<sub>2</sub>O; orange: 6% of Na<sub>2</sub>O; squares: initial heat release; triangles: compressive strength).**

Figure 4.5 presents the average results for the apparent density and porosity of pastes at 28 days. The standard deviation is indicated by the error bars. The green triangles represent the apparent density. Regarding the porosity, the pastes made with 4% Na<sub>2</sub>O are represented with hatched bars, while the 6% Na<sub>2</sub>O pastes are represented with solid bars. The apparent density values lay between 1.38 and 1.61 g/cm<sup>3</sup>, and the porosity mean values were between 33.92 and 36.62%. Unlike the compressive strength, it is possible to observe that the activation parameters' change did not significantly affect either the porosity or the apparent density. Regarding the

formulations made with 4% Na<sub>2</sub>O, a rise in the silica modulus (higher silicate content) increased the apparent density and porosity. This result may have been due to the fact that sodium silicate has a higher density than sodium hydroxide, yet its high viscosity negatively affected the workability of the pastes [31] and consequently increased the incorporated air in the paste. In contrast, pastes activated with 6% Na<sub>2</sub>O presented a more coherent behavior: the increase in silica modulus increased the porosity (same as the 4% pastes) and slightly decreased the apparent density.

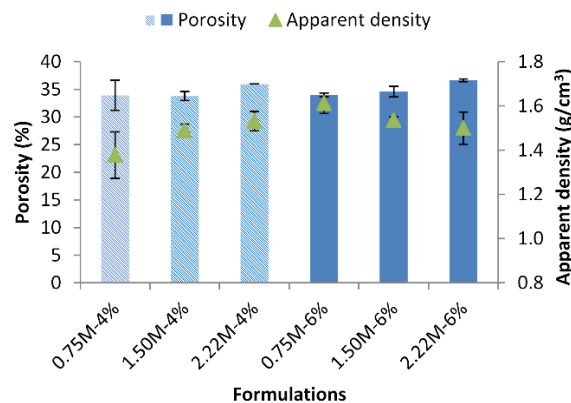


Figure 4.5 - Apparent density and porosity of pastes.

Overall, the paste porosity was highly related to the water-to-binder ratio (w/b), which played an important role in the consistency of the mixes [32]. It is important to state that the highest mean porosities were found for the 2.22M-4%, 1.50M-6% and 2.22M-6% pastes. They also had higher w/b values of 0.38, 0.40 and 0.40, respectively. You et al. [33] found that the use of SS as a binder increased the total porosity of GGBFS-based alkali-activated mortars. In contrast, Guo and Yang [10] found that an increase in the SS percentage of a PFA-based alkali-activated paste increases the apparent density. To the author's knowledge, no previous comprehensive study presented conclusive results on the influence of the activation parameters on the apparent density and/or porosity of alkali-activated SS paste.

#### 4.3.4. Structural and Microstructural Properties

##### 4.3.4.1. XRD Analysis

The XRD patterns of all pastes at 28 days are shown in Figure 4.6. Compared with the BOF slag pattern, the intensities of some diffraction peaks remarkably decreased and some peaks disappeared. The appearance of a broad hump below 10° 2θ and around 29° 2θ (dotted red circle) became clear, indicating that an amorphous phase structure, such as C-S-H/C-A-S-H gels, was formed [34,35,36]. The crystalline diffraction peaks of the calcium silicates and aluminates also decreased, suggesting that they dissolved (partially, at least) and reacted with an alkaline solution to produce the hydrated products in all pastes [13]. There was also calcium carbonate that resulted from the consumption of calcium hydroxide. No apparent changes were observed in the peaks

of wustite (FeO) or quartz (SiO<sub>2</sub>), suggesting that these phases did not participate in the alkali activation reaction [1].

Figure 4.7 presents the comparison of the mineralogical composition for two different pastes (0.75M-4% and 2.22M-4%) for the early (1 day) and later hydration (28 days). As can be seen, the main differences between both formulations were the peaks of Ca(OH)<sub>2</sub> at around 18° and 33° 2θ for the 0.75M-4% paste and the broader humps of C-S-H/C-A-S-H gels at about 10° and 29° 2θ for the 2.22M-4% paste. These findings were in accordance with the compressive strength results (Figure 4.2), showing that the hydrate gels were responsible for the strength development. Additionally, the presence of Ca(OH)<sub>2</sub> is known to promote the formation of reaction products in the system by increasing the Ca/Si ratio, which is beneficial for the formation of calcium silicate gels [4]. Thus, the crystalline phase in the 0.75M-4% pastes strongly suggested that the alkali reaction was weaker and fewer hydrates were formed.

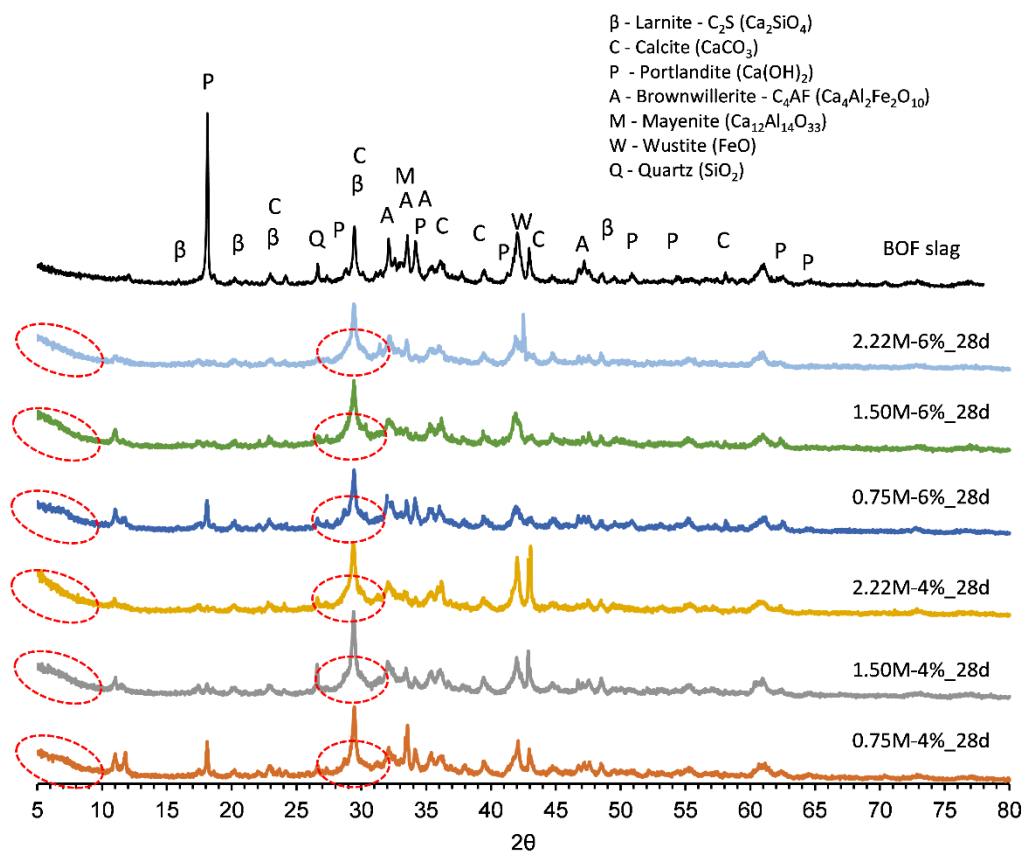


Figure 4.6 - XRD patterns of pastes at 28 days (dotted red circle: broad hump indicating amorphous phase structure).

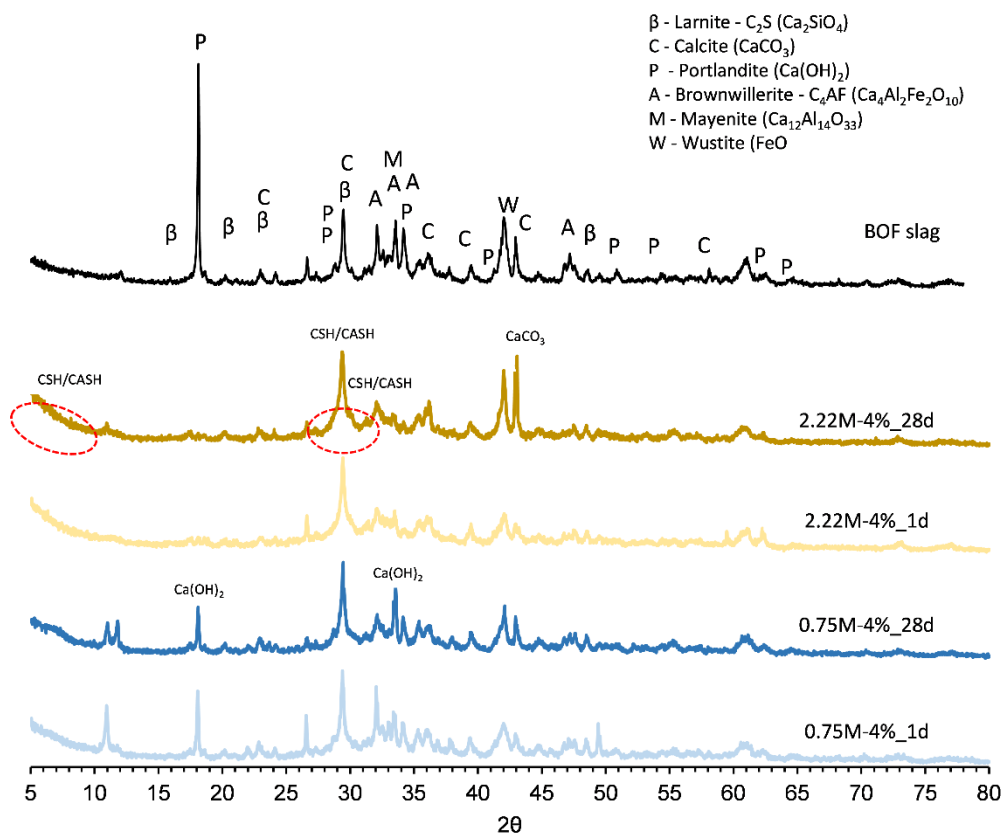


Figure 4.7 - Comparison of the XRD patterns of 0.75M-4% (blue) and 2.22M-4% (yellow) at 1 and 28 days (dotted red circle: broad hump indicating amorphous phase structure).

#### 4.3.4.2. TG/DTG Analysis

Thermogravimetric analysis is widely used to monitor the hydration process and identify and determine the content of reaction products, such as silicates, gels, other hydrates and carbonates. The TG/DTG of two different pastes (0.75M-4% and 2.22M-4%) as a function of the curing time are presented in Figure 4.8. The high mass loss below 120 °C was assigned to the complete release of physically bound water within the gel structure [37]. All pastes presented a shift toward high temperatures in the DTG peaks in this region as the curing progressed from 1 to 28 days (as represented in Figure 4.8). This suggested the formation of gels with more tightly bonded water as the reaction products developed [36]. The continuous mass loss after 120 °C until 600 °C was attributed to the decomposition of hydrated gels, such as C-S-H and C-(A)-S-H [38], and the dehydroxylation of residual  $\text{Ca(OH)}_2$  [37]. Notably, further mass loss can be observed at 600–800 °C, which was caused by the decomposition of calcium carbonate  $\text{CaCO}_3$  [36,37]. No other abrupt mass loss was observed until 1000 °C; all formulations had a slight and continuous mass loss.

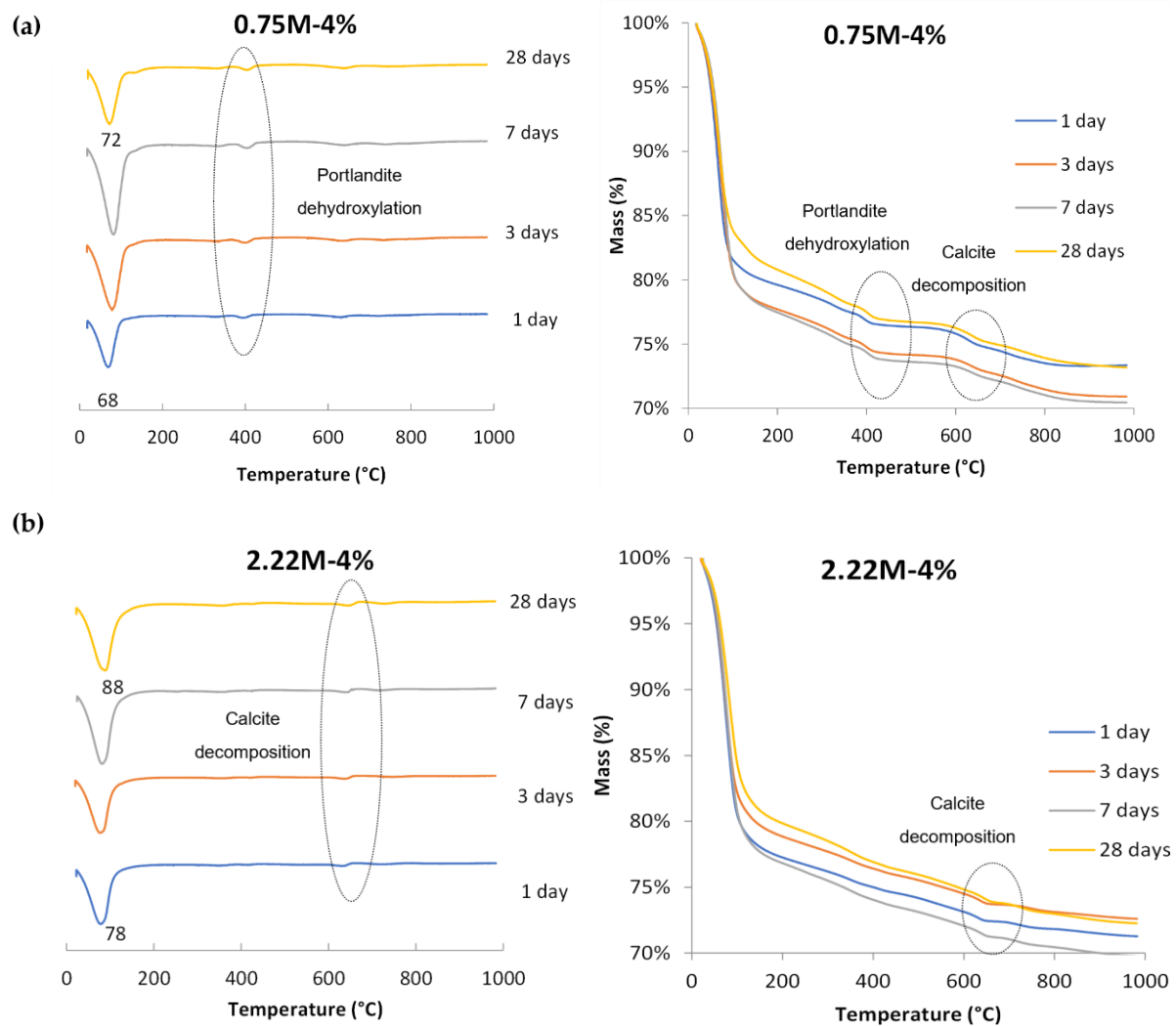


Figure 4.8 - TG/DTG of (a) 0.75M-4% and (b) 2.22M-4%.

Figure 4.8a presents the TG/DTG curves of the 0.75M-4% sample, representing the same behavior as the 0.75M-6% sample. It is possible to identify a more defined mass loss around 400 °C, probably due to the residual  $\text{Ca}(\text{OH})_2$  that was not totally consumed during the reaction. This was in line with the  $\text{Ca}(\text{OH})_2$  that was also identified in the XRD analysis for those formulations, as discussed in the previous section (Section 4.3.4.1—Figure 4.6). Alternatively, Figure 4.8b presents the TG/DTG curves of the 2.22M-4% sample as a representative curve for the remaining formulations. It is possible to observe the significant mass loss below 120 °C, the continuous mass loss above 120 °C, the calcite decomposition around 600 °C, and the constant and slight mass loss until 1000 °C.

Figure 4.9 presents the mass losses of all pastes as the curing progressed for two different temperature ranges (120–600 °C and 600–1000 °C). The curves showed an apparent increase in mass loss over the curing time for all formulations. Those two temperature ranges correspond to the decomposition of the main reaction products, namely, C-S-H/C-A-S-H gels and  $\text{CaCO}_3$ , respectively. The results confirmed the

findings of previous studies [42,43,44]. Moreover, the high content of reaction products primarily in the TGA 120–600 °C range correlated well with the strength development (Figure 4.10).

As the quantity and density of the gels increased, the mass loss also increased (Figure 4.9), which was revealed macroscopically as the enhancement in compressive strength [1]. Nevertheless, there was no correlation between mass loss and compressive strength. For instance, all formulations contained mass loss between 6.5–7.5% at 28 days but presented completely different mechanical behavior (Figure 4.10). It is essential to say that not all hydrates decomposed from 120–600 °C contributed to the strength development. In addition, other external factors are related to compressive strength, such as workability, casting/molding capacity, water content and internal porosity.

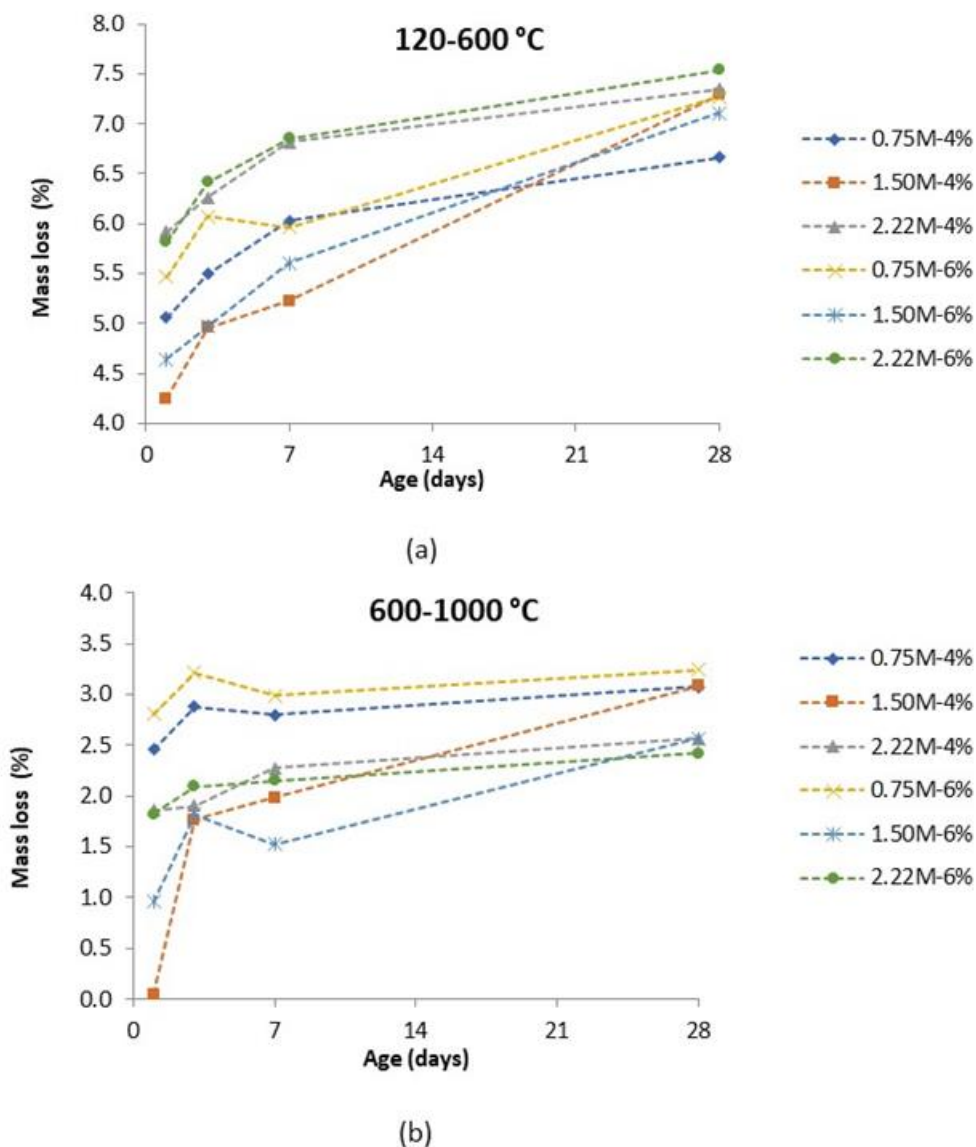


Figure 4.9 - Mass losses (%) for all pastes after 1, 3, 7 and 28 days of curing in different temperature ranges: (a) 120–600 °C and (b) 600–1000 °C.

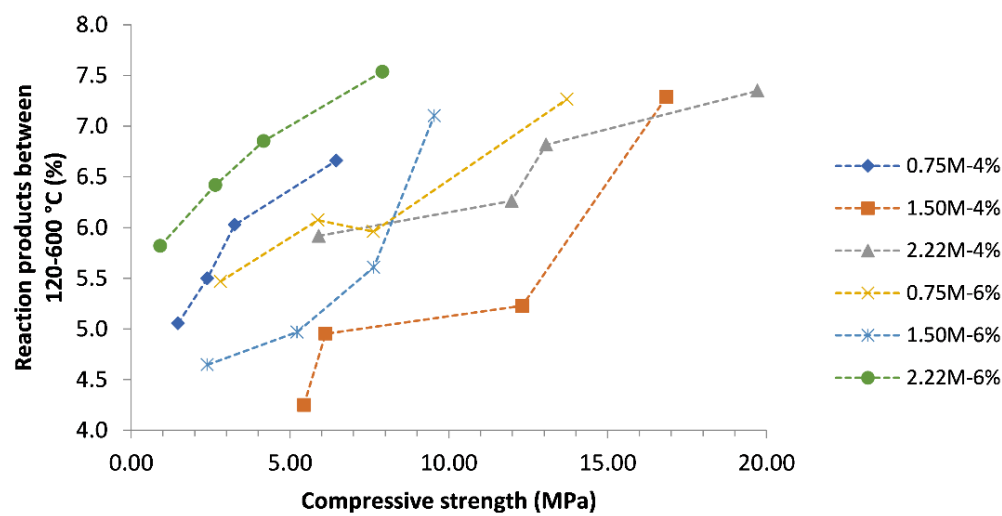


Figure 4.10 - Relationship between reaction product percentages and compressive strength for each paste. For each curve (formulation), each point is the value for each curing time (1, 3, 7 and 28 days).

The variation in the activation parameters affected the hydration process. Figure 4.11 presents the TGA mass loss at 28 days and the initial heat release found via calorimetry (Section 3.2) against the silica modulus and  $\text{Na}_2\text{O}$  concentration (4% and 6%). It is possible to see that the increase in the silica modulus (more soluble  $\text{Si}^{4+}$ ) was much more favorable at a low  $\text{Na}_2\text{O}$  concentration (4%) when it came to forming more reaction products, and consequently, improving the compressive strength (Figure 4.4). Overall, for a constant silica modulus, a high  $\text{Na}_2\text{O}$  concentration led to increased heat output and the formation of more hydrates (higher mass loss via TGA) due to the high alkali content [39].

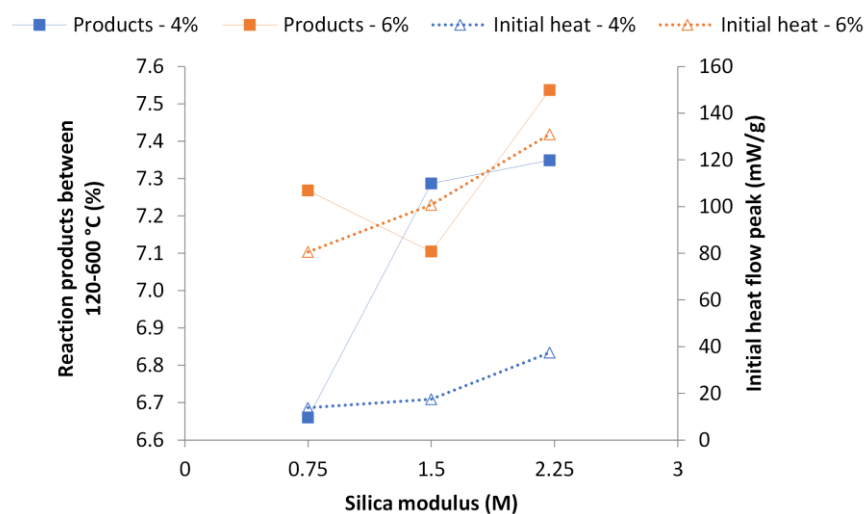
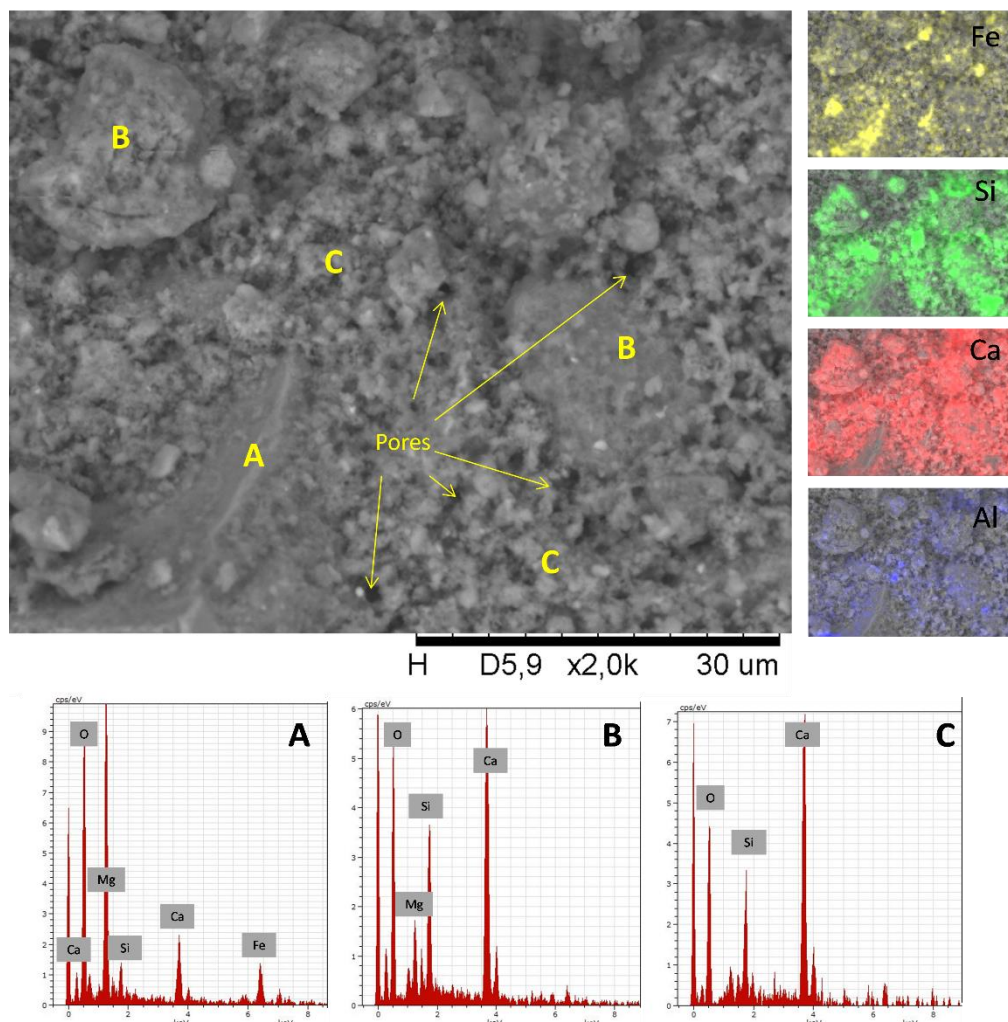


Figure 4.11 - Influence of activator parameters on the relationship between the reaction products and the initial heat release (blue: 4% of  $\text{Na}_2\text{O}$ ; orange: 6% of  $\text{Na}_2\text{O}$ ; squares: reaction products; triangles: initial heat release).

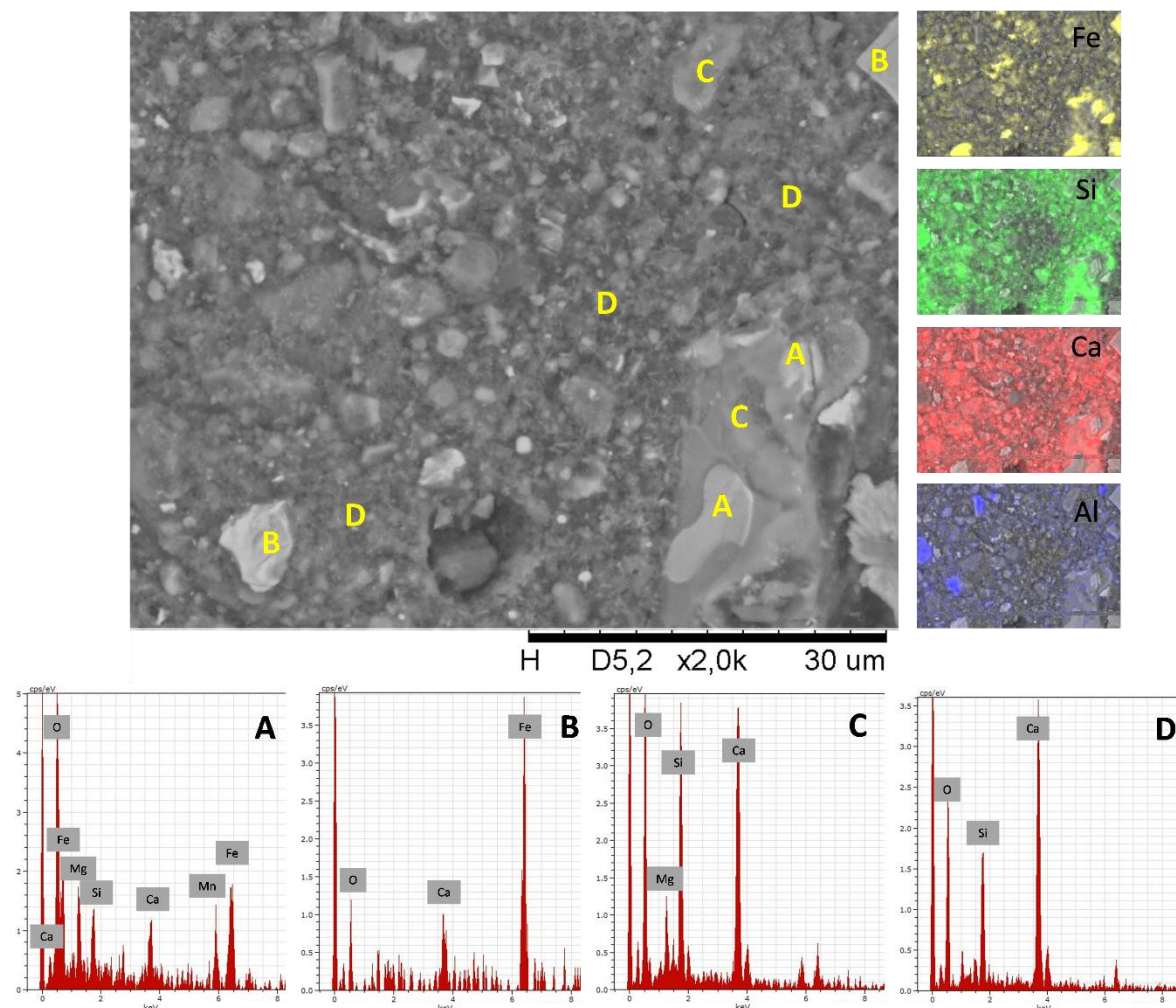
#### 4.3.4.3. SEM-EDX Analysis

Figure 4.12 and Figure 4.13 show the SEM micrographs with elemental mapping and EDX spot analyses for the formulations 0.75M-4% and 2.22M-4%, respectively. The major elements from the elemental mapping of the 0.75M-4% sample (Figure 4.12) were Si (from the activator) and Ca (from the BOF slag). The phases labeled A, B and C were, respectively, the RO phase, calcium silicate (from unreacted BOF slag particle) and C-S-H gel. The RO phase is an undissolved crystal phase commonly found in BOF slags and will remain like that even if hydrated for many years [40]. Figure 4.12 presents more unreacted BOF slag particles, which is in accordance with the lowest amount of reaction products found via TGA (Figure 4.9a) and the lowest compressive strength (Figure 4.3). An open microstructure with porous regions all over the matrix resulted from a poor hydration/activation process, which compromised the compressive strength development.



**Figure 4.12 - SEM image of 0.75M-4% (magnification of 2000×) with elemental mapping and EDX spectra of the scanning points: (A) RO phase, (B) calcium silicate (unreacted BOF slag particle) and (C) C-S-H (reaction product).**

Differently, Figure 4.13 presents the 2.22M-4% formulation with an entirely different microstructure. The elemental mapping showed an even greater predominance of Si and Ca in the matrix. Phases labeled A, B, C and D were, respectively, the RO phase embedded in the BOF slag particles, the remaining steel inclusion, calcium silicate (unreacted BOF slag) and C-S-H gel. In this case, the RO phase was embedded in the BOF slag particles, blocking these particles from dissolving and forming the reaction products (gel). A more homogeneous microstructure was observed, which was characterized by a smaller number of undissolved or partially dissolved BOF slag particles and lower porosity. More hydrates were formed (Figure 4.9a), which filled the existing pores (voids) and bonded the remaining solid particles together to form a continuous, dense and complete matrix [2]. Therefore, the denser microstructure resulted from a better hydration/activation process, and the high presence of hydrates reduced the microstructural porosity, resulting in higher compressive strength (Figure 4.3).



**Figure 4.13 - SEM image of 2.22M-4% (magnification of 2000×) with elemental mapping and EDX spectra of the scanning points: (A) RO phase (embedded in BOF particle), (B) steel particle, (C) calcium silicate (unreacted BOF slag particle) and (D) C-S-H (reaction product).**

#### 4.4. Concluding Remarks

This study explored the possibility of using SS as a single precursor in AAM. The effect of the variation of the activation parameters, namely, the  $\text{Na}_2\text{O}$  concentration and silica modulus, on the fresh and hardened properties of BOF slag-based AAM was evaluated through a series of experiments. The focus was given to the structural and microstructural behavior of the AAM pastes. The main conclusions were as follows:

- The BOF slag studied presented low pozzolanic behavior, low heat generation and may be considered a low-reactivity material. Nevertheless, the alkali activation process and hardening of pastes were confirmed in all studied cases.
- Crystalline phases of the BOF slag dissolved under the alkaline environment to produce hydrates in all studied formulations, as presented by the TGA and XRD results.
- The high initial heat release measured from the formulations with a high concentration of  $\text{Na}_2\text{O}$  and a high silica modulus may have contributed to the rapid setting, thus compromising the casting process of those formulations.
- All formulations presented the same behavior in terms of hydrate formation over the curing time. The TGA results showed the amount of hydrates by quantifying the mass loss, but no correlation with compressive strength development was determined. Other external factors are related to compressive strength, such as workability, molding process, water content and internal porosity.
- A low silica modulus combined with a low  $\text{Na}_2\text{O}$  concentration led to the identification of residual  $\text{Ca}(\text{OH})_2$  in the TGA and XRD results. This strongly suggested that the alkali reaction was weaker, and thus, less reaction products were formed, which jeopardized the strength development.
- A high silica modulus combined with a high  $\text{Na}_2\text{O}$  concentration increased the alkalinity in the solution, thus increasing the intensity and speed of the heat release. Moreover, the excess of silicate and  $\text{OH}^-$  limited the diffusion of ions, and thus, the reaction of  $\text{Ca}^{2+}$  with  $\text{Si}^{4+}$ . As a result, the casting process and the strength development were compromised.
- Finally, better strength performance was achieved when an optimized combination of activator sources was considered. In this study, a low  $\text{Na}_2\text{O}$  concentration (4%) with an intermediary silica modulus (1.50–2.22) presented the best mechanical results (compressive strength up to 20 MPa), a good amount of reaction products formed (C-S-H/C-A-S-H gel and  $\text{CaCO}_3$ ), and a low initial and cumulative amount of heat released. Although the compressive strength was lower than for the conventional ones, it is essential to highlight that BOF slag is an important industry waste that presents economic and environmental benefits and can be used in future engineering projects.

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## **5. BASIC OXYGEN FURNACE STEEL SLAG AS AGGREGATE ON ALKALI-ACTIVATED MATERIALS**

## Abstract

This study investigated basic oxygen furnace steel slag (BOF SS) as aggregate in alkali-activated mortars (AAM). It assesses the influence of wet-curing and carbonation pre-treatments on the mechanical, microstructural properties ( $\mu$ CT and SEM), and susceptibility to volumetric expansion (autoclave accelerated test). Untreated BOF SS, natural aggregate, and a Portland cement (PC) matrix were used for comparison. The results show the effectiveness of wet-curing pre-treatment, as it ensures sound mortars after accelerated testing. This curing regime provides a denser microstructure, less porous interface transition zone (ITZ) and absence of microcracks in the microstructure, which allows equivalent mechanical behavior to mortars made with natural aggregate. In contrary, the carbonated BOF SS aggregate negatively affected the strength development of AAM mortars due to the conversion of the activator into sodium carbonate in AAM. AAM and PC mortars with carbonated BOF SS also fail in accelerated expansion tests, like those containing untreated BOF SS.

## 5.1. Introduction

The construction and infrastructure industries are known to employ large quantities of natural resources [1,2]. This is a continuous process, as the current world housing deficit is estimated to be 1.3 billion [3] and the investment gap on infrastructure by 2040 is expected to be around 15 trillion dollars [4]. Construction works consume up to 60% of all raw materials extracted worldwide [5], which accounts for around 40% of the natural sand depletion, i.e. 10 billion tons per year [6]. This is a special issue mainly in developing countries, where the increasing demand for civil works results in large-scale mining of natural resources and major environmental damage and depletion [7,8]. Concrete and mortars are the main responsible materials since both are the most used construction materials and their production primarily rely on natural aggregates and Portland cement [9,10]. Moreover, natural sand is a locally available resource, which has made researchers explore possible alternative materials such as byproducts and industrial wastes to replace the former.

Compared to PC based materials, the investigation on the use of SS as aggregate replacement on AAM is considerably recent and few studies have been published so far [11–21]. Lu et al. [15] studied the use of BOF slag without any further treatment as fine aggregate in GGBFS-based AAM mortar and its effects on the mortar expansion. They found that the AAM mortar with BOF slag presented comparable compressive strength to a PC-based one and a little potential volume expansion. Lee et al. [19] also evaluated the use of an untreated BOF slag as fine aggregate in a PFA/GGBFS-based

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AAM; the authors concluded that the expansion of the SS was controlled within the AAM matrix. Mastali et al. [18], in contrary, studied the effect of using a carbonated BOF slag fine aggregate in a GGBFS/ladle slag-based AAM. They reported that the use of the carbonated BOF slag provided a denser matrix and enhanced the mechanical strength. Additionally, Jing et al. [20] reported that the interface between the BOF slag fine aggregate and GGBFS-based paste was denser, which enhanced the compressive strength. These findings indicate that the use of BOF slag as fine aggregate in AAM matrices could be promising. However, the low number of studies to fully understand the real influence of the SS aggregate on AAM properties endorses that this is still a ongoing topic of investigation among researchers. The SS pre-treatment process and its effects on the microstructural and durability-related properties are key factors that are scarcely addressed for AAM matrices [22].

This chapter investigated the influence of SS aggregate pre-treatment on the mechanical, microstructural, and durability-related properties to validate the use of BOF SS as a single aggregate in GGBFS-based AAM. Different AAM mortars were produced by changing the pre-treatment method, i.e., wet curing and carbonation. PC mortars were also produced as matrix comparison. The fresh properties were evaluated by the consistency test and the mechanical properties by compressive and flexural strength. The mortars were also submitted to X-ray microtomography ( $\mu$ CT) to assess the internal structure (pore network) and SEM to assess the microstructure changes, particularly at the ITZ between aggregates and matrices. The durability of the mortars was evaluated by measuring the volume stability using the autoclave testing method.

## 5.2. Experimental program summary

The complete description of the materials and methods used in this chapter is presented in chapter 3. Nine different mortars were studied by combining different binders (GGBFS and PC), the type of aggregate (BOF SS and natural aggregate), and the type of pre-treatment for the BOF SS aggregate (as received, cured under water, and carbonated), as presented in Table 5.1. The AAM were produced using a silica modulus in the activator of 1.50 and 4% of  $\text{Na}_2\text{O}$ . The water to binder ratio (w/b) was kept constant at 0.53 except for one mortar with natural aggregate when the water was adjusted considering the difference on the aggregates water absorption (7.16% for the BOF SS and 0.91% for the natural aggregate). The aggregate to binder ratio (a/b) was determined on previous laboratory work and kept constant at 2.0 by mass. The mortar with natural aggregate was prepared with an a/b of 1.71 to keep the same volume of aggregate considering the difference on the aggregate's density. The PC mortars were produced using a water to cement ratio (w/c) of 0.47, also determined on previous laboratory work.

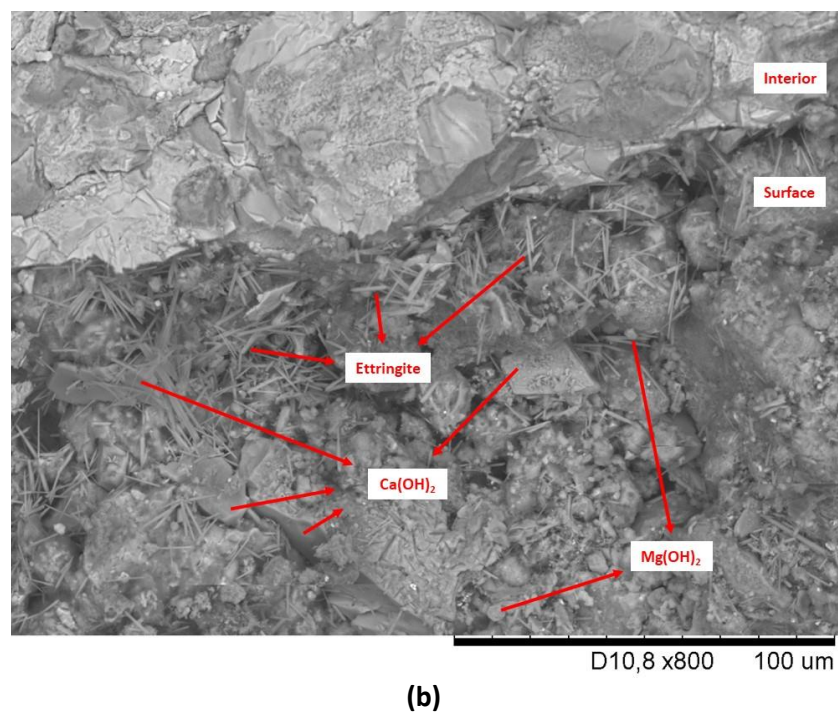
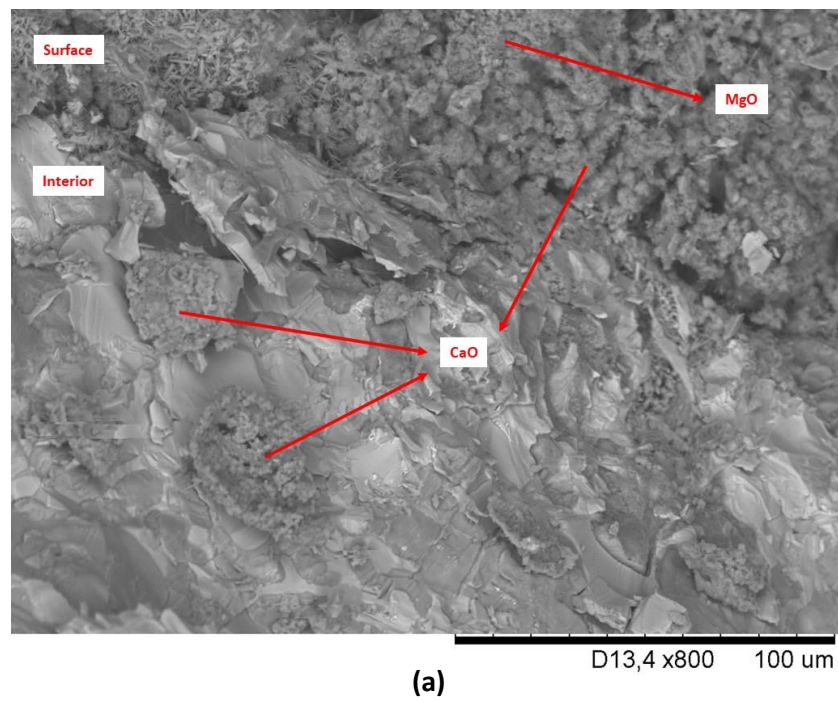
**Table 5.1 – Mix proportions.**

| Formulation | Type of aggregate  | Solution/binder | Water/binder | Proportions in mass |           |       |                                  |      |
|-------------|--------------------|-----------------|--------------|---------------------|-----------|-------|----------------------------------|------|
|             |                    |                 |              | Binder              | Aggregate | Water | Na <sub>2</sub> SiO <sub>3</sub> | NaOH |
| AAM1        | BOF SS as received | 0.63            | 0.53         | 1.0                 | 2.00      | 0.43  | 0.18                             | 0.02 |
| AAM2        | BOF SS water cured | 0.63            | 0.53         |                     | 2.00      | 0.43  | 0.18                             | 0.02 |
| AAM3        | BOF SS carbonated  | 0.63            | 0.53         |                     | 2.00      | 0.43  | 0.18                             | 0.02 |
| AAM4        | Natural aggregate  | 0.63            | 0.53         |                     | 1.71      | 0.43  | 0.18                             | 0.02 |
| AAM5        | Natural aggregate  | 0.50            | 0.40         |                     | 1.71      | 0.30  | 0.18                             | 0.02 |
| PC1         | BOF SS as received | -               | 0.47         | 1.0                 | 2.00      | 0.47  | -                                | -    |
| PC2         | BOF SS water cured | -               | 0.47         |                     | 2.00      | 0.47  | -                                | -    |
| PC3         | BOF SS carbonated  | -               | 0.47         |                     | 2.00      | 0.47  | -                                | -    |
| PC4         | Natural aggregate  | -               | 0.47         |                     | 1.71      | 0.47  | -                                | -    |

### 5.3. Results and discussion

#### 5.3.1. Pre-treatment of BOF slag aggregate

Figure 5.1 presents three SEM images of the BOF SS aggregate particles: (i) as received without any further treatment; (ii) wet cured and (iii) carbonated. In all cases it is possible to identify a well-defined interface between the core of the particles (denser area) and the surface, as marked on the images. The BOF SS aggregate as received (Figure 5.1a) presented free CaO and MgO solid solution [23]. Figure 5.1b presents the hydrated products formed after the wet curing; calcium, and magnesium hydroxides and ettringite. Figure 5.1c presents the crystalline carbonated products formed (calcium and magnesium carbonate) after carbonation [24]. Both pre-treatments were validated, ensuring that the expansive reactions of CaO and MgO took place prior to the use of the aggregate.



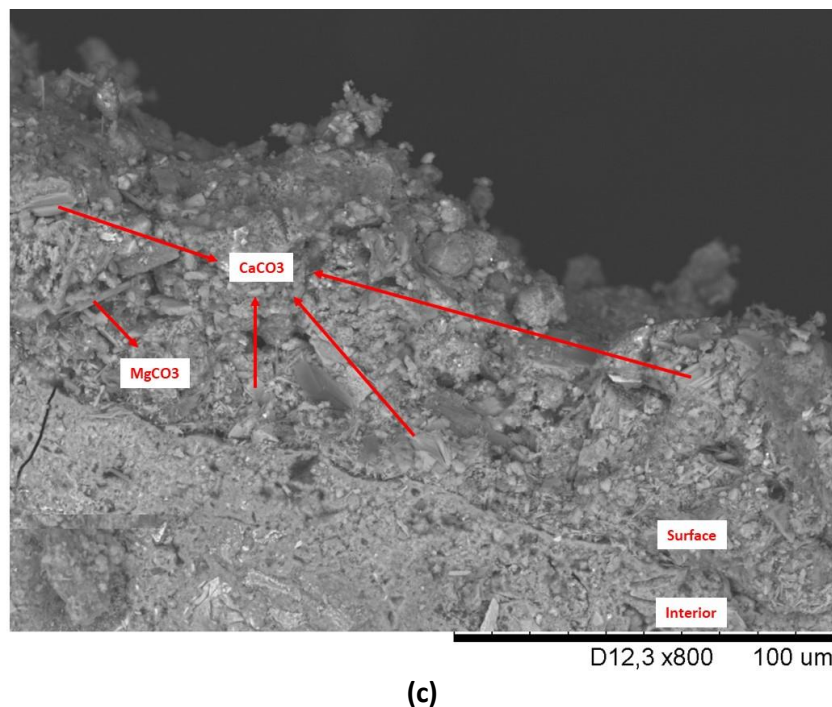
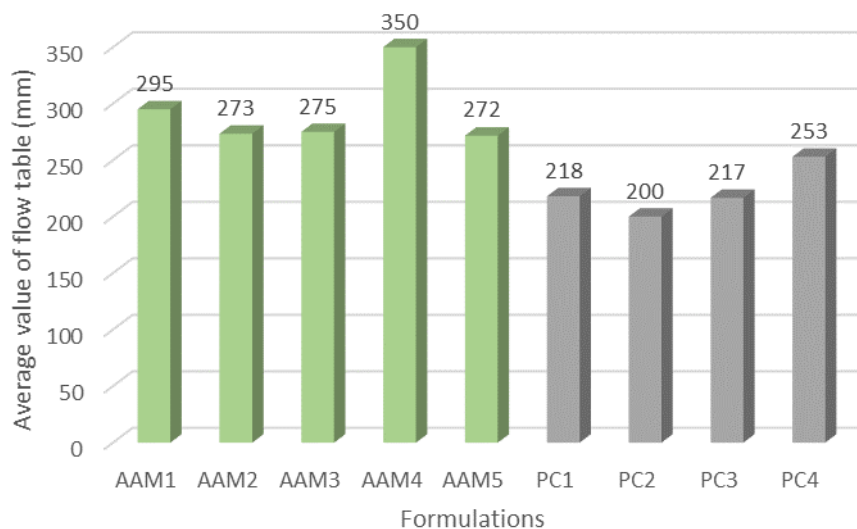


Figure 5.1 – SEM images of BOF SS aggregate particle: (a) as received, (b) wet curing, and (c) carbonation.

### 5.3.2. Consistency of the mortars

Figure 5.2 presents the results of the consistency of each mortar, i.e., 272 - 350 mm and 200 - 253 mm for AAM and PC mortars, respectively. The change of the aggregate or treatment directly affected the consistency in all cases. AAM4 presented the highest consistency among the AAM mortars due to the low water absorption of the natural aggregate. AAM5 is the same formulation with lower w/b; its consistency is therefore equivalent to the other mortars. The pre-treatments of the BOF SS aggregate considerably reduced the workability, varying from 295 mm to  $274 \pm 01$  mm, and in the same range that the natural aggregate. In other words, the employment of BOF SS aggregate after treatment didn't affect the workability of AAM mortars compared to the natural aggregate. Lee et al. [19] also reported a good workability using only BOF slags aggregates in a GGBFS/FA-based alkali-activated mortar.

The consistency of the PC mortar reduced when the wet-cured BOF SS aggregate replaced the aggregate as received (PC1 = 218 mm and PC2 = 200 mm). This is the same trend observed for the AAM mortars. However, the carbonation of BOF SS aggregate did not affect the consistency of the PC mortar (PC1 = 218 mm and PC3 = 217 mm). PC4 presented higher consistency due to the lower water absorption of the natural aggregate and the multi-angular and rough shape of BOF aggregate particles [25,26]. The decrease in the workability by using SS as fine aggregate into PC-based matrices was also observed by other authors. [9,27-32].

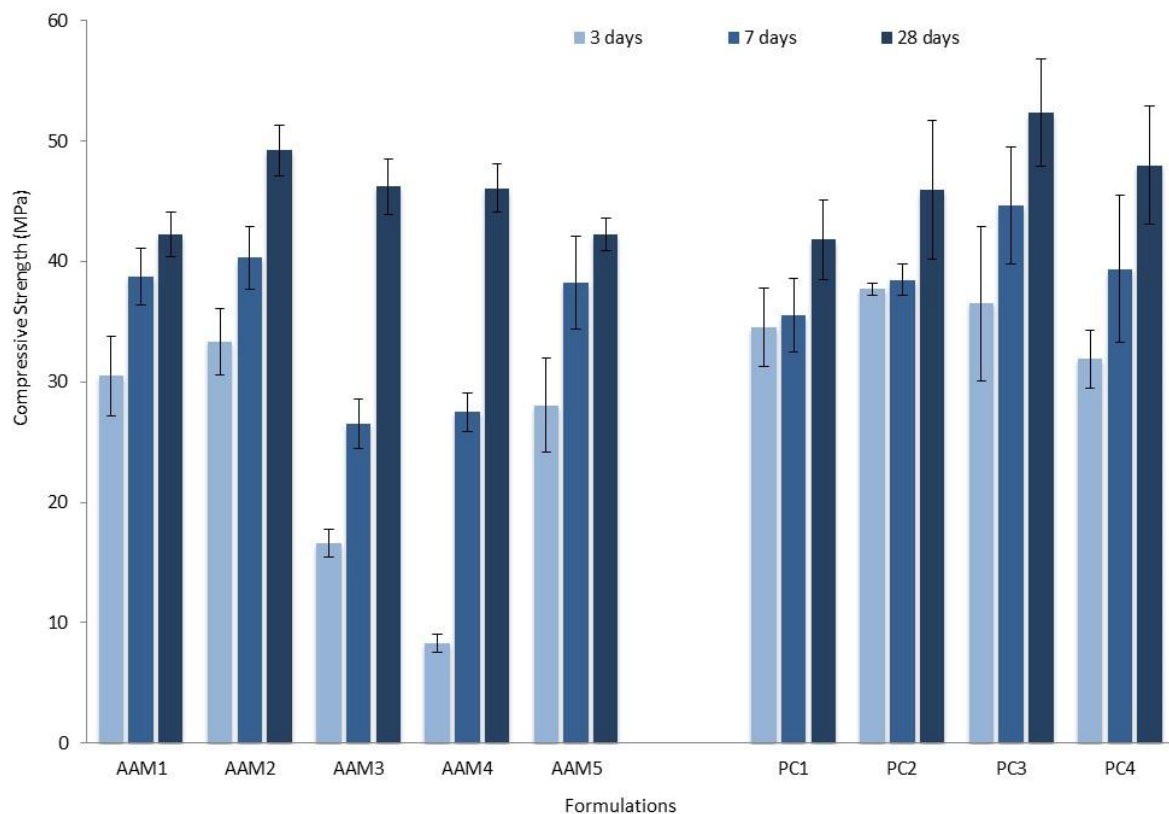


**Figure 5.2 – Consistency of fresh mortars.**

### 5.3.3. Compressive and flexural strength

Figure 5.3 presents the average results for the compressive strength of the studied mortars at 3, 7 and 28 days. The error bars represent the standard deviation. It is possible to observe a considerable development in the compressive strength from 3 to 28 days for all AAM mortars. The rise in the mechanical strength for AAM1 to AAM5 were 38.50%, 47.65%, 178.39%, 458.11% and 50.52%, respectively. The strength development over time was moderate for the PC mortars: 21.18%, 21.88%, 43.45% and 50.38%, respectively, for PC1 to PC4. The reason is the employment of a rapid-hardening cement, that presents a higher strength development at early age (3 days). A high compressive strength (42 MPa to 52 MPa) was achieved at 28 days for both the AAM and PC mortars, regardless of the type of aggregate used.

The use of BOF SS aggregate enhanced the compressive strength of AAM mortars at 28 days, especially after the pre-treatments (AAM2 and AAM3). The mortar with natural aggregate (AAM4) presented the lowest compressive strength at 3 days (8.26 MPa) and low compressive strength at 7 days (27.51 MPa) due to the excessive available water resulted from the low water absorption of the aggregate. This was improved by the adjustment on the w/b ratio (AAM5), which achieved a strength of 28.05 MPa and 38.26 MPa, respectively at 3 and 7 days. Nevertheless, the replacement for the natural aggregate with BOF SS aggregate increased the compressive strength at 28 days, especially after the treatments. The mean compressive strength rose 0.12% for the untreated BOF SS, 16.64% for wet cured BOF SS and 9.52% for carbonated BOF SS. These results emphasize that the BOF aggregate can be successfully used as an alternative fine aggregate in alkali-activated mortars, which is in line with previous studies [16,18,20,21].



**Figure 5.3 – Compressive strength of mortars.**

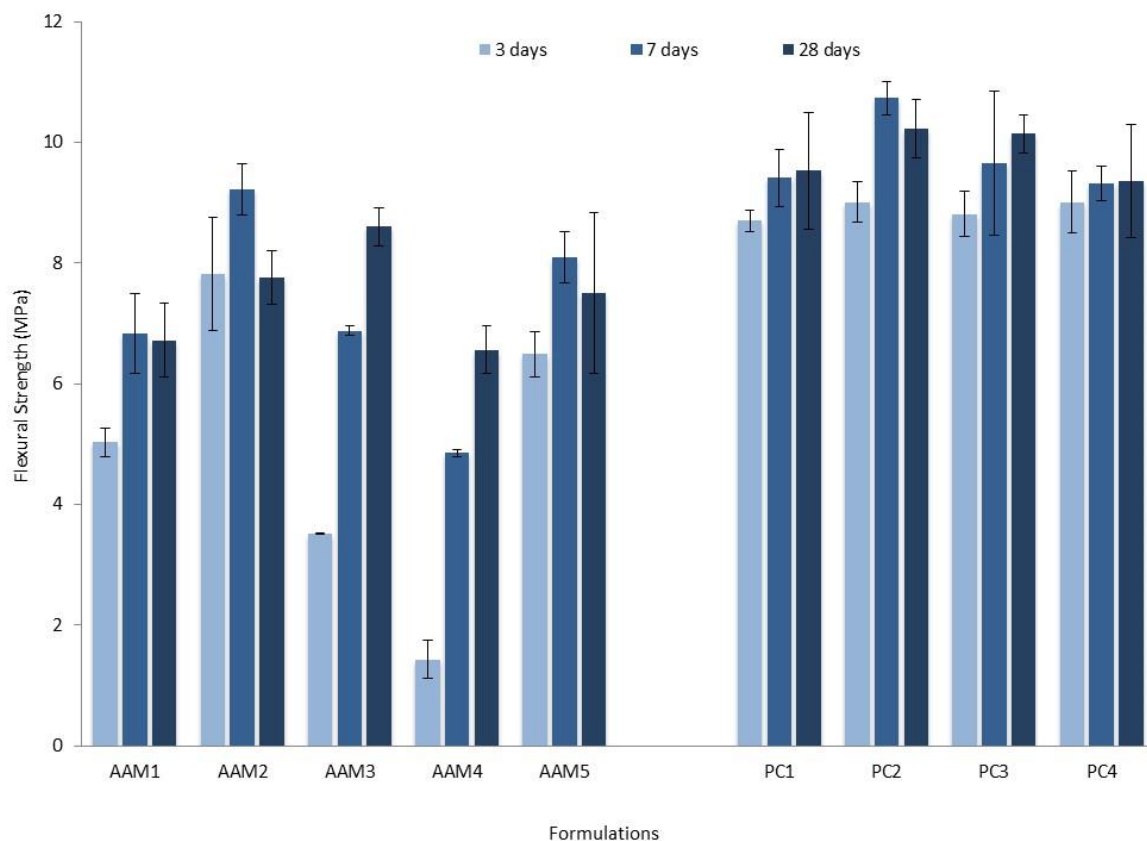
The BOF SS aggregate is known to positively affect the compressive strength because of its high strength and hardness, its rough surface and improved ITZ of the matrices. The rougher and irregular surface of the aggregate might have helped to increase the bonding between paste and aggregate. Additionally, Morone et al. [33], Liu et al. [34], and Nunes et al. [35] reported that BOF slag particles could react under alkaline conditions and form C-S-H/C-A-S-H gel, which could coexist with the gels from the activated binder (GGBFS) and improve the pore structure at the ITZ, enhancing the bonding between aggregate and matrix [21].

It is important to note that the strength development varied among the AAM mortars. The wet curing of the BOF SS aggregate may positively affected the volumetric stability of the SS (Figure 5.1b) with the hydrated compounds. Moreover, this pre-treatment might have densified the matrix and an improved bond at the ITZ for AAM2, leading to the highest mean compressive strength at all ages among all AAM mortars. This will be more evident during the microstructure assessment (Section 3.7). On the other hand, the carbonation process of the BOF SS aggregate negatively affected the strength development at early ages. The AAM3 mortar presented 16.61 MPa and 26.51 MPa of compressive strength at days 3 and 7, respectively, which are lower than the compressive strength at 3 days for AAM1 (30.52 MPa) and AAM2 (33.35 MPa). This will be further discussed in following sections 3.4 and 3.5, where calorimetry and an X-ray diffraction are presented.

In general, the replacement of natural aggregates with BOF SS did not negatively affect the strength of PC-based mortars (PC1 to PC4). The untreated BOF slag aggregate decreased the mean compressive strength at 28 days (12.88% lower). The higher water absorption of the SS may reduce the water available to the hydration of the Portland cement, weakening the cohesiveness between aggregate and paste [7]. Similar results were reported by Omur et al. [9] and Guo et al. [36] when high replacement of the natural aggregate by SS decreased the mechanical properties. On the other hand, both pre-treatments proved to be positive as they keep the compressive strength on the same level. The pre-treatments seemed to have improved the bond at the ITZ, increasing the mechanical behavior of the mortars. This is in accordance with the findings of Rehman et al. [27], Pang et al. [29], and Lai et al. [31], which reported the enhanced compressive strength by using SS as aggregate. The ITZ improvement will be further discussed in the following section (Section 3.7).

Both matrices (AAM and PC) performed very similar under compression, especially at 28 days. The use of the untreated and wet-cured BOF SS aggregate resulted in higher mean compressive strength for AAM mortars than on PC based, although the carbonated BOF SS aggregate did on PC mortars. Nevertheless, the mechanical evaluation of mortars with an industrial waste is only fulfilled when the durability is analyzed (see following Section 3.6).

Figure 5.4 presents the average results for the flexural strength of the studied mortars at 3, 7 and 28 days. The error bars represent the standard deviation. The flexural strength results are in line with the compressive strength. Flexural strength between 6 and 11 MPa was achieved at 28 days for AAM and PC mortars, regardless of the type of aggregate used. Overall, the replacement of the natural aggregate with BOF SS did not negatively affect their flexural strength at 28 days. Nevertheless, the mean strength values rose for the pre-treated aggregates (AAM2, AAM3, PC2 and PC3). In fact, the use of carbonated BOF aggregates was already reported to increase the flexural strength of a GGBFS alkali-activated mixtures [18], and an increase of flexural strength was also reported by Rehman et al. [27], when 80% of the natural aggregate was replaced by SS aggregate in a PC-based mortar. This behavior could be associated with the irregular shape of the BOF SS aggregate which might have improved the bonding between aggregate and paste [9].



**Figure 5.4 – Flexural strength of mortars.**

On the other hand, the strength development over time was different. The flexural strength at early ages was negatively affected by the carbonation process of the aggregate (AAM3), as happened in the compressive for the AAM. In contrary, the PC mortars presented higher strength at early ages regardless the type of aggregate and performed better in flexion at all ages. The results herein contradict what was found in the literature, i.e., higher flexural for alkali-activated slag than PC [37].

#### 5.3.4. Calorimetry

Calorimetry was only performed to explain the poor performance of the AAM mortar with carbonated-treated BOF SS. Figure 5.5 presents the heat flow rate and the cumulative heat release during the early ages of AAM1 and AAM3 mortars. The hydration process of an alkali-activated GGBFS is divided into five stages like in cement-based materials: the rapid initial dissolution, induction/reorganization, acceleration, deceleration, and stabilization periods [38-40]. The activation parameters and binders' composition are known to regulate and modify the activation kinetics [41]; however, these parameters were the same for AAM1 and AAM3. The only change was the aggregate, i.e., untreated and carbonated BOF SS, respectively.

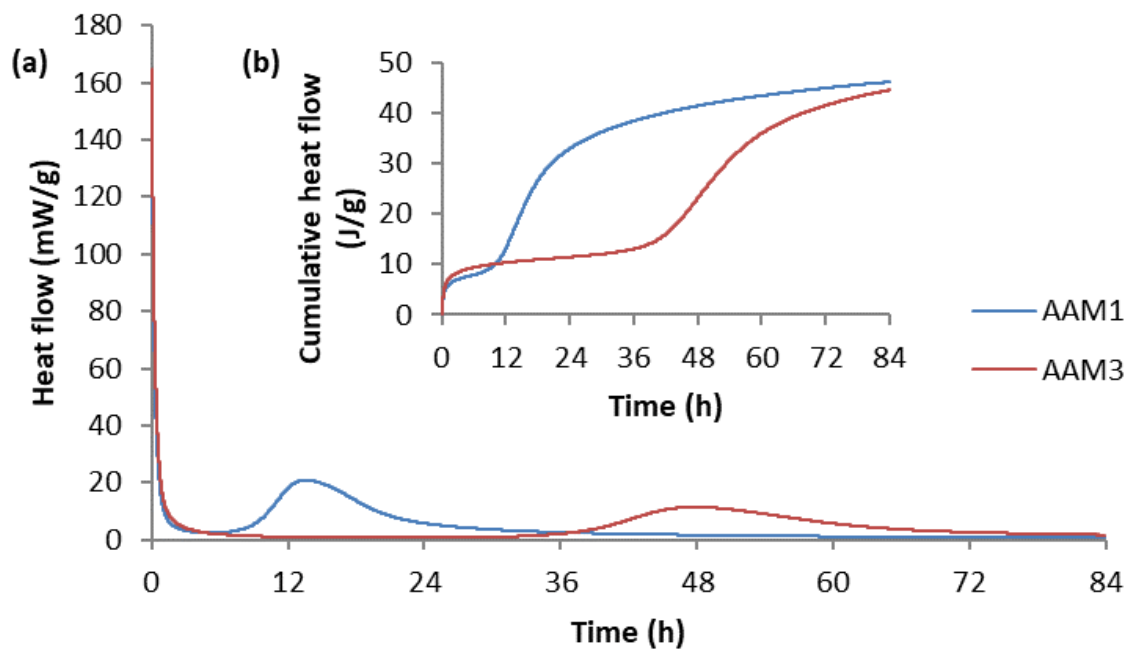


Figure 5.5 – Hydration kinetics of mortars: (a) heat flow and (b) cumulative hydration heat.

Figure 5.5 clearly presents a major difference between both hydration processes. A prolonged induction period is observed for AAM3 (up to 36 hours) after a fast dissolution period. This phase is characterized by the inhibition of the reaction. A second energy peak takes place around 48 hours. This led to a retardation of the acceleration phase where the large amount of hydration products is formed, directly affecting the strength development. In contrary, AAM1 had a much shorter induction period, and its second peak of energy took place at about 12 hours. The calorimetry results indicate that the carbonates formed all over the aggregate's surface, as presented in Figure 5.1c, interfered with the activation process. The results of calorimetry are in line with the mechanical strength, which have shown a significant late strength development of AAM3 compared to the other mortars (Figure 5.3).

### 5.3.5. X-ray diffraction (XRD)

XRD was carried out in addition to calorimetry to understand the unexpected results for AAM3. The explanation may lie on the presence of calcite on the aggregate's surface (Figure 5.1c). The calcium carbonate reacts with the sodium silicate solution resulting in sodium carbonate, as detected by the XRD analysis of the AAM3 mortar at 1 day (Figure 5.6). This finding is in accordance with the results published in the literature [42-44]. Part of the  $\text{Na}^+$  ions from the activator solution potentially react with the  $\text{CO}_3^{2-}$  provided by the calcium carbonate to form the sodium carbonate in solution. From that moment onwards, the alkali-activated process occurred with the coexistence of two alkali activators:  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  and the  $\text{Na}_2\text{CO}_3$  formed. That's the reason why the AAM3 presented a delay in strength development. Shi et al. [45,46] and Bernal et al. [47,48] have demonstrated in their studies that a prolonged induction period can be obtained when  $\text{Na}_2\text{CO}_3$  is used as activator in slag-based AAM.

The presence of  $\text{Na}_2\text{CO}_3$  among the activators slightly decrease the pH, leading to low rate of dissolution of the GGBFS [45]. At early ages, the formation of calcium carbonate and sodium-calcium carbonates are favored instead of the development of calcium silicate hydrate gels; the carbonate ions  $\text{CO}_3^{2-}$  from activator interact with the calcium ions  $\text{Ca}^{2+}$  from the dissolved GGBFS [47]. As the reaction progress, 2 to 3 days after casting, the precipitation of the C-S-H / C-A-S-H gels start [49], and the reaction continue like the reaction mechanism of  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  activated GGBFS [50,51]. The formation of C-S-H / C-A-S-H gels can be identified at the XRD pattern of the AAM3 at 3 days on Figure 5.6 (peaks at around  $29^\circ$ ,  $32^\circ$  and  $49^\circ$   $2\theta$  and the broader amorphous humps between  $5^\circ$  to  $10^\circ$  and  $25^\circ$  to  $35^\circ$   $2\theta$ ) [52,53].

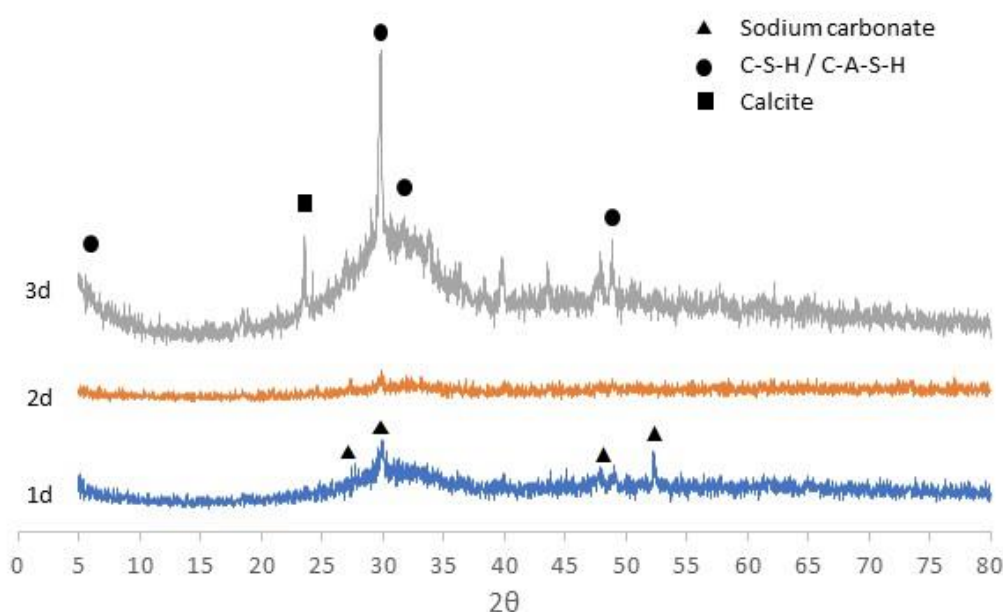
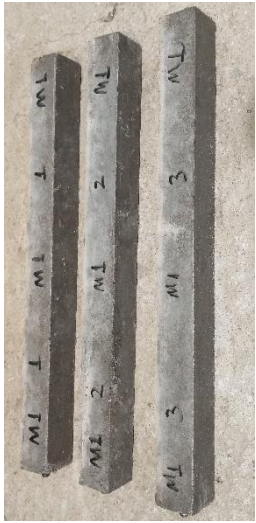


Figure 5.6 – XRD patterns of AAM3 mortar at early ages, 1, 2 and 3 days.

#### 5.3.6. Durability related assessment

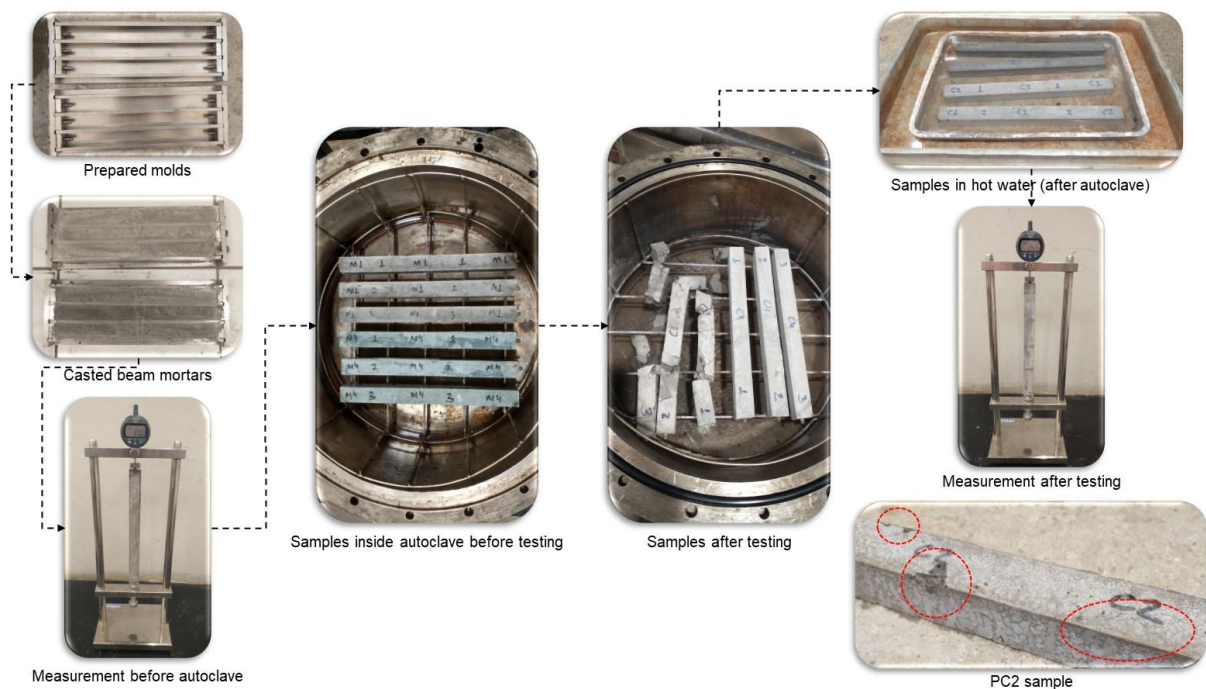
The testing procedure of the expansion autoclave testing is presented in Figure 5.7 and the results are summarized in Table 5.2. The results showed significant differences between the AAM and PC mortars. In some cases, the use of BOF slag as aggregate on AAM matrices presented better results of volume stability than on PC matrices. All 3 specimens of PC1 (untreated BOF slag) were completely destroyed after the accelerated testing, whereas 1 specimen of AAM1 was sound and 2 others locally broken in a single point. The better behavior of AAM mortar may be related to the reaction between the free silicon from the activator with the free oxides from the BOF slag forming stable silicates [19]. However, this mechanism is not enough to control 100% of the expansion. The remaining sound sample presented a length change of 7.56%.

**Table 5.2 – Autoclave expansion test results.**

| Formulation | Type of aggregate  | Expansion (%) |           |           |         | Photos of mortars beams                                                              |                                                                                     |
|-------------|--------------------|---------------|-----------|-----------|---------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|             |                    | Sample 01     | Sample 02 | Sample 03 | Average | Before                                                                               | After                                                                               |
| AAM1        | BOF SS untreated   | failed        | 7.56      | failed    | 7.56    |    |    |
| AAM2        | BOF SS water cured | 2.36          | 0.76      | 1.18      | 1.43    |    |    |
| AAM3        | BOF SS carbonated  | failed        | -         | -         | -       |   |   |
| AAM5        | Natural aggregate  | -1.60         | -2.40     | -0.58     | -1.53   |  |  |

**Table 5.2 – Autoclave expansion test results (cont.).**

| Formulation | Type of aggregate  | Expansion (%) |           |           |         | Photos of mortars beams                                                              |                                                                                     |
|-------------|--------------------|---------------|-----------|-----------|---------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|             |                    | Sample 01     | Sample 02 | Sample 03 | Average | Before                                                                               | After                                                                               |
| PC1         | BOF SS untreated   | failed        | failed    | failed    | -       |    |    |
| PC2         | BOF SS water cured | 0.94          | 2.37      | 2.32      | 1.88    |    |    |
| PC3         | BOF SS carbonated  | failed        | -         | -         | -       |   |   |
| PC4         | Natural aggregate  | 0.49          | 0.44      | 0.38      | 0.44    |  |  |



**Figure 5.7 – Autoclave expansion test procedure.**

The wet-cured specimens were all sound after testing for both AAM and PC mortars. Their length changes were in general low, i.e., average 1.43%, and 1.88%, respectively for AAM2 and PC2. In addition to a slightly higher expansion, PC2 also presented some spalling of the mortar and small cracks on the surface, as detailed in Figure 5.7. The carbonation process of the aggregate, on the other hand, seemed to improve the expansion resistance on the cementitious matrix (PC3) compared to PC1. But the expansion problem was not solved. Similar findings were reported by Pang et al. [29], when carbonated steel slag aggregate was used. The AAM3 was also heavily destroyed, and as it can be seen in the figures of Table 5.2. The sample was already broken before testing because of the lack of early mechanical strength of this matrix during the demolding process. The reason for that was discussed in the previous sections.

The reference mortars (natural aggregate) did not present any visual damage after the autoclave but presented different behavior. The AAM5 had a length change of -1.53%, which means that the alkali-activated matrix slightly shrunk. This has been previously reported in other studies [54]. The PC4 had a small expansion of 0.44%, which may be resulted from the cement expansion as presented by previous studies [32,55]. According to these results of the autoclave expansion test, the wet curing as a pre-treatment for the BOF slag aggregate is highly recommended, for AAM and PC matrices to control the delayed expansion producing stable hardened materials.

### 5.3.7. Structural and microstructural assessment

#### 5.3.7.1 X-ray computerized microtomography ( $\mu$ CT)

The  $\mu$ CT analysis was carried out on some chosen mortars: (i) AAM2 and PC2, the mortars that presented the best durability results, and (ii) AAM5 and PC4, both matrices with natural aggregate as comparative. The quantitative analysis results obtained by  $\mu$ CT are presented in Table 5.3. The results show highly interesting information. The total porosity, which includes all the entrapped air inside the sample, was found to be similar between the AAM mortars regardless of the type of aggregate. However, the use of the BOF SS aggregate considerably increased the total porosity of the PC mortars. Furthermore, the use of BOF SS aggregate increases the closed porosity within both pastes (AAM and PC). This suggests that the irregular surface of the BOF SS aggregate may hinders the air to escape from the paste during the casting process.

The OSRV is higher for AAM5 and PC4, which indicates that the BOF SS aggregate may promotes the complexity of the internal structure compared to the natural aggregate. Additionally, it was possible to identify approximately 2.5% of metallic material in the BOF SS aggregate for AAM2 and PC2 mortars, coming from residual steel particles that are not recovered in BOF SS with particle size below 4.8mm.

**Table 5.3 – Properties of the mortars obtained by  $\mu$ CT.**

| Formulation | Total porosity (%) | Paste      |                     |                             | Aggregate  |                     |                             | Metallic part from aggregate |                     |                             |
|-------------|--------------------|------------|---------------------|-----------------------------|------------|---------------------|-----------------------------|------------------------------|---------------------|-----------------------------|
|             |                    | Volume (%) | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) | Volume (%) | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) | Volume (%)                   | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) |
| AAM2        | 22.39              | 74.89      | 21.16               | 0.00614                     | 17.09      | 27.57               | 0.01930                     | 2.55                         | 1.36                | 0.01597                     |
| AAM5        | 22.72              | 82.09      | 15.90               | 0.00307                     | 17.75      | 33.80               | 0.04092                     | -                            | -                   | -                           |
| PC2         | 22.80              | 74.71      | 20.15               | 0.00657                     | 22.75      | 28.20               | 0.02145                     | 2.44                         | 1.46                | 0.01583                     |
| PC4         | 15.77              | 86.53      | 10.65               | 0.00653                     | 14.72      | 34.80               | 0.04193                     | -                            | -                   | -                           |

OSRV: object surface/volume ratio.

The distribution of paste and aggregate along the sample was also evaluated by  $\mu$ CT as a mean to identify possible segregation of the aggregate. Segregation is the unintentional separation of the particles of an aggregate, causing a lack of uniformity in their distribution within the mortar [56]. Figure 5.8 presents the percentage area of the paste and aggregate phases along the sample, top to bottom. None of the mortars presented a considerable segregation of the aggregates. However, AAM2 appears to have a more constant distribution with ~15% of aggregate and ~80% of paste top to bottom. Is possible to notice that the AAM5 and the PC mortars presented some aggregate segregation, with the following approximate distribution: (i) 7% to 20% top to bottom for AAM5 and (ii) 12% to 27% top to bottom for PC2 and 4% to 16% top to bottom for PC4. These findings may indicate that the use of BOF SS aggregate instead

of natural aggregate in AAM mortars improved the cohesion of the mortar and prevented segregation [56] even if the mortars presented the equivalent consistency in the fresh state (Figure 5.2). In addition, the use of BOF SS aggregate decreased the workability for the PC mortars (Figure 5.2) and yet some segregation was observed.

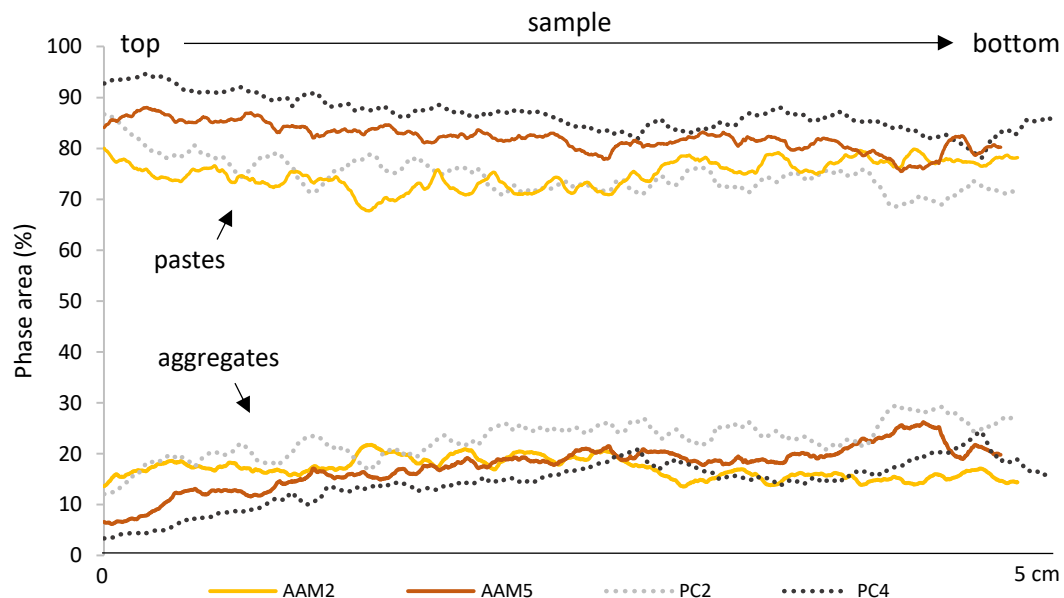
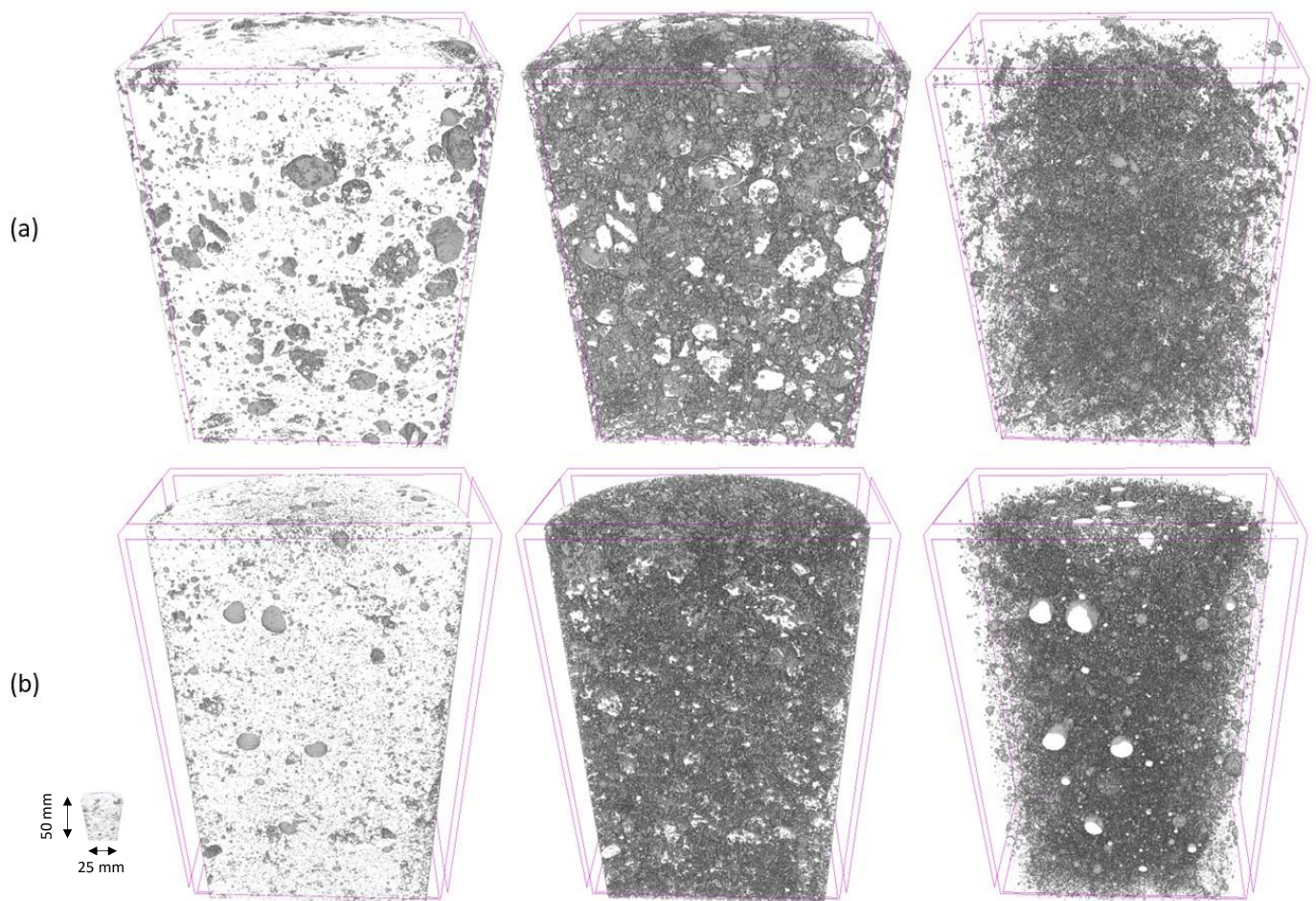


Figure 5.8 – Phase percent area distribution through the sample (Z axis).

Figure 5.9 and Figure 5.10 present the 3D images of the studied mortars generated by  $\mu$ CT. It is possible to observe the distribution of each phase within the sample with the 3D reconstruction of the real situation. It is important to point out the increased pores volume in the AAM mortars compared to the PC mortars, regardless the type of aggregate, and the increased volume of pores in the PC matrix when the BOF SS is used instead of natural aggregates. Another noteworthy visual observation in Figure 5.9a and Figure 5.10a is the irregular shape of the BOF SS aggregate and its influence on the morphology of the paste distribution. In general, the  $\mu$ CT has been revealed as a very valuable technique for volume quantification in mortars [57]. However, there is still no standard procedure for this type of characterization. Therefore, comparisons with other studies are complicated since the numerical results of this technique are strongly influenced by the adjustment of the test parameters. Nevertheless, the evaluation of the use of SS as aggregate in AAM mortars by  $\mu$ CT is an innovative feature of this present work.



**Figure 5.9 – 3D images from  $\mu$ CT of (a) AAM2, and (b) AAM5: paste (left, in white), aggregate (center, in grey), and pores (right, in grey).**

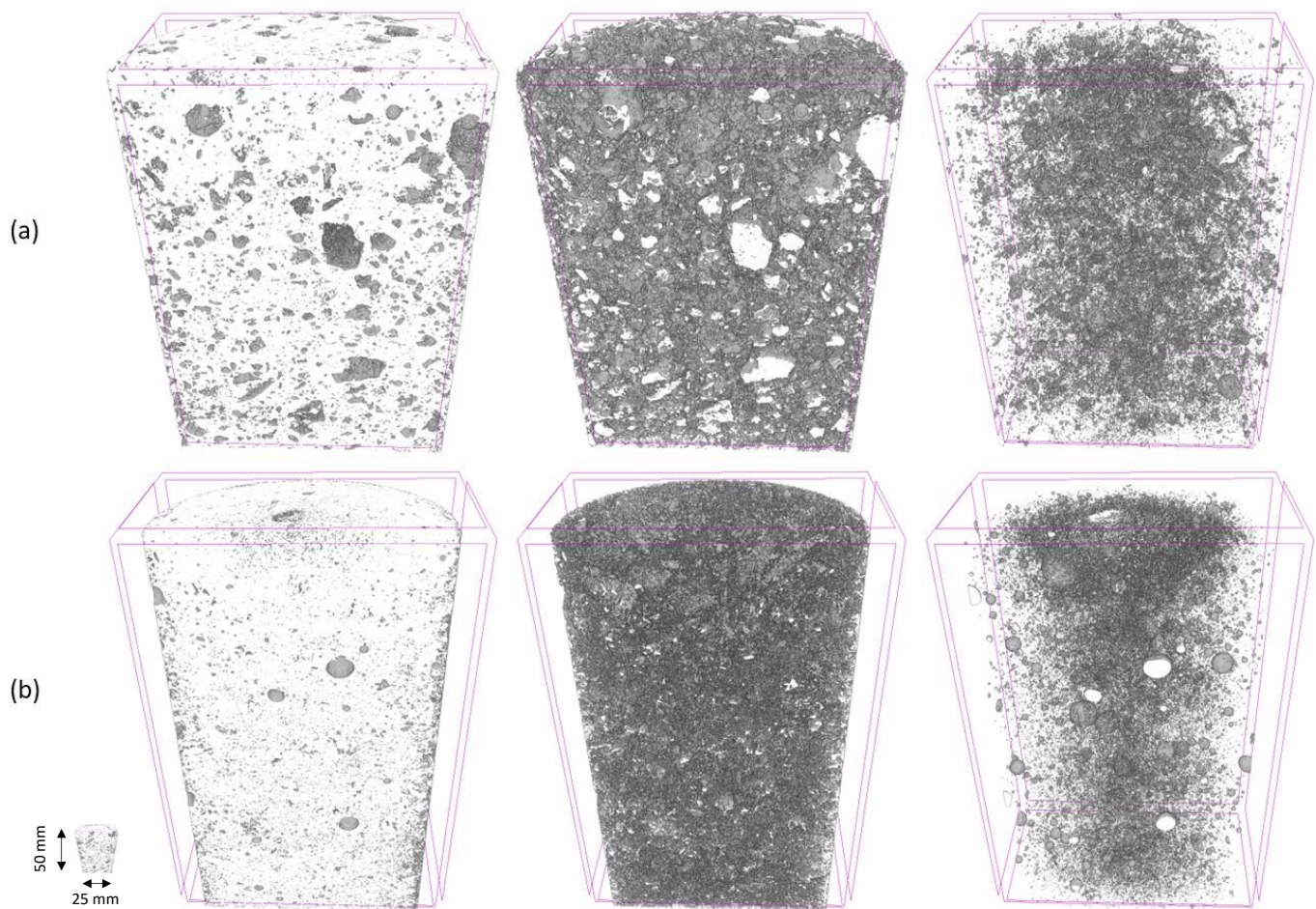


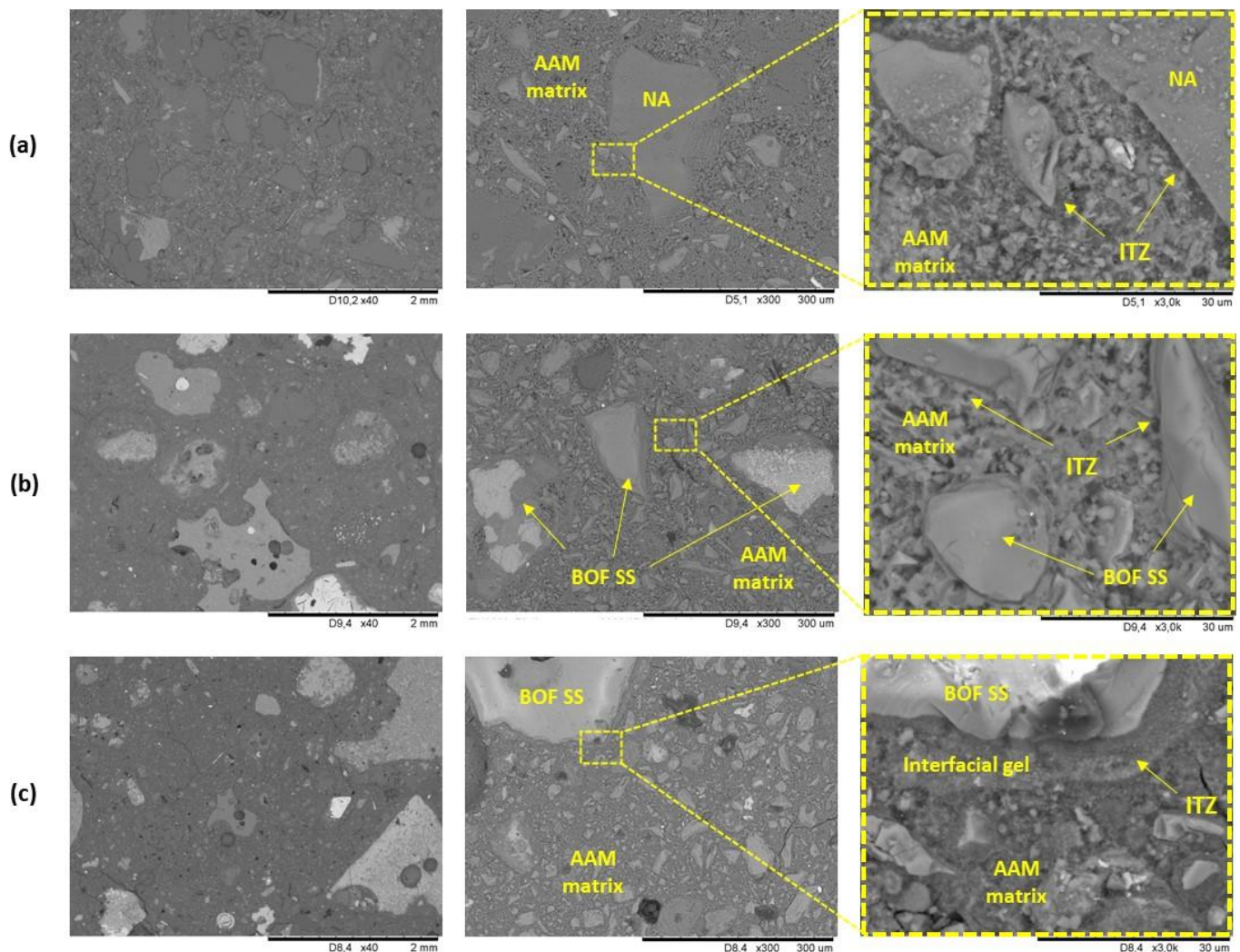
Figure 5.10 – 3D images from  $\mu$ CT of (a) PC2, and (b) PC4: paste (left, in white), aggregate (center, in grey), and pores (right, in grey).

### 5.3.7.2 Scanning electron microscopy (SEM)

The characterization of the microstructural composition of the mortars was carried out by using a SEM, after 28 days of curing. Figure 5.11 and Figure 5.12 show the SEM images of the microstructure of the AAM and PC mortars, respectively, highlighting the ITZ. Figure 5.11 also presents a comparison between the influence of the natural aggregate (Figure 5.11a), the untreated BOF SS aggregate (Figure 5.11b), and the wet cured BOF SS aggregate (Figure 5.11c) on the microstructure of the AAM mortars. The major differences between the matrices are the morphology of the aggregates, the densification of the matrix and the definition of the interface between aggregate and matrix. From the first image on the left (40x magnified) of each mortar in Figure 5.11 it is possible to see the irregular, porous and rougher surface of the BOF SS aggregate compared to the natural one, which leads to a well-defined ITZ of the latter for it does not adhere to the reaction products of the matrix surrounding them [16,21].

The high magnification (3000x) images of Figure 5.11 clearly show the difference in the densification of each matrix and the characteristics of the ITZ. The AAM5 mortar (Figure 5.11a) and the AAM1 mortar (Figure 5.11b) presented a porous and spongy

internal structure, while the AAM2 mortar (Figure 5.11c) presented a dense microstructure. Moreover, the latter presented a strong ITZ, no micro-cracks and the presence of a gel phase (most likely resulting from the reaction between the BOF SS in the alkaline system [35]) which promotes the bond between aggregates and paste. The less porous ITZ and denser matrix made with wet cured BOF SS aggregate (AAM2) explained the better mechanical performance (Figure 5.3).



**Figure 5.11 – SEM images showing the microstructure of (a) AAM5, (b) AAM1, and (c) AAM2 (NA: natural aggregate, BOF SS: BOF steel slag aggregate, ITZ: interfacial transition zone).**

The microstructure of the PC mortars (Figure 5.12) is also in line with the results of the mechanical properties. It is possible to see a clear distinction of the ITZ structure when natural (Figure 5.12a), untreated BOF SS (Figure 5.12b) and carbonated BOF SS (Figure 5.12c) aggregates are employed. A more porous ITZ is present in PC1 (Figure 5.12b), when the natural aggregate is replaced by the untreated BOF SS. This suggests, once again, that the higher water absorption of the SS reduced the hydration of the cement in this region. The consequence is the poor adhesion between aggregate and matrix [7]. This is in accordance with the lower compressive strength found for PC1 compared to PC4 (Figure 5.3). Alternatively, PC3 presented a denser ITZ (Figure

5.12c), with embedded paste on the aggregate's particles without micro-cracks or any voids. The improved adhesion between matrix and the carbonated BOF SS aggregate might explained the better mechanical performance (Section 1), which also is reported in Pang et al. [29].

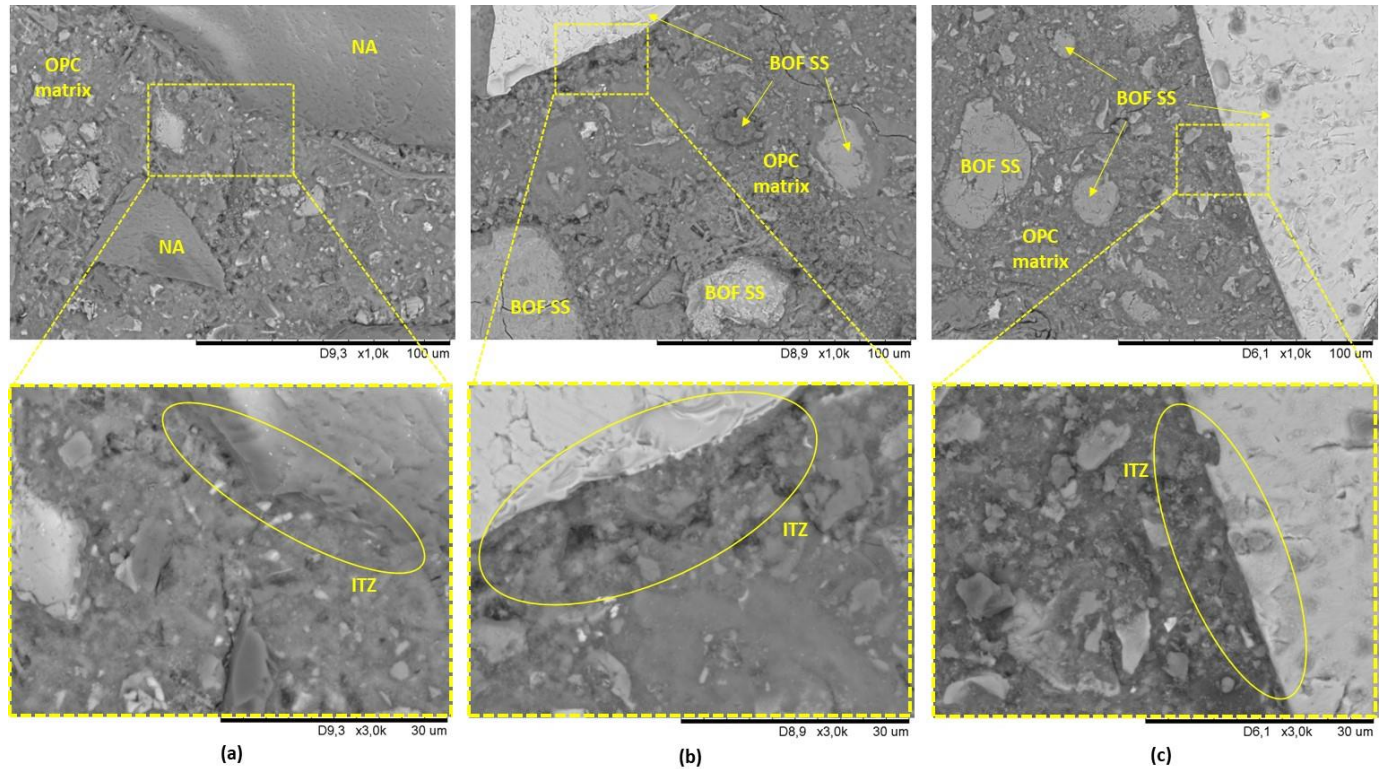


Figure 5.12 – SEM images showing the microstructure of: (a) PC4, (b) PC1, and (c) PC3 (NA: natural aggregate, BOF SS: BOF steel slag aggregate, ITZ: interfacial transition zone).

#### 5.4. Concluding remarks

The present study explored the possibility of using BOF SS as a single aggregate in an alkali-activated GGBFS-based mortar and in PC-based mortar. The effect of the pre-treatment (wet curing, and carbonation), on the fresh, hardened and durability (accelerated expansion test) properties of mortars was evaluated through a series of experiments. The focus was given to the mechanical, structural, and microstructural behavior of the mortars. The main conclusions are:

- The mechanical behavior of AAM and PC mortars was very similar regardless the type of aggregate used, especially at 28 days. In fact, the replacement of natural aggregate with BOF SS did not negatively affect the mechanical strength. However, the strength development at early ages of AAM was strongly affected when the carbonated BOF SS aggregate was used. This happened due to the formation of sodium carbonate at the beginning of the alkali-activated process, resulted from the reaction of  $\text{Na}^+$  ions from the activator and the calcium carbonate from the carbonated aggregate.

- Results of  $\mu$ CT show that the total porosity of AAM mortars is equivalent regardless the aggregate and increased in PC mortar when BOF SS aggregate is used. Moreover, the use of BOF SS aggregate promotes the complexity of the internal structure of mortars compared to natural aggregate. In addition, the use of wet-cured BOF SS aggregate instead of natural aggregate in AAM mortars improved the cohesion of the mortar and prevented segregation.
- Microstructural observation on SEM indicates a dense microstructure, less porous ITZ and no micro-cracks when wet-cured BOF SS aggregate is employed in AAM. The ITZ presented a gel phase (most likely resulting from the reaction of the BOF SS aggregate in the alkaline system) which promoted the bond between aggregates and paste. On the other hand, the carbonation process seemed to improved adhesion between aggregate and matrix only for the PC mortar.
- The wet curing as pre-treatment is highly recommended for AAM and PC matrices to control the delayed expansion of the BOF SS, as the former ensures the production of sound hardened materials after accelerated testing. Alternatively, the carbonation process appeared to slightly improve the expansion resistance only for PC matrix but does not solve the expansion issues.

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## **6. NOVEL ECO-FRIENDLY ALKALI-ACTIVATED BOF STEEL SLAG-BASED MORTAR**

## **6.1. Introduction**

The experimental work so far in this thesis assessed the activation parameters for using SS as precursor (Chapter 4) and the pre-treatment methods for using SS as aggregate (Chapter 5), both in alkali-activated matrices. The last step of the proposed experimental program is to develop a AAM mortar by using SS as the single raw material, as precursor and aggregate. This was carried out with the support of findings from the previous chapters.

The research on SS-based alkali-activated materials is still incipient with some controversial results [1]. Most of the results presented in the literature are restricted to the employment of SS as binder in AAM pastes [2–4]. Some studies also evaluated the use of SS as binder [5,6] or as aggregate [7,8] in AAM mortars. Lu et al [9] and Cristelo et al [10] are the only two studies found in the literature that combine SS as aggregate and as binder. However, they both mix SS with other binders in AAM mortars. So, the great research opportunity and novelty of this chapter is to study and present results of SS as the neat binder and aggregate in alkali-activated material matrices, as well as durability studies (accelerated expansion testing).

This chapter compares a SS-based AAM mortar using a wet-cured pre-treated BOF SS as the single aggregate with two reference mortars: (i) GGBFS-based AAM and (ii) PC-based. The early age hydration process was evaluated by calorimetry, the fresh properties were evaluated by the consistency test, the mechanical properties by compressive strength, and the physical properties by the water saturation method. The mortars were also submitted to mercury intrusion porosimetry (MIP) to assess the pore size distribution, X-ray microtomography ( $\mu$ CT) to assess the internal structure and SEM to assess the microstructure changes, particularly at the ITZ between aggregates and matrices. The durability of the mortars was estimated via accelerated expansion under autoclave conditions.

## **6.2. Experimental program summary**

The complete description of the materials and methods used in this chapter is presented in chapter 3. Three different mortars were studied by changing the precursor, as presented in Table 6.1. The AAMs were produced using an optimized combination of activator source determined on previous the chapter 4, with silica

modulus in the activator of 1.50 and 4% of  $\text{Na}_2\text{O}$ . The water to binder ratio (w/b) was kept constant at 0.53. The aggregate to binder ratio (a/b) was also determined on the chapter 5 and kept constant at 2.0 by mass. The PC mortars were made using a w/b of 0.47, determined on preliminary laboratory work.

**Table 6.1 – Mix proportions.**

| Formulation | Type of aggregate  | Solution/binder | Water/binder | Proportions in mass |           |       |                           |      |
|-------------|--------------------|-----------------|--------------|---------------------|-----------|-------|---------------------------|------|
|             |                    |                 |              | Binder              | Aggregate | Water | $\text{Na}_2\text{SiO}_3$ | NaOH |
| SS-AAM      | BOF SS water cured | 0.63            | 0.53         |                     | 2.00      | 0.43  | 0.18                      | 0.02 |
| GGBFS-AAM   | BOF SS water cured | 0.63            | 0.53         | 1.0                 | 2.00      | 0.43  | 0.18                      | 0.02 |
| PC          | BOF SS water cured | -               | 0.47         |                     | 2.00      | 0.47  | -                         | -    |

### 6.3. Results and discussion

#### 6.3.1. Fresh property

Table 6.2 presents the results of the consistency of each mortar. The AAM mortars had a very similar consistency; 277 mm for SS and 273 mm for GGBFS. On the other hand, the PC mortar presented a much lower workability, 200 mm. To the authors knowledge, there is no study that evaluates the influence of BOF SS aggregates on the workability of SS-based AAM. Lee et al. [11] reported a good workability using only BOF SS aggregates in a GGBFS/FA-based alkali-activated mortar. The reduced workability by using SS as fine aggregate into PC-based matrices was also previously observed by other authors [12-18].

**Table 6.2 – Consistency of fresh mortars.**

|                               | SS  | GGBFS | PC  |
|-------------------------------|-----|-------|-----|
| Average value flow table (mm) | 277 | 273   | 200 |

#### 6.3.2. Early hydration results via Calorimetry

The hydration process of alkali-activated slags is like cement-based materials, divided into rapid initial dissolution, induction, acceleration, deceleration, and stabilization periods [19]. Figure 6.1 presents the heat flow and the cumulative heat release for the two alkali-activated mortars up to 84 hours. It is possible to observe a clear difference between both hydration curves. The first exothermic peak observed in both mortars is due to the rapid dissolution of the calcium silicates and aluminates from the slags [20]. As shown in Figure 6.1a, the SS-AAM presented a higher intensity of this first peak,

221.14 mW/g, against 149.72 mW/g from the GGBFS. The second phase is the induction period, which is characterized by the inhibition of the reaction [21]. This region was significantly shortened for the SS-AAM mortar, since the aluminum phase of the BOF SS does not form crystalline products, then no reaction is delayed [20]. The second peak in Figure 6.1a corresponds to the acceleration and deceleration phase, when hydration products are formed [22]. The behavior of SS-AAM and GGBFS-AAM is considerably different at this stage. The peak starts before 1 hour for SS-AAM and around 12 hours for GGBFS-AAM. However, these results do not quantify the reaction products, but rather indicate when the hydration process occurred. The reaction products are more related to the mechanical strength development, which will be further discussed in the following section (Section 6.3.3).

Other significant difference between the hydration of SS-AAM and GGBFS-AAM was the cumulative heat output presented in Figure 6.1b. The activation parameters were constant, so the total heat cumulative was influenced by the slag's solubility [23]. GGBFS is much more amorphous than SS), with more soluble silica to react and increase the degree of reaction [24]. The cumulative heat values were 21.53 J/g and 46.19 J/g for SS and GGBFS, respectively. Still, the GGBFS mortar presented a lower heat release than other GGBFS-based alkali-activated pastes (80-200 J/g) [25], which may have been influenced by the BOF SS aggregate fine particles. The SS mortar presented a low cumulative heat value, which is in accordance with the previous findings of the authors [4].

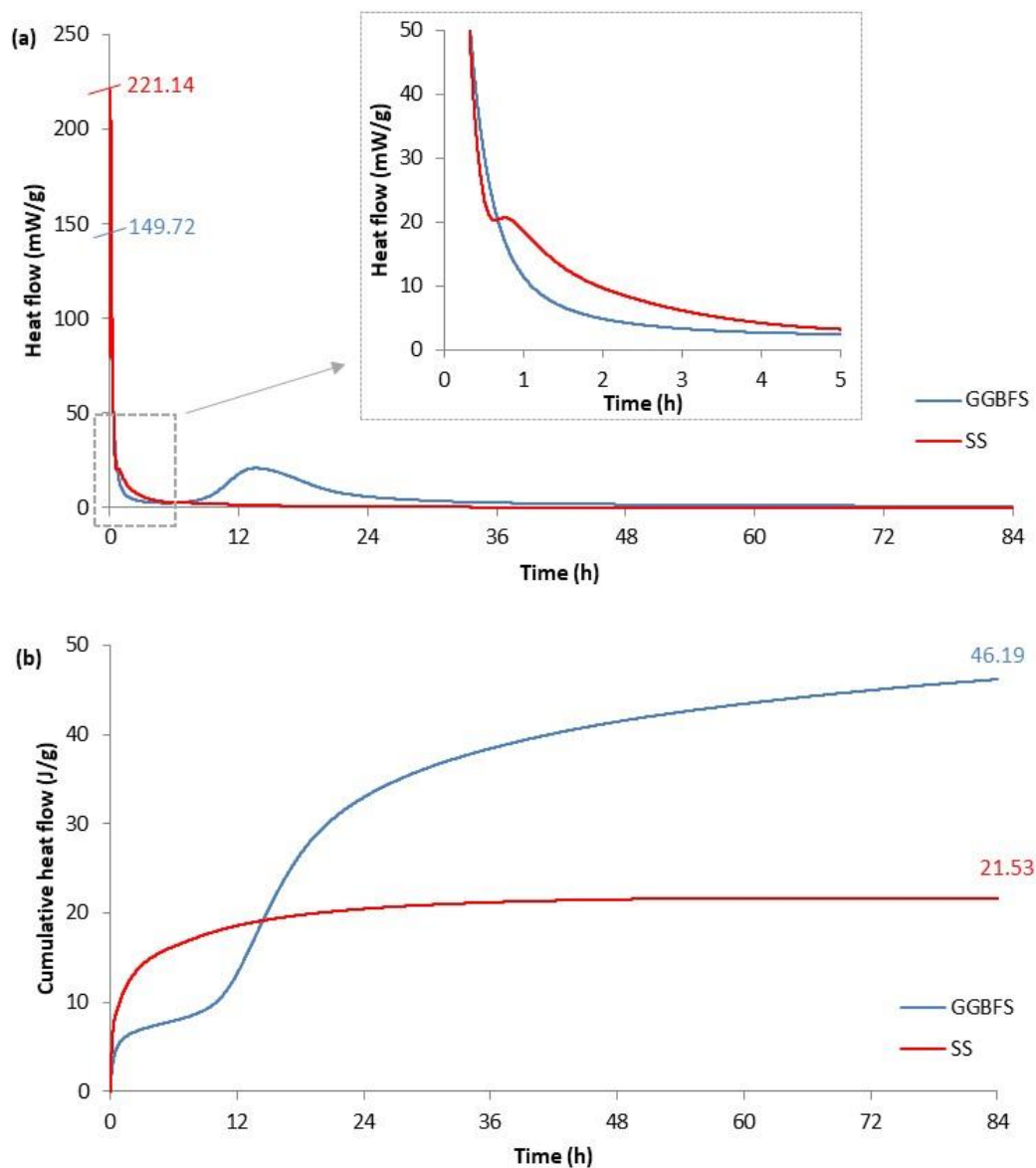
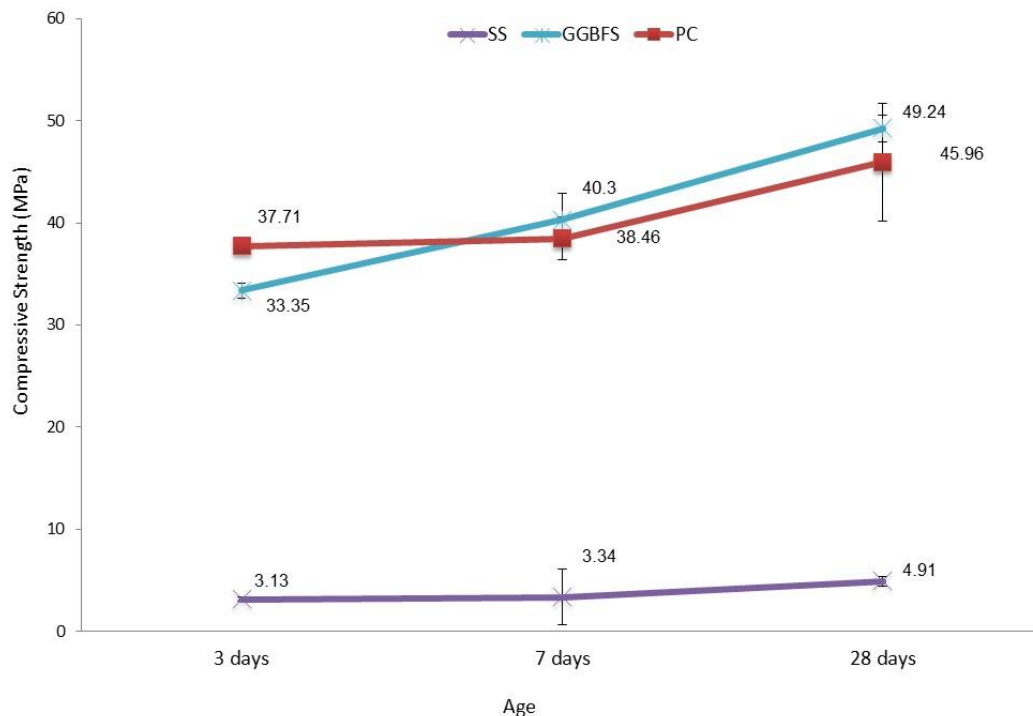


Figure 6.1 – Hydration kinetics of mortars: (a) heat flow and (b) cumulative hydration heat.

### 6.3.3. Hardened properties

Figure 6.2 presents the average results for the compressive strength of the studied mortars at 3, 7 and 28 days. The error bars represent the standard deviation. The three mortars increased the compressive strength over time, i.e. 56.87%, 47.65% and 21.88% for SS-AAM, GGBFS-AAM and PC, respectively. These results confirmed the alkali activation process of the BOF SS and the hardening of the matrix, such as it was found on previous chapter 4. However, the compressive strength of the SS-AAM is much lower. The GGBFS-AAM and PC mortars presented mechanical strength at 28 days between 45 to 50 MPa, which is typical for structural applications. On the other

hand, the SS-AAM achieved only 5 MPa, which restrict its employment to non-structural application.



**Figure 6.2 – Compressive strength of mortars.**

To the author's knowledge, there is no study in the literature using the SS as neat binder and aggregate in AAM mortars. Some studies did use the SS as the single binder in AAM pastes [2-4,19,22,26], some in AAM mortars but with natural sand as aggregate [5,6,27], and some in AAM mortars as the single aggregate but combining SS with other precursors [9,10]. Morone et al. [5] is the only study so far that used BOF SS as single precursor to produce AAM mortar, and they reported a compressive strength up to 2 MPa using a carbonation curing with elevated temperature. On the other hand, Ozturk et al. [6] studied the use of EAF SS as binder on the development of AAM mortar. The authors employed thermal curing of 40°C and 80°C and reported compressive strength of 5 MPa and 20 MPa, respectively. Additionally, Adesanya et al. [27] evaluated the properties of AAM mortar produced with ladle SS as binder. They also used thermal curing (60°C) and achieved up to 50 MPa of compressive strength. Lu et al [9] and Cristelo et al [10] were the only studies that evaluated the use of SS as both binder and aggregate, but they mixed the SS precursor with GGBFS [9] and PFA [10]. The first study studied the activation of 20% of BOF SS combined with 80% of GGBFS and BOF SS as fine aggregate in order to evaluate the effects on the mortar

expansion. They reported a compressive strength of 35 MPa for the AAM mortar [9]. The second assessed the activation of 50% of EAF SS combined with 50% of PFA and EAF SS as fine aggregate and reported compressive strength up to 20 MPa [10]. Therefore, the findings of this present research proved to be relevant and thus adds new knowledge to this field of study.

The average results for the apparent density, porosity, and water absorption of the mortars at 28 days are presented in Figure 6.3. The standard deviation is indicated by the error bars. The black triangles represent the apparent density, the solid bars represent the water absorption, and the hatched bars represent the porosity. The differences found in the physical properties are mainly due to the matrix, since the aggregate used to produce the mortars was the same. The apparent density of SS-AAM, GGBFS-AAM and PC mortars were  $2.04 \pm 0.02 \text{ g/cm}^3$ ,  $2.13 \pm 0.00 \text{ g/cm}^3$ , and  $2.21 \pm 0.02 \text{ g/cm}^3$ , respectively. The density of the mortar is related to the casting process, the amount of incorporated air and to the densification of the matrix (degree of hydration). One may note that SS (as binder) presented higher density than the GGBFS (Chapter 3 - section 3.2.1), which has no effect on the density of the mortars. This will be further discussed in the section 6.3.5.

The mean porosities were 35.71%, 30.87%, and 26.32%, respectively. Overall, the porosity is highly related to the w/b ratio, which plays an important role in the consistency of mortars [28]. It is important to state that the PC mortar was mixed with a lower w/b, i.e., 0.47 against 0.53 (Table 6.1). This may contribute to the lowest porosity and higher density of the PC mortar. To the author's knowledge, no previous study presented results on the influence of the BOF SS aggregate on the apparent density and porosity of AAM mortars.

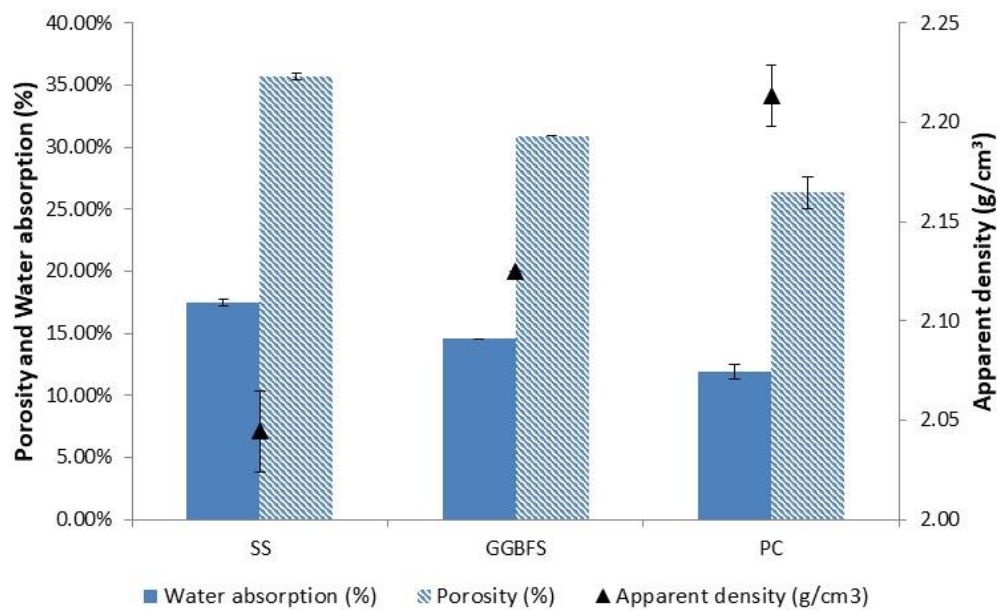


Figure 6.3 – Apparent density, porosity, and water absorption of mortars.

#### 6.3.4. Durability related assessment

The mortars were tested under the autoclave conditions to accelerate the expansive reactions. The results are presented in Table 6.3. The GGBFS-AAM and PC mortars presented a very good behavior in terms of volume stability. The employment of the wet-cured SS aggregate may have contributed to that. All three tested samples of GGBFS-AAM and PC were sound after testing with low average length changes, 1.43% and 1.88%, respectively. However, the PC mortar still presented some spalling of the mortar and small cracks on the surface. These results indicate that the AAM mortar (GGBFS) have excellent volume stability, which was also concluded by Liu et al. [9] in their study.

On the other hand, the SS-AAM samples were destroyed into fragments during autoclaving, as shown in the pictures of Table 6.3. Two out of three samples were already broken before testing because of the low early mechanical strength of the mortar (Figure 6.2) and the high slenderness of the samples. Hence, the SS-AAM did not presented sufficient mechanical strength to be evaluated by the accelerate autoclaving testing. No other study in the literature evaluated the volume stability of SS-based mortar to permit comparison.

Table 6.3 – Autoclave expansion test results.

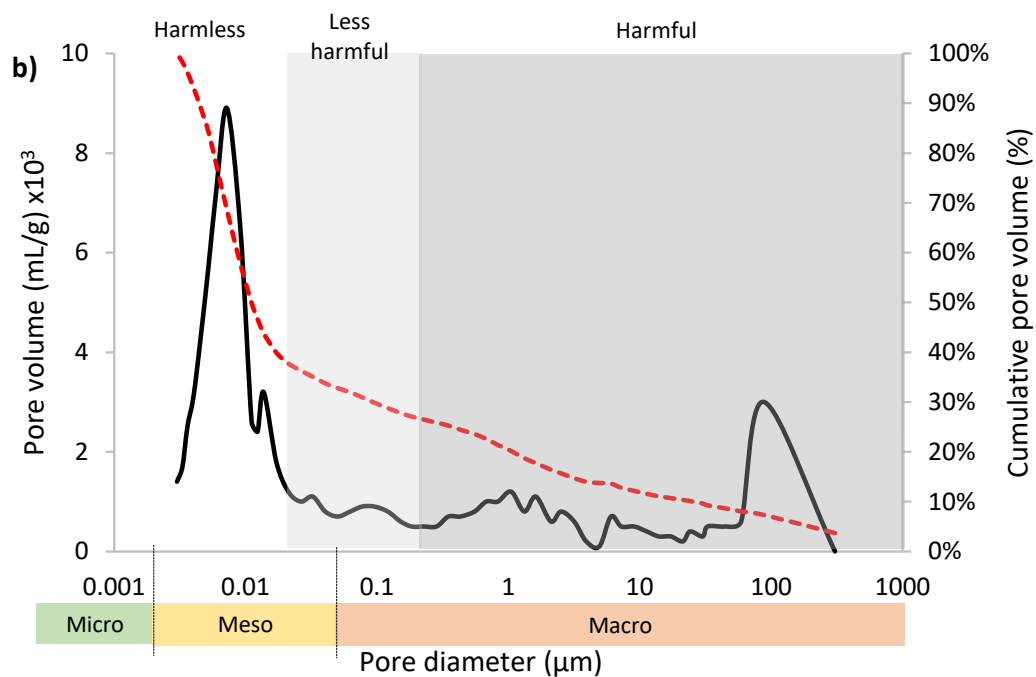
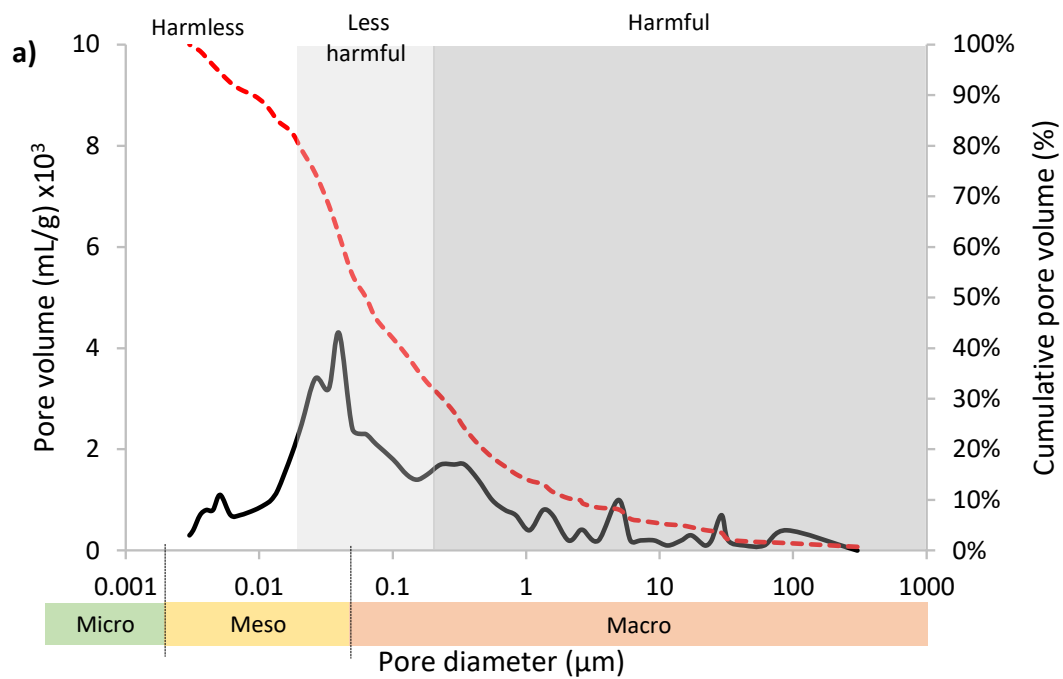
| Formulation | Expansion (%) |           |           | Photos of mortars beams |                                                                                                                                                                                                             |
|-------------|---------------|-----------|-----------|-------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|             | Sample 01     | Sample 02 | Sample 03 | Average                 |                                                                                                                                                                                                             |
| SS-AAM      | failed        | failed    | failed    | -                       | <div>Before</div>  <div>After</div>      |
|             |               |           |           |                         |                                                                                                                                                                                                             |
| GGBFS-AAM   | 2.36          | 0.76      | 1.18      | 1.43                    | <div>Before</div>  <div>After</div>      |
|             |               |           |           |                         |                                                                                                                                                                                                             |
| PC          | 0.94          | 2.37      | 2.32      | 1.88                    | <div>Before</div>  <div>After</div>  |
|             |               |           |           |                         |                                                                                                                                                                                                             |

### 6.3.5. Structural and microstructural assessment

#### 6.3.5.1 Mercury intrusion porosimetry (MIP)

The MIP pore size distributions are presented in Figure 6.4 and the quantitative results summarized in Table 6.4. Significant differences can be seen from the pore size distribution of the mortars. Most of the pores in the SS-AAM and PC mortars (Figure 6.4a and c, respectively) are distributed between 0.01  $\mu\text{m}$  and 1  $\mu\text{m}$ , but with a great difference in the pore volume: SS-AAM has total volume of 0.18 mL/g against 0.08 mL/g of the PC. This range is characteristic of meso and macropores and from the Portland cement hydration products (C-S-H gel) pores [29]. Similar pore size distribution of PC-based materials was also reported by Lu et al. [9]. On the other hand, the GGBFS-AAM (Figure 6.4b) mortar presented a massive concentration of pores around 0.01  $\mu\text{m}$  (mesopores) and some pores around 100  $\mu\text{m}$  (macropores). Higher mesopores volume is characteristics of alkali-activated GGBFS-based matrices [30], especially the ones activated using water glass (sodium silicate) [31]. The presence of those macropores is due to incorporated air during the casting process. The GGBFS-AAM total volume of pore is comparable to the PC mortar, 0.08 mL/g (Table 6.4).

The average pore diameter is considerably reduced on the GGBFS-AAM (10.50 nm) compared to the PC mortar (95.60 nm), which may be related to the ability of the GGBFS refine the pore structure [20]. The total porosity results showed that the SS-AAM have a much higher internal porosity e.g., 14.50%, than the others (GGBFS-AAM: 7.40%, PC: 7.90%). This finding is in accordance with the total porosity trend found in the saturation test (Figure 6.3).



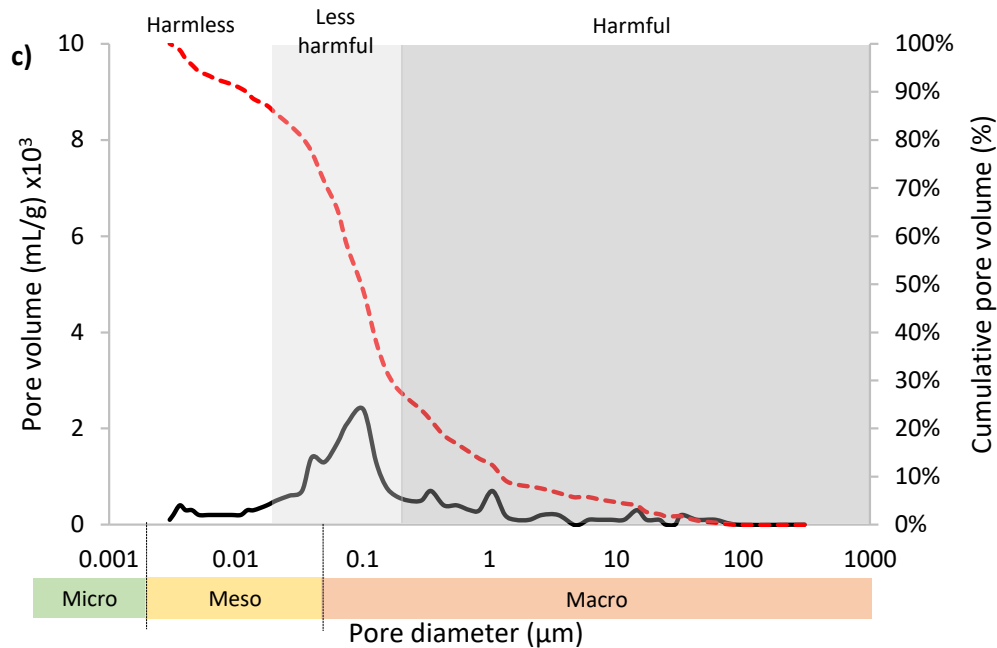


Figure 6.4 – Pore size distribution: (a) SS-AAM, (b) GGBFS-AAM, and (c) PC.

Table 6.4 – MIP results of mortars.

| Formulation | Average pore diameter (nm) | Total intruded volume (mL/g) | Total pore area (m <sup>2</sup> /g) | Porosity (%) |
|-------------|----------------------------|------------------------------|-------------------------------------|--------------|
| SS-AAM      | 66.20                      | 0.18                         | 23.47                               | 14.50        |
| GGBFS-AAM   | 10.50                      | 0.08                         | 31.87                               | 7.40         |
| PC          | 95.60                      | 0.08                         | 8.10                                | 7.90         |

The pore system in cement-based materials can be classified into three ranges according to the adverse effect on the matrix: (i) harmless pores (<20 nm), less harmful pores (20-200 nm), and harmful pores (>200 nm) [16,22]. Figure 6.5 brings the percentage of pores of the mortars distributed in those pore size envelopes. All three mortars present a majority of harmless and less harmful pores, which is preferred in terms of mechanical strength and durability of the material. An interesting finding is that the GGBFS-AAM presents most of its pores (62.26%) in the harmless range, much more than the others (SS: 20.85%, PC: 14.60%). This suggests that the GGBFS-AAM internal structure is denser. The microstructure of the mortars will be discussed in the following section 6.3.5.3. Results from the MIP indicate that the pore size distribution, average pore diameter, porosity, and pore volume distribution are more related to the matrix than to the aggregate. The use of the BOF SS aggregate do not present any negative effect in terms of those characteristic of the developed mortars.

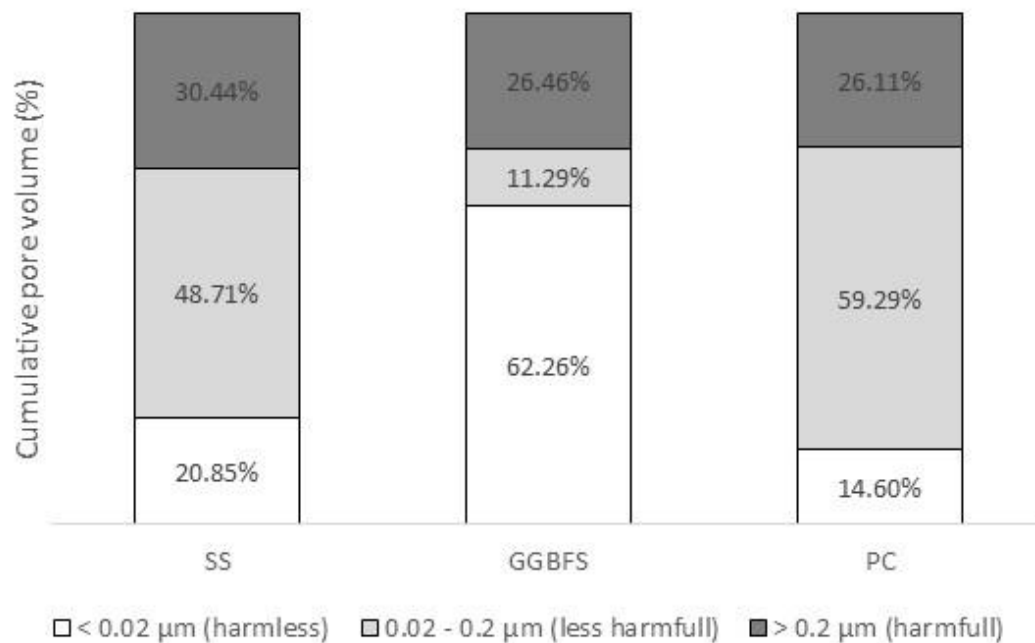


Figure 6.5 – Cumulative pore volume distribution.

#### 6.3.5.2 X-ray computerized microtomography

The results of the quantitative analysis obtained by  $\mu$ CT are presented in Table 6.5. The results show highly interesting information. Firstly, the total porosity of the SS-AAM, which includes all the entrapped air within the sample, is considerably higher than the others (10 to 12% higher). These results are in accordance with the results of porosity from the saturation method (Figure 6.3) and with the results of MIP (Table 6.4). The major contribution of the internal porosity is from the paste phase, where 23.09% of the SS-AAM paste was found to be closed porosity. This finding confirms that the SS-based matrix is more porous than a conventional AAM matrix, e.g., GGBFS-AAM (21.16%). Moreover, the aggregate phase is the same, so what really differentiates them is indeed the paste. Additionally, it was possible to identify approximately 2.44 – 2.68% of metallic material in the aggregate for all mortars. This result suggests that it is difficult to recover all the metal small particle sizes of BOF SS (< 4.8mm), and residual percentages of metallic phase will always be part of this byproduct.

**Table 6.5 – Properties of the mortars obtained by  $\mu$ CT.**

| Formulation | Total porosity (%) | Paste      |                     |                             | Aggregate  |                     |                             | Metallic part from aggregate |                     |                             |
|-------------|--------------------|------------|---------------------|-----------------------------|------------|---------------------|-----------------------------|------------------------------|---------------------|-----------------------------|
|             |                    | Volume (%) | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) | Volume (%) | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) | Volume (%)                   | Closed porosity (%) | OSVR ( $\mu\text{m}^{-1}$ ) |
| SS          | 25.07              | 72.39      | 23.09               | 0.00773                     | 25.13      | 28.47               | 0.02267                     | 2.68                         | 1.86                | 0.01662                     |
| GGBFS       | 22.39              | 74.89      | 21.16               | 0.00614                     | 17.09      | 27.57               | 0.01930                     | 2.55                         | 1.36                | 0.01597                     |
| PC          | 22.80              | 74.71      | 20.15               | 0.00657                     | 22.75      | 28.20               | 0.02145                     | 2.44                         | 1.46                | 0.01583                     |

OSRV: object surface/volume ratio.

Another quantitative information obtained from  $\mu$ CT was the distribution of paste and aggregate in the sample, in order to identify segregation of the aggregate. Segregation is the unintentional separation of the particles of an aggregate, causing a lack of uniformity in their distribution within the mortar [32]. Figure 6.6 presents the percentage area of each phase along the sample, top to bottom. None of the mortars presented a considerable segregation of the aggregates. However, the GGBFS-AAM appears to have a more constant distribution with ~15% of aggregate and ~80% of paste top to bottom. It is possible to notice that the SS-AAM and PC mortars presented some segregation. Both started with ~10% of aggregates in the top of the sample and reach 27-30% of aggregates in the bottom. These results indicate that: (i) the SS-AAM must be better designed to avoid excessive porosity (Table 6.5, Figure 6.3) and segregation of the aggregate even with a good workability (Table 6.2) in the fresh state, and (ii) the high density of the BOF SS aggregate ( $3.30 \text{ g/cm}^3$ ) tend to cause segregation in PC-based materials if improperly casted [33].

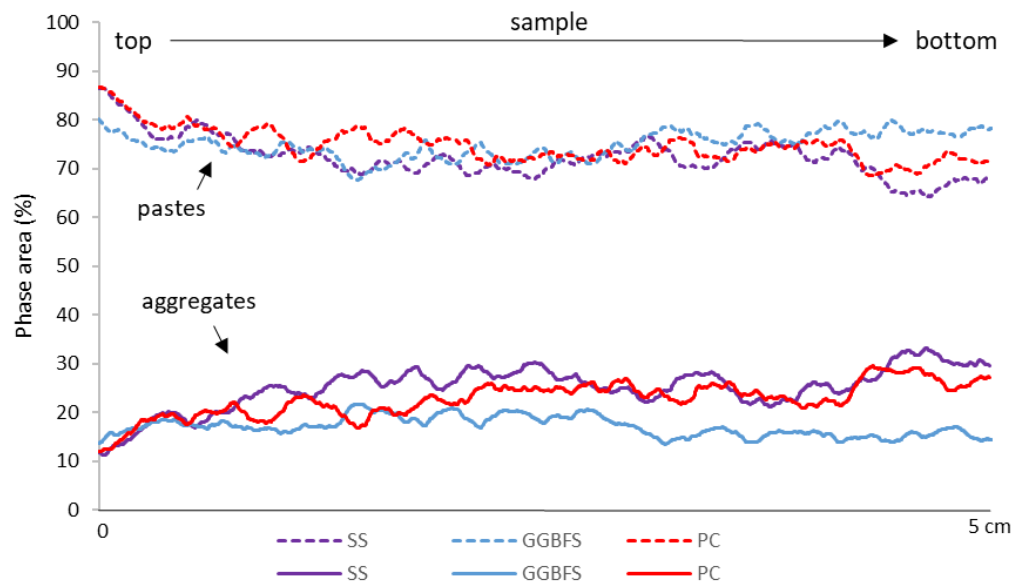


Figure 6.6 - Phase percent area distribution along the sample (Z axis).

Figure 6.7 to Figure 6.9 shows the 3D images of the studied mortars generated by  $\mu$ CT. It is possible to observe the distribution of each phase within the sample with the 3D reconstruction. It is interesting to point out that the irregular shape of BOF SS aggregate interfere directly on the morphology of the paste distribution regardless the type of precursor. Another interesting visual observation is how the pores presents a higher concentration in the inner part of the samples. Additionally, it is possible to visually confirm that none of the mortars presented considerable segregation of the aggregates, which is desired during the casting process.

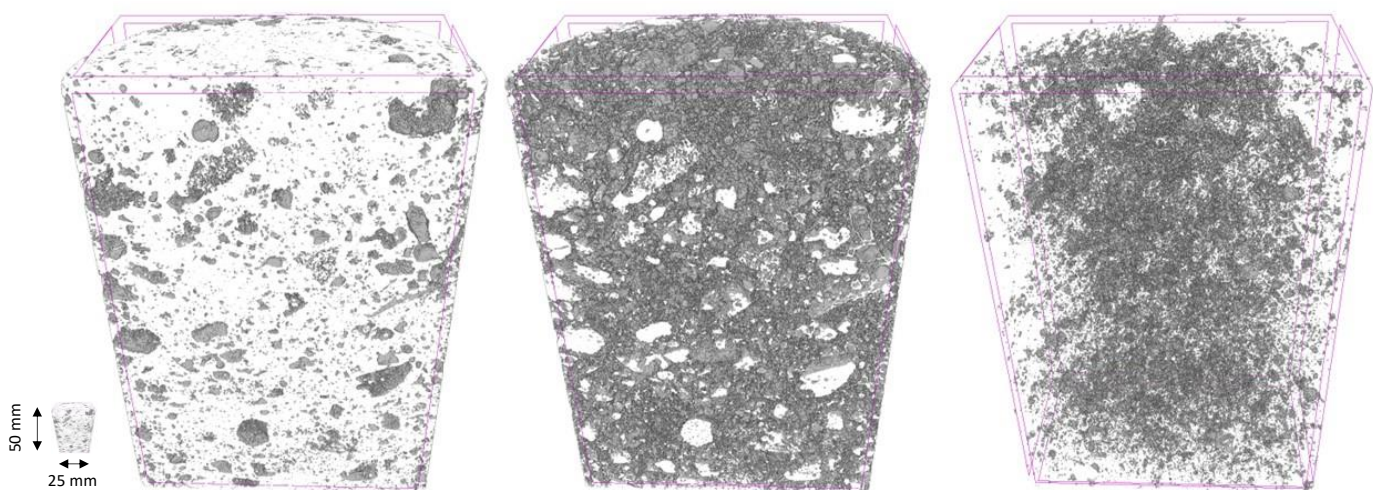
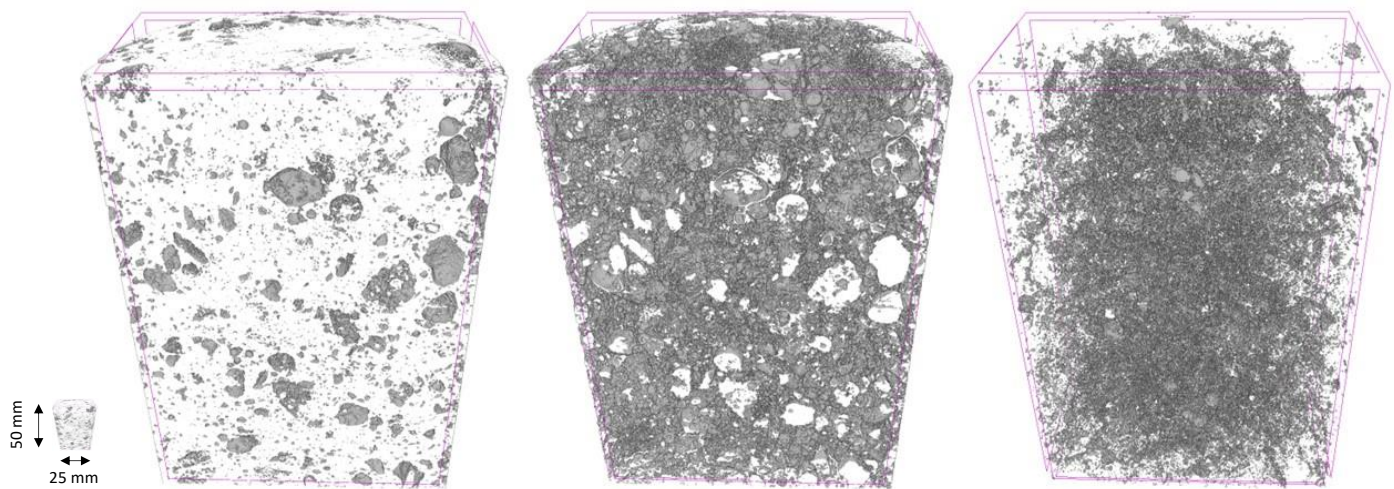
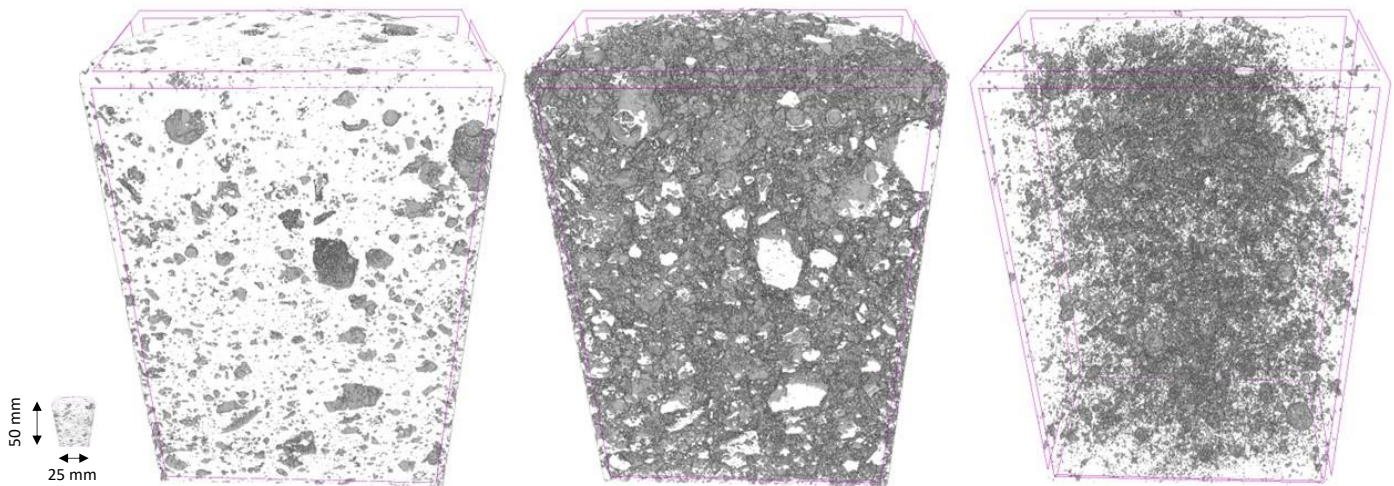


Figure 6.7 – 3D images from  $\mu$ CT of SS mortar: paste (left, in white), aggregate (center, in grey), and pores (right, in grey).



**Figure 6.8 - 3D images from  $\mu$ CT of GGBFS mortar: paste (left, in white), aggregate (center, in grey), and pores (right, in grey).**



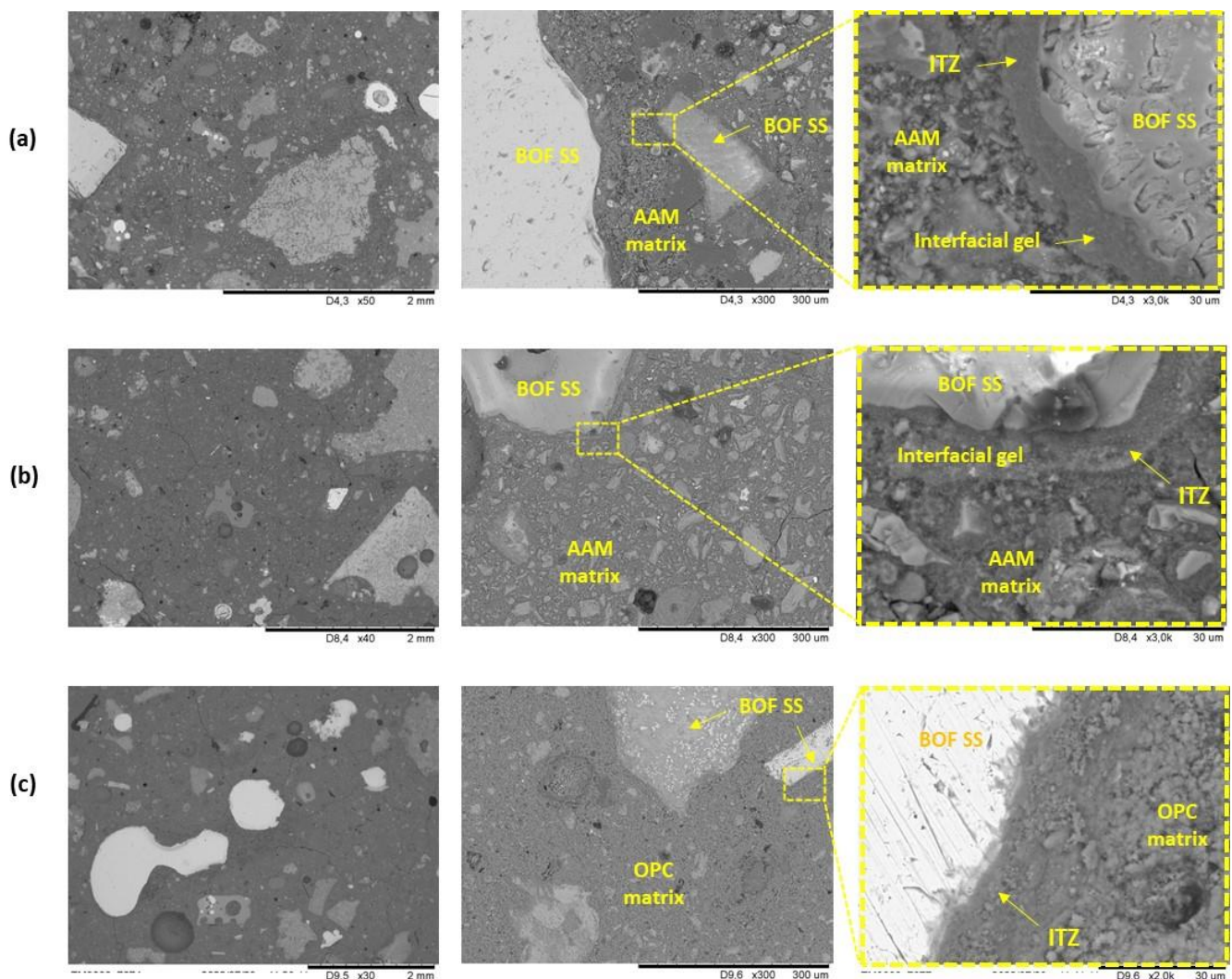
**Figure 6.9 - 3D images from  $\mu$ CT of PC mortar: paste (left, in white), aggregate (center, in grey), and pores (right, in grey).**

### 6.3.5.3 Scanning electron microscopy

Figure 6.10 shows the SEM images of the microstructure of the mortars highlighting the ITZ between aggregate and matrices. It is possible to observe the distribution of the aggregates, the densification of the matrices, and the definition of the ITZ. From the images on the left (at lower magnification) it is possible to see the irregular, porous and rougher surface of the BOF SS aggregate and some macropores in all the three mortars. A higher magnification helps the identification of a strong and well-defined transition zone between the particles of the aggregate and the AAM matrices, both SS and GGBFS (Figure 6.10a and b, respectively). In fact, an interfacial gel is formed, which can be associated with a gel type C-A-S-H [10] and may be positively influenced

the mechanical strength of the GGBFS-AAM (Figure 6.2). Moreover, the GGBFS-AAM (Figure 6.10b) presented a denser matrix than the others, which is consistent with the results found for the mechanical strength, MIP, and  $\mu$ CT analysis. In contrast, the SS mortar (Figure 6.10a) presented a porous matrix (Table 6.4) resulted from a weakened activation process, compromising the strength development (Figure 6.2).

Regarding the PC mortar, the use of a BOF SS aggregate seemed to improve the interfacial bonding with the cement paste, where no micro-cracks or voids were found. This behavior was also reported by Dai et al. [15] in their study comparing with natural aggregate and in the results from Chapter 5 comparing with natural aggregate and untreated BOF SS aggregate. This finding corroborates with the results from the previous sections (mechanical properties and structural assessment).



**Figure 6.10 – SEM images showing the microstructure of (a) SS-AAM, (b) GGBFS-AAM, and (c) PC (BOF SS: BOF steel slag aggregate, ITZ: interfacial transition zone).**

#### 6.4. Concluding remarks

This chapter compared the performance of three different mortars (SS-based AAM, GGBFS-based AAM and PC-based) using a pre-treated (wet-cured) BOF SS as the single aggregate. The behavior of the mortar was evaluated through a series of experiments, and focus was given to the mechanical, structural, and microstructural properties. The main conclusions are:

- The SS-AAM presented a shorter induction period compared to the GGBFS-AAM. In contrast, the GGBFSAAM presented a much higher cumulative heat output due to its higher solubility and amorphous character of the slag. However, the later presented a lower heat release than other GGBFS-based materials do, which may have been influenced by the BOF SS aggregate fine particles.
- The SS-AAM presented low compressive (up to 5 MPa), which restricts the application of this type of mortar to non-structural applications. Conversely, the use of BOF SS aggregate in the GGBFS-AAM and PC mortars did not jeopardize the mechanical strength. In fact, those mortars presented high strength (45- 50 MPa), which allow for structural applications.
- The GGBFS-AAM and PC mortars presented volume stability, although the PC-based still presented some spalling material and small cracks on the surface. The wet-curing of the BOF SS aggregate guarantee the volume stability of the mortars, specially the GGBFS-AAM. On the other hand, the SS-AAM does not have sufficient mechanical strength to be evaluated in an accelerated testing like the autoclave test. Thus, all the samples were destroyed into fragments during autoclaving. Alternative experimental methods should be proposed to evaluate the volume stability of SS-based mortars containing the BOF SS aggregate.
- The SS-AAM presented a much higher pore volume and higher total porosity than the other mortars. The major contribution of the internal porosity is derived from the SS-AAM paste phase. Additionally, the GGBFS-AAM presented the lowest average pore diameter and most of the pores below 20 nm (considered a harmless range), indicating that the GGBFS refines the pore structure thus leading to a denser internal structure.

- None of the mortars presented considerable segregation of the aggregate during the casting process, which was quantified and visually confirmed by the 3D images generated by  $\mu$ CT. However, the SS-AAM must be better designed to avoid excessive porosity. Both AAM matrices presented a strong and well-defined transition zone between the aggregate and the matrix, where an interfacial gel is formed (probably a C-A-S-H gel). Nevertheless, the SS-AAM presented a porous matrix resulted from the weakened activation process.

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## **7. SUMMARY OF RESULTS AND DISCUSSION**

This chapter summarizes the most relevant results from the experimental work of this thesis, which have already been presented in the previous chapters 4, 5, and 6. Additionally, some complementary discussions about these findings are also presented. The investigation was divided into three parts, evaluation of BOF SS as precursor, evaluation of BOF SS as aggregate, and comparative study between BOF SS based mortar and other mortars.

### **7.1. SS as precursor**

In the first part of the experimental program, the potential use of SS as single precursor in AAM was evaluated by changing the activation parameters, i.e., silica modulus and  $\text{Na}_2\text{O}$  concentration. Initially, the pozzolanic and the reactivity behaviors of the SS were assessed by two different methods. The pozzolanic index was 67.29%, which indicated that SS cannot be considered a pozzolanic material. The low pozzolanic behavior of the SS was expected based on the high content of crystalline phases presented in its mineralogical diffractogram. The reactivity results according to the modified  $R^3$  test showed a low reactivity from the SS based on its low heat released and calcium hydroxide consumption, 76 J/g SCM and 16 g/100 g SCM, respectively. It was still expected the alkali-activation process to take place despite those unpromising behavior of the SS.

In fact, the hydration/activation process of the SS was confirmed with the calorimetry analysis of several SS-based AAM pastes. The changes in the silica modulus and in the  $\text{Na}_2\text{O}$  concentration in the activator clearly modified the activation kinetics. First, a rise in both parameters helped the initial dissolution of the SS particles (calcium silicate and aluminate), thus increasing the formation of the initial dissolved silicates and aluminates units. The formation of hydration products (e.g. reaction gels and  $\text{Ca}(\text{OH})_2$  resulting from the hydration of the calcium silicate present in the SS) was only identified in the formulations with 4% of  $\text{Na}_2\text{O}$  and silica modulus of 0.75 and 1.50. However, these results do not necessarily indicate the absence of reaction products in the other formulations, but rather a retarded reaction when the silica modulus was increased.

A XRD and TG analyses were made to assess the structural changes of the hardened pastes and to monitor the reaction products. The main findings from the XRD analysis

were: (i) an amorphous phase structure, such as C-S-H/C-A-S-H gels was formed as indicated by a clear broad hump below  $10^\circ 2\theta$  and around  $29^\circ 2\theta$ ; (ii) the crystalline diffraction peaks of the calcium silicates and aluminates of the SS decreased, confirming that they dissolved (at least partially) and reacted with an alkaline solution to produce the hydrated products in all pastes; (iii) there was also calcium carbonate resulted from the consumption of calcium hydroxide; (iv) no apparent changes were observed in the peaks of wustite (FeO) or quartz (SiO<sub>2</sub>), suggesting that these phases did not take part in the alkali activation reaction. Moreover, the presence of the crystalline phase of Ca(OH)<sub>2</sub> in the pastes with silica modulus of 0.75 strongly suggested that the alkali reaction was weaker and fewer hydrates were formed in those formulations.

From the TG analysis it was possible to determine the content of the reaction products. The main findings from the TG analysis were: (i) all formulations presented a high mass loss below 120°C assigned to the release of physically bond water within the gel structure; (ii) increased DTG peak temperature in this region as the curing advance from 1 to 28 days suggesting the formation of gels with more tightly bonded water as the reaction products developed; (iii) increased mass loss over the curing time for all formulations in the temperature ranges (120–600 °C and 600–1000 °C) corresponding to the decomposition of the main reaction products, namely, C-S-H/C-A-S-H gels and CaCO<sub>3</sub>, respectively.

The mass loss increased proportionally to the quantity of the gels, which was correlated with the compressive strength enhancement of pastes. Considerable development in strength from 1 to 28 days was observed for all formulations. These results confirmed the alkali activation process of the SS and the hardening of all pastes. The lowest strength values were found for extremes in the activator's content: a low alkali concentration combined with a low silica modulus, or a high alkali concentration combined with a high silica modulus. Better strength performance could be achieved when an optimized combination of activator sources was considered. In this study, a low Na<sub>2</sub>O concentration (4%) with an intermediary silica modulus (1.50–2.22) presented the best mechanical results, increasing the compressive strength up to 20 MPa. Additionally, the change in the activation parameters significantly affect neither the porosity nor the apparent density of the pastes. In fact, the porosity of the

pastes was highly related to the water-to-binder ratio (w/b), which played an important role in the consistency of the mixes.

SEM-EDX analysis was made to support the previous findings in term of microstructure of the pastes. Two very different formulations were compared, 0.75M-4% and 2.22M-4%. It was possible to identify Si (from the activator) and Ca (from the SS) as the predominant elements in the element mapping. The paste 0.75M-4% presents more unreacted SS particles, which is in accordance with the lowest amount of reaction products found via TGA and the lowest compressive strength. An open microstructure with porous regions all over the matrix resulted from a poor hydration/activation process, which compromised the compressive strength development. On the other hand, a more homogeneous microstructure was observed at the paste 2.22M-4%, which was characterized by a smaller number of undissolved BOF SS particles and lower porosity. More hydrates were formed, which filled the existing pores (voids) and bonded the remaining solid particles together to form a continuous, dense, and complete matrix. Therefore, the denser microstructure resulted from a better hydration/activation process and the high presence of hydrates reduced the microstructural porosity, resulting in higher compressive strength.

## **7.2. SS as aggregate**

In the second part of the experimental program, the potential use of SS as aggregate was evaluated by assessing the effect of the SS pre-treatments (wet curing and carbonation) on various properties of AAM and PC mortars. The AAM mortars were prepared with a single binder (GGBFS) and a natural aggregate was also used as reference. Initially, the pre-treatments of the SS aggregate particles were evaluated via SEM to verify the presence of the hydrated and carbonated products that would prevent the expansive reactions of the SS elements, such as CaO and MgO. Both pre-treatments were validated.

The use of pre-treated SS aggregate did not affect the workability of AAM mortars compared to the natural aggregate. On the other hand, the workability was reduced for PC mortars. However, it is important to state that the high-water absorption of the SS aggregate (7.16%) must be taken into consideration when dosing the mortars, so the consistency is not affected.

Regarding the mechanical behavior of the mortars, the replacement of natural aggregates (NA) with SS aggregate enhanced the compressive strength of AAM mortars at 28 days, especially after the pre-treatments. The mean compressive strength rose 0.12% for the untreated SS, 16.64% for wet cured SS and 9.52% for carbonated SS. These results emphasize that the SS aggregate can be successfully used as an alternative fine aggregate in AAM. In fact, other studies have shown that the SS aggregate is known to positively affect the compressive strength because of its high strength, hardness, and rough surface. The rougher and irregular surface of the aggregate might have helped to increase the bonding between paste and aggregate at the ITZ. In general, the replacement of NA with SS aggregates did not negatively affect the strength of PC-based mortars. The pre-treatments seemed to have improved the bond at the ITZ, increasing the mechanical behavior of the mortars, which is in accordance with previously findings. Both matrices (AAM and PC) performed very similar under compression, especially at 28 days.

However, it is important to note that the strength development varied among the AAM mortars. The carbonation process of the SS aggregate negatively affected the strength development at early ages. Results from calorimetry and XRD explained the poor performance. The explanation may lie on the presence of calcite on the aggregate's surface. The calcium carbonate reacts with the sodium silicate solution at the beginning of the alkali-activated process resulting in sodium carbonate. Thus, the presence of  $\text{Na}_2\text{CO}_3$  among the activators slightly decrease the pH, leading to low rate of dissolution of the GGBFS. At early ages, the formation of calcium carbonate and sodium-calcium carbonates are favored instead of the development of calcium silicate hydrate gels. The mortar presented a delay in strength development consequently.

Regarding durability, the use of SS aggregate on AAM matrices presented better results of volume stability than on PC matrices in most of the cases, excepted in the carbonated case. The wet curing is highly recommended for both matrices to control the delayed expansion of SS, ensuring the production of sound-hardened materials after accelerated testing. In fact, the wet cured SS was the only SS aggregate that had the same behavior as the natural aggregate.

A structural assessment with a  $\mu$ CT was carried out to complete the evaluation of the mortars with best durability results. Results of  $\mu$ CT have shown that the total porosity of AAM mortars is equivalent regardless the aggregate and increased in PC mortar when SS aggregate is used. Furthermore, the employment of SS aggregate increases the closed porosity for both pastes (AAM and PC). This suggests that the irregular surface of the SS aggregate may hinder the air to escape from the paste during the casting process. Moreover, the use of SS aggregate promotes the complexity of the internal structure of mortars compared to natural aggregate. In addition, the use of wet cured SS aggregate instead of NA in AAM mortars improved the cohesion of the mortar and prevented segregation even if the mortars presented the equivalent consistency in the fresh state. The irregular shape of the SS aggregate and its influence on the morphology of the paste distribution is noteworthy in  $\mu$ CT analysis.

SEM analysis was made to support the previous findings. SEM images confirmed that the wet cured SS aggregate densified the matrix, while the mortars with natural aggregate and untreated SS presented a porous and spongy internal structure. Moreover, the former presented a strong ITZ, no micro-cracks and the presence of a gel phase (most likely resulting from the reaction between the SS aggregate in the alkaline system) which promotes the bond between aggregates and paste. The less porous ITZ and denser matrix made with wet cured SS aggregate explained its better mechanical performance.

### **7.3. Comparative study of mortars**

In the last part of the experimental program, an AAM mortar was developed by using SS as the single raw material, as binder and aggregate, and several properties were analyzed and compared with two mortars made with either alkali-activated GGBFS or PC as binder. Concerning the fresh properties of the mortars, both AAM mortars presented good consistency around 275 mm, unlike the PC-based which presented a much lower workability of 200 mm. This behavior is indicative that the use of SS as fine aggregate does not jeopardize the consistency of AAM mortars.

Some significant differences between the activation (hydration process) of the AAM mortars were found via calorimetry. First, the SS-AAM presented a faster dissolution of the calcium silicates and aluminates species as demonstrated by its higher first

exothermic peak. Then, the induction period was significantly shortened since no reaction was delayed by the formation of crystalline aluminum products. In addition, the second peak was also notably different between the two mortars, indicating that the formation of the hydration products was indeed different. In fact, the GGBFS-AAMr presented a much higher cumulative heat output due to its higher solubility and amorphous character.

Compressive strength at different ages, apparent density, porosity, and water absorption at 28 days were the hardened properties evaluated. The development of compressive strength was observed for all mortars. GGBFS-AAM and PC mortars had their mechanical strength at 28 days between 45 to 50 MPa, which is in the range for structural applications. On the other hand, the SS-AAM achieved 5 MPa, which was quite low and restricted the applications to non-structural materials. To the of the author's knowledge, there is no study on the literature using the SS as the sole binder and aggregate combined in AAM mortars.

The apparent density of SS, GGBFS and PC mortars were  $2.04 \pm 0.02 \text{ g/cm}^3$ ,  $2.13 \pm 0.00 \text{ g/cm}^3$ , and  $2.21 \pm 0.02 \text{ g/cm}^3$ , respectively. The density of the mortar is strongly related to the casting process, incorporated air and to the hydration (densification) of the matrix. The mean porosities were 35.71%, 30.87%, and 26.32%, respectively. Overall, the porosity is highly related to the w/b ratio, which plays an important role in the consistency of mortars. To the author's knowledge, no previous study presented results on the influence of the SS aggregate on the apparent density and porosity of AAM mortars.

The GGBFS-AAM and PC mortars presented the best results of volume stability after the accelerated autoclaved testing. All three tested samples of GGBFS-AAM and PC mortars were sound after testing and presented low average length changes, 1.43% and 1.88%, respectively. On the other hand, the SS-AAM was destroyed into fragments after the autoclave procedure. Samples were already broken before testing because of the low early mechanical strength of the mortar and the high slenderness of the samples. Hence, the SS-AAM does not have sufficient mechanical strength to be evaluated in an accelerated testing like the autoclave. No other study in the literature evaluated the volume stability of SS-based mortar to permit comparison.

The structural and microstructural evaluation of the mortars were carried out by MIP,  $\mu$ CT, and SEM. The SS-AAM presented a much higher pore volume (0.18 mL/g) and higher total porosity (14.50%) via MIP than the other two mortars; 0.08 mL/g and ~7.50% for GGBFS-AAM and PC mortars. Most of the pores of all mortars are distributed between 0.01 $\mu$ m and 1 $\mu$ m, characteristic of meso and macropores. Most of the pores can be classified according to the adverse effect on the matrix as harmless (<0.02 $\mu$ m) and less harmful (0.02-0.2 $\mu$ m) pores. Additionally, the GGBFS-AAM presented the lowest average pore diameter (10.50nm) and most of the pores in the harmless range (62.26%), indicating a refined pore structure and denser microstructure. Results from the MIP indicate that the pore size distribution, average pore diameter, porosity, and pore volume distribution are more related to the matrix than to the aggregate. Thus, the use of the SS aggregate does not present any negative effect in terms of those characteristic of the developed mortars.

Results from the  $\mu$ CT shows that the major contribution of the internal porosity of the SS-AAM is derived from the SS paste phase (23.09% of the paste phase was found to be closed porosity). Additionally, none of the mortars presented considerable segregation of the aggregates. The GGBFS-AAM showed a more constant distribution all over the sample than the other mortars. The irregular shape of the SS aggregate was found to interfere directly on the morphology of the paste distribution regardless the type of precursor. The results from  $\mu$ CT indicate that the SS-AAM must be better design to avoid excessive porosity and to prevent segregation of the aggregate.

Finally, SEM analysis supported the previous findings and has shown that both AAM matrices presented a strong and well-defined transition zone between the aggregate and the matrix, where an interfacial gel is formed. In fact, this may be associated with a gel type C-A-S-H and may positively affected the mechanical strength of the GGBFS-AAM (which also presented the denser matrix). However, the SS-AAM presented a porous matrix resulted from the weakened activation process, which may have compromised the strength development. Results from the microstructure analysis were consistent with the results found in the mechanical, MIP and  $\mu$ CT analysis.

## **8. CONCLUSIONS AND RECOMMENDATIONS**

## 8.1. Conclusions

The present thesis presented a better understanding of some important factors involved in the utilization of steel slag as binder and aggregate in AAM. The main general conclusion is that the use of steel slag as raw material in the development of a low environmental impact construction material is indeed feasible. The following specific conclusions can be drawn from the investigation:

- (i) The BOF SS studied presented low pozzolanic behavior, low heat generation and may be considered a low-reactivity material. Nevertheless, the alkali activation process and hardening of pastes were confirmed in all studied cases. Moreover, crystalline phases of the BOF SS dissolved under the alkaline environment to produce hydrates in all studied formulations, as presented by the TGA and XRD results. In this thesis, a paste with low  $\text{Na}_2\text{O}$  concentration (4%) and intermediary silica modulus (1.50–2.22) presented the best mechanical results (compressive strength up to 20 MPa), a good amount of reaction products formed (C-S-H/C-A-S-H gel and  $\text{CaCO}_3$ ), and a low initial and cumulative amount of heat released.
- (ii) The replacement of natural aggregate with BOF SS did not negatively affect the mechanical strength of AAM and PC mortars. However, the strength development at early ages of AAM was strongly affected when the carbonated BOF SS aggregate was used. This happened due to the formation of sodium carbonate at the beginning of the alkali-activated process, resulted from the reaction of  $\text{Na}^+$  ions from the activator and the calcium carbonate from the carbonated aggregate.
- (iii) Results of  $\mu\text{CT}$  and SEM shows that the total porosity of AAM mortars is equivalent regardless the aggregate and increased in PC mortar when BOF SS aggregate is used. Moreover, the use of BOF SS aggregate promotes the complexity of the internal structure of mortars compared to natural aggregate. In addition, the use of wet-cured BOF SS aggregate instead of natural aggregate in AAM mortars improved the cohesion of the mortar and prevented segregation. It also densifies the microstructure, presenting a

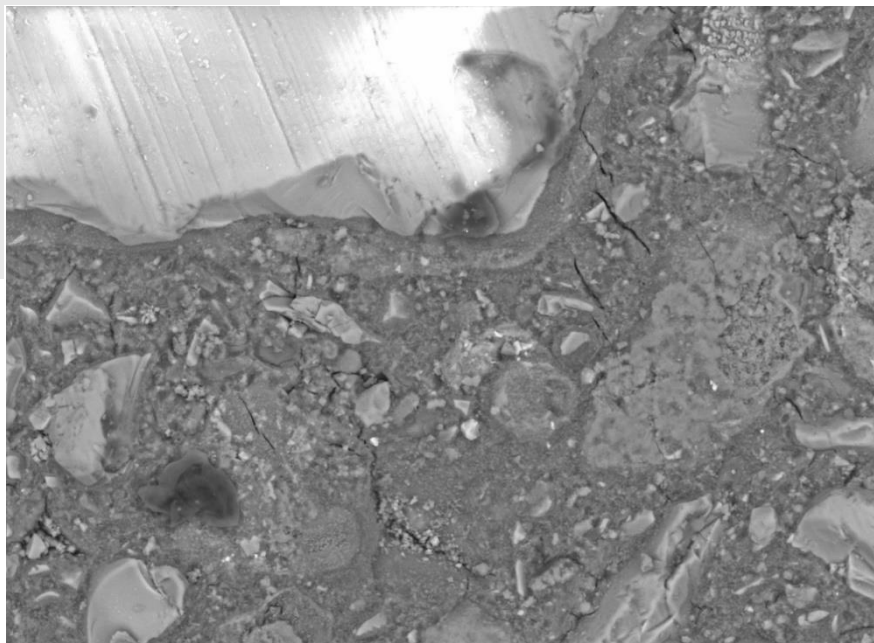
less porous ITZ and no micro-cracks. The ITZ presented a gel phase (most likely resulting from the reaction of the BOF SS aggregate in the alkaline system) which promoted the bond between aggregates and paste.

- (iv) The wet curing as pre-treatment is highly recommended for AAM and PC matrices to control the delayed expansion of the BOF SS, as the former ensures the production of sound hardened materials after accelerated testing. Alternatively, the carbonation process appeared to slightly improve the expansion resistance only for PC matrix but does not solve the expansion issues.
- (v) An AAM mortar designed with SS as the single binder and aggregate combined (greatest novelty of this thesis) presented mechanical strength up to 5 MPa, then restricted to non-structural applications. This mortar presented a much higher pore volume and higher total porosity than a GGBFS-AAM and PC mortars. It also did not present considerable segregation of the aggregate during the casting process; however, the mortar must be better design to avoid excessive porosity.
- (vi) The SS-based mortar also presented a strong and well-defined transition zone between the aggregate and the matrix, where an interfacial gel is formed. In fact, this may be associated with a gel type C-A-S-H and positively affected the mechanical strength. Nevertheless, the SS-AAM mortar presented a porous matrix resulted from the weakened activation process. Its low compressive strength at early and later ages prevents the evaluation in accelerated autoclaving testing. Finally, it is essential to highlight that the results of this research suggest that BOF SS is a promising raw material for AAM applications.

## **8.2. Recommendations for future research**

This present investigation offers important findings to validate the use of SS as raw material in AAM. Some recommendations for further research are:

- (i) Alternative expansion assessment: The SS-AAM mortar did not present sufficient mechanical strength to be evaluated in a accelerate testing like the autoclave test. So, alternative experimental methods should be proposed to evaluate the volume stability of SS-AAM mortars containing the BOF SS aggregate.
- (ii) Long-term age analysis: This study only evaluated the early age and the 28 days properties of the developed pastes and mortars. The long-term properties may present a better understand about the performance and durability of the materials, besides the autoclave expansion.
- (iii) Life cycle assessment: The environmental impact of the developed mortars was not addressed in this investigation. A life cycle assessment (LCA) is essential to validate the proposed solution as a sustainable, environmentally friendly alternative.



La escoria de acería (EA) es un residuo sólido generado durante el proceso de fabricación del acero con generación anual de 270 millones de toneladas de EA en todo el mundo. La EA se puede reutilizar como materia prima alternativa en varias aplicaciones debido a su composición química, propiedades mecánicas y físicas. Esta investigación investigó la viabilidad de EA como aglutinante y árido en materiales álcali-activados (MAA) a través de la determinación de los parámetros de activación óptimos y el proceso de pretratamiento necesario. Las propiedades mecánicas, microestructurales y de durabilidad se evaluaron mediante una serie de métodos de caracterización, como microscopía electrónica de barrido (MEB), microtomografía de rayos X ( $\mu$ CT), porosimetría de intrusión de mercurio (MIP) y expansión en autoclave, entre otros. Los resultados mostraron que, a pesar de la baja reactividad de la EA, se confirmaron el proceso de activación alcalina y el endurecimiento de las pastas a base de SS como aglutinante único. De hecho, los mejores resultados mecánicos (resistencia a la compresión hasta 20 MPa) se consiguieron con una combinación de baja concentración de  $\text{Na}_2\text{O}$  (4%) y módulo de silicio intermedio (1.50-2.22). En cuanto al uso como árido, el curado en húmedo como pretratamiento es muy recomendable para las matrices MAA y PC para controlar la expansión retardada de la EA, produciendo materiales endurecidos tras el ensayo acelerado. Además, la interfase presentó una fase gelatinosa (muy probablemente resultante de la reacción del árido EA en el sistema alcalino) que favorecía la interfase entre áridos y pasta. Por otro lado, la carbonatación como pretratamiento afectó fuertemente al desarrollo de la resistencia a edades tempranas de los morteros MAA debido a la formación de carbonato sódico en el activador. El mortero MAA diseñado únicamente con EA como ligante y árido presentó bajas resistencias mecánicas (hasta 5 MPa) y alta porosidad total. Como consecuencia, este mortero no tiene suficiente resistencia mecánica para ser evaluado en pruebas aceleradas. Los resultados de esta investigación demostraron que el uso de EA como materia prima es muy prometedor para el desarrollo de MAA.

Steel slag (SS) is a solid waste generated during the steelmaking process, with annual generation of 270 million tons of SS worldwide. SS can be reused as an alternative raw material in several applications due to its chemical composition, mechanical and physical properties. This research investigated the feasibility of SS as binder and aggregate in alkali-activated materials (AAM), by determining the optimum activation parameters and the pre-treatment process needed. Mechanical, microstructural and durability properties were evaluated via a series of characterization methods, such as scanning electron microscopy (SEM), X-ray microtomography ( $\mu$ CT), mercury intrusion porosimetry (MIP) and autoclave expansion, among others. Results showed that SS has low reactivity but may be alkali-activated as single binder. In fact, the best mechanical results (compressive strength up to 20 MPa) were achieved by using an activator with low  $\text{Na}_2\text{O}$  concentration (4%) and intermediary silica modulus (1.50-2.22). As aggregate, the wet curing as pre-treatment of the SS is highly recommended for AAM and PC matrices to control the delayed expansion of the former, producing sound materials after accelerated testing. In addition, the ITZ showed a gel phase (most likely resulting from the reaction of the SS aggregate in the alkaline system) which promoted the bond between aggregates and paste. On the other hand, the carbonation as pre-treatment of SS strongly affected the strength development at early ages of AAM mortars due to the formation of sodium carbonate in the activator. The AAM mortar designed with neat SS as binder and aggregate presented low mechanical strength (up to 5 MPa) and high porosity. Consequently, this mortar does not have sufficient mechanical strength to be evaluated in accelerated expansion testing. The findings of this research showed that the use of SS as raw material is very promising for AAM development.